MANGANIC ACETATE IN ANHYDROUS ACETIC ACID

PREPARATION, STRUCTURE AND SOME OXIDATION REACTIONS

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN
DE WISKUNDE EN NATUURWETENSCHAPPEN AAN
DE RIJKSUNIVERSITEIT TE LEIDEN, OP GEZAG VAN
DE RECTOR MAGNIFICUS DR P. MUNTENDAM,
HOOGLERAAR IN DE FACULTEIT DER GENEESKUNDE,
TEN OVERSTAAN VAN EEN COMMISSIE UIT DE SENAAT
TE VERDEDIGEN OP WOENSDAG 26 JUNI 1968
TE KLOKKE 14.15 UUR

DOOR

LOUWRENS WILLEM HESSEL

GEBOREN TE 's-GRAVENHAGE IN 1931

1968
BRONDER-OFFSET ROTTERDAM

PROMOTOR: PROF. DR E. C. KOOYMAN

respectfully to Dr F. S. Khair Ullah,
Principal of Murray College,
West Pakistan.

STELLINGEN

I

Zuiver azijnzuur is niet bestand tegen destillatie onder normale druk.

Dit proefschrift.

II

De waarde die de meest gebruikte hand- en leerboeken geven voor de cryoscopische constante van azijnzuur is ongeveer 10% te hoog.

Dit proefschrift.

III

Het is niet waarschijnlijk dat Kolling en Lambert bij hun bepaling van de dissociatieconstante van $Fe(OAc)_3 . HOAc$ deze verbinding inderdaad in handen hebben gehad.

O. W. Kolling and J. L. Lambert, Inorg. Chem. 3, 202 (1964)

IV

De argumenten die Ziffer c. s. geven voor de door hen voorgestelde configuratie van occidentalol zijn onvoldoende.

H. Ziffer, T. J. Batterham, U. Weiss and E. von Rudloff, Tetrahedron, 20, 67 (1964).

V

De veronderstelling van Walling en Gibian dat de door hen onderzochte waterstofabstractie reacties door benzofenon in de triplet toestand niet omkeerbaar zijn is onvoldoende gefundeerd.

C. Walling and J. Gibian, J. Am. Chem. Soc. 87, 3361 (1965).

VI

Tegen de uiteenzetting die Kauzmann geeft over het effect van de intermoleculaire attractie op de toestandsvergelijking van gassen zijn didactische bezwaren.

W. Kauzmann, "Thermal properties of matter", Vol. I, p. 70 W. A. Benjamin Inc. New York, 1966.

VII

De door Whitesides c.s. uitgevoerde bepaling van de relatieve substituentgrootte in 1- gesubstitueerde 3,3-dimethylbutanen is te onnauwkeurig om de door hen getrokken vergelijking met de substituentgrootte in overeenkomstige cyclohexanen zinvol te maken.

G.M. Whitesides, J.P. Sevenair and R.W. Goetz, J. Am. Chem. Soc. 89, 1135 (1967).

VIII

De uitspraak dat N,N'-digesubstitueerde hydrazines niet condenseren met de carbonylgroep is in zijn algemeenheid niet juist.

N.V. Sidgwick, "The organic chemistry of nitrogen", 3d revised edn., p. 523. Clarendon Press, Oxford, 1966.

IX

De nadruk die het orthodoxe christendom gelegd heeft op de goddelijke oorsprong van de bijbel en op de goddelijkheid van Christus heeft de inhoud van de bijbelboeken en de persoonlijkheid van Jezus van Nazareth afgeschermd voor Joden, Moslims en vele Christenen.

X

Vele der op de Nederlandse wegen geplaatste verkeersborden vormen een bedreiging voor de verkeersveiligheid.

L.W. Hessel

Leiden, 26 juni 1968.

CONTENTS

CHAPTER I

INTRODUCTION

Manganese salts play an important rôle as catalysts in many autoxidation reactions.

These autoxidations are free-radical chain reactions in which the processes of chain initiation, propagation and termination can usually be clearly distinguished.

The catalytic activity of manganese in these reactions is due to its ability to take part in oxidation-reduction cycles: as Mn(III) it can act as oxidising agent in the propagation and/or initiation steps and as Mn(II) it can react with peroxy radicals and/or hydroperoxides which are formed by the action of molecular oxygen on the primary radicals.

By a proper choice of the reaction conditions it has been possible to isolate several individual steps from these complicated reaction sequences and to study them separately.

In this way Van Helden and Kooyman found that the initiation step in the autoxidation of acetophenone in butyric acid is an attack of Mn(III) on the enol form of the substrate.[1]) They presumed the regeneration of Mn(III) to take place through a direct oxidation of Mn(II) by acylperoxy radicals. De Klein demonstrated the feasibility of this reaction by oxidising Mn(II) acetate to Mn(III) acetate by cyanoisopropylperoxy radicals.[2])

Autoxidation of toluene, xylenes and cumene under the catalytic influence of Mn and Co acetates in acetic acid yields the corresponding aromatic acids[3]), but when manganic acetate is allowed to react with aromatics in the absence of oxygen, substitution in the aromatic nucleus takes place.[4, 5]) Many other

oxidations by Mn(III) compounds have been studied.

For all these reactions a readily accessible Mn(III) compound is required which should also be soluble in the solvent which is chosen as the reaction medium. One of the few simple Mn(III) compounds of sufficient stability is manganic acetate dihydrate, which is known since 1883 when Christensen described it for the first time.[6] It is conveniently prepared from manganous acetate and potassium permanganate and readily soluble in acetic acid, which is a suitable solvent for oxidation reactions.

A survey of the various organic compounds which have been oxidised with manganic acetate in acetic acid was given by Van der Ploeg.[5]

A disadvantage of the use of hydrated manganic acetate is the involuntary introduction of water into the reaction medium. Many oxidations with manganic salts are known to be influenced by small amounts of water and some of them very strongly. Therefore De Korte, Den Hertog, Bronsdijk, De Klein and Van der Ploeg in their studies used anhydrous manganic acetate which they prepared from manganous acetate and potassium permanganate in the presence of acetic anhydride.[4,7,8,9,5]

However, the iodometric equivalent of their preparations did not quite correspond to the formula $Mn(OAc)_3$*, deviations of 5% from the expected value being often observed.

A second problem was the unexpected course of the thermal decomposition of this product in acetic acid. Van der Ploeg found that in the main decomposition reaction acetoxy radicals are not involved and concluded to a direct interaction between manganic acetate and acetic acid molecules producing CH_2COOH radicals.[5] He suggested a concerted mechanism but supporting evidence was not obtained.

Thirdly, $Mn(OAc)_2$ had a retarding influence on all oxidation reactions with manganic acetate which were studied so far. Explanations were given in terms of a disproportionation of Mn(III) acetate to Mn(II) acetate and Mn(IV) acetate[8], and of a charge-transfer complex between Mn(II) and Mn(III) acetate[9], but again there was no direct proof.

As these problems are closely related to the nature of anhydrous manganic acetate itself, and because of the continuing interest in oxidation reactions with anhydrous manganic acetate, a more detailed study of this compound seemed appropriate.

The main purposes of the present investigation were:

* Ac = acetyl.

a. to prepare pure anhydrous manganic acetate and to examine its structure, and
b. with the aid of this information to elucidate the mechanism of its thermal decomposition and the effect of manganous acetate on oxidation reactions with anhydrous manganic acetate.

As it became clear in the course of these studies that even traces of water in the solvent could not be tolerated, special attention was given to the preparation and handling of anhydrous acetic acid.

The analytical methods are discussed in chapter II. Various preparations of anhydrous manganic acetate are reported in the third chapter. Chapter IV and V are dealing with the structure of manganic acetate, including X-ray diffraction studies. Chapter VI describes the preparation of anhydrous acetic acid in connection with its disproportionation to acetic anhydride and water. Some oxidation reactions with anhydrous manganic acetate in anhydrous acetic acid are discussed in the last chapter.

REFERENCES:

1. R. van HELDEN and E.C. KOOYMAN, Rec. Trav. Chim. 80, 57 (1961).
2. W.J. de KLEIN and E.C. KOOYMAN, J. Catal. 4, 626 (1965).
3. R.M. STEPHENSON, "Introduction to the chemical process industries", Reinhold Publishing Cy., New York, 1966, chapter 16.
4. R.W. DE KORTE, Thesis, University of Leiden (1964).
5. R.E. VAN DER PLOEG, Thesis, University of Leiden (1967).
6. O.T. CHRISTENSEN, J. Prakt. Chem. 28, 1 (1883).
7. H.J. DEN HERTOG, Thesis, University of Leiden (1964).
8. J.M. BRONSDIJK, Thesis, University of Leiden (1965).
9. W.J. DE KLEIN, Thesis, University of Leiden (1967).

CHAPTER II

GENERAL METHODS FOR THE ANALYSIS OF ANHYDROUS MANGANIC ACETATE.

II.1 INTRODUCTION.

De Korte, Bronsdijk, De Klein and Van der Ploeg prepared anhydrous manganic acetate by the oxidation of $Mn(OAc)_2$ with $KMnO_4$ in a mixture of acetic acid and acetic anhydride at temperatures varying from 50 to 118°C. After partial evaporation of the solvent anhydrous manganic acetate was obtained as a dark brown precipitate. The iodometric equivalent of this product varied from 220 to 240, corresponding with an apparent $Mn(OAc)_3$ content of 105 - 95%. [1,2,3,4)]

The variations could easily be explained by assuming contamination of the samples with MnO_2 or $Mn(OAc)_2$, respectively. MnO_2 would be expected as one of the products of a disproportionation of manganic acetate to Mn(IV) and Mn(II) compounds, proposed by Bronsdijk on the basis of his kinetic results, and $Mn(OAc)_2$ would arise from the reducing action of the solvent above 90°C.

An alternative explanation would be to assume the presence of some basic acetate in the samples of low equivalent weight and coordinated acetic acid or "acetic acid of crystallisation" in the samples of high equivalent weight.

In order to establish the nature of these variations and with the purpose of obtaining information about the structure of manganic acetate we developed the following analytical methods:

A. Chromatographic analysis to test manganic acetate solutions in anhydrous acetic acid for Mn(II) and/or Mn(IV). (section II.2).

B. Chemical analysis (section II.3)

Determination of the following constituents:

a. Total Mn content by complexometric titration.

b. Mn(II) content by titration with $KMnO_4$.

c. Mn(III) content by iodometric titration.

d. Total acetate content by acidimetric titration.

e. Acetate-ion content by titration with perchloric acid in acetic acid solution.

f. Content of O as oxide or hydroxide by Karl Fischer titration.

Test on K or Pb.

C. Determination of the molecular weight by depression of the freezing point in acetic acid solution. (section II.4).

II.2. CHROMATOGRAPHY OF MANGANESE ACETATE SOLUTIONS IN ACETIC ACID.

II.2.1. INTRODUCTION.

Disproportionation of Mn(III) to Mn(II) and Mn(IV) compounds has been often observed.[5,6,7]

The disproportionation of manganic acetate in acetic acid would be expected to proceed according to the equilibrium:

$$2\ Mn(OAc)_3 \rightleftarrows Mn(OAc)_4 + Mn(OAc)_2 \qquad (1)$$

with the disproportionation constant:

$$K = \frac{\left[Mn(OAc)_2\right]\left[Mn(OAc)_4\right]}{\left[Mn(OAc)_3\right]^2}$$

Bronsdijk interpreted the kinetics of the oxidation of thioanisole by manganic acetate on the basis of this equilibrium, which was supposed to be established very rapidly.[2] K was calculated as 5.6×10^{-3} at $40^{\circ}C$, corresponding to a Mn(II)/Mn(total) or Mn(IV)/Mn(total) ratio of 7.5%, but a direct proof for the disproportionation was not obtained.

The disproportionation products would be expected to contaminate samples of manganic acetate in different and varying proportions, making the preparation of pure $Mn(OAc)_3$ impracticable.

We tried to verify the existence of equilibrium (1) by

a. examining the stability and detectability of Mn(IV) acetate in acetic acid solution, and

b. testing solutions of Mn(III) acetate for Mn(IV) acetate.

The detection of Mn(IV), rather than Mn(II) seemed the more reliable test for the disproportionation, as Mn(II) could equally well be formed as the product of some reduction reaction.

Chromatographic techniques were employed for the separation of the various manganese acetates.

II. 2. 2. PREPARATION AND DETECTION OF Mn(IV) ACETATE IN SOLUTIONS OF Mn(III) ACETATE.

The existence of tetravalent manganese acetates has been reported by several investigators.

Schönbein claimed the formation of $Mn(OAc)_4$ from Pb_3O_4 and $MnSO_4$ in acetic acid solution. [8])

Sem prepared solutions of Mn(IV) acetate by anodic oxidation of $Mn(OAc)_2$ in 70% acetic acid solutions, but the average oxidation state of Mn did not increase beyond 3. 6. [9])

Zonis and Pesina prepared samples of solid manganese tetraacetate by Sem's method and stated that the "percentage of active oxygen was 2.89, corresponding to 53% of the theory". [10]) As $Mn(OAc)_3 \cdot 2H_2O$ would require an active oxygen content of 2. 98%, it is doubtful whether their preparations contained any tetravalent Mn at all.

We could easily oxidise $Mn(OAc)_2$ beyond the trivalent stage by $KMnO_4$ or O_3 in acetic acid solution, but the maximum average oxidation state obtained was 3. 8. These higher-valent manganese acetates were characterised by fast-travelling spots (R_f = 0. 6 - 0. 7) on thin-layer silicagel plates, whereas manganic acetate was strongly retained.

With excess $Pb(OAc)_4$ the oxidation could not be carried beyond the Mn(III) stage.

From the oxidation products of $Mn(OAc)_2$ with O_3 we isolated by means of short-column chromatography a Mn(III-IV) complex of the approximate composition $MnO_2 \cdot Mn(OAc)_3$. This complex behaved on thin-layer silicagel plates as a single compound (R_f = 0. 7) and was, when freshly prepared, soluble in benzene (neither manganic acetate nor MnO_2 are soluble in benzene).

By prolonged ozonisation of $Mn(OAc)_2$ products could be obtained in which the average oxidation state of Mn was 3.8, but short-column chromatography of these products yielded the same Mn(III-IV) complex. Several other bands were observed which were much more strongly retained in the column and probably consisted in part of MnO_2 or oxidation products of the solvent.

Apparently Mn(IV) forms only stable solutions in acetic acid when complexed with sufficient Mn(III), and the species to be looked for as one of the disproportionation products of manganic acetate would be this Mn(III-IV) complex, rather than $Mn(OAc)_4$.

Saturated solutions of manganic acetate (0.25%) in acetic acid showed on thin-layer silicagel plates only a single spot of manganic acetate with R_f value 0.1, whereas with solutions of 0.25% manganic acetate and 0.001% Mn(III-IV) acetate the Mn(III-IV) acetate spot with R_f value 0.7 was clearly visible. It follows that, if manganic acetate disproportionates at all, the ratio Mn(IV)/Mn(III) is smaller than 1%. Consequently, disproportionation is very unlikely to be the cause of the variations in the oxidative equivalent of manganic acetate, although the stability of Mn(IV) as the Mn(III-IV) complex would not prohibit a reversible disproportionation reaction.

This conclusion was confirmed by De Klein, who demonstrated the absence of Mn(II) in solutions of manganic acetate by E.S.R. studies.[3])

II.2.3. EXPERIMENTAL.

Oxidation experiments. - Results are summarised in table 1. Three species of Mn are recognisable by their different retention times on thin-layer silicagel plates: Mn(II) with R_f=0.4 (colourless); Mn(III) with R_f=0.1 (reddish brown) and the Mn(III-IV) complex with R_f=0.7 (brown).

An average oxidation state of IV for Mn can apparently not be reached; with excess $KMnO_4$ or O_3 the solvent is severely attacked as evidenced by the oxidising capacity of the reaction mixture falling below 100% and the appearance of additional spots on the chromatograms.

Preparation of the Mn(III-IV) complex. - a. *From $KMnO_4$.* By shaking 17.5 mmole $Mn(OAc)_2$ with 7.5 mmole $KMnO_4$ in acetic acid for 20 min. and evaporating the solvent a dark brown residue was obtained which, on extraction with benzene, left 95% of the calculated quantity of KOAc as colourless crystals. On evaporation of the benzene the Mn(III-IV) complex was obtained as an amorphous product which we were unable to free from the last traces of K.

b. *By ozonization.* Ozone was passed into a solution of 1 g $Mn(OAc)_2$ in 50 ml AcOH till a drop of the reaction mixture showed only a very faint manganic acetate spot on a silicagel plate. The solvent was evaporated in vacuo and the residue, dissolved in $\frac{1}{2}$ ml AcOH passed through a 17 cm x 25 cm^2 silicagel column. The eluate containing the band with the smallest retention time (about 10 h) was collected, and after evaporation of the solvent in vacuo left the Mn(III-IV) complex as a brown amorphous product. Calcd for $Mn(OAc)_3 \cdot MnO_2$: Mn, 34.4; OAc, 55.5; equiv wt, 106; Found: Mn, 33.8; OAc, 54.0; equiv wt, 108.

On thin-layer silicagel plates the complex produced a single spot with R_f=0.7.

The second band had a retention time of about 13 h and corresponded with the spot with R_f=0.6 on the silicagel plates. The average oxidation state of Mn in the eluate containing this band was also

TABLE 1

OXIDATION OF $Mn(OAc)_2$ BY VARIOUS OXIDISING AGENTS.

Intake $Mn(OAc)_2$, mmole	Oxidising agent.	Intake oxidising agent, mmole	Reaction time, min.[b]	Average oxidation state of Mn on completion of reaction, calculated	Average oxidation state of Mn, found.[a]	Oxidising capacity of reaction mixture, % of intake oxidising agent.[a]	Chromatographic analysis of reaction mixture, Spots at R_f values: 0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0 [h]
1.5	none	-	-	2.0	-	-					+++(k)						
18.0	$KMnO_4$	2	10[c]	2.5	2.5	100		++			++(k)						
18.0	"	4.5	10	3.0	3.0	100		+++									
18.0	"	6	20	3.25	3.25	99		+++						++			
17.5	"	7.5	20	3.5	3.48	98		+					+	+++			
7.0	"	3	30	3.6	3.57	98		(+)					+	+++			
13.0	"	7	30	3.75	3.71	98							+	+++			
37.5	"	25	120[e]	4.0	3.79[f]	93[f]							++	+++			
15.0	"	15	300[e]	4.5	3.83[f]	88[f]					+ + + + + + +			+ +++(j)			
7.0[g]	"	3	20	3.6	3.57	98		(+)					+	+++			
7.0[g]	"	4.5	60	3.96	3.82	93					+		+	+++			
30.0	$Pb(OAc)_4$	15	5	3.0	3.0	100		+++									
15.0	"	15	60[e]	4.0	-	-		+++									
2.4	O_3	-	15	-	2.9	-		+++			++(k)						
2.4	"	-	30	-	3.2	-		++					+	++			
2.4	"	-	60	-	3.6	-		(+)			+ + + + + + + + + +			++(d)(j)			
2.4[l]	"	-	120	-	3.8	-			+ + + + + + + + + + + + + +					++(j)			

[a]) by iodometric titration.

[b]) time, required for complete dissolution of oxidising agent c.q. time during which O_3 was passed into solution.

[c]) gentle heating required to dissolve all $Mn(OAc)_2$.

[d]) black precipitate formed, analysis: 32.0% Mn(total), 54.7% OAc, oxidative equivalent: 107.5.

[e]) time after which undissolved oxidising agent was removed by filtration.

[f]) after making allowance for the quantity undissolved $KMnO_4$.

[g]) solvent: AcOH + 25% Ac_2O.

[h]) (+) very faint; + faint; ++ strong; +++ very strong.

[j]) severe tailing.

[k]) these spots were colourless and became only visible after spraying with benzidine and KOH.

[l]) solvent: AcOH + equal volume Ac_2O.

Reactions with $KMnO_4$ and $Pb(OAc)_4$ were carried out by shaking suspensions of the finely powdered reactants in 50 ml Baker A.R. glacial acetic acid.
In the ozonisation experiments oxygen containing about 5% O_3 was passed into well stirred solutions of $Mn(OAc)_2$ in 50 ml Baker A.R. acetic acid at a rate of about 5 $^{l}/_{h}$.
Thin-layer chromatograms were developed immediately after completion of the oxidation reactions. In all reaction mixtures precipitates formed after some time.

3.5. It seems no decomposition product of the above Mn(III-IV) complex, neither does it appear in solutions of Mn(III) or Mn(III-IV) acetate to which acetoxy acetic acid or succinic acid have been added. Its true nature was not established.

Chromatography. - 0.25 mm thin-layer silicagel plates, prepared in the usual way from Merck silicagel H, were pretreated by drying for 2 hours at 150°C in vacuo and storing over anhydrous acetic acid. On air-dried silicagel plates the Mn(III) and Mn(III-IV) acetates could not be separated due to tailing.

Spots of Mn compounds were detected by drying the plates and spraying with N KOH and 0.05% benzidine.[11]) Mn(III) and Mn(IV) spots, except those produced with the smallest concentrations were also recognisable by their brown colour.

The silicagel column for the separation of the Mn(III-IV) complex was prepared according to Rigby and Hunt[12]). Silicagel was Merck grade H (particle size 10-40 μ). According to the specifications this grade contains up to 0.03% Fe, which proved sufficient to interfere in the complexometric Mn determinations in the eluate. It was freed from Fe by extraction with 1:1 HCl at room temperature for 24 hrs, washing with demineralised water till acid-free, followed by drying at 150°C in vacuo. The column was operated under a pressure of 10 cm mercury; the flow rate was about 1 ml/min.

The eluent in all chromatography experiments was Baker A.R. glacial acetic acid.

Preparation of starting materials and analytical. - $Mn(OAc)_2$ was prepared by dehydrating $Mn(OAc)_2 . 4H_2O$ in vacuo at 100°C.

Manganic acetate, prepared according to section III.2, contained less than 0.01% Mn(II) as determined by the $KMnO_4$ titration of section II.3.2.b.

Acetic acid, used for making the manganic acetate solutions, was prepared according to chapter VI.

Lead tetraacetate was recrystallised from AcOH containing 5% Ac_2O and contained 97% $Pb(OAc)_4$ according to iodometric titration.

Potassium permanganate was A.R. quality containing 99.5% $KMnO_4$, according to iodometric titration. It was finely powdered and sieved to a maximum particle size of 0.2 mm.

The oxidising capacity of Mn(III) and Mn(III-IV) acetate solutions was determined iodometrically by adding a known volume of the solution to excess ice-cold 2% KI and titrating the iodine liberated with 0.05N thiosulphate using sodium starch glycollate as the indicator.

Complexometric titrations of Mn and OAc contents were performed according to section II.3.2. The Mn(III-IV) complex was brought into solution with a few drops H_2O_2 and a known quantity of 0.1 N $HClO_4$ which was taken into account in the calculation of the acetate content.

II. 3. CHEMICAL ANALYSIS OF Mn(III) ACETATE.

II. 3. 1. DISCUSSION.

In order to establish the nature of the constituents which cause the variations in the oxidative equivalent of manganic acetate we developed analytical methods for the determination of Mn(II), Mn(III) and Mn(IV) content, acetate-ion and total acetate content and oxide or hydroxide content.

a. The total Mn content was determined by complexometric titration with EDTA* by means of an adaptation of the method of Pribil.[13])

b. For determining Mn(II) in the presence of Mn(III) we employed the method of Lingane and Karplus, consisting of potentiometric titration of Mn(II) to Mn(III) in pyrophosphate solution with standard

* EDTA = ethylenediamine tetraacetate disodium salt.

$KMnO_4$.[14]) MnO_2 might interfere, but its presence in samples which contain $Mn(OAc)_2$ would seem unlikely.

c. The iodometric equivalent weight was determined in the usual way. The percentages Mn(III) and Mn(IV) can be calculated from the relations: 100 x at. wt. Mn = %Mn(III) x eq. wt. + 2 x %Mn(IV) x eq. wt., and: %Mn(total) = %Mn(III) + %Mn(IV).

The calculations are based on the assumption that Mn(II) and Mn(IV) are not both present in the same sample and that the samples contain no oxidising components but Mn(III) and Mn(IV).

d. Two methods were employed for determining the total acetate content, both based on the assumption that no other acidic constituents were present.

d. 1. The first method is an adaptation of Cheronis' procedure and consists of percolation of a suitably prepared solution of the sample through a strongly acidic ion exchange column, followed by titration of the free acetic acid in the percolate.[15])

d. 2. Because method d. 1. was rather time-consuming for routine-analysis we developed a second method for the determination of the total acetate content, consisting of complexing Mn with the calculated amount of EDTA and titration of the free acetic acid with standard barium hydroxide solution. The determination was carried out after converting all Mn to Mn(II). Sharp and reproducible end-points were observed, which agreed to within 0. 5% with the results of the ion-exchange method. It can be calculated that under the conditions of our determinations (pH = 9 and analytical Mn and EDTA concentrations about 10 mmole/l) hydrolysis of the Mn^{++} ion is negligeable.

e. In order to obtain information about the character of the acetate groups we titrated samples of manganic acetate in acetic acid solution with perchloric acid by the method of Casey and Starke, using a potentiometric end point detection.[16])

In simple acetates the acetate groups have ionic character and can be titrated as a weak base with perchloric acid in acetic acid solution. If manganic acetate is a complex salt, only part of the ace-

tate groups might be ionised, the others being covalently bound and not titratable as a base.

From the ratio of acetate-ion content to the total acetate content valuable information was gathered about the structure of manganic acetate (section IV. 3).

f. If samples of manganic acetate contained some basic acetate, a direct determination of the oxide and/or hydroxide content would be desirable. We converted manganic acetate, suspended in acetic acid, to $Mn(OAc)_2$ by means of anhydrous oxalic acid and titrated the water which was formed with Karl Fischer reagent.

As far as Mn was linked to acetate groups, only $Mn(OAc)_2$ and AcOH would be produced:

$$2\ Mn(OAc)_3 + H_2C_2O_4 \rightarrow 2Mn(OAc)_2 + 2AcOH + 2CO_2$$

but any OH groups or oxide functions would produce water:

$$2\ Mn(OH)(OAc)_2 + H_2C_2O_4 \rightarrow 2\ Mn(OAc)_2 + 2H_2O + 2\ CO_2, \text{ and:}$$

$$2\ MnO(OAc) + H_2C_2O_4 + 2\ AcOH \rightarrow 2Mn(OAc)_2 + 2H_2O + 2\ CO_2$$

The method is applied in section IV. 1.

g. Samples of manganic acetate, prepared from $KMnO_4$, were tested for K by the sodium cobaltinitrite test after conversion of all Mn to Mn(II). [11]) The large excess of Mn(II) did not interfere.

Samples of manganic acetate, prepared from $Pb(OAc)_4$ were tested for Pb with hydrogen sulphide.

The quantitative methods were tested on anhydrous manganous acetate and on manganic acetate dihydrate. Manganous acetate tetrahydrate was not suitable as a model substance because of variations in the water content. Results are summarised in table 2.

TABLE 2

Testing of the quantitative analytical methods on manganous acetate and hydrated manganic acetate.

	$Mn(OAc)_2$		$Mn(OAc)_3.2H_2O$	
	found	calculated	found	calculated
% Mn total	31.6	31.8	20.3	20.5
% Mn(II)	31.7	31.8	0.15	0.0
% Mn(III)	-	0.0	20.7	20.5
% OAc total (ion-exchange method)	68.2	68.2	66.2	66.1
" " (EDTA method)	67.9	68.2	66.4	66.1
% OAc ion	68.4	68.2	-	-
% O as oxide or hydroxide	-	-	13.5	13.4

II. 3. 2. EXPERIMENTAL.

Total Mn and total acetate content were determined in a solution "S" prepared as follows: a 1-g sample of manganic acetate was suspended in about 25 ml of water, all Mn was converted to Mn(II) by the addition of a few drops H_2O_2, and the volume was brought to 100 ml in a volumetric flask.

a. *Total Mn content.* - 20 ml of solution S were warmed with about $\frac{1}{2}$ g hydroxylamine hydrochloride to 80° and diluted to 100 ml. The solution was brought to pH 7 with conc. ammonia and after addition of the prescribed quantities of buffer solution, triethanolamine and eriochrome black titrated with 0.05 N EDTA. EDTA solutions were standardized on A.R. Zn pellets.

b. *Mn(II) content.* - A 1-g sample of manganic acetate was dissolved in 100 ml saturated $Na_4P_2O_7$ solution which had previously been brought to pH 7 with conc. H_2SO_4. The solution was again neutralized to pH 7 with KOH solution and titrated with 0.1 N $KMnO_4$, using Pt and calomel electrodes for the potentiometric end point detection.

c. *Iodometric equivalent.*-A 200-mg sample was added to 100 ml ice-cold 2% KI solution which had been acidified with 1 ml 2 N H_2SO_4. After the solid had dissolved the liberated iodine was titrated with 0.05 N thiosulphate using sodium starch glycollate as the indicator.

d.1. *Total acetate content, ion-exchange method.* - A column "Amberlite H 120" ion-exchange resin of 30 cm x 2 cm^2 was rinsed with CO_2-free demineralised water till the eluate contained less than 0.02 meq/l acid. A 10-ml portion of solution "S" was pipetted on top of the resin layer and allowed to percolate at a rate of about 2 ml/min. The column was washed with 100 ml CO_2-free demineralised water. The combined percolate was titrated with 0.05 N barium hydroxide solution in the usual way.

d.2. *Total acetate content, EDTA method.* - To a 20-ml sample of solution "S" (see above) a volume 0.05 N EDTA was added, exactly equal to the EDTA consumed in the Mn determination of the same solution (II.3.2.a.) The solution was then titrated with 0.05 N barium hydroxide in the usual way.

e. *Acetate-ion content.* - About 0.5 g manganic acetate was dissolved in 70 ml glacial acetic acid by heating to 80°C. After cooling to room temperature and adding 20 ml acetic anhydride a "Radiometer GK2021B" combined glass/calomel electrode was inserted and the solution rapidly titrated with 0.1 N $HClO_4$ in acetic acid.

The titration curves of manganic acetate did not show a very sharp potential break; determination of the equivalence point with a sensitivity of $\pm$ 2% was possible. As will be reported in chapter IV only ~12.5% of the total acetate content was found as acetate ion, corresponding to 1 acetate ion per 3 Mn atoms. Manganous acetate behaves in glacial acetic acid as a diacidic base, both acetate groups being ionised. Accordingly, even a small percentage of $Mn(OAc)_2$ as a contaminant in manganic acetate caused the result to be

much too high.

f. *Percentage O as oxide or hydroxide.* - Karl Fischer reagent was standardized on sodium tartrate dihydrate; detection of the end points was by the dead stop method.

A 8.5% solution of anhydrous oxalic acid in acetic acid was prepared and the water content determined by titration of 5-ml portions. About 13 g manganic acetate was suspended in 50 ml of this solution and gently warmed with stirring till the brown colour had disappeared. The bulky precipitate of $Mn(OAc)_2$ was allowed to settle and 2-ml portions of the clear supernatant solution were titrated with the Karl Fischer solution. Best results were obtained if these 2-ml portions were diluted with 10 ml methanol of known water content before the titration. The excess oxalic acid appeared to cause little esterification, end points being sharp and reproducible.

g.1. *Test for K.* - 1 mg manganic acetate was suspended in a drop of water on a microscopic slide. After converting Mn(III) to Mn(II) with a small drop 3% H_2O_2, a few crystals of sodium cobaltinitrite were added. A yellow precipitate indicated the presence of K. Test samples containing 0.05% K showed a clearly positive reaction.

g.2. *Test for Pb.* - 0.5 g manganic acetate was suspended in 5 ml water, all Mn was converted to Mn(II) with a drop of H_2O_2, and H_2S was passed into the solution. The appearance of a black precipitate indicated the presence of Pb.

Titrations were carried out with "Metrohm" piston burettes.

$Mn(OAc)_2$ as a test substance was prepared by recrystallising A.R. $Mn(OAc)_2 . 4H_2O$ from acetic acid containing 5% Ac_2O.

$Mn(OAc)_3 . 2H_2O$ was prepared according to Christensen.[17]) It should not be dried for a long period over KOH or quicklime, as Christensen recommends, because it slowly loses water as well as acetic acid and passes into a compound of the approximate composition MnO(OAc).

II. 4. DETERMINATION OF THE MOLECULAR WEIGHT OF MANGANIC ACETATE IN ACETIC ACID.

II. 4. 1. DISCUSSION.

In chapter III it will be reported that manganic acetate invariably contains about 2. 5% oxygen as oxide or hydroxide, corresponding to approximately 1 atom O per 3 $Mn(OAc)_3$ units. If this substance consists of a single compound a molecular weight of 640 would be required. The value found by De Korte from the depression of the freezing point in acetic acid was 228 ± 8.[1]) Therefore a re-determination of the molecular weight seemed desirable.

The hygroscopic character of manganic acetate and its thermal instability above 80°C limited the number of conventional procedures suitable for its molecular-weight determination to the cryoscopic method. The solubility of manganic acetate in anhydrous acetic acid is about 2, 5 g/l, corresponding to about 10 mat/1 Mn, which on the basis of a molecular weight of 640, would produce a maximum depression of the freezing point of 0.015°C.

If a reliable value for the molecular weight is to be deduced from freezing-point determinations, the total level of impurities in the solvent should, on a

molar basis, be far below the manganic acetate concentration. Accordingly the acid should contain far less than 10 mmole/l or 0.02% water. The preparation of high-purity acetic acid and the precautions to be taken in handling it are the subject of chapter VI of this thesis.

The molecular weight determinations are used in section IV.4 for establishing the trinuclear character of dissolved manganic acetate.

II.4.2. EXPERIMENTAL.

Freezing-point determinations were carried out in an atmosphere of dry nitrogen in an all-glass apparatus, consisting of a tall three-necked test tube equipped with air jacket, magnetic stirrer and Beckmann thermometer. The apparatus was protected against atmospheric moisture by drying tubes with "siccapent".

Portions of about 100 ml acetic acid, prepared according to section VI.3 were siphoned into the apparatus in a current of dry nitrogen. After cooling to 0.5°C below the freezing point crystallisation was induced by pressing a lump of solid carbon dioxide against the outside of the tube. The apparatus was then placed in a thermostatically controlled water bath which was kept at a temperature of 0.2°C below the freezing point of acetic acid. Temperature readings were taken at 1-min intervals and became constant after 5 min. There was no observable drift of the freezing point for at least 15 min.

Portions of about 125 mg manganic acetate were introduced through a nitrogen lock and dissolved by warming to 50°C. The freezing point was re-determined after cooling and saturating the liquid with dry nitrogen by vigorously shaking the contents of the tube.

The molecular weight of dissolved manganic acetate was calculated on the basis of a cryoscopic constant of 3.65°C kg mol^{-1} (section IV.4 and VII.8).

II.5 REFERENCES

1. R.W. de KORTE, Thesis, University of Leiden (1964).
2. J.M. BRONSDIJK, Thesis, University of Leiden (1965).
3. W.J. de KLEIN, Thesis, University of Leiden (1967).
4. R.E. van der PLOEG, Thesis, University of Leiden (1967).
5. R.G. SELIM and J.J. LINGANE, Anal. Chim. Acta 21, 536 (1959).
6. H. DIEBLER and N. SUTIN, J. Phys. Chem. 68, 174 (1964).
7. A.Y. DRUMMOND and W.A. WATERS, J. Chem. Soc. 1953, 435.
8. C.F. SCHÖNBEIN, J. Prakt. Chem. 74, 315 (1858).
9. M. SEM, Z. Elektrochemie 21, 426 (1915).
10. S.A. ZONIS and A.G. PESINA, J. Gen. Chem. USSR, 20, 1223 (1950).
11. F. FEIGL, "Qualitative analysis by spot tests", Elsevier, New York - Amsterdam (1947).
12. B.J. HUNT and W. RIGBY, Chem. Ind. (London), 1967, 1868.
13. R. PŘIBIL, Collect. Czech. Chem. Commun. 19, 465 (1954).
14. J.J. LINGANE and R. KARPLUS, Anal. Chem. 18, 191 (1946).
15. N.D. CHERONIS and T.S. MA, "Organic functional group analysis by micro and semi-micro methods", Interscience, London, 1964, p. 117.
16. A.T. CASEY and K. STARKE, Anal. Chem. 31, 1060 (1959).
17. O.T. CHRISTENSEN, J. Prakt. Chem. 28, 1 (1883).

CHAPTER III

PREPARATION OF ANHYDROUS MANGANIC ACETATE.

III. 1. DISCUSSION AND RESULTS.

Two methods for the preparation of anhydrous manganic acetate have been recorded in the chemical literature:

1. Späth claimed the preparation of anhydrous $Mn(OAc)_3$, $Cr(OAc)_3$ and $Fe(OAc)_3$ by the action of acetic anhydride on the corresponding hydrated metal nitrates. The reported analyses agreed with the expected values for metal and acetate contents. [1])

Weinland and Reihlen criticised Späth's paper as far as $Fe(OAc)_3$ and $Cr(OAc)_3$ were concerned and showed that with these metals not the neutral acetates but trinuclear basic acetates are formed. [2])

Chretien and Varga employed Späth's method for the preparation of anhydrous manganic acetate which they used as a starting material for their preparation of $MnCl_3$. [3]) Their procedure has been recommended by Brauer in his "Handbuch der praeparativen anorganischen Chemie". [4])

2. The second method is based on Christensen's procedure, who obtained the dihydrate by oxidising $Mn(OAc)_2$ with $KMnO_4$ in glacial acetic acid, adding "a few cc. of water to facilitate crystallisation". [5])

De Korte, den Hertog, Bronsdijk, De Klein and Van der Ploeg carried out the reaction in the presence of excess acetic anhydride and obtained anhydrous manganic acetate, but the iodometric equivalent of their preparations varied from 220 to 240, whereas $Mn(OAc)_3$ would require a value of 232.

We analysed the products obtained by both methods under a wide variety of reaction conditions. When we were unable to obtain preparations of the empirical formula $Mn(OAc)_3$, we also studied the products formed by the oxidation of $Mn(OAc)_2$ with $Pb(OAc)_4$ and O_3. Finally we examined the effect of recrystallisation on samples of manganic acetate of various compositions.

The results, summarised in tables 3, 4, 5, 6 and 7 lead to the following conclusions:

1. Preparations of approximately the same composition can be obtained by oxidation of $Mn(OAc)_2$ with $KMnO_4$, O_3 and $Pb(OAc)_4$, by the reaction of hydrated Mn(II) nitrate with Ac_2O and by recrystallisation of Mn(III) acetate of various origins.

2. These products are practically free from Mn(II) provided the temperature is not raised above 90°C in the presence of excess Ac_2O.

3. Products of a composition corresponding to the formula $Mn(OAc)_3$ (calculated: 23.7% Mn; 76.3% OAc) cannot be obtained under the present conditions. The total of acetate and manganese contents falls invariably a few percent short of 100%.

4. Mn(total) and OAc contents of preparations, obtained at 80°C or higher, and with excess Ac_2O, correspond to the empirical formula $Mn_3(OAc)_8OH$.

Products obtained at lower temperatures and with less Ac_2O tend to have higher acetate and lower manganese contents; their composition seems to depend strongly on small changes in the reaction conditions. In some cases the analyses correspond closely to the formula $Mn_3(OAc)_8OH$. AcOH.

Manganic acetate, obtained at low temperatures (typical analysis: 23.1% Mn; 74.0% OAc) was usually microcrystalline and lost 3-5% of its acetic acid when stored for a month in vacuo over KOH. This loosely held acetic acid is not merely absorbed, but forms part of the crystal structure as is apparent from the fact that X-ray powder diagrams of these preparations are different from those of manganic acetate obtained at 80°C.

Manganic acetate obtained at about 80°C in the presence of Ac_2O precipitated as larger crystals and could be dried at 50°C in vacuo without loss of weight. It was therefore selected for our further investigations.

In the remaining part of this thesis the name manganic acetate refers to this product (typical analysis: 25.3% Mn, 72.0% OAc).

The recommended procedure for its preparation is given in the experimen-

TABLE 3

OXIDATION OF Mn(II) ACETATE TO Mn(III) ACETATE BY $KMnO_4$ UNDER VARIOUS CONDITIONS.

REACTANTS			SOLVENT				ANALYSIS OF PRODUCT.						
mmole $Mn(OAc)_2$	mmole $Mn(OAc)_2.4H_2O$	mmole $KMnO_4$	ml AcOH	ml Ac_2O	Reaction temperature, °C	Temperature during crystallisation, °C	% Mn(II)	% Mn(III)	% Mn(total)	% OAc	% (Mn + OAc)	apparent % $Mn(OAc)_3$ (a)	
	20	5	50	15	50 - 118	20	2.0	22.3	24.2	72.7	96.9	94.2	
	20	5	70	100	75 - 95	20	0.15	23.0	23.3	74.5	97.8	97.0	
	20	5	50	15	70	20	0.1	23.2	23.3	73.9	97.2	98.3	
	20	5	50	10	40	20		23.6	23.5	73.4	96.9	99.5	
	20	5	50	12	20	20		22.8	22.7	74.4	97.1	96.2	
	20	5	25	10	20	20			23.5	73.7	97.2		
	20	5	25	15	20	20			23.0	74.8	97.8		
	20	5	40	15	20	20		24.9	24.8	73.0	97.8	105.0	
	20	5	50	20	20	45		24.7	24.5	73.2	97.7	104.2	
	20	5	65	10	20	70	0.01		25.1	72.4	97.5	105.9	
	20	5	65	20	20	70	0.01		24.9	71.8	96.7	105.1	
	20	5	25	11	20	60	0.01		25.0	72.4	97.4	105.5	
	20	5	25	15	20	80			25.2	72.4	97.6		(b,c)
						20	12.8	12.3	25.0	74.6	99.6	51.9	(d)
	20	4.75	50	12	20	20	0.1	22.8	22.9	74.4	97.3	96.2	
	20	5.25	40	12	20	20		23.1	23.2	75.0	98.2	97.9	
	20	5	50	0									(e)
20		5	50	0	20	20		23.8		74.0	97.8	99.7	(f)
20		5	70	0	118	20	0.06		23.3	73.7	97.0	98.4	
20		5	75	15	80	80	0.1	25.3	25.1	72.0	97.1	106.7	(g)
20		5	40	10	50	20			23.1	73.5	96.6	97.5	
20		5	42	8	20	20		23.1	23.1	73.7	96.8	97.5	
20		5	30	4	20	20	0.16	24.1	24.1	72.6	96.7	101.7	
							0.1		25.3	72.2	97.5	106.8	(h)
20		5	30	10	20	5		26.2	26.3	66.2	92.5	110.7	
20		5	40	6	20	20	0.01	22.8	23.0	73.7	96.7	97.1	(b)
								23.1	23.1	73.6	96.7	97.5	(d)
								23.4	23.1	74.0	97.1	97.5	(h)
								25.4	23.9	73.2	97.1	100.8	(i)
Calculated for $Mn(OAc)_3$:							0.0	23.7	23.7	76.3	100.0	100.0	
Calculated for $Mn_3(OAc)_8OH$:							0.0	25.2	25.2	72.2	97.4	106.3	
Calculated for $Mn_3(OAc)_8OH.AcOH$:							0.0	23.1	23.1	74.4	97.5	97.5	

(a) calculated on the basis of the iodometric equivalent.

(b) first fraction.

(c) mixture kept at 80°C for 7 hrs.

(d) second fraction.

(e) after several days only traces of a brown colloidal precipitate obtained.

(f) yield only 60%.

(g) mixture kept at 80°C for 1 hr.

(h) third fraction.

(i) fourth fraction.

TABLE 4

REACTION PRODUCTS OF $Mn(NO_3)_2 \cdot 6H_2O$ and Ac_2O.

Reactants and solvent $Mn(NO_3)_2 \cdot 6H_2O$ mmole	Ac_2O ml	AcOH ml	Reaction conditions	Temperature during crystallisation °C.	Analysis of products. % Mn(II)	% Mn(III)	% Mn(total)	% OAc	%(Mn+OAc)	% $Mn(OAc)_3$ (apparent) (a)
35	40	0	Mixture heated to induce reaction, then left to cool to ambient temperature	20	0.2	22.5	22.8	73.0	95.8	95.0
duplicate experiment :			do	20	0.1	22.0	22.0	72.8	94.8	92.8
35	60	0	do	20	0.2		22.6	73.2	95.8	94.6
35	90	0	do	20	13.1	13.0	25.9	73.0	98.9	54.8(b)
					3.5		24.9	72.2	97.1	90.4(c)
35	160	0	mixture kept at 60°C for 90 min.	60 - 20	0.1	23.2	23.2	73.4	96.6	97.9
35	40	0	mixture kept at 120°C for 8 min. after reaction had subsided	20			24.7	69.2	93.9	(d)
							19.2	67.2	86.4	(e)
30	13	50	mixture boiled for 2 min.	20	0.3		22.8	74.7	97.5	95.0(f)

(a) calculated on the basis of the iodometric equivalent.

(b) first fraction.

(c) second fraction.

(d) second fraction, obtained after ten days; a first fraction of 2.5 g $Mn(OAc)_2$ precipitated in the course of the first five days and was removed by filtration.

(e) obtained after evaporation of most of the solvent.

(f) second fraction, obtained after ten days; a first fraction of 2 g $Mn(OAc)_2$ precipitatted in the course of the first four days and was removed by filtration.

TABLE 5.

OXIDATION OF $Mn(OAc)_2$ to Mn(III) ACETATE by $Pb(OAc)_4$ UNDER VARIOUS CONDITIONS.

Reactants		Solvent		Reaction temp.	temp. during	Analysis of products.					
$Mn(OAc)_2$, mmole	$Pb(OAc)_4$, mmole	AcOH, ml	Ac_2O ml	°C	Crystallisation, °C	% Mn(II)	% Mn(III)	% Mn(total)	% OAc	%(Mn+OAc)	% $Mn(OAc)_3$ (apparent) (a)
20	10	50	2	20	20	0.01	23.6	23.5	74.0	97.5	99.6
20	20	80	3	118	20		22.9	22.8	74.3	97.1	96.8
20	10	50	5	20	20			24.3	72.9	97.2	102.5
20	10	40	0	118	118 - 20			24.3	71.5	95.8	102.5

(a) calculated on the basis of the iodometric equivalent.

TABLE 6.

OXIDATION OF $Mn(OAc)_2$ TO Mn(III) ACETATE BY O_3 UNDER VARIOUS CONDITIONS.

Intake $Mn(OAc)_2$, mmole (a)	AcOH ml	Ac_2O ml	H_2O ml	Time during which O_3 was passed into the solution, min.	Ac_2O added after passing O_3 into the the solution, ml	Temperature during crystallisation, °C	Analysis of products				
							% Mn(III)	% Mn(total)	% OAc	%(Mn+OAc)	apparent % $Mn(OAc)_3$ (b)
55	100	0	0	60	0	20	23.5	23.5	73.1	96.6	99.2(c)
55	100	10	0	60	0	20		24.0	72.4	96.4	(c)
55	100	0	4.5	60	25	20		33.8	52.2	86.0	(d)
55	100	0	4.5	60	25	20		24.2	73.1	97.3	(e)

(a) $Mn(OAc)_2$ obtained by dehydration of $Mn(OAc)_2.4H_2O$ in vacuo at 100°C.

(b) Calculated on the basis of the iodometric equivalent.

(c) precipitate fromed during ozonisation.

(d) mixture was homogeneous at the end of the ozonisation period, precipitate began to form after about 24 hours; its oxidative equivalent was 104, corresponding to an average oxidation state of 3.56 for Mn.

(e) the average oxidation state of Mn in the homogeneous solution at the end of the ozonisation period was determined by complexometric and iodometric titration. Then an amount of $Mn(OAc)_2$ was added, equal to the quantity calculated for converting all Mn to Mn(III).

TABLE 7.
RECRYSTALLISATION OF MANGANIC ACETATE.

SOLVENT							Analysis of starting material and of recrystallised product.					
Intake crude manganic acetate, g.	AcOH, ml.	H_2O, ml.	Ac_2O, ml.	Temperature at which crude material was dissolved, °C	Time of heating, min.	Ac_2O added after dissolution crude material, ml.	Temperature during crystallisation, °C.	% Mn(II)	% Mn(total)	% OAc	% (Mn+OAc)	apparent % $Mn(OAc)_3$ (a)	
				Crude material:				<0.1	23.8	73.3	97.1	100.5	
1.2	100	-	-	70	60	-	70-20	<0.1	23.0	73.5	96.5	97.0	
				Crude material:				<0.1	23.0	73.7	96.7	97.0	
1.0	100	-	-	60	90	-	60	<0.1	24.8	72.1	96.9	104.7	
1.0	90	-	10	60	90	-	60	<0.1	24.9	71.7	96.6	105.0	
				Crude material:				<0.1	25.2	72.2	97.4	106.3	
4.0	100	-	-	118	5	-	118-20	<0.1	25.1	72.0	97.1	105.8	
4.0	100	-	-	118	5	5	118-20	0.1	25.1	71.8	96.9	105.8	
4.0	97	-	3	118	60	-	118-20	0.7	23.4				
				Crude material:				0.1	23.3	73.5	96.8	98.4	
4.0	90	-	10	118	1	-	60	0.1	25.2	72.5	97.7	106.3	
4.5	100	0.4	-	118	1	-	20	<0.1	23.0	74.7	97.7	97.0	
4.5	100	0.4	-	118	1	40	118-20	0.1	24.6	72.2	96.8	103.8	
				Crude material:				0.1	24.1	72.6	96.7	101.7	
4.0	100	-	-	118	20	-	70	<0.1	25.1	71.8	96.9	105.8	
do	do			do	do	-	20	<0.1	25.1	71.7	96.8	105.8	
				Crude material:				<0.1	28.5	59.7	88.2	120.0	(b)
6.0	100	-	-	20	-	30	20	<0.1	25.0	71.6	96.6	105.5	
6.0	100	-	10	20	-	-	20	<0.1	24.8	72.3	97.1	104.7	
6.0	100	-	10	20	-	-	70	<0.1	25.3	72.4	97.7	106.8	
				Crude material:				0.1	24.7	73.7	98.4	104.2	
4.0	100	0.4	-	118	1	-	20	<0.1	22.9	74.6	97.5	96.6	
				Crude material:				0.2	20.3	66.6			(c)
10.0	100	-	-	80	5	-	-						(d)
10.0	100	-	-	80	5	10	20	0.1	22.7	75.0	97.7	95.8	
35.0	100	-	-	80	15	30	20	0.1	22.4	75.1	97.5	94.5	
do	do	-	-	do	do	do	60	<0.1	24.8	72.7	97.5	104.7	
do	do	-	-	do	do	do	70	<0.1	25.0	72.7	97.7	105.5	
				Crude material:					23.0	74.8	97.8	97.0	
30	100	4	-	50	30	70	70	<0.1	24.8	72.6	97.4	104.7	
30	100	4	-	80	10	70	40	<0.1	24.8	72.6	97.4	104.7	
do	do	do	-	do	do	do	20	0.1	24.8	72.3	97.1	104.7	
30	100	3.3	-	80	30	70	90	0.2	25.1	72.5	97.6	105.8	(e)
do	do	do	-	80	30	70	80	0.5	25.1	72.3	97.4	105.8	(f)
30	100	5.0	-	60	20	30	80	0.1	25.0	72.2	97.2	105.5	
Calculated for $Mn(OAc)_3$:								0.0	23.7	76.3	100.0	100.0	
Calculated for $Mn_3(OAc)_8OH$:								0.0	25.2	72.2	97.4	106.3	
Calculated for $Mn_3(OAc)_8OH.AcOH$:								0.0	23.1	74.4	97.5	97.5	

(a) calculated on the basis of the iodometric equivalent.

(b) samples of manganic acetate which had been exposed to the atmosphere for a week.

(c) manganic acetate dihydrate.

(d) only traces of a brown colloidal precipitate obtained.

(e) mixture kept at 90°C for 3 hours.

(f) " " " 80°C " 5 " .

tal part of this chapter.

The solubility behaviour of manganic acetate in acetic acid of various water contents is noteworthy. In dry acetic acid the solubility of anhydrous manganic acetate is less than 3 g/l at room temperature. On addition of water the solubility increases rapidly; in acetic acid containing about 2% H_2O more than 150 g/l anhydrous manganic acetate can be dissolved. Increasing the water content still further results in precipitation of the dihydrate; its solubility in acetic acid containing about 10% H_2O is almost negligeable. Manganic acetate dihydrate can be dissolved in dry acetic acid by gentle warming to concentrations of more than 160 g/l. On cooling these solutions no precipitates are obtained; the amount of water introduced (about 20 g per l solvent) is apparently sufficient to prevent precipitation. On addition of 50 - 80 ml water per l solvent the dihydrate is recovered. Adding Ac_2O results in precipitation of the anhydrous salt. These properties were utilized in the purification of manganic acetate (section III. 2) and in the preparation of crystals suitable for X-ray analysis (section V. 2).

III. 2. EXPERIMENTAL.

General. - Acetic acid, acetic anhydride and manganous nitrate were AR reagents; other starting materials were the same as in section II.2.3. Analyses were carried out as indicated in section II.3.

Oxidation of $Mn(OAc)_2$ by $KMnO_4$ (table 3). - Christensen carried out the reaction at the boiling point of acetic acid[5]), and this has been the common practice for preparing the dihydrate[11]) as well as the anhydrous salt[6-10]). We found that the oxidation proceeds smoothly at room temperature, provided the solid reactants are finely powdered. $Mn(OAc)_2$, obtained by dehydrating the tetrahydrate at 100°C in vacuo is preferable to recrystallized $Mn(OAc)_2$ because of its higher solubility in acetic acid.

Reactions at room temperature were carried out by shaking the suspensions of the reactants in a conical flask for 10 - 30 min, when dark brown homogeneous solutions were obtained.

Reactions at higher temperatures were carried out by stirring the reactants for 1 - 2 hours.

At room temperature it took about a week for the products to precipitate completely; at higher temperatures precipitation was complete in a few hours.

The precipitates, obtained in 70 - 90% yields were thoroughly washed with AcOH and dried in vacuo on KOH for 24 hours. Tests on K were negative.

Reactions between $Mn(NO_3)_2.6H_2O$ and Ac_2O (table 4). - According to Späth[1]) 10 g $Mn(NO_3)_2.6H_2O$ are heated in 40 ml Ac_2O till the reaction starts. After the reaction has subsided the solution is heated for a further 8 min. and cooled to room temperature. After several hours 2.2 g $Mn(OAc)_2$ have precipitated, which are removed by filtration, and from the filtrate 6.6 g manganic acetate crystallize in the course of some days.

Chretien and Varga heated a mixture of the same composition till the reaction started but omitted the additional heating period. They did not obtain $Mn(OAc)_2$ as the first fraction of the precipitate and claimed a yield of 85% $Mn(OAc)_3$.[3])

We found that a mixture of the specified composition did not react below 60°C. The reaction, once started, was of almost explosive violence and could hardly be kept under control. Increasing

the proportion of Ac_2O or diluting the mixture with AcOH had a moderating influence. We suspect the precipitates to be contaminated with succinic acid, which is the main reaction product when Ac_2O is allowed to react with manganic acetate above 80°C (chapter VII).

Precipitates, obtained in 40 - 70% yields were thoroughly washed with AcOH and dried in vacuo over KOH for 24 hours.

Oxidation of $Mn(OAc)_2$ by $Pb(OAc)_4$ (table 5).- Reactions at room temperature were carried out by shaking the reactants in a conical flask for 10 min. when dark brown homogeneous solutions were obtained. Reactions at higher temperatures were carried out by stirring the reactants for 1 - 2 hours. Precipitates, obtained in 50 - 70% yields, were thoroughly washed with AcOH and dried in vacuo over KOH for 24 hours. All manipulations with the precipitates were carried out in a drybox. Tests on Pb were very faintly positive.

Oxidation of $Mn(OAc)_2$ by Ozone (table 6). - Oxygen containing about 5% O_3 was passed at room temperature into the well stirred solutions of $Mn(OAc)_2$ at a rate of about 20 l/hr. Products, obtained in 40 - 70% yield were thoroughly washed with AcOH and dried in vacuo over KOH for 24 hours.

Recrystallization of manganic acetate (table 7). - Samples of manganic acetate prepared in different ways, but of approximately the same composition yielded the same products when recrystallized in the same way. Precipitates, obtained in 60 - 90% yields were thoroughly washed with AcOH and dried in vacuo over KOH for 24 hours.

Preparation of anhydrous manganic acetate. - A suspension of 34.6 g finely powdered $Mn(OAc)_2$ (0.2 mole) and 7.9 g finely powdered $KMnO_4$ (0.05 mole) in 150 ml glacial acetic acid is shaken in a 250 ml stoppered conical flask for 30 min or until the solids have dissolved. The solution is filtered through a G3 fritted filter crucible and after addition of 30 ml acetic anhydride (0.3 mole) heated to 75°C for 2 hours. After cooling to ambient temperature the mixture is set aside for 24 hours to allow manganic acetate to precipitate completely. The dark brown crystalline product is filtered on a fritted glass Büchner funnel, extracted with 100 ml warm glacial acetic acid to remove potassium acetate and dried for 2 hours in vacuo at 50°C. The yield is 49 g (90%).

The product may be purified as follows: 40 g manganic acetate are dissolved in a mixture of 150 ml AcOH and 7 ml H_2O by gentle warming. After filtration 45 ml acetic anhydride are added and the solution is kept at 70°C for 4 hours. After cooling to ambient temperature the precipitate is filtered on a fritted glass Büchner funnel, washed with 100 ml warm glacial acetic acid and dried at 50°C in vacuo for 2 hours. The yield is 32 g (80%).

III.3. REFERENCES

1. E. SPATH, Monatsh. Chem. 33, 242 (1912).
2. R. WEINLAND and H. REIHLEN, Z. Anorg. Chem. 82, 426 (1913).
3. A. CHRETIEN and G. VARGA, Bull. Soc. Chim. Fr. 3, 2386 (1936).
4. G. BRAUER, "Handbuch der praeparativen anorganischen Chemie", Bd. II, Ferdinand Enke Verlag, Stuttgart, 1960, p. 1282.
5. O.T. CHRISTENSEN, Z. Anorg. Chem. 27, 321 (1901).
6. R.W. de KORTE, Thesis, University of Leiden (1964).
7. H.J. den HERTOG, Thesis, University of Leiden (1964).
8. J.M. BRONSDIJK, Thesis, University of Leiden (1965).
9. W.J. de KLEIN, Thesis, Leiden (1967).
10. R.E. van der PLOEG, Thesis, Leiden (1967).
11. P.J. ANDRULIS, M.J.S. DEWAR, R. DIETZ, R.L. HUNT, J. Am. Chem. Soc. 88, 5473 (1966).

CHAPTER IV

THE SUPPOSED STRUCTURE OF MANGANIC ACETATE.

IV. 1. THE EVIDENCE FOR AN OXIDE BRIDGE BETWEEN THE Mn ATOMS.

According to section III. 1. the analysis of manganic acetate (25.3% Mn, 72.0% OAc, 2. 7% unaccounted for) is compatible with the empirical formula $Mn_3(OAc)_8OH$.

Our acetate determinations were based on the assumption that apart from acetate groups no other potentially acidic constituents were present. When we prepared manganic acetate from precisely equivalent proportions $KMnO_4$ and $Mn(OAc)_2$, neither the precipitate nor the mother liquor contained detectable traces of Mn(II). This means that the solvent was not oxidised to any appreciable extent and that the only organic components which could be present were acetate groups and/or groups of the same oxidation level as acetic acid.

The Karl Fischer titration, performed according to section II. 3. 2. f. yielded an oxygen content of 2.6%, which raised the percentage of components accounted for to 99.9% and was in reasonable agreement with the formula $Mn_3(OAc)_8OH$ (calc. : 2. 45% O).

The presence of OH groups bound to Mn seems not very likely under the conditions of our experiments. Most probably therefore, there is an oxygen atom present as a bridge between 2 or 3 manganese atoms.

IV. 2. THE EVIDENCE FOR ACETIC ACID MOLECULES IN MANGANIC ACETATE.

If manganic acetate is a trinuclear complex containing an oxygen bridge,

the Mn atoms would be able to bind only 7 acetate groups and consequently the complex should contain one molecule of acetic acid.

Infra-red spectra of our samples showed a strong sharp maximum at 1710 cm^{-1}, which is the same wave number as observed for the C=O stretching vibration in liquid acetic acid.* The maximum persisted undiminished under strictly anhydrous conditions, in KBr and KCl discs as well as in mulls with nujol or polychlorotrifluoroethylene.

Taking into account that our samples did not lose any acetic acid when kept in vacuo at 50°C for several hours, we considered this maximum as an indication for the presence of acetic acid molecules in the crystal structure of manganic acetate.

IV. 3. THE CHARACTER OF THE ACETATE GROUPS IN MANGANIC ACETATE.

In the preceding sections it was made plausible that one of the eight OAc groups in manganic acetate is present as an acetic acid molecule. In order to examine whether there is any further differentiation in the character of the remaining seven OAc groups we titrated manganic acetate with perchloric acid in acetic acid solution according to section II. 3. 2. e.

The acetate-ion content, determined in this way amounted to 9. 1 ± 0. 2%. The total percentage of OAc groups was 72. 0 (section III. 1), accordingly only one out of the total number of eight acetate groups is capable of dissociation, the others being covalently bound.

The equivalent conductivity of a 0. 006 molar solution in acetic acid was 0. 05 mho cm^2/mole, comparable with that of sodium acetate (0. 06 mho cm^2/mole for a 0. 02 molar solution) and considerably higher than that of manganous acetate (0. 02 mho cm^2/mole for a 0. 02 molar solution). [6])

Similar cases in which only part of the acetate groups in a complex salt could be titrated with perchloric acid have been reported by Casey and Starke for iron, aluminium and chromium compounds. [2])

* Infra-red spectra were recorded on a Beckmann IR-10 spectrophotometer. The IR spectrum of manganic acetate of different composition was recorded and interpreted by De Klein. [1]) He observed a strong maximum at 1730 cm^{-1} and assigned it to the C=O stretching vibration of free acetic acid. The IR spectrum reported by De Klein resembled the spectra which we recorded for our samples of higher acetate content.

IV. 4. THE MOLECULAR WEIGHT OF MANGANIC ACETATE.

All information gathered so far pointed to a trinuclear complex of the empirical formula $Mn_3(OAc)_8OH$. The only discrepancy was the molecular weight of 228 ± 8, found in earlier studies[3]); the above formula would require a value of 654.

We redetermined the molecular weight in acetic acid of high purity according to the procedure of section II. 4. and found a value of 640 ± 75. Although the accuracy of this figure is not very high, the trimeric character of manganic acetate is clearly confirmed.

IV. 5. CONCLUSION.

On the basis of the arguments in the preceding sections manganic acetate could be represented by the formula:

$$\left[Mn_3O(OAc)_6\right]^+\left[OAc\right]^- . AcOH$$

The composition of the cation suggests trigonal symmetry, which would involve a central O atom surrounded by three Mn atoms in a plane. The six acetate groups would form three pairs of bridges between the Mn atoms above and below this plane.

In crystalline manganic acetate the seventh acetate group might bridge two Mn atoms from two different trinuclear units so that with one acetic acid molecule the octahedral coordination shells of all Mn atoms would be filled. The polymeric structure formed in this way could be represented by the formula:

$$\left[Mn_3O(OAc)_6 . AcOH . AcO\right]_n$$

In solution the octahedral coordination about the Mn atoms might be completed, either by the acetate ion together with two acetic acid molecules or by three acetic acid molecules. In the latter case the best representation would be:

$$\left[Mn_3O(OAc)_6 . 3AcOH\right]^+\left[OAc\right]^-$$

Comparable trinuclear complexes have been observed with the hydrated acetato chlorides of Fe and Cr.[4,5]) The complex cations of these compounds

have the same structure as suggested above for manganic acetate but the octahedral coordination of the metal atoms is completed by water in stead of acetic acid molecules, and the anion is a chloride ion.

The evidence on which the proposed structure is based is summarized in table 8.

TABLE 8

ANALYTICAL EVIDENCE FOR THE STRUCTURE OF MANGANIC ACETATE.

	Calculated for $\left[Mn_3O(OAc)_6 . AcOH . OAc\right]_n$	found
Percentage Mn (total)	25.2	25.3
" OAc "	72.2	72.0
" OAc(ionic)	9.0	9.1
" O (as oxide or hydroxide)	2.45	2.6
Molecular weight in solution	654	640 $\pm$ 75
Acetic acid	one molecule	evidence from IR spectrum.

IV.6. REFERENCES

1. W.J. de KLEIN, Thesis, University of Leiden (1967).
2. A.T. CASEY and K. STARKE, Anal. Chem. 31, 1060 (1959).
3. R.W. de KORTE, Thesis, University of Leiden (1964).
4. K. STARKE, J. Inorg. Nucl. Chem. 13, 254 (1960).
5. A. EARNSHAW, B.N. FIGGIS and J. LEWIS, J. Chem. Soc. 1966, 1656.
6. I.M. KOLTHOFF and A. WILLMAN, J. Am. Chem. Soc. 56, 1007 (1934).

CHAPTER V

X-RAY ANALYSIS OF MANGANIC ACETATE*.

V. 1. INTRODUCTION.

In the preceding chapter substantial evidence was brought forward for the trinuclear character of manganic acetate, but the structure proposed for the $Mn_3O(OAc)_6$ - unit was largely hypothetical.

Because of our investigation into a possible concerted mechanism for the thermal decomposition of manganic acetate the spatial arrangement of the acetate groups with respect to the manganese atoms in dissolved manganic acetate had our special interest. The value of 640 for the molecular weight of manganic acetate, found by the cryoscopic method, suggests that the $Mn_3O(OAc)_6$ - unit remains intact on dissolution in acetic acid. We therefore considered it worth while to attempt a structure determination of crystallised manganic acetate by X-ray analysis.

V. 2. EXPERIMENTAL.

Preparation of single crystals. - Crystals suitable for X-ray analysis were obtained by dissolving 2 g manganic acetate in 50 ml AcOH containing 1% H_2O. After addition of 3 ml Ac_2O the mixture was kept at 85°C for 36 hours. On filtration of the hot solution 0.3 g manganic acetate was obtained in the form of lath-shaped crystals from which a few suitable single crystals could be selected. Analysis: 25.1% Mn(total); 72.5% OAc(total).

Specimens on which diffraction-intensity measurements were taken measured about 0.6 mm x 0.07 mm x 0.01 mm.

* The investigations in this chapter were carried out under the supervision of Dr C. Romers.

Photographs. - Oscillation photographs about the needle axis (to be called c) were taken with Ni-filtered Cu K_α radiation.

For the determination of unit-cell dimensions equatorial Weissenberg photographs 0kl and hk0 were taken with unfiltered copper radiation ($\lambda(\alpha_1) = 1.5405$ Å). The photographs were superposed with aluminium powder lines for calibration.

For intensity measurements equi-inclination Weissenberg photographs hk0 - hk8, 0kl, and 1kl were taken with V-filtered Cr K_α radiation ($\lambda(\alpha_1) = 2.2935$ Å) at room temperature. Exposure times were 40 - 80 hours. In order to prevent decomposition the crystals had to be coated with paraffin oil and were sealed in lithium borate capillaries.

Due to extraneous scattering by the capillary wall, coating liquid and air in the camera the quality of the photographs was poor. Chromium radiation was used in stead of copper radiation in order to avoid anomalous scattering, but the question arises whether the gain in quality outweighs the disadvantage of the longer exposure time necessitated by the softer character of the chromium radiation.

There was no serious loss in resolution due to the longer wavelength of chromium radiation because films exposed with copper radiation "died out" near $\theta = 50^\circ$.

Intensity measurements and processing of data. - Relative intensities were estimated visually by the multiple film technique and comparison with an intensity scale. The intensity range was 1 to 2700.

Corrections for Lorentz and polarization effects were made but the quality of the films did not warrant the application of absorption corrections.

The number of independently observed reflexions was 1157, i.e. 68% of the reflexions possible within the chromium reflexion sphere.

Initial scaling and temperature factors were obtained by Wilson's method. Scaling factors employed in the structure determination were the averages of the Wilson scaling factors and factors obtained by comparing common reflexions on photographs of different reciprocal lattice layers.

All relevant calculations in this chapter were carried out on the I.B.M. 360-50 computer of the "Centraal Rekeninstituut", University of Leiden.

V. 3. UNIT CELL, SPACE GROUP AND MOLECULAR WEIGHT.

From the symmetry and systematic extinctions on the oscillation photographs about c and the hk0 and hk1 equi-inclination Weissenberg photographs it was concluded that manganic acetate crystallises in the orthorhombic space group Pbca with eight molecules in general position or four molecules at centra of symmetry in the unit cell.

Unit-cell dimensions were determined from 47 reflexions on the 0kl and hk0 Weissenberg photographs and refined by the least squares method.

Cell dimensions with their standard deviations are, at room temperature:

$a = 16.07 \pm 0.03$ Å

$b = 19.84 \pm 0.03$ Å

$c = 15.80 \pm 0.02$ Å

Volume $V = 5037 \pm 20$ Å^3

The density, determined by the flotation method in CH_3I - CCl_4 mixtures was 1.75 g cm^{-3}.

On the basis of these data a molecular weight of 663 ± 10 for a-centric or

1326 ± 20 for centrosymmetric molecules would be calculated. Afterwards it will be shown that the structure consists of polymer chains of a-centric units. Accordingly the corresponding monomeric unit weight is 663 ± 10 (calculated for $Mn_3O(OAc)_6$. AcOH. OAc:654).

V. 4. PATTERSON FUNCTION.

With the purpose of finding the three manganese atoms in the asymmetric unit a three-dimensional Patterson function P(u, v, w) was calculated. Due to severe overlap from non-equivalent interactions the manganese atoms could not be located directly from the Harker sections and -lines.

On the basis of the structure proposed in section IV. 5 and assuming Mn-O bond lengths of about 1. 9 Å, (the approximate metal-oxygen distance in the trinuclear Fe and Cr acetates; see section IV. 5) the manganese atoms should be

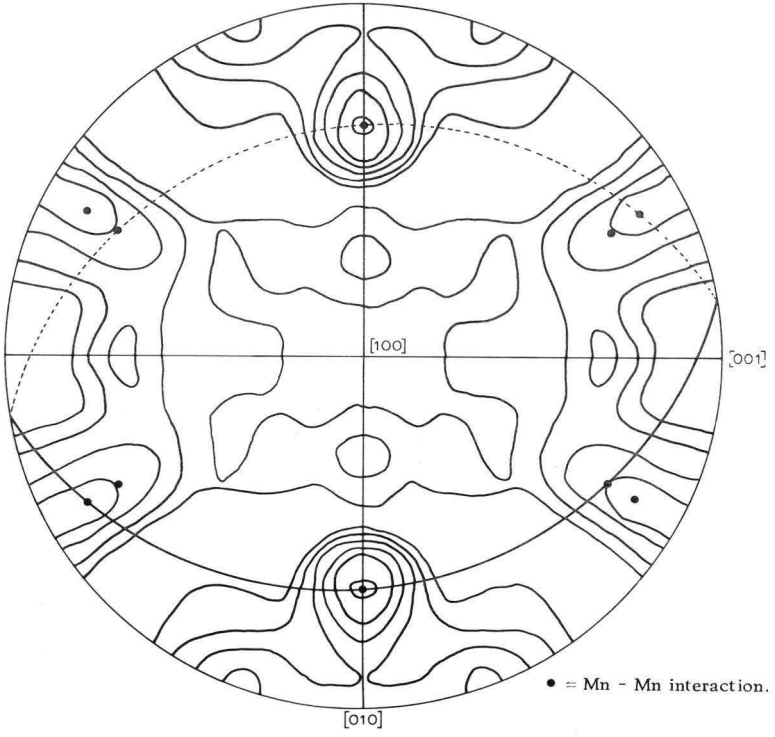


Fig. 1

Patterson function at 3.3 Å from the origin, represented in stereographic projection. Contour lines are drawn at an arbitrary scale.

situated at the corners of an equilateral triangle with sides 3.3 Å. On this assumption a sphere of radius 3.3 Å was constructed about the origin and the values of P(u, v, w) on the surface of this sphere were plotted in a stereographic projection.

From this projection the plane of the manganese atoms containing the non-equivalent interactions Mn(1)-Mn(2), Mn(2)-Mn(3) and Mn(1)-Mn(3) was found (see fig. 1). Then sets of symmetry-equivalent interactions at

$$x_2-x_1,\quad y_2-y_1,\quad z_2-z_1,$$
$$\tfrac{1}{2}-x_2-x_1,\quad \tfrac{1}{2}+y_2-y_1,\quad z_2-z_1,$$
$$\tfrac{1}{2}+x_2-x_1,\quad \tfrac{1}{2}-y_2-y_1,\quad -z_2-z_1,\quad \text{etc. could be recognised.}$$

By correlating systematically all symmetry-equivalent interactions between the manganese atoms a unique solution for their positional parameters in the a-symmetric unit was found.

V. 5 REFINEMENT OF THE STRUCTURE.

The oxygen and carbon atoms were located by calculations of structure factors and Fourier maps according to the method used in the heavy-atom technique. Results are summarised in table 9.

TABLE 9.

LOCATION OF OXYGEN AND CARBON ATOMS BY CALCULATIONS OF STRUCTURE FACTORS AND FOURIER MAPS.

Number of cycle	Atoms on which the structure factor calculation was based.	Resulting R-factor.	Additional atoms found from corresponding Fourier maps.
1.	Mn(1)-Mn(3)	54%	0(5), 0(10), 0(15), 0(16).
2.	Mn(1)-Mn(3), 0(5), 0(10), 0(15), 0(16).	50%	0(1)-0(4), 0(6)-0(8), 0(11)-0(14)
3.	Mn(1)-Mn(3), 0(1)-0(8), 0(10)-0(16).	38%	0(9), 0(17), C(1)-C(12), C(15), C(16).
4.	Mn(1)-Mn(3), 0(1)-0(17), C(1)-C(12), C(15), C(16)	25%	C(13), C(14).
5.	All Mn atoms, all 0 atoms, all C atoms.	22.2%[1])	
6.	do.	20.9%[2])	

[1]) after refinement by least squares method with one overall B of 2.4 Å^2

[2]) after refinement by least squares method with individual isotropic B's. Atomic B's varied from 0.0 to 6.4 Å^2.

The rather high final value of the agreement factor R is apparently due to the set of data being incomplete and of poor quality. That the atomic thermal parameters B do not "blow up" but assume constant and not very high values is an indication that the calculated structure is essentially correct.

Positional parameters are listed in Table 10. Standard deviations vary from about 0.01 Å for the manganese atoms to about 0.06 Å for the carbon atoms.

V. 6. DISCUSSION OF THE STRUCTURE.

From fig. 2 it can be seen that the trinuclear unit of one oxygen atom, three manganese atoms and six acetate bridges has the approximate trigonal symmetry ($\bar{6}$m2 or D_{3h}) suggested in the preceding chapter.

The Mn atoms lie at the apices of an almost equilateral triangle and each is surrounded by six oxygen atoms in a distorted octahedral arrangement. The three octahedra share 0(16) at their common vertex. The carboxylate groups form bridges between the Mn atoms.

The trinuclear units are linked one-dimensionally by the acetate bridges 0(15)-C(13)-0(5). Oxygen atom 0(10) is part of a single acetic acid molecule 0(10)-C(15)-C(16)-0(17) with an intramolecular hydrogen bridge of 2.7 Å between 0(9) and 0(17).

Accordingly crystallised manganic acetate is a linear polymer. The polymer chains are parallel to the needle axis **c** of the crystals.

A summary of interatomic distances and valency angles is given in table 11.

The relatively low precision of the atomic parameters does not warrant detailed conclusions with respect to bond character or valency angles.

With the exception of Mn(2)-0(10) the spread in Mn-0 bond lengths is ten times the standard deviation in the Mn-0 distances, indicating the octahedra to be distorted. The valency angles 0-Mn-0 involving the outer oxygen atoms 0(5), 0(10), and 0(15) are considerably smaller than the corresponding 0-Mn-0 angles involving the central oxygen atom 0(16); thus the impression is gained that the Mn atoms are drawn from the centra of the octahedra towards the central oxygen atom 0(16).

The bond Mn(2)-0(10), connecting acetic acid molecule 0(10)-C(15)-C(16)-0(17) to manganese atom Mn(2) is 0.3 Å larger than the mean value of the other Mn-0 distances.

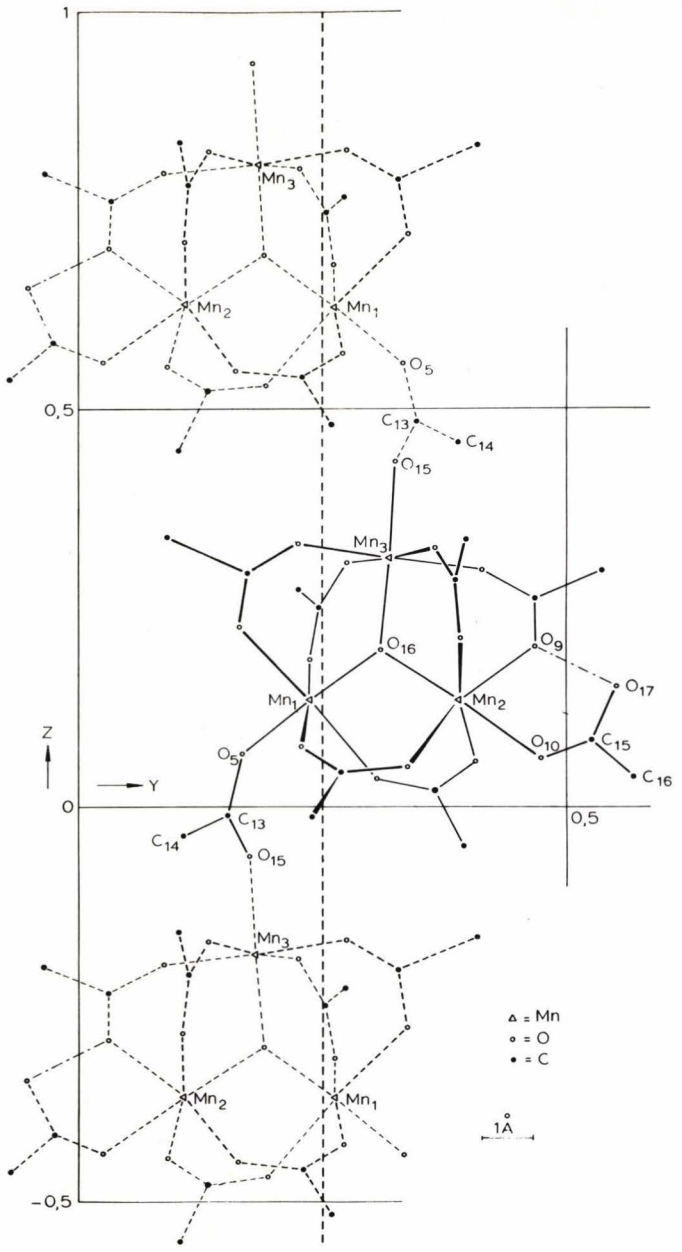


fig. 2

The crystal structure of manganic acetate, projection along the a-axis. Only the glide-plane operation $\frac{1}{2}\bar{c}$ perpendicular to the b-axis has been shown. All other symmetry operations have been omitted.

TABLE 10.

FINAL ATOMIC COORDINATES OF MANGANIC ACETATE IN FRACTIONS OF THE CELL EDGES.

		x/a	y/b	z/c
Manganese atoms:				
	Mn(1)	0.057	0.239	0.131
	Mn(2)	0.152	0.392	0.132
	Mn(3)	0.078	0.319	0.311
Oxygen atoms linked to Mn 1:				
	O(1)	0.008	0.306	0.031
	O(2)	0.168	0.228	0.074
	O(3)	0.099	0.164	0.223
	O(4)	-0.058	0.239	0.182
	O(5)	0.016	0.165	0.061
Oxygen atoms linked to Mn 2:				
	O(6)	0.062	0.409	0.050
	O(7)	0.211	0.337	0.048
	O(8)	0.251	0.391	0.211
	O(9)	0.110	0.470	0.203
	O(10)	0.222	0.477	0.059
Oxygen atoms linked to Mn 3:				
	O(11)	0.031	0.418	0.297
	O(12)	0.202	0.368	0.326
	O(13)	0.130	0.227	0.330
	O(14)	-0.042	0.276	0.308
	O(15)	0.059	0.327	0.434
Oxygen atom linked to Mn 1, Mn 2, and Mn 3:				
	O(16)	0.094	0.311	0.195
Oxygen atom linked to C and H:				
	O(17)	0.230	0.555	0.149
Carbon atoms of carboxylate groups:				
	C(1)	0.216	0.270	0.041
	C(3)	0.015	0.370	0.023
	C(5)	0.056	0.470	0.262
	C(7)	0.259	0.389	0.285
	C(9)	0.134	0.174	0.296
	C(11)	-0.088	0.249	0.249
	C(13)	-0.003	0.153	-0.015
	C(15)	0.258	0.524	0.082
Carbon atoms of methyl groups:				
	C(2)	0.284	0.242	-0.016
	C(4)	-0.041	0.399	-0.054
	C(6)	0.031	0.539	0.297
	C(8)	0.340	0.400	0.333
	C(10)	0.169	0.111	0.333
	C(12)	-0.173	0.227	0.272
	C(14)	-0.071	0.106	-0.041
	C(16)	0.320	0.570	0.036

The standard deviations in the parameters were, in Å, :

for the Mn atoms: 0.008 to 0.010
for the O atoms: 0.027 to 0.048
for the C atoms: 0.040 to 0.072

Numbering of atoms refers to fig. 2.

TABLE 11.

INTERATOMIC DISTANCES AND ANGLES IN ONE MOLECULE OF MANGANIC ACETATE.

	Smallest distance, resp. angle observed.	Largest distance, resp. angle observed.
A. DISTANCES.		
Distance between the Mn atoms	3.27 ± 0.02 Å	3.38 ± 0.02 Å
Length of Mn-O bonds[1])	1.85 ± 0.04	2.24 ± 0.04
" " C-O "	1.16 ± 0.07	1.34 ± 0.07
" " C-C "	1.48 ± 0.08	1.63 ± 0.08
B. VALENCY ANGLES.		
Mn-O-Mn	118° [2])	124°
O-C-O	116	132
O(5)-Mn(1)-O [3])	85	88
O(10)-Mn(2)-O [3])	80	86
O(15)-Mn(3)-O [3])	85	90
O(16)-Mn-O [3])	91	100

Numbering of atoms refers to fig. 2

Length of O(9)-O(17) hydrogen bridge: 2.70 ± 0.09 Å.

[1]) except Mn(2)-O(10) = 2.35 ± 0.08 Å.

[2]) standard deviations in the valency angles are about 3°

[3]) excluding valency angles near 180°.

CHAPTER VI

PREPARATION AND THERMAL STABILITY OF ANHYDROUS ACETIC ACID

VI.1. INTRODUCTION

In section II.4.1 it was pointed out that reliable conclusions with respect to the molecular weight of dissolved manganic acetate could only be arrived at if the freezing-point determinations were carried out in very pure acetic acid. Also for the mechanistic studies reported in the seventh chapter high demands had to be made upon the purity of the acetic acid used as the solvent.

A sensitive criterion for the purity of acetic acid is its melting point, 16.60° being a generally accepted value.

In spite of many attempts we were unable to obtain acetic acid of higher melting point than 16.58°C by any of the established purification procedures except fractional crystallisation. The product invariably contained traces of water and/or acetic anhydride after the final distillation at atmospheric pressure.

Investigating the widely employed procedure for the removal of water by distillation from boron acetate [1,2,3], we found that with a small excess of boron acetate the distillate still contained water. Using a large excess of boron acetate the product contained acetic anhydride and traces of boron as revealed by Gravestein's test. [4]

In some cases to our surprise the quality of the acid was lowered by fractional distillation as indicated by a decrease in melting point of some 0.02°C. Precise water determinations revealed an increase in the total water content

upon distillation. As the effect persisted under the most careful exclusion of atmospheric moisture, the only explanation seemed a partial disproportionation of acetic acid to acetic anhydride and water according to the reaction:

$$2\ AcOH \rightleftarrows Ac_2O + H_2O \qquad (1)$$

with the equilibrium constant $K = \frac{[Ac_2O]\,[H_2O]}{[AcOH]^2}$ (2)

The detection of a considerable quantity of acetic anhydride in the distillation residue confirmed this hypothesis.

We are aware of only one publication in which allusions are made to the instability of acetic acid under such surprisingly mild conditions. In 1962 Child and coworkers studied the thermal decomposition of acetic acid to acetic anhydride and water in the temperature range 169°-248°C. [5] By extrapolation of the log K - 1/T plot they concluded that "absolutely pure acetic acid should decompose to the extent of 0.028% at the boiling point, if held at this temperature for a sufficiently long time". In the same paper reference is made to a private communication by Bruckenstein, stating that "after the careful purification of acetic acid, the last step of which involves fractional distillation, very small and approximately equimolar amounts of anhydride and water are present".

The implications of this article have not been recognized. Fractional distillation under atmospheric pressure has continued to be considered as a suitable final purification step for the preparation of high-purity acetic acid. [6, 7] In one publication the acid was distilled after it had been "frozen out many times"! [8]

Purification of acetic acid by fractional crystallization avoids its thermal decomposition, but is a cumbersome method for large quantities. Therefore we developed a purification procedure which likewise precludes the thermal decomposition but is more suitable for large amounts of acetic acid.

Because of the extensive use of acetic acid as a solvent a direct determination of its stability near the boiling point seemed very desirable. For this purpose we determined the equilibrium constants K in the temperature range 80°-130°C.

VI. 2. DISCUSSION AND RESULTS

We freed acetic acid from oxidisable impurities in the conventional way by boiling with CrO_3, followed by distillation. The acid was then freed from water by the addition at room temperature of an exactly equivalent proportion of acetic anhydride, together with 1 mmole/l of sulphuric acid as a catalyst. After adding 2 mmole/l of sodium acetate we distilled the acid under reduced pressure at about 25°C and thus avoided disproportionation.

A slight adaptation of Bruckenstein's procedure [9]) provided a sufficiently sensitive method for the determination of water in acetic acid.

Acetic acid treated in this way contained less than 0.3 mmole/l of Ac_2O or H_2O (i.e. 30 ppm Ac_2O and 5 ppm H_2O), and was stored under dry nitrogen.

Equilibrium constants K were determined by measuring the equilibrium concentrations of acetic anhydride, generated in anhydrous acetic acid at 80°, 100°, 118°, and 130°C. Results are represented in table 12, together with values of K, found by extrapolation of Child's data. [5]) The agreement seems fair, taking into account the minute concentrations of acetic anhydride which had to be measured at the lower temperatures.

The disproportionation is very strongly accelerated by sulphuric acid; conversely, traces of sodium acetate almost completely inhibit the reaction.

From the table it follows that kinetic measurements in acetic acid above 80°C could be impaired by the instability of the solvent. However, in solutions of manganic acetate the disproportionation reaction is likely to be very slow because of the basic character of the solute. If manganic acetate for cryoscopic measurements is dissolved below 60°C interference by disproportionation products of acetic acid is negligeable (section II. 4. 1).

VI. 3. EXPERIMENTAL

Analytical procedure. - Water and acetic anhydride determinations were based on Bruckenstein's spectrophotometric procedure. [9]) Acetic anhydride concentrations were measured directly from the uv absorbance at 250 nm. As the acetic anhydride maximum appears as a small shoulder on the side of the strong acetic acid band, its absorption has to be measured with reference to pure acetic acid and with wide open slit and consequently low resolution. This results in a dependence of λ_{max} and of the apparent molar absorptivity ϵ_{app} on the characteristics of the spectrophotometer (as already pointed out by Bruckenstein) as well as on the cell path length.

A positive temperature difference Δt between sample and reference cell, both filled with pure acetic acid, gave rise to a maximum at about the same position as the anhydride maximum. Its extinction $D_{\Delta t}$ was proportional to Δt and amounted to $0.03°C^{-1}$ at 245 nm in 1 cm-cells on a Cary 15 spectrophotometer. In 1 mm-cells $D_{\Delta t}$ was $0.02°C^{-1}$ at 234 nm on the same instrument. It is therefore essential to have sample and reference compartments thermostatted to within 0.1°C.

TABLE 12

EQUILIBRIUM CONSTANTS OF THE REACTION $2\ AcOH \rightleftharpoons Ac_2O + H_2O$.

Temperature, °C	$[Ac_2O]$ at equilibrium, mmole/l	$K_d = ([Ac_2O] / [AcOH])^2$	Approximate time required for attaining equilibrium, without a catalyst	Approximate time required for attaining equilibrium, with 5 μmole/l of H_2SO_4 as a catalyst	K_e*
130	6.0	$(1.2 \pm 0.1) \times 10^{-7}$	3 h	5 min	1.3×10^{-7}
118	4.2	$(0.58 \pm 0.08) \times 10^{-7}$	7 h	20 min	0.8×10^{-7}
100	2.4	$(0.19 \pm 0.05) \times 10^{-7}$	24 h	1 h	0.3×10^{-7}
80	1.2	$(0.05 \pm 0.03) \times 10^{-7}$	120 h	2 h	0.09×10^{-7}
60	0.5**	-	-	-	-

* Calculated from the results of Child c.s. [5]) by linear extrapolation of the log K - 1/T plot..

** Calculated by extrapolation.

In the presence of 2 mmole/l NaOAc the Ac_2O concentration generated in 1 hour at 130°C was below 0.5 mmole/l.

This maximum seems to be caused by the broadening of the acetic acid absorption band on increase in temperature, the surprisingly large magnitude of the effect being due to the steepness of the absorption curve. Other solvents such as acetone, benzene and carbon tetrachloride showed effects of the same order of magnitude.

Acetic anhydride concentrations were determined on a Perkin Elmer 137 uv spectrophotometer with cell compartments thermostatted at $30 \pm 0.1^{\circ}C$. Using 1 cm-cells and with slit width 0.6 mm, λ_{max} was 250 nm with ϵ_{app} 33.9 l $mole^{-1} cm^{-1}$.

Water concentrations were determined as follows: to a 3 ml-sample of acetic acid in a 1 cm quartz cell was added 10 µl Ac_2O, and the absorbance at 250 nm was determined. Then 1 µl 2M H_2SO_4 in AcOH was added and after about 30 min the absorbance was redetermined. From the decrease in Ac_2O absorbance the water content was calculated. For larger proportions of water, as in the purification process, larger quantities of Ac_2O had to be added; the initial concentrations were then calculated from the weights of Ac_2O and AcOH.

The spectrophotometer was sensitive to within 0.01 absorbance unit, corresponding to 0.3 mmole/l of Ac_2O or H_2O.

All additions to the cells were made either in a dry box or in a current of dry nitrogen.

Purification of Acetic Acid. - 3 l of Baker A.R. glacial acetic acid were stirred with 15 g chromium trioxide at 90° for 10 hours and then rapidly distilled. The first 200 ml of the distillate were rejected and a main fraction of 2.5 l was collected. The water content was determined and the calculated quantity of acetic anhydride added, together with 1.2 ml 2M H_2SO_4 in AcOH. After about 1 hr. the acid was tested for water or acetic anhydride and if necessary a final adjustment was made by adding the component which was not in excess. After another 30 min. about 500 mg anhydrous sodium acetate was added and the acid distilled in vacuo: b.p. $25^{\circ}/10$ mm. The product contained no detectable amounts of water or acetic anhydride; m.p. 16.60°.*

Variations in the above procedure produced the following effects:

1. Oxidation with CrO_3 omitted: m.p. 16.59°.
2. Careful fractional distillation trough a 6 ft Vigreux column following the oxidation step: no difference.
3. No addition of sodium acetate: slight contamination with sulphuric acid (and/or derivatives), causing 30x more rapid disproportionation; m.p. 16.60°.

The acid was stored and transferred to other vessels as needed in an atmosphere of dry nitrogen.

Upon prolonged boiling the m.p. dropped to 16.57°. At room temperature the equilibrium was re-established extremely slowly: even after three days there was no detectable increase in m.p. Addition of 0.1 mmole/l H_2SO_4 caused the m.p. to rise to its original value of 16.60° in less than 24 hours.

Determination of the equilibrium constants K. - 3 ml-samples of anhydrous acetic acid containing 0.5 mg/l H_2SO_4 were kept at the desired temperature in a quartz spectrophotometercell with well fitting PTFE stopper. After regular intervals the cell was quenched in a dry ice - acetone mixture and the increase in absorbance at 250 nm redetermined at 30° with reference to pure acetic acid.

At each temperature the absorbance reached a constant value from which the equilibrium concentration of acetic anhydride was calculated.

The same equilibrium concentrations were observed in runs starting from acetic acid containing 10 mmole/l. both of water and acetic anhydride.

Runs without a catalyst led to the same equilibrium constants but in some cases the absorbance readings became abnormally high, probably due to dissolution of some of the cell or stopper material during the long reaction times required.

* Thermometer calibrated at "Physikalisch-Technische Bundesantalt", Braunschweig, Germany. Certified accuracy : 0.01°C. All recorded melting points are for AcOH in equilibrium with dry nitrogen of atmospheric pressure.

REFERENCES

1. W. EICHELBERGER and V.K. LA MER, J. Am. Chem. Soc. 55, 3633 (1933).
2. K. HEYMANN and H. KLAUS in: G. JANDER, H. SPANDAU and C.C. ADDISON, "Chemie in nichtwassrigen ionisierenden Lösungsmitteln", Band IV, Teil 1, Vieweg & Sohn, Braunschweig.
3. I.M. KOLTHOFF and S. BRUCKENSTEIN, J. Am. Chem. Soc. 78, 1 (1956).
4. H. GRAVESTEIN and A.W.F. MIDDELBURG, Molisch Festschrift, 154 (1936), quoted by: C.J. van NIEUWENBURG and J.W.L. van LIGTEN, "Kwalitatieve Chemische Analyse", D.B. Centen, Amsterdam.
5. J.A. KNOPP, W.S. LINNELL and W.C. CHILD, J. Phys. Chem. 66, 1513 (1962).
6. P.D.T. COULTER and R.T. IWAMOTO, J. Electroanal. Chem. 13, 21 (1967).
7. T.W. MARTIN, J.M. BURK and A. HENSHALL, J. Am. Chem. Soc. 88, 1097 (1966).
8. A.J. DEITSCH, W. BRANDEL, M. BARANOWNA, Z. Phys. Chem. (Leipzig), 235, 1 (1967).
9. S. BRUCKENSTEIN, Anal. Chem. 31, 1757 (1959).

CHAPTER VII

OXIDATION OF THIOANISOLE, ACETIC ACID AND ACETIC ANHYDRIDE BY MANGANIC ACETATE

VII.1. INTRODUCTION

In the preceding chapters the structure of crystalline anhydrous manganic acetate was established. Determinations of the freezing-point depression and perchloric acid titrations pointed to the preservation of the trinuclear character of manganic acetate when dissolved in acetic acid. The equivalent conductivity indicated partial dissociation into ions.

Consequently, if the trinuclear unit does not rearrange upon dissolution the oxidising species can be represented as the ion-pair $[Mn_3O(OAc)_6 . nAcOH]^+ [OAc]^-$, the cation being coordinated by one or more acetic acid molecules as described in section IV.5 and pictured in fig. 2.

The relevance of this information for the second part of our investigations seems twofold:

a. Interaction of $Mn(OAc)_2$ with $Mn_3^{III}O(OAc)_6^+$ ions might well produce uncharged $Mn_2^{III}Mn^{II}O(OAc)_6$ species which could be less reactive in oxidation reactions than the corresponding cations. This might explain the retarding effect of $Mn(OAc)_2$ on many oxidations by manganic acetate.

b. In crystalline manganic acetate the spatial arrangement of the acetic acid molecules does not favour the transfer of a methyl hydrogen atom to an acetate oxygen atom in the way Van der Ploeg proposed in order to account for

the formation of $^{\cdot}CH_2COOH$ radicals in the thermal decomposition of manganic acetate solutions. [1]) There are no obvious reasons why the situation in dissolved manganic acetate should be different.

In accordance with the two kinds of OAc groups present in manganic acetate two pathways for its thermal decomposition suggest themselves, characterised by either electron transfer from the coordinated acetic acid molecules to the $Mn_3O(OAc)_6^+$ system, or by fission of Mn-O bonds in the Mn-acetate-Mn bridges.

We first investigated the hypothesis mentioned under a. by trying to obtain direct evidence for the interaction of $Mn(OAc)_2$ with manganic acetate.

VII. 2. COMPLEX FORMATION BETWEEN MANGANOUS ACETATE AND MANGANIC ACETATE IN ACETIC ACID SOLUTION

We studied the interaction between manganic acetate and manganous acetate by means of cryoscopic measurements, attempts to isolate a Mn(II)-Mn(III) complex, and uv spectroscopy.

Results are summarised in table 13 and fig. 3.

Apparently manganic acetate does not react with $Mn(OAc)_2$ in acetic acid, provided the solvent is sufficiently dry. In the presence of traces of water the two compounds strongly interact and probably form a complex.

In previous kinetic experiments [2]) with manganic acetate in acetic acid the water content of the solvent has not been specified and may have been considerable because of the hygroscopic character of dry acetic acid. Therefore, the retarding influence of $Mn(OAc)_2$ on the reaction rate in these experiments may have been due to the complexation of manganic acetate by $Mn(OAc)_2$. If that were the only effect $Mn(OAc)_2$ should not retard reactions of manganic acetate in dry acetic acid.

TABLE 13.

INTERACTION BETWEEN MANGANIC ACETATE AND MANGANOUS ACETATE IN ACETIC ACID.

A. SOLVENT: DRY ACETIC ACID (less than 5 ppm H_2O)	B. SOLVENT: ACETIC ACID CONTAINING 0.15% H_2O (about 5 mmole H_2O/mole AcOH)
I. Cryoscopy.	
3.5 mmole/l manganic acetate gave the normal freezing-point depression (0.013°C, corresponding to a mol.wt. of 670) in a solution of 27 mmole/l manganous acetate.	5.5 mmole/l manganic acetate gave no depression of the freezing point in a solution of 40 mmole/l manganous acetate.
II. Isolation of a complex.	
Warm solutions of mixtures of manganic and manganous acetate yielded on cooling or partial evaporation only the starting materials.	Evaporation of a warm solution of 9.5 g/l manganic acetate and 7.1 g/l manganous acetate yielded no crystalline precipitate of either of the starting materials, but a brown oil, soluble in benzene. In the benzene solution a precipitate of $Mn(OAc)_2$ formed in the course of some days.
III. UV spectroscopy.	
Very little influence on the uv spectrum of 1.3 mmole/l manganic acetate by addition of 5 mmole/l $Mn(OAc)_2$. Molar extinction at 460 nm decreased from 317 to 315 l mole^{-1}cm^{-1}.	UV spectrum of 1.3 mmole/l manganic acetate strongly affected by addition of 5 mmole/l $Mn(OAc)_2$. Molar extinction at 460 nm decreased from 315 to 304 l mole^{-1}cm^{-1}.

The region near the absorption maximum at 460 nm is the most sensitive part of the spectrum for the combined influence of $Mn(OAc)_2$ and water. Fig. 3 shows the influence of higher concentrations of water and $Mn(OAc)_2$ on the molar extinction at 460 nm.

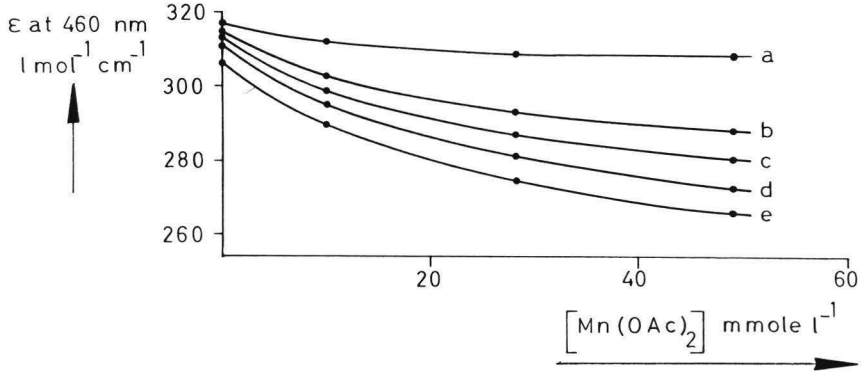


Fig. 3. Influence of $Mn(OAc)_2$ on molar extinction of manganic acetate in acetic acid solution at 460 nm. Water content of the solvent: a ⟨0.001%, b 0.1%, c 0.2%, d 0.5%, e 1.0%.

VII. 3. OXIDATION REACTIONS OF MANGANIC ACETATE IN DRY ACETIC ACID - SELECTION OF SUBSTRATES AND REACTION CONDITIONS

Reduction of manganic acetate, $Mn_3O(OAc)_6^+(OAc)^-$, to manganous acetate, $Mn(OAc)_2$, yields an equivalent quantity of water.
Consequently, kinetic studies in dry acetic acid had to be carried out by measuring initial reaction rates and assuming a zero water concentration as a first approximation.

We studied the oxidation by manganic acetate of the following three substrates in the presence of varying amounts of $Mn(OAc)_2$:

a. Thioanisole, for which we could compare our results with the extensive studies by Bronsdijk. [3])

b. Acetic acid, which was studied as a substrate by De Korte [4]) and Van der Ploeg [1]) and in which we took a special interest because of the mechanism of the thermal decomposition of manganic acetate solutions.

c. Acetic anhydride. In the course of our work on manganic acetate we found that acetic anhydride is much more readily oxidized than acetic acid. We determined the products of this reaction and carried out some exploratory kinetic experiments.

All three substrates can be conveniently obtained water-free and do not yield water as one of their primary oxidation products.

VII. 4. OXIDATION OF THIOANISOLE BY MANGANIC ACETATE IN DRY ACETIC ACID

We determined spectrophotometrically the initial rates v_o of the reaction between manganic acetate and thioanisole in dry acetic acid at 30°C, in the presence of varying amounts of manganous acetate.

The experiments were carried out under dry nitrogen because, in contrast with Bronsdijk's observations, we found a retarding influence of oxygen on the rate of disappearance of manganic acetate. Initial reaction rates were up to 7

times as high as the rates reported by Bronsdijk at the same temperature.

In accordance with Bronsdijk we found v_o proportional to the manganic acetate concentration $[Mn^{III}]_o$ and to the substrate concentration $[C_6H_5SCH_3]_o$. Even under the most careful exclusion of moisture v_o decreased sharply with increasing manganous acetate concentration $[Mn^{II}]_o$.

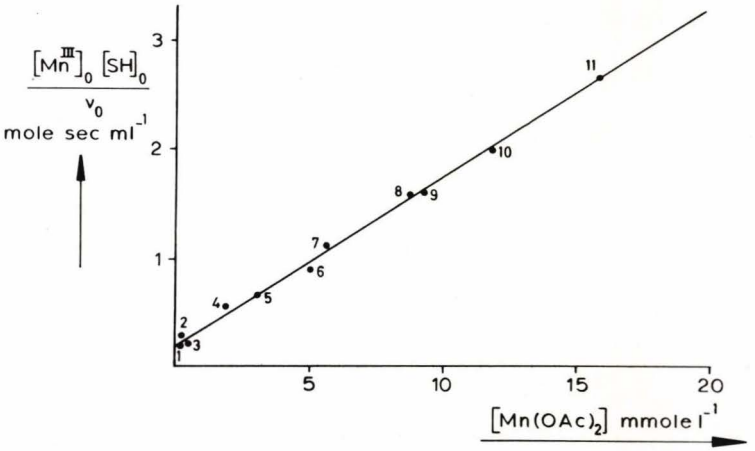


Fig. 4. Influence of manganous acetate on kinetics of thioanisole oxidation by manganic acetate at 30°C in dry acetic acid under nitrogen.
Initial concentrations:

		1	2	3	4	5	6	7	8	9	10	11
$[Mn^{III}]_o$,	mmole/l	1.15	0.54	1.15	0.87	1.30	0.24	1.09	1.19	1.26	1.30	1.25
$[C_6H_5SCH_3]_o$,	mmole/l	9.1	19.0	18.0	86.0	128.0	109.0	124.0	704.0	259.0	300.0	346.0

As can be seen from fig. 4 a plot of the quantity $\frac{[Mn^{III}]_o\,[C_6H_5SCH_3]_o}{v_o}$ against $[Mn^{II}]_o$ is a straight line which nearly passes through the origin.

Bronsdijk obtained a linear plot of $\frac{v_o}{[Mn^{III}]_o\,[C_6H_5SCH_3]_o}$ against $[Mn^{III}]_o / [Mn^{II}]_o$, but as he did not vary $[Mn^{III}]_o$ this dependence may equally well be interpreted as the same proportionality as was found by us.

According to section II. 2. 2 the retarding influence of $Mn(OAc)_2$ cannot be explained in terms of a disproportionation of Mn(III) to Mn(II) and Mn(IV). Complexation of Mn(III) by Mn(II) in dry acetic acid was ruled out in section VII. 2. The only explanation left seems to assume that the oxidation takes place in steps and that $Mn(OAc)_2$ is able to reduce a reactive intermediate, possibly

according to the following reaction scheme:

$$Mn_3^{III}O(OAc)_6^+ OAc^- + C_6H_5SCH_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_6H_5^{\cdot}SCH_3^+ OAc^- + Mn_2^{III}Mn^{II}O(OAc)_6 \quad (1)$$

$$C_6H_5^{\cdot}SCH_3^+ OAc^- \xrightarrow{k_3} C_6H_5SCH_2^{\cdot} + AcOH \quad (2)$$

$$C_6H_5SCH_2^{\cdot} + Mn_3^{III}O(OAc)_6^+ OAc^- \xrightarrow{fast} C_6H_5SCH_2OAc + Mn_2^{III}Mn^{II}O(OAc)_6 \quad (3)$$

$$C_6H_5^{\cdot}SCH_3^+ OAc^- + Mn(OAc)_2 \underset{k_5}{\overset{k_4}{\rightleftharpoons}} C_6H_5SCH_3 + Mn(OAc)_3 \quad (4)$$

For simplicity the acetic acid molecules which complete the coordination shells of the Mn atoms have been omitted. In subsequent reactions the $Mn(OAc)_3$ and the $Mn_2^{III}Mn^{II}O(OAc)_6$ species will either oxidise additional molecules of thioanisole or rearrange to manganic acetate $Mn_3^{III}O(OAc)_6^+ OAc^-$ and manganous acetate $Mn(OAc)_2$.

Reaction (1) is a possibly reversible electron abstraction from the substrate producing the cation radical $C_6H_5^{\cdot}SCH_3^+$ together with a hypothetical mixed Mn(III)-Mn(II) acetate. The cation loses a proton in reaction (2), probably by internal proton transfer within the ion pair, and the resulting radical is rapidly oxidised to the main reaction product acetoxymethylphenyl sulphide. The retarding action of $Mn(OAc)_2$ is accounted for by reaction (4) in which part of the reactive intermediates is withdrawn from the reaction sequence.

On the basis of these equations the rate of disappearance of the Mn(III) species is given by the relation:

$$-dMn^{III}/dt = k_1[C_6H_5SCH_3][Mn_3^{III}O(OAc)_6^+ OAc^-] - k_2[C_6H_5^{\cdot}SCH_3^+ OAc^-] \cdot$$

$$\cdot [Mn_2^{III}Mn^{II}O(OAc)_6] + k_3[C_6H_5^{\cdot}SCH_3^+ OAc^-] - k_4[C_6H_5^{\cdot}SCH_3^+ OAc^-][Mn(OAc)_2]$$

$$+ k_5[C_6H_5SCH_3][Mn(OAc)_3] \quad (5)$$

Application of the steady-state approximation to the $C_6H_5^{\cdot}SCH_3^+ OAc^-$

concentration yields the following rate expression:

$$v = -dMn^{III}/dt =$$

$$2k_3[C_6H_5SCH_3]\frac{k_1[Mn_3^{III}O(OAc)_6^+OAc^-] + k_5[Mn(OAc)_3]}{k_2[Mn_2^{III}Mn^{II}O(OAc)_6] + k_3 + k_4[Mn(OAc)_2]} \qquad (6)$$

On the assumption that the concentration of $Mn(OAc)_3$ as a secondary reaction product may be neglected during the initial stages of the reaction the expression for the initial reaction rate v_o becomes:

$$\frac{[C_6H_5SCH_3]_o\,[Mn_3^{III}O(OAc)_6^+OAc^-]_o}{v_o} = \frac{k_2[Mn_2^{III}Mn^{II}O(OAc)_6] + k_3}{2k_1k_3} + \frac{k_4[Mn(OAc)_2]}{2k_1k_3} \qquad (7)$$

If $k_2[Mn_2^{III}Mn^{II}O(OAc)_6] \ll k_4[Mn(OAc)_2]$, then equation (7) reduces further to:

$$\frac{[C_6H_5SCH_3]_o\,[Mn_3^{III}O(OAc)_6^+OAc^-]_o}{v_o} = \frac{1}{2k_1} + \frac{k_4}{2k_1k_3}[Mn(OAc)_2] \qquad (8)$$

which is in agreement with the observed kinetics.

Rate constants, calculated with the help of (8) from fig. 4 are:

$k_1 = 2.5 \times 10^{-3}$ l mole^{-1}sec^{-1} and $k_4/k_3 = 0.8 \times 10^3$ l/mole, and substitution of these values in (8) yields:

$$\frac{[C_6H_5SCH_3]_o\,[Mn_3^{III}O(OAc)_6^+OAc^-]_o}{v_o} = 200 + 16 \times 10^4[Mn(OAc)_2]\ \text{mole sec l}^{-1} \qquad (9)$$

VII. 5. OXIDATION OF ACETIC ACID BY MANGANIC ACETATE

We reinvestigated the kinetics of the oxidation of acetic acid by manganic acetate in the presence of varying amounts of $Mn(OAc)_2$ by measuring initial reaction rates v_o at 110°C under nitrogen. The decrease in manganic acetate concentration was followed by iodometric titration.

TABLE 14.

OXIDATION OF ACETIC ACID BY MANGANIC ACETATE AT 110°C UNDER DRY NITROGEN.

Water content of acetic acid, % by weight	Initial concentration of manganic acetate $\left[Mn_3^{III}\right]_o$, mmole/l	Initial concentration of manganous acetate $\left[Mn(OAc)_2\right]_o$, mmole/l	$v_o / \left[Mn_3^{III}\right]_o$, h^{-1}
0.000	2.4	0.0	0.19
do	10.3	0.0	0.15
do	20.3	4.0	0.13
do	2.9	15.0	0.15
do	26.0	20.0	0.15
do	31.0	60.0	0.13
do	10.0	90.0	0.15
0.15	12.0	0.0	0.13
do	2.3	15.0	0.012
do	9.0	92.0	0.13
0.000	10.0*	0.0	0.13

* Added: 10 mmole/l $HClO_4$

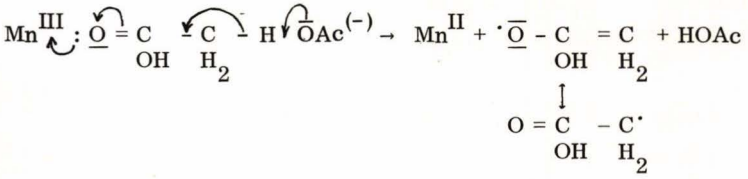
From the results, summarised in table 14, it can be seen that the effect of $Mn(OAc)_2$ in dry acetic acid is hardly detectable.

The solvent seems to take an active part in the decomposition. Crystalline manganic acetate could be heated in vacuo (10 mm) at 85°C for two hours without loss of weight. At 110°C the decrease in weight was about 3% for the first hour. This decrease is apparently due to evolution of acetic acid and not to internal oxidation, the Mn(II) content of the samples remaining below 0.05% after 3 hours at 110°C.

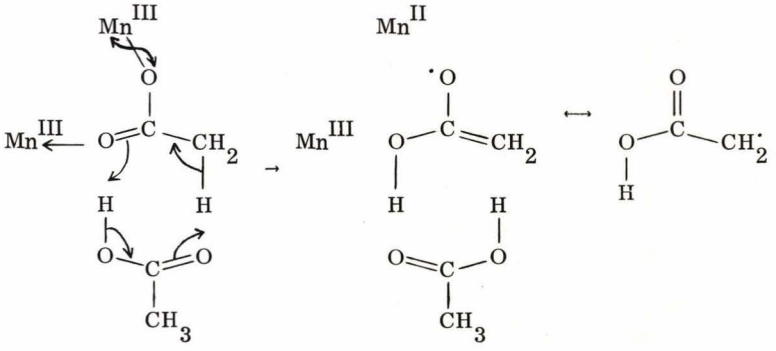
According to Steggerda manganic propionate is thermally more stable in benzene solution than in propionic acid solution, which also points to the participation of the solvent acid in the decomposition reaction. [5])

Two reaction mechanisms seem to account well for the above observations, in accordance with the two reaction paths suggested in section VII.1:

a. Electron transfer from acetic acid molecules to Mn(III), facilitated by simultaneous proton removal from the CH_3 group by, e.g., acetate ions:



b. Fission of an Mn-O bond attended by enolisation of the acetate bridge involved by an acetic acid molecule. Starting from a particular resonance structure of the acetate bridge, and omitting all other ligands:



Both mechanisms account for the formation of $\cdot CH_2COOH$ radicals and the failure of $Mn(OAc)_2$ to retard the decomposition reaction.

In mechanism a. the importance of the solvent lies in the provision of OAc^- ions at the proper place; according to b. acetic acid molecules would be needed for the enolisation.

In fast subsequent reactions the $\cdot CH_2COOH$ radicals will either be oxidised to acetoxyacetic acid (the main reaction product) or dimerise to succinic acid. [1])

The last experiment in table 15 was carried out with equimolar quantities of manganic acetate and perchloric acid, i.e. in a solution in which the available acetate ions have been replaced by far less basic ClO_4^- ions. From the fact that the decomposition proceeds at the same rate it might be inferred that acetate ions do not play the important rôle which a. ascribes to them. However, in stead of acetate ions, which are always present in small amounts, the acetic acid molecules themselves could be the proton acceptors, which means that an electron-transfer mechanism cannot be excluded on the basis of this experiment.

Further work to decide in favour of either a. or b. seems necessary.

VII. 6. OXIDATION OF ACETIC ANHYDRIDE BY MANGANIC ACETATE IN ACETIC ACID

Manganic acetate oxidised acetic anhydride smoothly at 80°C, i.e. at a temperature of about 30°C lower than required for the oxidation of acetic acid.

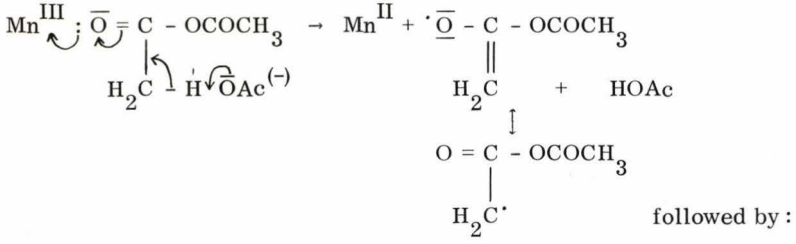
The reaction product was succinic acid (about 60%, calculated on Mn^{III}; most probably present as anhydride in the reaction mixture), with traces of acetoxyacetic acid (about 4%, calculated on Mn^{III}; perhaps present as mixed anhydride with acetic acid).

At constant initial concentrations of 1.32 mmole/l manganic acetate and 670 mmole/l acetic anhydride the term $\frac{[Mn_3^{III}]_o\,[Ac_2O]_o}{v_o}$ increased from 2×10^3 to 6×10^3 mole sec l^{-1} when $Mn(OAc)_2$ was increased from 0.0 to 20.0 mmole/l.

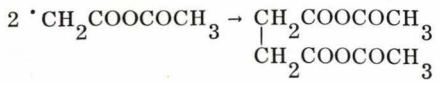
Reaction rates were determined spectrophotometrically by measuring the decrease in optical density at 460 nm in glass cells under nitrogen at 82°C.

The nature of the main product indicates the reaction to proceed through the formation of $\cdot CH_2COOCOCH_3$ radicals, which for the major part seem to dimerise to a succinic acid derivative.

The following simplified reaction scheme involves electron-transfer from acetic anhydride to the oxidising agent, attended by proton removal from a methyl group:



followed by:



mixed anhydride of succinic and acetic acid.

or:

$$Mn^{III} + {}^{\cdot}CH_2COOCOCH_3 \rightarrow \underset{\underset{OCOCH_3}{|}}{CH_2}COOCOCH_3$$

mixed anhydride of acetoxy-acetic acid and acetic acid.

A redistribution of acid and anhydride functions could produce succinic anhydride and acetoxyacetic acid respectively. In the working-up process (consisting of esterification with ethanol) diethyl succinate and ethyl glycolate are produced from all succinic acid and glycolic acid derivatives respectively.

The retarding influence of $Mn(OAc)_2$ is small and might well be due to a salt effect or to occupation of the coordination positions at the Mn atoms by acetate ions at the cost of acetic anhydride molecules.

VII. 7. CONCLUSION

$Mn(OAc)_2$ can retard oxidation reactions of manganic acetate in acetic acid for at least two reasons:

a. It is able to reduce the cation radicals which are formed as intermediates in some oxidation reactions. (Oxidation in dry acetic acid of thioanisole).

b. Small proportions of water cause $Mn(OAc)_2$ to interact with manganic acetate thereby reducing the activity of the oxidising species (Oxidation of thioanisole and acetic acid in the presence of traces of water).

The mechanism that leads to the formation of ${}^{\cdot}CH_2COOH$ radicals in the decomposition of manganic acetate solutions has not been established unequivocally.

VII. 8. EXPERIMENTAL

Starting materials. - Acetic acid was purified as indicated in section VI. 3. Merck A.R. acetic anhydride was subjected to fractional distillation and stored under dry nitrogen. Thioanisole was purified by fractional distillation under reduced pressure and stored under dry nitrogen.

Freezing-point determinations. - Conflicting statements have appeared in the chemical literature with respect to the cryoscopic constant K_F of acetic acid. The value of 3.90°C kg $mole^{-1}$ given in the "International Critical Tables" and quoted in most textbooks is based on Raoult's determinations of 1884 on 40 different substances.[6])

From the latent heat of fusion Eichelberger (1934) calculated an average value of 3.59°C kg $mole^{-1}$ and Bourne c.s. (1957) found 3.66°C kg $mole^{-1}$ for the molar depression of diphenyl and naphthalene,[7,8]) but Jander (1955) found 3.90 for benzil and benzoic acid.[9])

Repeating Jander's experiment with 0.02, 0.05 and 0.07 molar solutions of benzoic acid in dry

acetic acid we found the freezing-point depression proportional to the solute concentration with K_F = 3.65 ± 0.02°C kg mole^{-1}. This value we have used in our calculations.

Freezing-point depressions of water in acetic acid were proportional to the water concentration upto 0.15%. The molecular weight, calculated from the relation.

$$M_{solute} = 3.65 \times \frac{\text{concentration solute in g per kg solvent}}{\text{freezing-poin depression in °C}} \quad (10)$$

was 18.3.

With $Mn(OAc)_2$ freezing-point depressions increased less than proportionally to the solute concentration. The apparent molecular weight, calculated from (10) increased proportionally from 174 for 1 g $Mn(OAc)_2$ per kg AcOH to 189 for 6.5 g $Mn(OAc)_2$ per kg AcOH. By extrapolation to zero concentration a molecular weight of 172 was found. The formula weight of $Mn(OAc)_2$ is 173. Apparently $Mn(OAc)_2$ is only little associated in dilute acetic acid solution.

Freezing-point determinations were carried out as described in section II.4.2.

Spectrophotometric determination of reaction rates. - Reactions were carried out in a glass spectrophotometer cell of about 3 ml contents and provided with a well fitting stopcock. After flushing the cell with dry nitrogen the manganic acetate solution was introduced by means of a hypodermic syringe through the bore of the stopcock. Oxygen was removed from the solution by repeated freezing in vacuo and thawing under dry nitrogen. The cell was placed in the thermostatted cell compartment of a Perkin Elmer model 137 uv spectrophotometer for at least 15 min. The substrate (thioanisole or acetic anhydride) was introduced in the same way as the manganic acetate solution and after mixing the contents of the cell the optical density at 460 nm with respect to a reference cell with pure acetic acid was recorded automatically.

Reaction rates were calculated from the decrease in optical density during the period corresponding to 0 - 10% conversion. Where relevant initial $Mn(OAc)_2$ concentrations were corrected for the quantity of manganous acetate formed during this period.

The optical density at 460 nm of manganic acetate in dry acetic acid was proportional to the concentration.

Iodometric determination of reaction rates. - Portions of about 150 ml pure acetic acid were transferred under dry nitrogen to a three-necked flask provided with a magnetic stirrer and a thermometer. After addition of the desired quantity of $Mn(OAc)_2$, air was removed by repeated freezing in vacuo and thawing under dry nitrogen. The flask was suspended for at least 15 min. in a thermostatted oil bath and the desired quantity of manganic acetate was added through a nitrogen lock. The decrease in manganic acetate concentration was followed by withdrawing 3 - 20 ml samples from the reaction mixture and titration with 0.01 N iodine solution using sodium starch glycolate as the indicator.

Reaction products of the oxidation of acetic anhydride by manganic acetate. - A mixture of 2 g manganic acetate, 50 ml acetic anhydride and 50 ml pure dry acetic acid was kept at 90°C for 5 h under nitrogen. After 24 h at room temperature the precipitated Mn salts were removed from the reaction product by filtration (yielding filtrate A), dissolved in a minimum quantity of distilled water, and passed through a 50 cm x 2 cm^2 column of Amberlite 120H ion-exchange resin. The column was rinsed with 100 ml distilled water and the combined eluates evaporated to dryness at 80°C in vacu (yielding residue B). Filtrate A was concentrated to about 10 ml in vacuo at 80°C, combined with residue B, and quantitatively (trans-)esterified by boiling for 12 h with about 10 g Amberlite 120 H in 300 ml absolute ethanol. In this way succinic acid (or anhydride) was converted to ethyl succinate and acetoxyacetic acid to ethyl glycolate. Water produced during the esterification was removed continuously by inserting a Soxhlet apparatus containing a thimble with 40 g "Molecular Sieves 3 Å" between the boiling flask and the reflux condenser. Superheating was reduced by heating the boiling flask in an oil bath and adding a few platinum cuttings.

After boiling for 12 h, the ion-exchange resin was filtered, the filtrate concentrated to about 10 ml by distillation from a boiling water bath and the residue analysed by glpc on a 10' x 1/8" 10% Apiezon L on 60/80 mesh chromosorb W column at 170°C and on a 10' x 1/8" 10% Versamid 900 on 60/80 mesh chromosorb W column at 140°C.

Treatment of a test sample of 0.7 g succinic acid and 0.8 g acetoxyacetic acid in the same way yielded a recovery of 95 - 100% of diethyl succinate and ethylglycolate.

The yield of the products in the oxidation experiment, calculated on the basis of manganic acetate intake was 62% succinic acid and 4% acetoxyacetic acid.

Ethyl succinate as a reference substance for glpc analysis was Merck A.R. quality. Ethyl glycolate was prepared by esterification of glycolic acid with absolute ethanol according to the method described above.

The identity of the main reaction product, succinic acid, was confirmed independently by evaporating acetic acid and acetic anhydride from the reaction mixture, passing an aqueous solution of the residue through an Amberlite 120H column, evaporating the eluate to dryness and recording the ir spectrum of the residue.

VII.9. REFERENCES

1. R.E. van der PLOEG, Thesis, University of Leiden (1967).
2. Chapter I, references 4,5,7,8 and 9.
3. J.M. BRONSDIJK, Thesis, University of Leiden (1965).
4. R.W. de KORTE, Thesis, University of Leiden (1964).
5. W.A. STEGGERDA, not published.
6. F.M. RAOULT, Ann. Chim. Phys. 6 [2], 66 (1884).
7. W.C. EICHELBERGER, J. Am. Chem. Soc. 56, 799 (1934).
8. E.J. BOURNE, J.C. TATLOW and R. WORRALL, J. Chem. Soc. 1957, 315.
9. G. JANDER and H. KLAUS, J. Inorg. Nucl. Chem. 1, 228 (1955).

SUMMARY

Oxidation reactions by manganic acetate in acetic acid have been the subject of many investigations, partly in connection with the catalysis of autoxidations by compounds of transition metals. The present thesis deals mainly with the preparation and structure of anhydrous manganic acetate. The incentive for these studies is outlined in the first chapter.

In chapter II the methods are described which were developed for the determination of Mn(II), Mn(III), total acetate, acetate-ion and oxide content of manganic acetate. Ozonisation of $Mn(OAc)_2$ yielded a Mn(III)-Mn(IV) complex which was isolated by chromatography. The failure to detect this complex in solutions of manganic acetate in acetic acid disproved the hypothesis that manganic acetate in acetic acid disproportionates to Mn(II) and Mn(IV) acetates.

In chapter III the preparation of manganic acetate by oxidation of $Mn(OAc)_2$ by $KMnO_4$, $Pb(OAc)_4$ or O_3 is reported. The samples could easily be obtained free from Mn(II), but Mn and total acetate contents showed variations of several percents and there was always a shortage of about 3% in the total of the analyses. Reproducible samples for further work were prepared at about 80^oC; their analysis was in agreement with the empirical formula $Mn_3(OAc)_8OH$.

The structure of manganic acetate in acetic acid solution is discussed in chapter IV. Per three Mn atoms there was one oxide or hydroxide group (determined by Karl Fischer titration), one acetate ion (determined by perchloric acid titration) and consequently one acetic acid molecule (qualitatively confirmed by infra-red spectrum). The molecular weight indicated the presence of three Mn

atoms per molecule.

X-Ray analysis of manganic acetate is the subject of chapter V. The space group was Pbca with 8 molecules in the unit cell in general position. On Weissenberg photographs the intensities of about 1150 independent reflexions were estimated and from these the positional parameters of all atoms except hydrogen could be found by means of Patterson synthesis and conventional heavy-atom techniques. The final agreement factor was 22%.

Crystalline manganic acetate is a linear polymer of $-Mn_3O(OAc)_6 . AcOH . AcO-$ units. The Mn atoms in one unit are arranged in an almost equilateral triangle about a central oxygen atom and are connected by three pairs of acetate bridges. The octahedral coordination about one of these Mn atoms is completed by a molecule of acetic acid and about the other two by the acetate bridges which link the $Mn_3O(OAc)_6$ groups to each other in the polymer chains.

A separate chapter (VI) is devoted to acetic acid. Anhydrous acetic acid partially disproportionated to acetic anhydride and water when heated above $80^{o}C$. Equilibrium constants for the disproportionation were determined in the temperature range 80 - $130^{o}C$. Acetic acid with a water content of less than 5 ppm could be prepared by treating glacial acetic acid with the calculated proportion of acetic anhydride in the presence of a trace of sulphuric acid, followed by distillation under reduced pressure.

Chapter VII reports on the oxidation of thioanisole, acetic acid and acetic anhydride by manganic acetate. The strongly retarding influence of $Mn(OAc)_2$ on the thioanisole oxidation was attributed to its ability to reduce intermediate $C_6H_5^{\cdot}SCH_3^{+}$ species.

$Mn(OAc)_2$ did not reduce the oxidation rate of acetic acid if free from water. Reaction mechanisms characterized by either oxidation of coordinated acetic acid molecules or by fission of Mn-acetate bonds were proposed.

Exploratory experiments showed that acetic anhydride is much more readily oxidized than acetic acid, yielding succinic acid as the main product.

SAMENVATTING

Oxydatie reacties van mangani acetaat in azijnzuur zijn het onderwerp geweest van vele onderzoekingen, gedeeltelijk in het kader van de studie van autoxydaties die gekatalyseerd worden door overgangsmetalen. Dit proefschrift is voornamelijk gewijd aan bereiding en structuur van mangani acetaat. De wenselijkheid van een nader onderzoek in deze richting is uiteengezet in het eerste hoofdstuk.

Hoofdstuk II beschrijft de methoden die ontwikkeld werden ter bepaling van Mn(II), Mn(III), totaal acetaat, acetaat-ion en oxyde gehalte in mangani acetaat. Ozonisatie van $Mn(OAc)_2$ leverde een Mn(III)-Mn(IV) complex dat chromatografisch geisoleerd kon worden. De afwezigheid van een dergelijk complex in oplossingen van mangani acetaat wees er op dat mangani acetaat in azijnzure oplossing niet disproportioneert in Mn(II) en Mn(IV) acetaten.

In hoofdstuk III wordt de bereiding van mangani acetaat uit $Mn(OAc)_2$ en $KMnO_4$, $Pb(OAc)_4$ of O_3 beschreven. De preparaten konden gemakkelijk vrij van Mn(II) worden verkregen, maar het Mn en totaal acetaat gehalte vertoonde variaties van enkele procenten en er was een systematisch tekort van ongeveer 3% in het totaal van de analyses. Reproduceerbare preparaten voor het verdere onderzoek werden verkregen door de bereiding uit te voeren bij $80^{o}C$; de analyse van deze kwaliteit mangani acetaat kwam overeen met de empyrische formule $Mn_3(OAc)_8OH$.

De structuur van mangani acetaat in azijnzure oplossing wordt besproken in hoofdstuk IV. Er is per drie mangaan atomen een oxyde of hydroxyde groep (bepaald door titratie volgens Karl Fischer), een acetaat ion (bepaald door

perchloorzuur titratie) en derhalve een azijnzuur molecuul (kwalitatief bevestigd aan de hand van het infra-rood spectrum). Het molecuul gewicht wees op de aanwezigheid van drie mangaan atomen per molecuul.

Het onderwerp van hoofdstuk V is de Röntgen analyse van mangani acetaat. De ruimte groep was Pbca met 8 moleculen in de elementair cel in algemene positie. De intensiteiten van ongeveer 1150 onafhankelijke reflecties op Weissenberg foto's werden geschat en met behulp van Patterson functies en gebruikelijke "heavy-atom" technieken werden de plaatsparameters van alle atomen behalve waterstof gevonden. De tenslotte bereikte overeenstemmingsfactor R was 22%.

Kristallijn mangani acetaat is een lineair polymeer van $-Mn_3O(OAc)_6$. AcOH. AcO- eenheden. De Mn atomen in één eenheid liggen in een vrijwel gelijkzijdige driehoek om een centraal zuurstof atoom en zijn verbonden door drie paren acetaat bruggen. De octaëdrische omringing van een van deze mangaan atomen wordt voltooid door een azijnzuur molecuul, die van de andere twee mangaan atomen door de acetaat bruggen die de $Mn_3O(OAc)_6$ groepen onderling verbinden in de polymeer ketens.

Een apart hoofdstuk (VI) is gewijd aan azijnzuur. Boven 80^oC disproportioneert anhydrisch azijnzuur merkbaar in azijnzuur anhydride en water. Evenwichtsconstanten voor de disproportionering werden bepaald in het temperatuurgebied $80-130^oC$. Azijnzuur met een water gehalte van minder dan 5 ppm kon worden verkregen door ijsazijn met de berekende hoeveelheid azijnzuur anhydride te behandelen in aanwezigheid van een spoor zwavelzuur als katalysator en het daarna onder verminderde druk te destilleren.

Hoofdstuk VII betreft de oxydatie van thioanisool, azijnzuur en azijnzuur anhydride met mangani acetaat. De sterk vertragende invloed van $Mn(OAc)_2$ op de oxydatiesnelheid van thioanisool werd toegeschreven aan de reductie van intermediaire $C_6H_5SCH_3^+$ deeltjes door $Mn(OAc)_2$.

$Mn(OAc)_2$ vertraagde de oxydatie van azijnzuur niet indien dit watervrij was. Reactie mechanismen, gekenmerkt door hetzij oxydatie van gecoördineerde azijnzuur moleculen, hetzij homolyse van Mn-acetaat bindingen werden voorgesteld.

Voorlopige onderzoekingen wezen uit dat azijnzuur anhydride veel gemakkelijker geoxydeerd wordt dan azijnzuur en dat barnsteenzuur het hoofdproduct is van deze oxydatie.

Op verzoek van de Faculteit der Wiskunde en Natuurwetenschappen volgen hier enkele persoonlijke gegevens.

Na het afleggen van het eindexamen HBS-B in 1948 studeerde ik Chemische Technologie aan de Technische Hogeschool te Delft waar ik in 1953 het eind-diploma behaalde. Het afstudeerwerk stond onder leiding van Prof. Dr. Ir. P. E. Verkade en had betrekking op de synthese van fosfatidezuren.

Van 1953 tot 1955 vervulde ik de militaire dienstplicht; daarna werkte ik tot 1957 op het Koninklijke/Shell-Laboratorium als research chemicus.

Na van 1957 tot 1960 werkzaam te zijn geweest als leraar natuur- en scheikunde en godsdienstonderwijs aan het Christelijk Lyceum te Apeldoorn ben ik vanaf 1961 als scheikunde docent verbonden aan het Murray College te Sialkot, West Pakistan.

De onderzoekingen, beschreven in dit proefschrift, werden verricht in een driejarige verlofperiode van 1965 tot 1968. Gedurende deze tijd was ik hoofdassistent bij het Laboratorium voor Organische Chemie te Leiden.

Speciale dank ben ik verschuldigd aan Mevrouw L. Willemsen-Brouwer die van mijn kristallen mangani acetaat bruikbare röntgen opnamen heeft weten te maken, aan Drs. R. A. G. de Graaff die met grote volharding de verwerking van de kristallografische gegevens door de computer heeft verzorgd en aan de Heer L. Pison voor het verzorgen van de grafieken en tekeningen.

Yet it is people, not things, that matter.