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Intermediate Steps in Autoxidation

IV. Reactions of Mn^{III} Acetate in Acetic Acid with Methyl Benzoate and with Benzoic Acid(s)

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Mn^{III} acetate in acetic acid reacts with methyl benzoate at 110°C in the same way as toluene, chlorobenzene, and anisole, viz., with formation of *o*-, *m*-, and *p*-derivatives mainly containing $—CH_2COOH$ and $—CH_2OAc$ substituents as a result of homolytic nuclear attack by $HOOC—CH_2\cdot$ radicals.

Benzoic acid gave analogous *m*- and *p*-substituted compounds, but instead of the corresponding *ortho*-derivatives, biphthaloyl ($C_{16}H_8O_4$) was formed. Toluic acid reacted similarly, yielding normal 3-substituted products in addition to dimethylbiphthaloyl. It is shown that the biphthaloyls as well as other dimeric 2-substituted products are formed via homophthalic acid(s).

It is suggested that there is a relation between the formation of these homophthalic acid derived products and the fact that transition metal catalyzed autoxidations of alkylbenzoic acids in acetic acid are proceeding much more slowly than those of their esters.

INTRODUCTION

In Part III (*1*) it was demonstrated that Mn^{III} acetate in anhydrous acetic acid reacts with benzene, chlorobenzene, and toluene at 100–110°C to give (*o*-,*m*-, and *p*-)substitution products mainly containing $-CH_2COOH$ and $-CH_2OAc$ groups. The phenylacetic acids were shown to be the precursors of the benzyl acetates. A mechanism was proposed, starting from the $HOOC—CH_2\cdot$ radical generated by the Mn^{III} acetate/acetic acid reagent. Heiba *et al.* (*2*) showed that a similar scheme is operative for the reaction with anisole; their data are in agreement with ours (*1*, *3*), confirming that except in the case of reactants having low ionization potentials, product formation is due to nuclear substitution or side-chain attack by $HOOC—CH_2\cdot$ radicals rather than to electron transfer reactions involving Mn^{III} acetate as such.

We are now presenting information regarding the behavior of benzoic acid(s) compared with that of methyl benzoate. This comparison seemed of interest in view of the well-known difference in autoxidation behavior between free alkylbenzoic acids and their esters. Thus, Mn- or Co-catalyzed autoxidation of *p*-toluic or *p*-isopropylbenzoic acid in the usual solvent acetic acid is normally much slower than that of the corresponding esters; industrial processes have been developed for the manufacture of terephthalic acid in which *p*-toluic acid is first esterified and subsequently oxidized (*4*), or in which *p*-toluic acid is oxidized by reagents other than molecular oxygen. Since the Hammett substituent constants for *p*-COOH and *p*-$COOCH_3$ are very similar, the difference in the autoxidation rates must be due to a different chemical behavior of the two substituents as such.

EXPERIMENTAL

A. Mn^{III} *Acetate and Benzoic Acid*

As an example, a representative run will be described (see part III). Mn^{III} acetate, 18 g (about 77 mmoles), 800 ml of anhydrous acetic acid and 10 g (82 mmoles) of benzoic acid were reacted at 110°C for 24 hr (10 half-lives), when all the Mn^{III} had disappeared.

The resulting yellow solution was evaporated to dryness at reduced pressure. The residue was then treated with 500 ml of a 5% solution of HCl in water and the solution again evaporated to dryness. Acetone extraction left 95% of the manganese as $MnCl_2 \cdot 4H_2O$ (14.4 g, 73 mmoles).

The yellow acetone extract was evaporated to yield 10.2 g of products. These were shaken with diethyl ether and a dilute aqueous sodium hydroxide solution. The ethereal solution yielded about 200 mg of biphthaloyl (0.8 mmoles) after recrystallization from acetic acid (I). The aqueous alkaline solution was acidified and the precipitate repeatedly washed with hot water to remove benzoic acids. The residue ((X), about 250 mg), presumed to be dimeric acids related to homophthalic anhydride, retained 1–3% of Mn even after several attempts at purification.

The acidic aqueous solution was extracted with ether to yield 9.5 g of material. Esterification with methanol/sulfuric acid followed by distillation yielded 7 g of methyl benzoate. The distillation residue contained another 0.40 g of methyl benzoate and 1.35 g of a mixture of substituted methyl benzoates (see Table 1, *b–e*).

Carbon dioxide formation, as determined by weighing the barium carbonate formed in a barium hydroxide trap connected to the reaction vessel, amounted to 12 mmoles, i.e., 16% based on intake Mn^{III} acetate. Methane amounted to 1.5 mmoles (2%).

Assuming the above 1.35 g of normal substitution products to have the average composition of $-CH_2OAc$ derivatives ($M = 208$) they account for 26 ($= 4 \times 6.5$) milliequivalents (meq) of Mn^{III}. The biphthaloyl (200 mg, 0.8 mmoles) required $12 \times 0.8 = 10$ meq. If it is assumed that the insoluble dimeric acids have the average composition of (III) the 250 mg isolated (0.7 mmoles) required $6 \times 0.7 = 4$ meq of Mn^{III}. Further, part of the carbon dioxide (total 12 mmoles) has been consumed in the formation of nonaromatic products (*1*), so that well over 50% of the intake Mn^{III} (> 40 meq) has been accounted for. Handling losses probably mainly involved the "anomalous" products, since the primary nuclear substitution pattern to be expected for attack by $HOOC—CH_2\cdot$ radicals suggests that about 40–50% of the aromatic reaction products should be *ortho*-derivatives; only 3 mmoles (0.7 + 0.8 mmoles of dimers) were isolated compared with 6.5 mmoles of $m + p$ derivatives.

B. *Reaction of Homophthalic Anhydride with* Mn^{III}

Homophthalic anhydride (1.62 g, 10 mmoles, readily obtained by dehydration of pure commercial homophthalic acid with acetic anhydride) was dissolved in 200 ml of anhydrous acetic acid. Small portions of Mn^{III} acetate in 200 ml acetic acid, totalling 1.30 g (56 mmoles), were gradually added at room temperature in an atmosphere of nitrogen. Reaction was practically instantaneous. Similar runs were made at 100°C. The work up was as described for the runs with benzoic acid. In the runs carried out at room temperature, the ether layer only contained (IV); at 100°C, biphthaloyl (I) was the only nonacidic ether-soluble product.

C. *Standard Samples and Starting Materials*

Anhydrous acetic acid and Mn^{III} acetate were made as described recently (*9*). Kinetic runs—with and without added *p*-toluic acid—led to a unimolecular rate constant of decomposition of Mn^{III} acetate in acetic acid amounting to 0.29 hr^{-1}; this corresponds to a half-life of 2.4 hr. 2,2′-Dicarboxydibenzyl was prepared as reported by Fischer and Wolffenstein (*10*). *o*-Carboxybenzyl acetate (2-HOOC-C_6H_4-CH_2OAc) appears to be unknown in the literature. It was synthesized from phthalide:

Phthalide (7 g, 52 mmoles) was heated with a solution of 6 g (107 mmoles) of KOH in 20 ml of water for about 15 min, when the phthalide had completely dissolved. The solution was evaporated to dryness. To the dry material, presumably containing the potassium salt of 2-hydroxymethylbenzoic acid, 10 ml of acetic anhydride were added dropwise at 20°C. After the evolution of heat had subsided, water was added and then the solution was slowly acidified with dilute hydrochloric acid. Organic products were extracted with benzene. The organic acid was taken up in a dilute sodium bicarbonate solution and isolated by precipitation with dilute hydrochloric acid. The yield was only moderate, viz., 1.2 g (12%). The white crystals melted at 116–118°C. Calculated for $C_{10}H_{10}O_4$ (194):61.85% C, 5.16% H; found 61.76% C, 5.29% H. The acidimetric equivalent weight was 196. The ir spectrum was in agreement with the presence of a carbonyl group and an *ortho*-substituted benzene. The NMR spectrum (Varian A60) showed four types of hydrogens, viz., three at 1.1 ppm, two at 2.80 ppm; four at 3.75–4.1 ppm and one at 5.68 ppm (TMS standard) as required for a carboxybenzyl acetate (CH_3,CH_2, C_6H_4, COOH).

Most other compounds used (see Table 1) were commercially available, purities being checked by gas–liquid chromatographic (glc) methods.

D. *Analytical Methods*

The glc analyses and separations were made using a Becker Multigraph instrument, Carbowax Column (4 m), 190°C, 1.4 atm H_2.

Mass spectrometric data were obtained using a double focusing AEI (MS 902) instrument with direct-inlet system. Molecular formulas were derived from parent ion peaks in combination with the C and H isotopic distribution patterns.

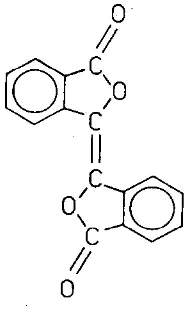
RESULTS AND DISCUSSION

A. *General*

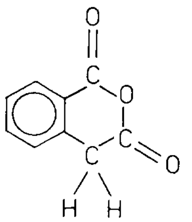
Using the procedures described in Part III, several runs were made with benzoic acid. A small number of experiments was carried out with methyl benzoate and with *p*-toluic acid; a single tentative run was made with terephthalic acid. Reaction time, 24 hr, temperature, 110°C.

Methyl benzoate gave the expected *o*-, *m*-, and *p*-substitution products analogous to those formed from toluene, chlorobenzene, and anisole. Reaction mixtures derived from benzoic and *p*-toluic acid were more difficult to analyze. Acidic products were first esterified with methanol so as to make them amenable to (glc); mass spectrometric analyses (MS) were generally made on samples isolated by glc. Methylation offered the additional advantage of a partial product overlap, side-chain derivatives of *p*-toluic acid being also formed via nuclear *para*-substitution in benzoic acid and methyl benzoate. Isomer ratios were not determined; in general, *m*- and *p*-isomers could not be completely separated on glc but were believed to be present in comparable proportions.

Benzoic acid gave the normal *m*- and *p*-substituted products, but no mononuclear *ortho*-derivatives. Instead, biphthaloyl (I)



Biphthaloyl (I)



Homophthalic Anhydride (II)

was formed. *p*-Toluic acid behaved similarly; normal 3-substituted products were obtained, in addition to dimethylbiphthaloyl. Both acids further yielded dimeric (perhaps oligomeric) *o*-substituted acidic compounds, structurally related to homophthalic anhydride (II), which could not be definitely identified. Terephthalic acid only gave the latter type of products.

A survey of the various compounds detected, together with brief references as to identifications, is given in Table 1. For identifications of biphthaloyls and other "anomalous" compounds see Section B.

TABLE 1

PRODUCTS OBTAINED FROM Mn^{III} ACETATE/ACETIC ACID AND VARIOUS BENZOIC ACID DERIVATIVES

	Substituent groups introduced[a]				
Reactant	—CH_2COOH	—CH_2OAc	—CHO (or —$CH(OAc)_2$)	—COOH	Other products
Benzoic acid	*m,p*[b] (No *ortho*)	*m,p*[c] (No *ortho*)	*m,p*[d] (No *ortho*)	*m,p*[e] (No *ortho*)	Biphthaloyl (I)[f] *Ortho*-substituted dimers
Methyl benzoate	*o,m,p*[g]	*o,m,p*[h]	*o,m,p*[i]		
p-Toluic acid		3-isomer[j] only	3-isomer[k] only	3-isomer[l] only	Dimethylbiphthaloyl[m] Dimers Side chain-derived products

[a] These product data refer to methyl esters.

[b] Molecular formula $C_{11}H_{12}O_4$ (MS), two compounds incompletely separated by glc, one of which identical with authentic sample of dimethylhomoterephthalate (no *ortho* on the basis of MS and ir).

[c] Molecular formula $C_{11}H_{12}O_4$ (MS), different from cpds (*a*), two compounds, incompletely separated by glc.

[d] Same as *c*, but molecular formula $C_9H_8O_3$.

[e] Molecular formula $C_{10}H_{10}O_4$ (MS); identical with authentic samples of dimethyl tere- and isophthalate, incomplete separation on glc.

[f] See Section B.

[g] As (*b*), but with an additional isomer (*ortho*), separable from *m,p* on glc.

[h] As (*c*), but with an additional isomer (*ortho*), separable from *m,p* on glc.

[i] As (*d*), but with an additional isomer (*ortho*), separable from *m,p* by glc.

[j] Molecular formula $C_{12}H_{14}O_4$ (MS), single compound (glc), identical with authentic sample of 3-acetoxymethyl derivative, synthesized from 3-methylol derivative of *p*-toluic acid according to H. Diesbach *et al.*, *Helv. Chim. Acta* **23**, 1249 (1940).

[k] Molecular formula of 2,4-dinitrophenylhydrazone $C_{16}H_{14}O_6N_4$ (358 MS).

[l] Single compound; molecular formula $C_{11}H_{12}O_4$ (MS).

[m] Section B. Side-chain derived products were the *p*-CH_2OAc, *p*-CHO, and the *p*-$COOCH_3$ derivative, also present in the pairs (*c*, *h*), (*d*, *i*) and in (*e*), respectively (glc). The *p*-CH_2 acetate was identical with an authentic sample synthesized from *p*-tolunitrile by the procedure of C. Barkenbus and J. B. Holtzclaw, *J. Amer. Chem. Soc.* **47**, 2192 (1925).

B. *Product Identification*[1]

Biphthaloyl (I) analyzed 72.7% C and 3.0% H, as required for a compound $C_{16}H_8O_4$. The mass spectrum showed a parent peak at 264; the C and H isotopic pattern agreed with molecular formula $C_{16}H_8O_4$ (=264). Fragment peaks appeared to be due to the consecutive loss of four molecules of CO, viz., at 236, 208, 180, and 152. A moderately strong peak at 76 (benzyne) proved the product to be *ortho*-substituted. Infrared spectra showed carbonyl (1786 cm^{-1}) and *ortho*-substitution bands (757 cm^{-1}). The product was identical in all respects with an authentic sample of biphthaloyl, prepared from phthalic anhydride and triethyl phosphite (*5*). The yellow crystals (from acetic acid) sublimed at 310°C and melted in a closed melting point capillary at 354°C (lit. 354°C).

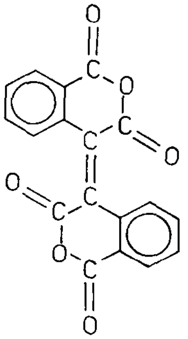
Dimethylbiphthaloyl closely resembled biphthaloyl. The mass spectrum displayed a parent peak at 292, as required for $C_{18}H_{12}O_4$; fragment peaks at 264, 236, 208, 180, and 90 again showed that four molecules of CO are lost consecutively. The peaks at 90 and 180 should be due to 4-methylbenzyne and its dimers.

Incompletely identified dimers (*X*). These products were obtained from benzoic acid (110°C) as well as from homophthalic anhydride (20°C, 100°C) and from homophthalic acid (80°C). They all retained small percentages of bivalent manganese (1–3% according to elemental analysis and ESR (*8*)).

Products isolated from different runs did not show constant carbon and hydrogen contents, viz., 61–65% C and 3–3.9% H. Dehydro-dimers (III) of homophthalic anhydride ($C_{18}H_{10}O_6$, $M = 322$) require 67.1% C and 3.1% H; corresponding dibasic acids ($C_{18}H_{12}O_7$, $M = 340$) require 63.5% C and 3.5% H. The ir spectrum of the brown-yellow material showed hydroxyl (3400 cm^{-1}), carbonyl (1700–1760 cm^{-1}), and *ortho*-substitution (760 cm^{-1}) bands. Titration with alkali, using phenolphthalein as the indicator, indicated the acidimetric equivalent weight to be about 175, end points being fuzzy due to the brownish color of the solution. Further oxidation with Mn^{III} acetate/acetic acid failed to yield biphthaloyl or other identifiable products. These admittedly inconclusive data suggest that the substance consists of dehydro-dimers of (II) and their hydrolysis products. Assuming that (II) is oxidized via the enol form (see Section C), the enol radicals may dimerize in various ways, viz., with formation of a C—C *meso*- or *dl*-dimer or with formation of a C—O linkage. The latter type of compound cannot be oxidized to (I).

$$\mathrm{II} \rightarrow \rightarrow \text{Enol radical} \rightarrow \left\{ \begin{array}{l} \text{IIIa,b } (\textit{meso-} \text{ and } \textit{d,l}\text{-dimer via C—C bond}) \\ \text{IIIc (Dimer formed by C—O bond)} \end{array} \right.$$

Tetra-dehydrodimer of homophthalic anhydride (*IV*) (see Section C). This compound was isolated—together with (X)—only from runs starting from homophthalic anhydride and Mn^{III} acetate at room temperature. Its mass spectrum showed a parent peak at 320 and a fragment peak at 248. The C and H isotopic pattern was in agreement with a molecular formula $C_{18}H_8O_6$ ($M = 320$); the loss of a fragment 72 suggested the presence of a OC—O—CO group. The yellow compound melted (broadly) at 190°C; its ir spectrum showed carbonyl as well as *ortho*-substitution bands. These data and the formation of biphthaloyl upon further oxidation with Mn^{III} acetate indicate the structure to be (IV), presumably formed by dehydrogenation of a C—C dimer (IIIa,b):



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[1] For mononuclear (normal) products see Table 1 and Experimental.

C. *Mechanisms*

The formation of *o*-, *m*-, and *p*-substitution products from methyl benzoate is in line with our earlier results on chlorobenzene and toluene as well as with those of Heiba *et al.* on anisole. The formation of related *m*- and *p*-substituted derivatives from benzoic acid and of 3-substituted compounds from *p*-toluic acid can be also regarded as normal. Rates of reduction of Mn^{III} were approximately the same as in the absence of aromatic reactants; accordingly, substitution products should be primarily due to HOOC—CH_2 radicals adding on to the aromatic nucleus. The formation of (I) and of other *ortho*-substituted dimeric products is therefore probably preceded by that of homophthalic acid.

In agreement with this, homophthalic acid was found to be oxidized by Mn^{III} acetate/acetic acid to form the same dimeric products as benzoic acid, but at a higher rate than those observed when starting from other substituted phenylacetic acids (*1*).

Presumably, homophthalic acid rapidly forms the cyclic anhydride (II). This compound was found to react with Mn^{III} even at room temperature; slightly larger proportions of dimeric acids (X) were obtained and compound (IV) could be isolated but no biphthaloyl. At 100°C, only (X) and (I) were obtained; (IV) was shown to be rapidly oxidized to biphthaloyl. The anhydride (II) is known to enolize and may even contain an appreciable proportion of the enol form in solution (*6*). In earlier papers (*3, 7*) we have shown that enols are readily oxidized by Mn^{III} with formation of radicals prone to dimerization even in the presence of oxygen. The C—C dimer(s) (IIIa and/or IIIb) are assumed to be further dehydrogenated via the enol stage to (IV). The dimeric acidic compounds (X) may arise either from C—O dimers of (II) or from a C—C dimer escaping further oxidation to (IV).

No attempts were made to establish the nature of the further degradation of (IV) to biphthaloyl. Since no carbon monoxide was detected, it probably involves the formation of two molecules of carbon dioxide, which would require four equivalents of Mn^{III}. This brings up the total number of equivalents of Mn^{III} consumed in the formation of biphthaloyl from benzoic acid to 12. The stoichiometry of the scheme suggested thus becomes[2];

$$12\,Mn(OAc)_3 + 2\,C_6H_5COOH \rightarrow 12\,Mn(OAc)_2 + 2\,CO_2 + 10\,CH_3COOH + C_{16}H_8O_4$$

A summary of the reactions proposed is given below.

Several experiments were done to detect other precursors of (I) or (X) than (II), starting from the fact that degradation of phenylacetic acids (1) normally proceeds via the corresponding benzyl radicals. However, oxidation runs with a number of *o*-carboxybenzyl derivatives, viz., with *o*-carboxybenzyl acetate, phthalide (conceivably formed by a ring closure reaction) as well as with the dimer 2,2′-dicarboxydibenzyl, all failed to yield (I) or type (X) compounds; rates of Mn^{III} reduction were so slow that detectable amounts of the starting material should have survived in runs started from benzoic acid. Treatment of homophthalic acid in acetic acid with di-*t*-butylperoxide as an indirect source of HOOC—$CH_2\cdot$ radicals in the absence of Mn^{III} did not yield biphthaloyl either and only small amounts of dimeric products were formed.

The latter data indicate that the *o*-carboxybenzyl radical is not an intermediate in the formation of (I) and is probably not formed at all. In view of the high rate of degradation of homophthalic acid by Mn^{III}, it seems likely that the normal decarboxylation sequence of phenylacetic acids is outrun by the cyclization enolization–oxidation sequence

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[2] The manganic acetate used by us was not the dihydrate but a "basic" trimer $Mn_3O(OAc)_7\cdot HOAc$, the composition and crystal structure of which were determined recently. In solution the compound is also a trimer (9b). For simplicity it is here designated as $Mn(OAc)_3$.

Stepwise formation of biphthaloyl, etc., from benzoic acid and $\mathrm{Mn^{III}}$ acetate/acetic acid

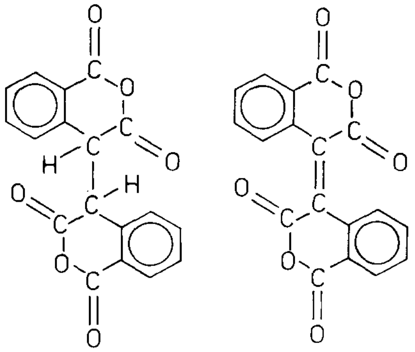
$$\text{Benzoic acid} \xrightarrow[\text{2 steps}]{\text{HOOC—CH}_2\cdot} \text{Homophthalic acid} \qquad \text{(a)}$$

$$\text{Homophthalic acid} \underset{H_2O}{\rightleftarrows} \text{Homophthalic anhydride (II)} \qquad \text{(b)}$$

$$\text{(II)} \rightleftarrows \text{Enol form of (II)} \qquad \text{(c)}$$

$$\text{Enol form of (II)} \xrightarrow{\mathrm{Mn^{III}}} \text{Enol radical} \qquad \text{(d)}$$

$$\text{2 Enol radicals} \longrightarrow \begin{array}{l}\text{C—C dimers (}\textit{meso}\text{ and }\textit{d,l}\text{ (IIIa,b))}\\ \text{C—O dimers (precursors of X?)}\end{array} \qquad \text{(e)}$$



$$\text{C—C dimer (III)} \xrightarrow[2\,\mathrm{Mn^{III}}]{} \text{Tetra-dehydrodimer (IV)} \qquad \text{(f)}$$

$$\text{(IV)} \xrightarrow[4\,\mathrm{Mn^{III}}]{} \text{Biphthaloyl (I)} \qquad \text{(g)}$$

(b, c, d). The experiment with di-*t*-butylperoxide shows that hydrogen removal by HOOC—$CH_2\cdot$ *t*-butoxy, and methyl radicals is inefficient compared with the steps (b, c, d), the rate of (d) probably being very high. Thus, whereas the formation of phenylacetic acids merely depends on the availability of HOOC—$CH_2\cdot$ radicals (*1*), that of dimeric *o*-derivatives (I, IV, X) is due to the characteristic property of $\mathrm{Mn^{III}}$ acetate to be both a highly efficient oxidant for enols and a source of HOOC—$CH_2\cdot$ radicals. The different behavior of benzoic acid and its methyl ester towards $\mathrm{Mn^{III}}$ acetate/acetic acid is attributed to the fact that in acetic acid a COOH substituent is readily capable of forming a cyclic anhydride with an adjacent -CH_2COOH group, whereas the $COOCH_3$ group is unable to do so.

It should be noted that the aromatic products are due to solvent degradation. According to our scheme of reactions, the central C=C bond of (I) originates from two methyl carbon atoms of acetic acid. Application of the same scheme to propionic acid fails at reaction (f); with isobutyric acid, the cyclic anhydride formed in step (b) is unable to enolize, etc.

D. *The Possible Significance of the Formation of Biphthaloyls, etc., in Autoxidations*

In order for small proportions of transition metal compounds to be effective catalysts in autoxidations, the formation of the higher and of the lower valency stage of the metal compounds has to proceed at the same (high) rate. Thus, rapid reduction of $\mathrm{Mn^{III}}$ with formation of a radical prone to dimerization rather than to addition of molecular oxygen leads to chain termination. In that case, the regeneration of Mn^{III} from Mn^{II} ($R\cdot + O_2 \rightarrow ROO\cdot$; $ROO\cdot + Mn^{II} \rightarrow ROO^- + Mn^{III}$ (*8*)) fails to be effective. (See Part II (*7*).)

It seemed of interest, therefore, to ascertain whether the radicals involved in the degradation of homophthalic acid to biphthaloyl would be capable of readily adding on molecular oxygen with subsequent regeneration of Mn^{III} as outlined above.

As a first approach, a number of simple autoxidation runs was performed (1 atm of oxygen bubbled through for 4 hr, 110°C) : a) Mn^{III}acetate/*p*-xylene/acetic acid (4, 94, and 2500 mmoles, respectively); b) same, but with Mn^{II} rather than Mn^{III} acetate; d) As c), but with Mn^{III} rather than Mn^{II} acetate.

Runs a) and b) produced about the same amount of *p*-toluic acid, viz., 7 mmoles; both mixtures contained Mn^{III}. Runs c) and d) both failed to produce any *p*-toluic acid; the product mixtures did not contain Mn^{III}. Work up consisted in extraction with alkali.

These data show that homophthalic acid is capable of rapidly reducing Mn^{III} with formation of radicals unable to maintain or build up a sufficiently high level of Mn^{III} for the autoxidation of *p*-xylene to proceed at a perceptible rate. In combination with the results described in the foregoing sections, the data suggest a close relation between formation of dimeric products from alkylbenzoic acids and their resistance to autoxidation in acetic acid.

This relation may consist in termination reactions caused by the rapid reduction of Mn^{III} and concomitant formation of radicals incapable of oxygen addition, and/or in the formation of dimeric polyfunctional acids (X) acting as powerful chelating agents for Mn^{II}, thereby impeding their oxidation to Mn^{III}.

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