Effect of Strong Acids on the Oxidation of Alkylarenes by Manganic and Cobaltic Acetates in Acetic Acid

By **Jacques Hanotier,* Monique Hanotier-Bridoux,** and **Pierre de. Radzitzky,** Labofina S.A., Research Laboratories of the Petrofina Group, 1120 Brussels, Belgium

The oxidation of alkylarenes by both manganic and cobaltic acetates in acetic acid is so enhanced by strong acids that extensive transformations can be achieved at room temperature. Under these conditions, only products from side-chain oxidation are obtained and the formation of nuclear adducts reported in previous studies with manganic acetate has not been observed. The products obtained are different according to whether oxygen is present or not. Under nitrogen, benzylic acetates predominate whereas carbonyl compounds are favoured when oxygen is present. The activating effect of strong acids on the oxidizing properties of manganic and cobaltic acetates seems to be primarily related to their ability to release protons. In the case of cobaltic acetate, this effect appears to be partly the result of a modification in the association state of cobalt atoms. In concentrated systems, Co^{III} and Co^{II} are apparently associated in dimeric structures and the effect of strong acids may be to dissociate such dimers with liberation of reactive cobaltic species. The mechanism of attack of alkylarenes is discussed.

ALTHOUGH the efficiency of manganese and cobalt salts as catalysts for the air oxidation of alkylbenzenes has been recognized for a long time, the mechanism by which they work has not been completely elucidated. Their ability to dissociate hydroperoxides together with much other experimental, mainly kinetic, evidence has led to the widely accepted opinion that their function is primarily to generate free radicals [reactions (1) and (2)].

$$ROOH + M^{2+} \longrightarrow RO\cdot + M^{3+} + OH^- \quad (1)$$

$$ROOH + M^{3+} \longrightarrow ROO\cdot + M^{2+} + H^+ \quad (2)$$

However, the fact that in several oxidation processes, large amounts of cobalt salt [1] and/or the use of various promoters, *e.g.* aldehydes,[2,3] ketones,[4] epoxides,[5] or

---

[1] Y. Ichikawa, G. Yamashita, M. Tokashiki, and T. Yamaji, *Ind. and Eng. Chem.*, 1970, **62**, 38.

[2] D. C. Hull, U.S.P. 2,673,217.

[3] M. Yamamoto, T. Minoda, H. Nishino, and T. Imoto, *J. Appl. Res.*, 1967, **17**, 293.

[4] W. F. Brill, *Ind. and Eng. Chem.*, 1960, **52**, 837.

[5] J. W. Patton and N. F. Seppi, *Ind. and Eng. Chem. (Product Res. and Development)*, 1970, **9**, 521.

ozone,[6] are required for oxidation has led to the conclusion that direct attack of the hydrocarbon substrate by high-valency species [reaction (3)] may also be operative.[7]

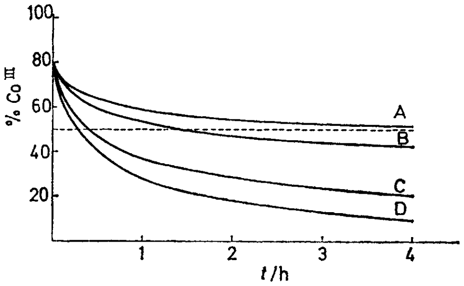
$$RH + M^{3+} \longrightarrow R\cdot + M^{2+} + H^+ \qquad (3)$$

It is surprising, however, that relatively few studies have been made to determine the theoretical and practical importance of such electron-transfer processes in the oxidation of hydrocarbons. One of the reasons for this may be that manganic and cobaltic acetates which are soluble in acetic acid and therefore are particularly suitable for studying the oxidation of water-insoluble substrates are in fact relatively weak oxidizing agents at low temperature.

Recently, we reported that the oxidizing activity of cobaltic acetate in acetic acid is greatly enhanced by strong acids to such an extent that relatively inert hydrocarbons such as paraffins can be significantly oxidized at temperatures as low as 20—40 °C.[8] Under the same conditions, cobaltic and manganic acetates were shown to react readily with alkylarenes to afford high yields of specific products.[9] We present here the results obtained in the latter case, with particular emphasis on the mechanism of action of strong acids.

RESULTS

Effect of Strong Acids on the Reduction of Manganic and Cobaltic Acetates.—Table 1 shows that when manganic acetate is heated in acetic acid at 70 °C for 30 min in the presence of *m*-diethylbenzene, practically no reduction of Mn^{III} occurs. However, when 1·0M-sulphuric acid is added to the system, almost complete reduction takes place within 10 min at only 25 °C. This rapid reduction of Mn^{III} is clearly the result of a reaction with *m*-diethylbenzene since no significant reduction is observed in the same conditions when the alkylaromatic substrate is omitted. Table 1 also shows that 1·5M-trichloroacetic acid has the same effect on the reduction of cobaltic acetate in the presence of 2-ethylnaphthalene. Similar results can be obtained with other strong organic or inorganic acids, *e.g.* perchloric acid, phosphoric acid, and trifluoroacetic acid and even with boron trifluoride. It has been pointed out elsewhere [8] that the strongest acids, *e.g.* sulphuric acid, perchloric acid, or benzenesulphonic acid, enhance the oxidizing power of cobaltic acetate to such a degree that extensive reduction of Co^{III} takes place at 25 °C in the absence of any hydrocarbon substrate, by reaction with acetic acid used as solvent. As shown here, trichloroacetic acid has a more selective action. Still weaker acids such as chloroacetic acid have practically no effect. On the other hand, trichloroacetic acid, by contrast with sulphuric acid, has no effect on the oxidation of *m*-diethylbenzene by manganic acetate although it markedly activates the oxidation of the more reactive 2-ethylnaphthalene. Apparently the activating effect of acids on the oxidizing power of manganic and cobaltic acetates is related to their strength, *i.e.* their ability to release protons, more than to the nature of their anion. The effect of the concentration of trichloroacetic acid on the rate of reduction at 25 °C of 0·5M-cobaltic acetate in acetic acid containing ethylbenzene is shown in the Figure.



Effect of trichloroacetic acid on the rate of reduction under nitrogen of 0·5M-cobaltic acetate in acetic acid in the presence of 2·5M-ethylbenzene. [CCl_3CO_2H], A, 0M; B, 0·3M; C, 0·9M; D, 1·8M. Temperature, 25 °C; Co^{III} preparation, solution (see Experimental section)

TABLE 1

Effect of strong acids on the reduction of manganic and cobaltic acetates in acetic acid in the presence of alkylarenes under nitrogen

[Oxidant] (mol l⁻¹)		Substrate (0·2M)	[Acid] (mol l⁻¹)		Temp. (°C)	Time (min)	Oxidant reduced (%)
Mn^{III}	0·04	*m*-Diethylbenzene			70	30	3
Mn^{III}	0·03	*m*-Diethylbenzene	H_2SO_4	1·0	25	10	98
Mn^{III}	0·03		H_2SO_4	1·0	25	10	2
Co^{III}	0·05	2-Ethylnaphthalene			25	15	2
Co^{III}	0·05	2-Ethylnaphthalene	CCl_3CO_2H	1·5	25	15	96
Co^{III}	0·05		CCl_3CO_2H	1·5	25	15	1

Co^{III} Preparation, powder (see Experimental section).

Kinetic Studies.—According to Andrulis and his coworkers,[10] the electron-transfer oxidation of *p*-methoxytoluene by manganic acetate in acetic acid at 70—100 °C obeys the kinetic equation (4). By assuming, as required

$$-d[Mn^{III}]/dt = k[Mn^{III}][\text{Substrate}]/[Mn^{II}] \qquad (4)$$

by the stoicheiometry of the reaction, that two equiv. of Mn^{II} are consumed per mole of substrate transformed, expression (5) can be derived by integration of equation (4)

$$k = \frac{1}{t}\frac{2}{2b-a}\left(a\ln\frac{a}{x} - 2b\ln\frac{2b}{x+2b-a}\right) \qquad (5)$$

---

[6] A. S. Hay, J. W. Eustance, and H. S. Blanchard, *J. Org. Chem.*, 1960, **25**, 616.

[7] T. Morimoto and Y. Ogata, *J. Chem. Soc.* (*B*), 1967, 62.

[8] J. Hanotier, Ph. Camerman, M. Hanotier-Bridoux, and P. de Radzitzky, *J.C.S. Perkin II*, 1972, 2247; Belg. P. 719,094 and 727,873; B.P. 1,214,417.

[9] Belg. P. 727,874; B.P. 1,206,268.

[10] P. J. Andrulis, M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Amer. Chem. Soc.*, 1966, **88**, 5473.

where $x = [\mathrm{Mn^{III}}]$, $a = [\mathrm{Mn^{II}}]_0$ and $b = [\mathrm{Substrate}]_0$, with the further assumption that $[\mathrm{Mn^{III}}]_0 = 0$.

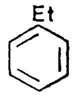
Table 2 quotes the kinetic constants calculated from equation (5) from data obtained by reacting manganic acetate at 25 °C with compounds (1)—(3) in the presence of 0·5M-sulphuric acid.

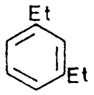
TABLE 2

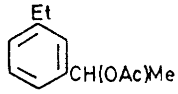
Kinetics of the reduction of manganic acetate activated by 0·5M-sulphuric acid in acetic acid in the presence of ethylarenes [a]

t/min	10^5k/sec^{-1} [b] (1)	(2)	(3)
2	6·4	40·7	6·2
4		47·5	5·5
6	7·3	45·1	5·7
8	6·9	43·6	5·9
10	6·8	44·8	5·7

[a] 0·0973M-Ethylbenzene (1); 0·0535M-m-diethylbenzene (2); 0·0908M-1-(m-ethylphenyl)ethyl acetate (3). [b] Calculated from expression (5). For m-diethylbenzene, both ethyl substituents have been considered as substrate, *i.e.* b = 0·1070M.


(1)


(2)


(3)

The constants thus determined do not show any systematic variation with time which suggests that the kinetics determined by Andrulis *et al.* still hold when manganic acetate is activated by strong acids. The constant determined by these authors for p-methoxytoluene at 100 °C was *ca.* 6·5 × 10^{-5} s^{-1}, *i.e.* of similar magnitude to that determined in the present work for the much less reactive ethylbenzene at 25 °C. Under the same conditions m-diethylbenzene has a reactivity per ethyl substituent about six times higher than ethylbenzene.

TABLE 3

Products from the oxidation of alkylarenes by 0·2M-manganic acetate in acetic acid in the presence of strong acids

Expt. no.	Atmosphere	[Substrate] (mol l^{-1})		[Acid] (mol l^{-1})		Temp. (°C)	Time (min)	Conversion [a] (%)	Products (mol %) [b] (I)	(II)	(III)	(IV)	Yield (%) *vs.* Substrate [c]	Mn$^{\mathrm{III}}$ [d]
1	N_2	Toluene	0·10	H_2SO_4	1·0	25	60	61	62	12	25	1	89	85
2	N_2	p-Chlorotoluene	0·10	H_2SO_4	1·0	25	120	66	55	19	26	*e*	93	86
3	N_2	p-Methoxytoluene	0·10	H_2SO_4	1·0	0	1	61	100	0	0	*e*	4	4
4	N_2	Ethylbenzene	0·10	H_2SO_4	1·0	25	60	62	81	12	7	0	91	93
5	N_2	Ethylbenzene	0·09	CCl_3CO_2H	1·5	60	1440	1	54	0	0	46		58
6	N_2	Cumene	0·10	H_2SO_4	1·0	25	60	64	0	16	75	9	32	40
7	N_2	m-Diethylbenzene	0·05			25	60	0						
8	N_2	m-Diethylbenzene	0·05	H_2SO_4	1·0	25	60	100	93	1	6	*e*	90	85
9	N_2	m-Diethylbenzene	0·10	H_2SO_4	1·0	25	3	85	92	7	1	*e*	100	
10	N_2	m-Diethylbenzene	0·05	$HClO_4$	1·0	25	60	90	91	4	5	*e*	100	100
11	O_2	Toluene	0·10	H_2SO_4	1·0	25	60	66	21	3	71	5	98	
12	O_2	m-Diethylbenzene	0·05	H_2SO_4	1·0	25	60	100	75	8	17	*e*	94	99

[a] Calculated from the amount of substrate not transformed as determined by analysis. [b] Products resulting from oxidation of the side chain: (I), acetate; (II), alcohol; (III) aldehyde or ketone; (IV), acid. With m-diethylbenzene as substrate, all possible products resulting from the oxidation of one or both ethyl groups have been identified; the values given in the Table refer to substituents. [c] Mole % of the products from side-chain oxidation *vs.* substrate transformed. [d] Based on the stoicheiometry of 2 moles of manganic acetate consumed per mole of acetate or alcohol produced, 4 moles of manganic acetate per mole of aldehyde or ketone, and 6 moles of manganic acetate per mole of acid (when determined). [e] Not determined.

A more detailed study of the kinetics of ethylbenzene oxidation by cobaltic acetate in the presence of trichloroacetic acid will be reported later.[11] Co$^{\mathrm{II}}$ was shown to have a retarding action on the reduction of Co$^{\mathrm{III}}$ as also established by Sakota and his co-workers for the oxidation of toluene by cobaltic acetate in the absence of an acidic activator.[12]

Product Studies.—Table 3 gives the results obtained by oxidation with manganic acetate of a number of alkylarenes under various conditions. When oxygen is excluded from the reaction mixture, the principal product is a benzylic alcohol mainly in the form of an acetate. The only exception is observed with cumene (experiment 6). When the reaction is carried out in the presence of oxygen, the principal product from toluene is benzaldehyde (experiment 11). For ethyl substituted hydrocarbons, the effect of oxygen is less clear; more acetyl compounds are produced but the proportion of ethyl groups transformed into CH(OAc)Me radicals is still high (experiment 12). The products generally account closely for the amount of substrate and Mn$^{\mathrm{III}}$ consumed (see last two columns in Table 3). Low yields were observed only with p-methoxytoluene and cumene (experiments 3 and 6). The former was so reactive under the conditions used that 61% was consumed within 1 min at 0 °C and the low yield of the expected anisyl acetate may be explained by overoxidation.

The effect of strong acids is clearly shown by experiment 8 in which m-diethylbenzene was completely transformed within 1 h at 25 °C in the presence of sulphuric acid whereas no products at all could be detected when sulphuric acid was omitted (experiment 7). As already mentioned, trichloroacetic acid is inefficient in activating Mn$^{\mathrm{III}}$ (experiment 5). The results of Table 3 also show the great reactivity of m-diethylbenzene already evident from kinetic data. This is especially illustrated by experiment 9 in which 85% of this hydrocarbon was transformed at 25 °C within only 3 min.

The results obtained with cobaltic acetate are quoted in Table 4. Here also products from side-chain oxidation are

---

[11] J. Hanotier and M. Hanotier-Bridoux, *J.C.S. Perkin II*, in the presss.

[12] K. Sakota, Y. Kamiya and N. Ohta, *Canad. J. Chem.*, 1969, **47**, 387.

formed in fairly high yields except from cumene (experiment 25). The dependence on the presence of oxygen is more marked than with manganic acetate as oxidizing agent. Thus, under oxygen, acetophenone is produced predominantly from ethylbenzene (experiment 24) while in the same conditions toluene is converted entirely into benzoic acid (experiment 23) most probably through oxidation of the benzaldehyde formed intermediately. An important difference with manganic acetate is the fact that when oxygen is present, the yield with respect to Co^{III} consumed regularly exceeds 100% which demonstrates that extensive regeneration of the oxidant takes place. In the case of toluene, the yield of benzoic acid with respect to Co^{III} is 1628%, *i.e.* the process is almost catalytic.

TABLE 4

Products from the oxidation at 25 °C of alkylarenes by 0·2M-cobaltic acetate[f] in acetic acid in the presence of strong acids

Expt. no.	Atmosphere	[Substrate] (mol l^{-1})		[Acid] (mol l^{-1})		Time (min)	Conversion[a] (%)	Products (mol %)[b]				Yield (%) *vs.*	
								(I)	(II)	(III)	(IV)	Substrate[c]	Co^{III}[d]
13	N_2	*p*-Methoxytoluene	0·10	CCl_3CO_2H	1·5	2	45	62	18	20	*e*	81	77
14	N_2	Ethylbenzene	0·09	CCl_3CO_2H	1·5	30	13	75	13	9	3	100	77
15	N_2	Ethylbenzene	0·10			1440	12	0	0	67	33	78	127
16	N_2	Ethylbenzene (no AcOH)		CCl_3CO_2H	1·5	120		2	32	63	3		
17	N_2	Ethylbenzene	0·10	CF_3CO_2H	1·4	1440	61	80	6	9	5	92	89
18	N_2	Ethylbenzene	0·10	BF_3	1·5	180	36	85	2	5	8	77	
19	N_2	*m*-Diethylbenzene	0·05	CCl_3CO_2H	1·5	120	82	88	6	6	*e*	100	88
20	N_2	*m*-Diethylbenzene	0·05	H_3PO_4	0·5	60	67	77	5	18	*e*	83	70
21	N_2	*m*-Diethylbenzene	0·05	$HClO_4$	1·0	60	99	87	4	9	*e*	100	97
22	N_2	2-Ethylnaphthalene	0·10	CCl_3CO_2H	1·5	30	63	90	8	2	*e*	90	83
23	O_2	Toluene	0·10	CCl_3CO_2H	1·5	240	95	0	0	0	100	85	1628
24	O_2	Ethylbenzene	0·10	CCl_3CO_2H	1·5	240	73	8	7	79	6	92	214
25	O_2	Cumene	0·10	CCl_3CO_2H	1·5	240	61	0	35	50	15	28	115
26	O_2	*m*-Diethylbenzene	0·05	CCl_3CO_2H	1·5	120	80	16	12	72	*e*	100	211

[a] See Table 3 for notes *a*—*e*. [f] Preparation of cobaltic acetate: experiments 13, 18, and 21—25, solution; others, powder (see Experimental section).

The effect of strong acids on the activity of Co^{III} is clearly shown by the data of Table 4 (compare, for instance, experiments 15 and 17). It is noteworthy that in addition to this effect on the rate, strong acids have a driving action on the selectivity as only carbonyl compounds are produced in the absence of added acid even when oxygen is carefully excluded (experiment 15).

A further conclusion can be drawn from Table 4. Experiment 16 shows that when ethylbenzene is oxidized by activated cobaltic acetate under nitrogen atmosphere but in the absence of any solvent, practically no acetate is produced. This result suggests that the acetyl radical in esters produced in acetic acid originates from the solvent instead of from acetate ligands of Co^{III}, probably through reaction of an intermediate carbonium ion with acetic acid.

DISCUSSION

Most previous work on the reaction of manganic acetate with alkylarenes in acetic acid was for the temperature range 90—120 °C and, even so, long periods were generally required for complete reduction of Mn^{III}.[13-15] A salient feature of previous work is that products having more carbon atoms than the substrate are always in excess over products expected for side-chain oxidation. For instance, methylbenzyl acetate and/or tolylacetic acid are mainly obtained from toluene instead of benzyl acetate. The formation of these products is widely considered as resulting from addition on the aromatic nucleus of $\cdot CH_2CO_2H$ radicals generated by thermolysis of manganic acetate. The small amount of benzyl acetate produced in these conditions is even attributed to hydrogen abstraction from the side chain by carboxymethyl radicals more than to direct attack by Mn^{III}. It is only for substrates with low ionization potential such as *p*-methoxytoluene that electron-transfer oxidation becomes predominant[10] although the formation of nuclear adducts is still observed.[14]

By contrast with those results, the low-temperature reaction of alkylarenes with manganic acetate in the presence of a strong acid, *e.g.* sulphuric acid, appears to proceed exclusively through electron transfer as only products from side chain oxidation are formed, often in high yield. The fact that in these conditions the kinetics of Mn^{III} consumption are similar to those determined for the electron-transfer oxidation of *p*-methoxytoluene[10] is further evidence for this interpretation. With acid-activated cobaltic acetate, the same products are formed as with manganic acetate and kinetic evidence is also in favour of a pure electron-transfer mechanism.[11]

More insight into this mechanism is provided by the fact that different products are formed according to whether oxygen is present or not, especially with cobaltic acetate as oxidizing agent. This demonstrates that a benzylic free radical is produced from the substrate. In the absence of oxygen, this radical appears to be further oxidized to a carbonium ion to afford an acetate by reaction of the latter with acetic acid [reactions (6) and (7)]. In the presence of oxygen, the

$$Ar\dot{C}HR + Co^{III} \longrightarrow Ar\overset{+}{C}HR \qquad (6)$$

$$Ar\overset{+}{C}HR + AcOH \longrightarrow ArCH(OAc)R \qquad (7)$$

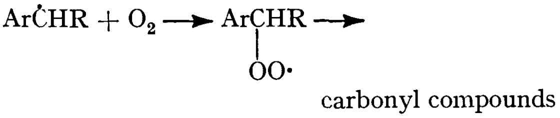
---

[13] R. E. van der Ploeg, R. W. de Korte, and E. C. Kooyman, *J. Catalysis*, 1968, **10**, 52.

[14] E. I. Heiba, R. M. Dessau, and W. J. Koehl, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 138.

[15] H. Finkbeiner and J. B. Bush, jun., *Discuss. Faraday Soc.*, 1968, **46**, 150.

incipient free radical will give a peroxyl radical which is known to be the first precursor of carbonyl compounds in metal-catalysed oxidations [reaction (8)].



$$\mathrm{Ar\dot{C}HR} + O_2 \longrightarrow \underset{\displaystyle \mathrm{OO}\cdot}{\underset{|}{\mathrm{ArCHR}}} \longrightarrow \text{carbonyl compounds} \qquad (8)$$

This scheme also accounts for the high yields with respect to Co^{III} observed for the reactions performed in the presence of oxygen. Such high yields indicate that extensive regeneration of the oxidant takes place as in catalytic systems.

Cobaltic salts of inorganic acids, *e.g.* sulphuric, perchloric, or nitric acids, are known to be powerful oxidizing agents in aqueous media and the oxidation thereby of a wide variety of organic compounds, *e.g.* alcohols, ketones, aldehydes, ethers, and acids, has been extensively investigated.[16] Recently, Meenakshi and Santappa have confirmed the earlier observation that the rate of such reactions is inversely dependent on acidity and they have shown that it is increased by added cobaltous ions.[17] Opposite effects are observed with cobaltic acetate in acetic acid. Bawn and Sharp have reported that cobaltic acetate was a weak oxidizing agent for olefins unless sulphuric acid was added to the system.[18] More recently, the positive effect of a variety of strong acids has been recognized with other substrates, *e.g.* paraffins,[8] aromatic hydrocarbons,[9,19] and radicals.[20] A similar effect of strong acids has been shown for the decarboxylation of acids by manganic acetate.[21]

The second difference is the fact that the oxidizing activity of manganic and cobaltic acetates in acetic acid is inhibited by the presence of M^{II} and Co^{II} ions respectively. Recently, the retarding effect of added Mn^{II} on the reduction of Mn^{III} in pivalic acid has been noted and ascribed to the formation of mixed valence species.[21] This explanation is certainly valid for cobaltic acetate as shown in the present study by the fact that the reduction of Co^{III} does not proceed beyond the 50% stage in the absence of strong acid (see Figure). This phenomenon which is regularly observed whatever substrate is present and even at relatively high temperatures, *e.g.* 80—100 °C,* can hardly be explained except by assuming that Co^{II} is associated with Co^{III} in dimeric species inactive for oxidation. In this respect, it is noteworthy that the retarding effect of added Mn^{II} on the reduction of Mn^{III} in pivalic acid has also been observed for added Co^{II} which was explained by the formation of dinuclear Mn^{III}–Co^{II} complexes.[21]

However, in view of the available kinetic data, it is difficult to explain the retarding effect of Co^{II} and Mn^{II} only by formation of inactive mixed valence species. Indeed, the inverse dependence on $[Co^{II}]$ of the rate of reduction of Co^{III} has been observed even in the presence of strong acids.[8,11] Under these conditions, however, association between both species is probably small as attested by the fact that the reduction of Co^{III} proceeds well beyond the 50% stage and even up to completion when the concentration of the acid is sufficiently high (see Figure). Moreover, as pointed out by Andrulis and his co-workers,[10] ' removal of Mn^{III} by formation of an inert complex with Mn^{II} could lead to a simple dependence of the rate on Mn^{II} concentration only if the latter were much greater than the concentration of Mn^{III} ' which is generally not the case in the kinetic studies cited above. To account for their experimental results, the same authors suggested reactions (10) and (11) for the oxidation of *p*-methoxytoluene where $(ArMe)^+$ is an

$$Mn^{III} + ArMe \rightleftharpoons Mn^{II} + (ArMe)^+ \qquad (10)$$

$$(ArMe)^+ \longrightarrow ArCH_2\cdot + H^+ \qquad (11)$$

intermediate radical-cation derived from the substrate by loss of a π electron. The high reactivity of *m*-diethylbenzene towards Mn^{III} as shown above when compared with ethylbenzene is consistent with this hypothesis more than with the attack by Mn^{III} on a benzylic C–H bond. However, the fact that oxygen has little influence on the products obtained from *m*-diethylbenzene throws some doubt on the generality of step (11) in which a free radical is produced. Obviously, more experimental work is needed to reconcile the data now available.

EXPERIMENTAL

Preparation of Manganic and Cobaltic Acetates.—Manganic acetate was prepared by oxidation of commercial manganous acetate with potassium permanganate in acetic acid. The procedure used was a modification of the method of Pascal.[22] The resulting product had the manganese content of the pure dihydrate $Mn(OAc)_3,2H_2O$. It is a stable compound which can be stored for long periods without losing activity. For use in oxidation experiments, it was heated in acetic acid at 70 °C and the resulting solution was filtered to remove undissolved material.

Cobaltic acetate was prepared from commercial cobaltous acetate by co-oxidation with acetaldehyde in the presence of oxygen.[23] The reaction mixture was further treated as described previously to obtain either a solution in acetic acid of highly active cobaltic acetate (85—95% Co^{III} *vs.* total cobalt) or a less active but more stable powdered preparation.[8]

Both Mn^{III} and Co^{III} were determined by reaction with

---

* Provided that the concentration of cobalt is sufficiently high. With diluted solutions, *e.g.* 0·02M, reduction of Co^{III} goes to completion. Similarly, Anderson and Kochi noted that modifications of the absorption spectrum of Mn^{III} by added Mn^{II} were not observed in dilute systems.[21]

[16] For a review see W. A. Waters and J. S. Littler in ' Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Academic Press, New York and London, 1965, p. 186.

[17] A. Meenakshi and M. Santappa, *J. Catalysis*, 1970, **19**, 300.

[18] C. E. H. Bawn and J. A. Sharp, *J. Chem. Soc.*, 1957, 1866.

[19] E. I. Heiba, R. M. Dessau, and W. J. Koehl, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 6830.

[20] Sh. S. Lande and J. K. Kochi, *J. Amer. Chem. Soc.*, 1968, **90**, 5196.

[21] J. M. Anderson and J. K. Kochi, *J. Amer. Chem. Soc.*, 1970, **92**, 2450.

[22] P. Pascal, ' Nouveau Traité de Chimie Minérale,' Masson, Paris, 1960, vol. XVI, p. 995.

[23] W. O. Walker and U. Kopsch, U.S.P. 1,976,757.

an excess of aqueous ammonium iron(II) sulphate and back titration of ferrous ions with either ammonium cerium(IV) nitrate in the presence of *o*-phenanthrolineiron(II) as indicator or with potassium dichromate in the presence of sodium diphenylsulphonate.

Mn^{III} *and* Co^{III} *Reduction Experiments.*—In most cases, the reduction of Mn^{III} or Co^{III} in an oxygen-free atmosphere was performed on 2—6 ml of reaction mixture in closed test-tubes immersed, without agitation, in a thermostat, the tubes being flushed with nitrogen before introduction of the reactants. With Co^{III}, the introduction of cobaltic acetate as a concentrated solution in acetic acid was taken as zero time. With the less soluble manganic acetate, it was more convenient to start the reaction with introduction of the acidic activator. To stop the reaction, an excess of ferrous ions was added to the system and Mn^{III} or Co^{III} were determined as described above.

Determination of the Oxidation Products.—The experiments for determining the products formed by oxidation of alkylarenes were performed by the method already described for the oxidation of paraffins.[8] At the end of the experiment, unchanged Mn^{III} or Co^{III} was reduced with aqueous ammonium iron(II) sulphate and the internal standards for g.l.c. were added. An aliquot portion of the resulting solution was diluted with ether and then neutralized after cooling with anhydrous sodium carbonate. The ether solution was then analysed by g.l.c. to determine neutral oxidation products. For the experiments with toluene, ethylbenzene, or cumene as substrate, benzoic acid was determined by direct g.l.c. of another aliquot portion. For the experiment without solvent the same procedure was applied except that no ether was used. All products were identified by comparison with known samples and determined against internal standards with similar retention times.

We thank the ' Institut Belge pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture (I.R.S.I.A.),' for partial support and Labofina personnel who participated in this research, particularly G. Lobet and R. Remacle

[2/1165 *Received, 22nd May,* 1972]