

GENERAL DISCUSSION

Dr. J. Vepřek-Šiška (*Inst. Inorg. Chem., Czechoslovak Acad. Sci., Prague*) (*partly communicated*): With reference to the papers by Cullis *et al.* and Williams *et al.*, some oxidation-reduction reactions, generally considered as uncatalyzed, are in fact catalyzed by trace metals, which are present as impurities.¹⁻⁴ The catalytic effects of trace metals were proved in the following reactions (table 1):

TABLE 1.—TRACE METAL CATALYZED REACTIONS

| | | | |
|--|--|------------------------|----------------------------------|
| 4MnO_4^- | $+4\text{OH}^- = 4\text{MnO}_4^{2-} + \text{O}_2$ | $+2\text{H}_2\text{O}$ | $\text{Ni}^{2+}, \text{Co}^{2+}$ |
| 4RuO_4^- | $+4\text{OH}^- = 4\text{RuO}_4^{2-} + \text{O}_2$ | $+2\text{H}_2\text{O}$ | $\text{Ni}^{2+}, \text{Co}^{2+}$ |
| 4FeO_4^{2-} | $+2\text{H}_2\text{O} = 4\text{FeO}_7^{2-} + 3\text{O}_2$ | $+4\text{OH}^-$ | $\text{Ni}^{2+}, \text{Co}^{2+}$ |
| $2[\text{Fe}(\text{CN})_6]^{3-} + \text{SO}_3^{2-}$ | $+2\text{OH}^- = 2[\text{Fe}(\text{CN})_6]^{4-} + \text{SO}_4^{2-}$ | $+ \text{H}_2\text{O}$ | Cu^{2+} |
| $2[\text{Fe}(\text{CN})_6]^{3-} + 2\text{NH}_2\text{OH}$ | $+2\text{OH}^- = 2[\text{Fe}(\text{CN})_6]^{4-} + \text{N}_2$ | $+4\text{H}_2\text{O}$ | Cu^{2+} |
| $2[\text{Fe}(\text{CN})_6]^{3-} + \text{N}_2\text{H}_4$ | $+4\text{OH}^- = 2[\text{Fe}(\text{CN})_6]^{4-} + \text{N}_2$ | $+4\text{H}_2\text{O}$ | Cu^{2+} |
| $2[\text{Fe}(\text{CN})_6]^{3-} + \text{CN}^-$ | $+2\text{OH}^- = 2[\text{Fe}(\text{CN})_6]^{4-} + \text{CNO}^-$ | $+ \text{H}_2\text{O}$ | Cu^{2+} |
| $2[\text{Fe}(\text{CN})_6]^{3-} + 2\text{SHCH}_2\text{COO}^-$ | $+2\text{OH}^- = 2[\text{Fe}(\text{CN})_6]^{4-} + (\text{SCH}_2\text{COO})_2^{2-} + 2\text{H}_2\text{O}$ | | Cu^{2+} |
| $2[\text{Fe}(\text{CN})_6]^{3-} + \text{C}_6\text{H}_{12}\text{O}_6$ | $= 2[\text{Fe}(\text{CN})_6]^{4-} + \text{products}$ | | Cu^{2+} |

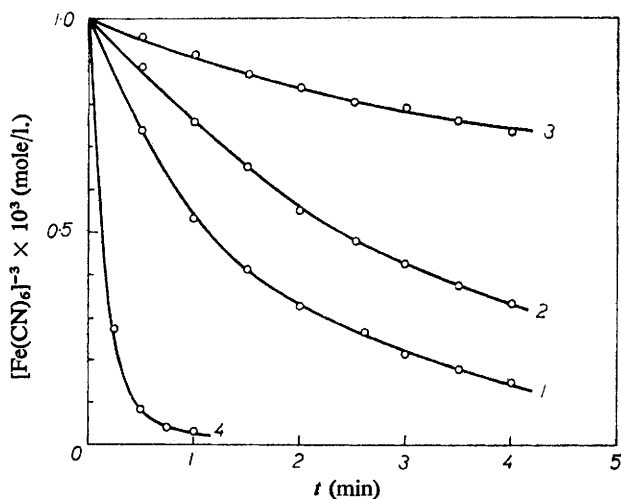


FIG. 1.—Effect of CuCl_2 and Na_2EDTA on the oxidation of hydrazine by hexacyanoferrate(III). $[\text{Fe}(\text{CN})_6]_{t=0} = 1 \times 10^{-3}$ mole/l.; $[\text{N}_2\text{H}_4]_{t=0} = 2.5 \times 10^{-2}$ mole/l.; Britton-Robinson buffer; pH 10.5; N_2 atmosphere; 25°C ; 1, no additions; 2, 2×10^{-5} mole/l. Na_2EDTA ; 3, 2×10^{-4} mole/l. Na_2EDTA ; 4, 1×10^{-5} mole/l. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

Using extremely pure chemicals it was found that the reaction of permanganate is catalyzed by traces of nickel and cobalt salts.¹ The rate of the uncatalyzed reaction is almost immeasurably low. The decomposition of perruthenate and the decomposition of ferrate is catalyzed by trace amounts of nickel and cobalt salts as well.² The rates of hexacyanoferrate(III) reductions are reduced by the additions of complexing

¹ J. Vepřek-Šiška and V. Ettel, *J. Inorg. Nucl. Chem.*, 1968, in press.

² J. Vepřek-Šiška and V. Ettel, *Chem. and Ind.*, 1967, 548.

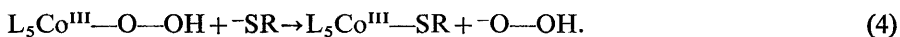
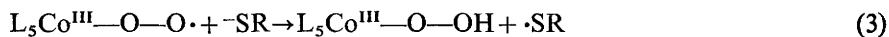
agents; addition of cupric salt in trace concentration appreciably enhances the reaction velocity.^{1, 2} The effect of copper salt and that of EDTA in the oxidation of hydrazine are demonstrated in fig. 1.

The reduction of permanganate by hydroxyl ions and the reductions of hexacyanoferrate(III) by various substrates (table 1) are considered to occur by outer-sphere electron transfer.^{3, 4} The specific catalytic effects of cations in trace concentrations cannot, however, be explained by either of the theories of outer-sphere reactions.

Similarly, the so-called specific effects of inert salts is often caused by various amounts of catalytically-active trace impurities in the chemicals used. The unusual effects of inert electrolytes noted in some of the Discussion papers may also be due to this cause.

Prof. C. F. Cullis (*The City University*) (*communicated*): I was interested to learn that Vepřek-Šiška had also found that some nominally uncatalyzed oxidation reactions are in fact catalyzed by trace quantities of metals. Trimm and I have studied the oxidation of a number of thiols in alkaline solution and in the absence of added metal catalysts. Our results show that trace impurities have a pronounced effect on the kinetics of the reaction. Thus, the addition of copper at concentrations as low as 10^{-7} M has a marked influence on the rate of oxidation of several alkanethiols and it is probably not valid to claim purity of this order even under conditions of minimal impurity concentration. We have therefore paid special attention to determining the kinetics of the reaction in the presence of additives which would be expected to reduce the catalytic activity of metal ions by forming stable complexes. For example, the addition of cyanide ions to the reacting solutions appears to have the desired effect of metal ion deactivation, although there is some evidence that the whole course of reaction may be altered in the presence of this additive. Experiments with other complexing agents, such as ethylenediamine and ethylenediamine-tetraacetic acid, are, however, characterized by irreproducibility and this may be due to the fact that metal ions are being introduced with the reagents. In general, the addition of ethylenediamine seems to have the greatest retarding effect as might be expected from the high stability constants of metal-ethylenediamine complexes.

Prof. W. A. Waters (*Oxford University*) said: With reference to the paper by Cullis *et al.*, a simpler inner sphere mechanism is



The observed kinetics follow if (2) is the slow reaction. Appropriate ligands L must be selected. Reaction (4) above is a simple S_N2 displacement. The reaction $2RS \cdot \rightarrow RSSR$ is too fast for the detection of simple thiyl radicals by e.s.r. and thiols are easily oxidized to disulphides by alkaline hydrogen peroxide. I would favour this destruction of the peroxide to the authors' reaction (5).

Following the comments of Pithethly and others, I would add that if there is strong evidence that hydrogen peroxide is not formed in this catalytic autoxidation

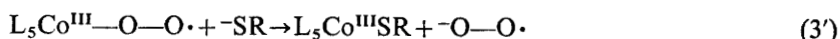
¹ J. Vepřek-Šiška and A. Hasnedl, *Chem. Comm.*, 1968, 1167.

² J. Vepřek-Šiška and A. Hasnedl, *Coll. Czech. Chem. Comm.*, 1968, submitted for publication.

³ M. C. R. Symons, *J. Chem. Soc.*, 1953, 3956.

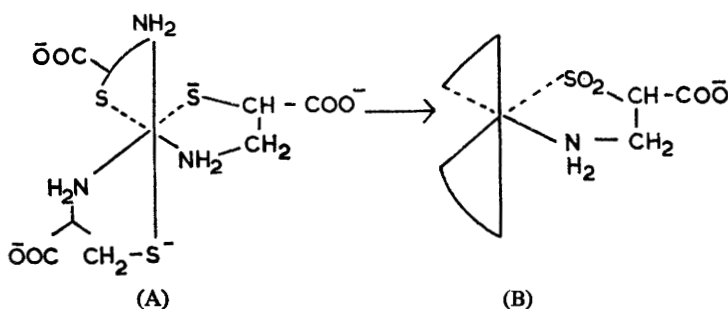
⁴ W. A. Waters, *Mechanisms of Oxidation of Organic Compounds* (J. Wiley & Sons, New York, 1964), pp. 87, 138.

of thiols then in place of my reactions (3) and (4) the S_N2 displacement (3') might occur after which fast reactions (5') and (6') can rationally be postulated

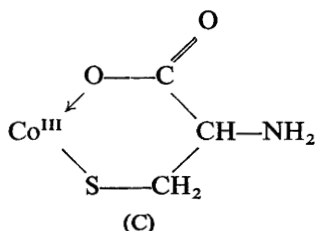


Dr. D. L. Trimm (*Imperial College, London*) said: In reply to Waters, although the inner-sphere reaction mechanism proposed in the present paper must be regarded as speculative, it does appear to explain some observations which have been made on the metal-catalyzed system.³ For example, no trace of RS-radicals could be found in the system when suitable trapping agents were added to the solutions. Again, no trace of hydrogen peroxide could be detected amongst the reaction products and the addition of peroxides and of peroxide-destroying agents both had the effect only of slightly increasing the rate, a trend which tended to disappear on careful removal of traces of metal ion from the additives. The direct oxidation of thiols by alkaline hydrogen peroxide was fairly slow in comparison with the rates of the inner-sphere reactions. I would agree with Waters that the proposed reaction (5) is the least satisfactory step in the reaction sequence. The disadvantage of the reaction sequence (3'), (5') and (6') lies in the production of thiyl radicals, for which no evidence has been obtained. The possibility of metal catalysis in the context of reaction (5) is certainly attractive.

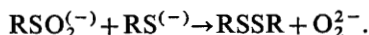
Dr. R. D. Gillard (*University of Kent*) said: With reference to the paper by Cullis *et al.*, the properties of $RS-Co^{III}L_5$, involved in the "inner sphere" mechanism of their paper, are a subtle reflection of the ligands L. For example, with cysteine as a ligand, attached to cobalt(III) as shown in (A), all the $RS-Co^{III}$ units react extremely



readily with hydrogen peroxide to give the sulphinic acid, still attached through sulphur to cobalt(III), as in (B). However, the isomeric complex with cysteine attached through oxygen and sulphur (as in (C)),

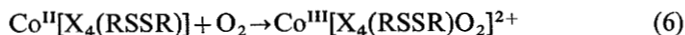


is unaffected by hydrogen peroxide. One or two similar reactions of other metal-thiolate species (though not cobalt) with peroxide have been briefly mentioned in the literature. It is also known that sulphinate reacts with thiols.

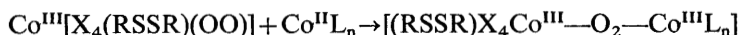


Could such reactions be important in the autoxidation of thiols, in particular, as an alternative pathway to that outlined in reactions (7) and (8) of the paper by Cullis and Trimm?

A second reaction which may be of importance would be a consequence of (6):



Since this cobalt(III) product contains a superoxo ligand, one might then expect a rapid reaction with any Co^{II} species,



and such cobalt^{III} peroxo-bridged dimers with sulphur ligands would themselves be highly reactive species.

Dr. D. L. Trimm (*Imperial College, London*) (*communicated*): Gillard's observations are particularly interesting in the context of the catalytically active species. As discussed above, the addition of peroxide did not affect the course of the overall reaction. The reaction between sulphinate and thiol has been proposed¹ as part of the overall oxidation of thiols to disulphides or to sulphinic and sulphonic acids. No trace of sulphinate could be found in oxidations in aqueous solution. Experiments have been confined to alkane and arane thiols in the present system. The presence in the thiol molecule of groups such as $-\text{COO}^-$ and $-\text{NH}_2$ will almost certainly affect the strength of bonding of the complexes, and hence may well influence the course of reaction. I was also interested to learn that dimeric cobalt species are reactive. Investigation of complexes in solution indicated that polymeric compounds may be present, and it might be that the inner-sphere reaction mechanism should be re-written in terms of more than one cobalt centre.

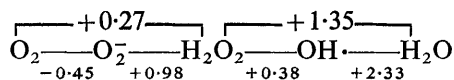
Dr. J. M. Pratt and **Dr. R. J. P. Williams** (*Oxford University*) (*communicated*): There may be several different mechanisms for the catalysis of the autoxidation of thiols reported by Cullis *et al.* We refer first to the mechanism of catalysis by cobalt corrinoids which has also been studied by Peel.² These cobalt catalysts have the advantages that at least four of the co-ordination positions of the metal are blocked and the different oxidation states and complexes are readily followed by spectrophotometry. On adding a thiol to the cobalt(III) aquocomplex (vitamin B_{12a}) at high pH the thiol-Co(III) complex is first formed; reduction to cobalt(II), i.e., B_{12r} , follows and then B_{12r} is re-oxidized by molecular oxygen. The last step is not a simple autoxidation because the oxidation of B_{12r} is much slower (half life ~ 20 min) in the absence of the thiol. Thiols appear to act in two redox steps; the reduction of cobalt(III), and the oxidation of cobalt(II) by oxygen. We have found that the autoxidation of B_{12r} can also be catalyzed by other reducing agents such as quinol, p-phenylenediamine, ascorbic acid, and sulphite.

It has often been reported that the rapid autoxidation of iron(II) chelate complexes, and especially the iron-porphyrin complexes which occur in naturally occurring

¹ H. Berger, *Rec. Trav. Chim.*, 1963, **82**, 773.

² J. L. Peel, *Biochem. J.*, 1963, **88**, 296.

proteins, requires the presence of a source of reducing equivalents. A good example is that of cytochrome oxidase which is only autoxidized in the presence of cytochrome-c.¹ These studies, together with those on vitamin B₁₂, autoxidation, suggest that oxygen is a poor one-electron oxidizing agent, as one might expect from the redox potentials given by P. George²



The potentials (in V) show that a metal ion in a complex which could only undergo a one-electron oxidation, and for which the redox potential is around 0.0 V, might well be only slowly oxidized by molecular oxygen in the absence of a second electron donor such as a thiol, quinol, or a second transition metal cation.

A more complex situation can develop for O. Warburg³ showed that the autoxidation of cysteine by Fe(II) cations was greatly accelerated by bispyridine Fe(II) porphyrins. This reaction has a close parallel with the catalysis of autoxidation of cysteine, p-phenylenediamine or ascorbic acid by the combined action of cytochrome oxidase and cytochrome-c.⁴ In these examples two metal catalysts are required for optimal autoxidation of cysteine and we assume that one acts as a source of electrons for the other so as to make the reduction of oxygen possible by a process which involves at least two electrons before the reduced oxygen molecule is released from one of the metals. We would ask whether Cullis and Trimm have made any similar observations.

Dr. D. L. Trimm (*Imperial College, London*) (*communicated*): The observation by Pratt and Williams that the oxidation of cobalt by oxygen may be catalyzed by thiols is gratifying. Although the present results indicate that re-oxidation of the metal ion is rate-determining, this process would be expected to be much slower than the overall oxidation of thiol. This seeming paradox could be explained for the phthalocyanine and vitamin B₁₂ systems in terms of their roles as oxygen carriers (i.e., the oxygen is located in the appropriate position to favour metal re-oxidation) but catalysis of the re-oxidation by thiol provides an attractive and more general explanation. We have not observed thiol catalysis of the oxidation of metal, but we would be unlikely to see any such effects under the conditions of our experiments. I would also add that the use of cobalt catalysts, in which four co-ordination positions may be blocked, does allow a direct measure of the importance of reaction mechanisms involving more than one metal centre. As a result of the stability of thiol complexes, metal porphyrin complexes appear to be the only such complexes identified in the present work; cobalt corrinoids could well provide further examples of this type of catalyst.

Dr. C. F. Wells (*Birmingham University*) said: With regard to the discussion by Halpern and Williams (following the paper by Cullis *et al.*) concerning the preferred form of reduced oxygen, O₂²⁻ (doubly ionized hydrogen peroxide) or •O₂⁻ (ionized hydroperoxy radical), the mechanism of the autoxidation of Fe(II) in acidic aqueous

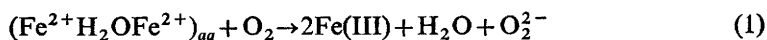
¹ I. Sekuzu, S. Takemori, Y. Orii and K. Okunuki, *Biochim. Biophys. Acta*, 1960, **37**, 64.

² *Oxidases and Related Redox Systems*, ed. T. E. King, H. S. Mason and M. Morrison (Wiley, New York, 1964), p. 3.

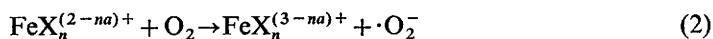
³ *Heavy Metal Prosthetic Groups* (Oxford: University Press, 1949), p. 91.

⁴ D. Keilin, *Proc. Roy. Soc. B.*, 1930, **106**, 418; E. C. Slater, B. F. van Gelder and K. Minnaert in *Oxidases and Related Redox Systems*, ed. T. E. King, H. S. Mason and M. Morrison (Wiley, New York, 1964), p. 667.

media¹ is of interest. In perchlorate media the rate $\propto [\text{Fe(II)}]^2 p\text{O}_2$,² and the rate-determining step is a simultaneous double-electron transfer¹ involving a small concentration of a Fe(II) dimer³ to produce doubly-reduced oxygen as in eqn. (1)

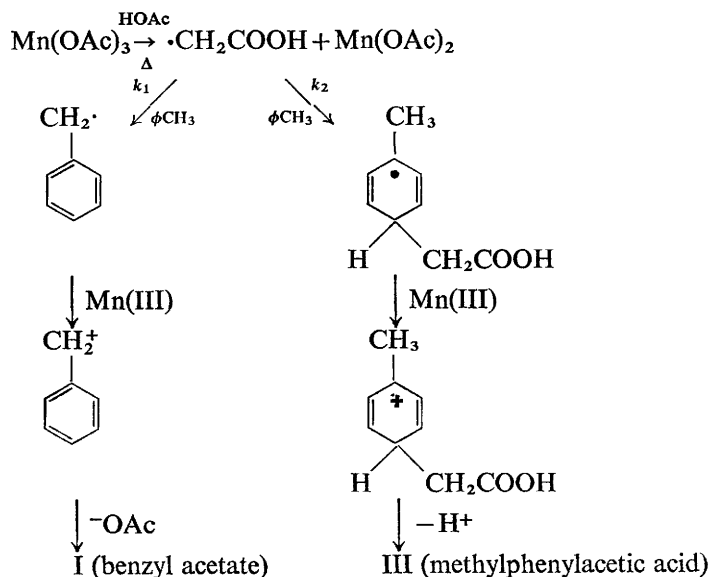


where Fe(III) may be a complex species of the ferric ion. The near $[\text{H}^+]$ -independence is explained by pre-equilibria in the formation of the Fe(II) dimer.^{1, 2} However, with complexing anions X^{a-} present (except SO_4^{2-}), the singly-reduced form of oxygen is produced (eqn. (2)).¹



When $\text{FeX}_n^{(2-na)+}$ and uncomplexed aquoiron(II) ions co-exist,⁴ reaction (2) predominates,¹ suggesting that singly-reduced oxygen is preferred.

Dr. E. I. Heiba and Dr. R. M. Dessau (*Mobil Research and Development Corp., Princeton, N.J.*) (*communicated*): We have, independently, conducted studies on the reaction of aromatic hydrocarbons and olefins with manganic acetate, similar to those reported by H. Finkbeiner and J. B. Bush, Jr.⁵ Our studies support the free radical mechanism proposed independently by van der Ploeg, deKorte, and Kooyman,⁶ involving the carboxymethyl radical ($\cdot\text{CH}_2\text{COOH}$) which is formed directly from the thermolysis of the manganic acetate complex. Thus, the reaction of manganic acetate with toluene gave three major products: benzyl acetate (I), methylbenzyl acetates (II), and methylphenylacetic acids (III), according to the free radical mechanism:



¹ C. F. Wells, *J. Inorg. Nucl. Chem.*, 1968, **30**, 893.

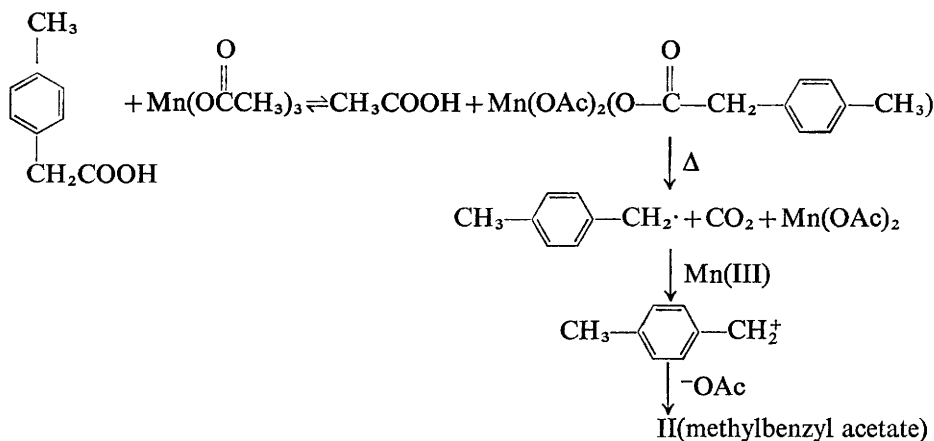
² P. George, *J. Chem. Soc.*, 1954, 4349.

³ C. F. Wells and M. A. Salam, *J. Chem. Soc. A*, 1968, 24.

⁴ C. F. Wells and M. A. Salam, *Trans. Faraday Soc.*, 1967, **63**, 620; *J. Chem. Soc. A*, 1968, 308.

⁵ H. Finkbeiner and J. B. Bush, Jr., this Discussion.

⁶ R. E. van der Ploeg, R. W. deKorte and E. D. Kooyman, *J. Catalysis*, 1968, **16**, 52.



This mechanism is similar to that proposed for lead tetra-acetate,¹ but there are several distinct differences in the oxidation of toluene by manganic acetate. Unlike the lead tetra-acetate oxidation, no xylenes were detected, indicating that the free methyl radicals are not produced from manganic acetate. In addition, the relative

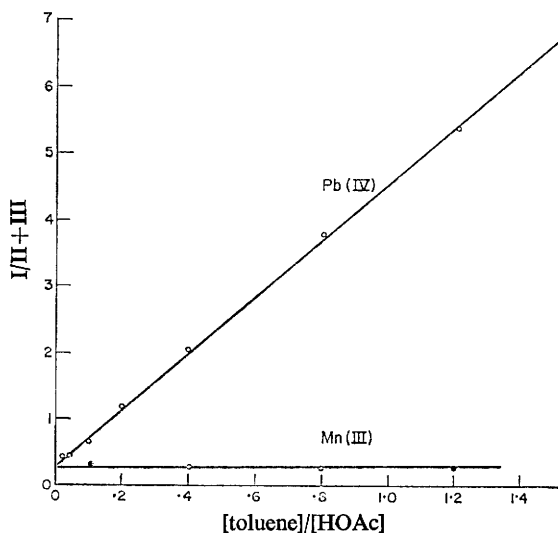


FIG. 1.—Oxidation of toluene: effect of [toluene]/[acetic acid] ratio on the product distribution.

yield of (I) to be sum of (II) and (III) was constant and independent of the [toluene]/[acetic acid] ratio used, which is unlike the linear variation observed with lead tetra-acetate (see fig. 1). This indicates that the $\cdot\text{CH}_2\text{COOH}$ radicals are formed directly from the manganic acetate complex. In the above mechanism it is assumed that the $\cdot\text{CH}_2\text{COOH}$ radical is oxidized relatively slowly to the corresponding carbonium ion, in contrast to the benzylic radical² or the cyclohexadienyl radical, due to its relatively high ionization potential.³ The high yield of benzylacetate, methylbenzyl acetate,

¹ E. I. Heiba, R. M. Dessau and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, 1968, **90**, 1082.

² J. K. Kochi, J. D. Bacha and T. W. Bethea, III, *J. Amer. Chem. Soc.*, 1967, **89**, 6538.

³ Gas phase I.P. of $\cdot\text{CH}_2\text{COOH}$ is expected to be similar to cyanomethyl radical whose I.P. = 10.87 eV, while that of benzylic radical is 7.76 eV (R. W. Kaiser, *Introduction to Mass Spectrometry and its Applications* (Prentice-Hall, 1965), p. 319.

and methylphenyl-acetic acid obtained indicates that the $\cdot\text{CH}_2\text{COOH}$ radical reacts with toluene faster than it is oxidized by Mn(III) . Further support for the intermediacy of the $\cdot\text{CH}_2\text{COOH}$ radical is the observation that the addition of Cu(OAc)_2 , which is a good radical oxidant,¹ decreased by more than 90 % the yield of these products obtained.

Also, the determined ratio of $(\text{I})/[(\text{II}) + (\text{III})] = 0.3$ using manganic acetate agrees well with the value obtained from the oxidation of toluene by lead tetra-acetate extrapolated to infinite toluene dilution. This ratio represents the relative rate constants of α -hydrogen abstraction (k_1) to that of nuclear addition (k_2) by the $\cdot\text{CH}_2\text{COOH}$ radical. The $\cdot\text{CH}_2\text{COOH}$ radical, unlike the more reactive methyl radical, adds to toluene faster than it abstracts the benzylic hydrogen atom. This difference in behaviour can be attributed to the greater stability of $\cdot\text{CH}_2\text{COOH}$ radical and partly to its electrophilicity. The more stable radical would be expected to favour the reaction of lower activation energy, which in this case is addition to the ring.²

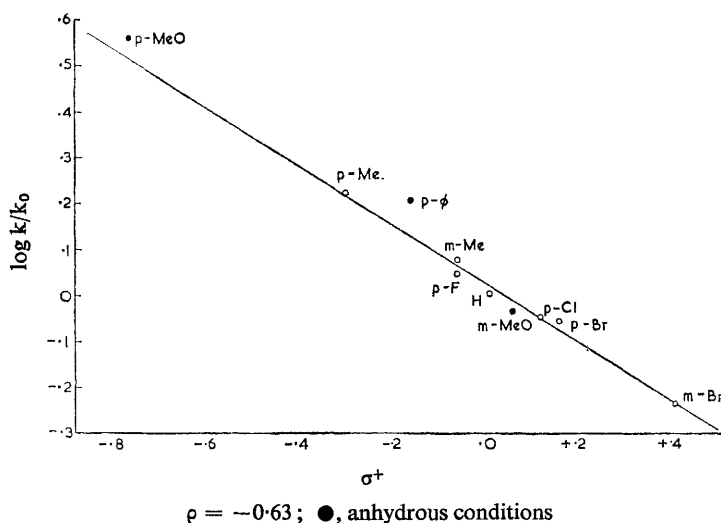


FIG. 2.—Relative reactivity of substituted toluenes towards hydrogen abstraction by the carboxymethyl radical at 130°.

The electrophilic character of the $\cdot\text{CH}_2\text{COOH}$ radical was deduced from the relative reactivities, using a competitive technique, of substituted toluenes towards hydrogen abstraction by this radical, and were calculated from the relative ratio of the reaction products, the corresponding benzylic acetates. The relative reactivities of substituted toluenes show a good correlation with σ^+ (fig. 2), yielding a ρ value of -0.63 . The good linear $\sigma-\rho$ fit obtained with all substituted toluenes indicates that a single free radical mechanism is operative for these compounds.

Further support of the free $\cdot\text{CH}_2\text{COOH}$ radical can be deduced from the isomer distribution of its addition products to substituted benzenes. With anisole, the isomer distribution of the methoxybenzyl acetates which were obtained in better than 75 % yield (78 % ortho, 5 % meta, and 17 % para) is inconsistent with an ionic

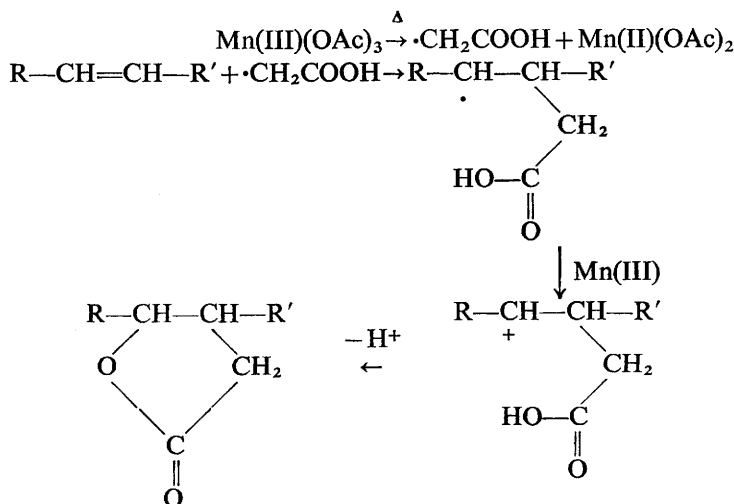
¹ Preliminary experiments indicate that Cu(II) oxidizes secondary alkyl radicals at least 100 times faster than Mn(III) .

² M. Cher, C. S. Hollingsworth and F. Sicilio, *J. Physic. Chem.*, 1966, **70**, 877.

mechanism since the ionic chloro-formylation of anisole yields a product which is 90 % para and 10 % ortho.¹

A second pathway involving electron-transfer operates with hydrocarbons of relatively low ionization potential (≤ 8.0 eV) under certain conditions. The reaction of manganic acetate with p-methylanisole in refluxing acetic acid yielded p-methoxybenzyl acetate as the predominant product, along with the isomeric $-\text{CH}_2\text{OAc}$ adducts in a 20 : 1 ratio (the free acid formed was negligible). The large preference for side-chain attack is inconsistent (fig. 2), with the reactivity of the $\cdot\text{CH}_2\text{COOH}$ radical. Since the $\cdot\text{CH}_2\text{COOH}$ radical abstracts benzylic hydrogen atoms from p-methoxytoluene only 3.6 times faster than from toluene, and since its rate of addition to toluene is approximately 3.3 times greater than its rate of hydrogen abstraction from toluene, approximately equal amounts of side-chain attack and nuclear addition would be expected for p-methoxytoluene, assuming the rate of addition to p-methoxytoluene to be the same as for toluene. Actually the rate of addition of $\cdot\text{CH}_2\text{COOH}$ to p-methoxytoluene is probably greater than that of toluene, in view of the fact that anisole reacts three times faster than t-butylbenzene. The large preponderance of side-chain acetoxylation in the manganic acetate oxidation of p-methoxytoluene is inconsistent with the free radical scheme alone. This indicates a second competing pathway which leads exclusively, or almost exclusively, to p-methoxybenzyl acetate. Probably, this is the electron-transfer process originally suggested by Dewar *et al.*²

Competition between these two competing pathways can be drastically affected by the addition of acetate ion and by rigorous drying of the system with acetic anhydride. Thus, in the reaction with *p*-methoxytoluene, in refluxing acetic acid, the side-chain acetate predominated over the $-\text{CH}_2\text{OAc}$ adducts by a ratio of about 20 : 1 (table 1). In the presence of added potassium acetate (300 g/l. acetic acid), the relative yield of $-\text{CH}_2\text{OAc}$ adducts increased to one-third of the side-chain acetate. Rigorous drying of the system by preconditioning with acetic anhydride and using anhydrous manganic acetate caused a further marked increase in the relative yield of the $-\text{CH}_2\text{OAc}$ adduct, to the point where they constituted the major product of the reaction.



¹ R. Quelet and M. Anglade, *Compt. rend.*, 1936, **203**, 262.

² P. J. Andrulis, Jr., M. J. S. Dewar, R. Dietz and R. H. Hunt, *J. Amer. Chem. Soc.*, 1966, **88**, 5473.

We have, also, found that the reaction of manganic acetate with olefins yielded the corresponding γ -butyrolactones in good yields.¹ The γ -butyrolactones are produced by a free radical mechanism similar to that invoked to explain the formation of γ -lactones from the oxidation of olefins with lead tetra-acetate in acetic acid.² The manganic acetate reaction differs from the lead tetra-acetate reaction in two fundamental respects: (i) no methyl-acetate adducts are produced even at relatively high olefin concentrations; (ii) only traces of CO_2 (0.03 mole/mole Mn^{+3}) and methane (0.004 mole/mole Mn^{+3}) are formed during the decomposition of manganic acetate in the presence of olefins. These results indicate that the $\cdot\text{CH}_2\text{COOH}$ radical is formed directly from the thermolysis of manganic acetate. The free radical nature of the intermediate is again supported by the effect of added Cu(II) which greatly reduced the yield of the γ -lactone obtained.

As for the specific objections raised by Finkbeiner and Bush, Jr.,³ in regard to the free radical mechanism, (i) the distribution of isomers in the methylation and phenylation of aromatic substrate is not significantly different from that observed in this reaction. The slight difference in the isomer distribution can be attributed to the greater electrophilicity of the $\cdot\text{CH}_2\text{COOH}$ radical as evidenced by its ρ value. (ii) The absence of significant polymerization of styrene in presence of metal oxidants is expected in view of the rapid oxidation of the benzylic radical by Mn(III) . The

TABLE 1.—EFFECT OF REACTION CONDITIONS ON THE PRODUCTS OF THE OXIDATION OF p-METHOXYTOLUENE BY MANGANIC ACETATE

| conditions | $-\text{CH}_2\text{OAc}$ adducts/side-chain acetate |
|---|--|
| glacial HOAc, 130° | 0.04 |
| 1 M KOAc, 130° | 0.10 |
| 1 M KOAc + 0.2 M Mn(II) , ^a 130° | 0.22 |
| 1 M KOAc, Ac_2O | |
| anhyd. Mn(III) , 130° | 0.73 |
| 300 g KOAc/1000 ml HOAc, 138° | 0.34 ^b |
| 300 g KOAc/1000 ml HOAc, 138° | |
| anhyd. Mn(III) , Ac_2O dried | 1.50 ^b |

^b This is twice the initial Mn(III) concentration; ^a Some carboxylic acid was detected.

addition of metal oxidants is a well known technique for inhibiting radical polymerization. In the reaction of lead tetra-acetate with styrene, which proceeds by a free radical pathway, no significant amount of styrene polymer was observed. (iii) Contrary to the statement that methyl benzoate is inert towards manganic acetate, we found that not only methyl benzoate but even nitrobenzene, reacts with manganic acetate. The relative reactivity of various substituted benzenes as measured by the competitive disappearance of the starting material was: C_6H_6 (1.0), $\text{C}_6\text{H}_5\text{Br}$ (1.0), $\text{C}_6\text{H}_5\text{Cl}$ (1.0), $\text{C}_6\text{H}_5\text{-t-Bu}$ (1.1), $\text{C}_6\text{H}_5\text{COOCH}_3$ (1.3), $\text{C}_6\text{H}_5\text{NO}_2$ (1.5), $\text{C}_6\text{H}_5\text{OCH}_3$ (3.0). This order of reactivity is more consistent with a free radical attack than a carbonium ion attack on the ring. (iv) The extensive formation of succinic acid and other dimeric products in the oxidation of carboxylic acids in the absence of the aromatic substrate, also supports the intermediacy of the $\cdot\text{CH}_2\text{COOH}$ radical.

Dr. C. F. Wells and Mr. C. Barnes (Birmingham University) (communicated): With reference to the paper by Finkbeiner and Bush, our results of the oxidations of simple carboxylic acids by monomeric Mn(III) in strongly acidic aqueous perchlorate

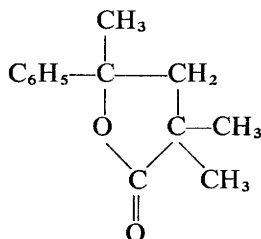
¹ E. I. Heiba, R. M. Dessau and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, in press.

² E. I. Heiba, R. M. Dessau and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, 1968, **90**, 2706.

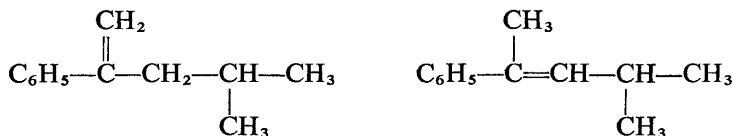
³ H. Finkbeiner and J. B. Bush, Jr., this Discussion.

media may be contrasted with those in carboxylic acid media of Finkbeiner and Bush given in table 5 of their paper. We have identified acetone and isopropanol as the main products from isobutyric acid and acetone as the main product from α -hydroxyisobutyric acid using thin layer chromatography of 2,4-dinitrophenylhydrazones and VPC, and no formic acid is detected, i.e., decarboxylation occurs. The initiation of vinyl polymerization suggests that intermediate free radicals are formed. The predominant rate-determining step involves the outer-sphere reaction of the hexa-aquomanganese (III) ion with an unprotonated molecule of carboxylic acid: this compares with the oxidation of secondary alcohols by Mn(III) in perchlorate media.¹

Dr. H. Finkbeiner (*G. E. Res. Dev. Centre, Schenectady*) said: In a series of experiments with isobutyric acid, α -methylstyrene and manganese (III), the maximum yield of lactone that



we were able to obtain was 11 %. The major products were



presumably arising from the attack of an isopropyl radical (or carbonium ion) on the α -methyl styrene. This result strongly suggests that the initial oxidation product of isobutyric acid is the same in both aqueous perchloric acid and in isobutyric acid. In turn it also suggests that the initial product formed in aqueous perchloric acid might be trapped by species other than water. Presumably this is what is occurring in the initiation of vinyl polymerization.

Dr. C. F. Wells and **Mr. C. Barnes** (*Birmingham University*) (*communicated*): In reply to Finkbeiner and Bush, we have evidence other than the initiation of vinyl polymerization that the free radical formed by the initial attack of Mn(III) on isobutyric acid in perchlorate media can react in more than one way. The yield of acetone varies considerably between anaerobic and aerobic conditions, and we interpret this as a competition for the free radical (probably the isopropyl radical) with Mn(III) and solvent on the one hand to form isopropanol and with oxygen on the other to form a peroxy radical which ultimately gives acetone.

Dr. C. F. Wells (*Birmingham University*) said: With reference to the papers by Bawn *et al.*, and Waters, many redox reactions of Co(III) are rapid despite high energies of activation. Values of the energy and entropy of activation for the *overall* reactions of Co(III) with various substrates are compared in table 1 with E and ΔS^\ddagger for other cations, all determined in perchlorate media.

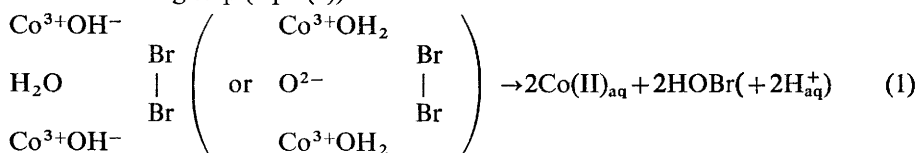
¹ C. F. Wells and G. Davies, *Trans. Faraday Soc.*, 1967, **63**, 2737; C. F. Wells, C. Barnes and G. Davies, *Trans. Faraday Soc.*, 1968, **64**, 3069.

The reactions of Co(III) and Mn(III) with secondary alcohols and isobutyric acid are outer-sphere, and the much higher reactivity of Co(III) mainly derives from the high positive values of ΔS^* . All the reactions of Co(III) in table 1 (except with H_2O_2)

TABLE 1

| substrate | oxidant | E kcal mole ⁻¹ | ΔS^* cal deg. ⁻¹ mole ⁻¹ | comments | ref. |
|------------------------|------------------------------|--------------------------------|---|---|--------|
| secondary alcohols | Co(III) | 29-32 | +36-+43 | no intermediate complexes detected | 1 |
| secondary alcohols | $\text{Mn}_{\text{aq}}^{3+}$ | 20-25 | -8-+5 | no intermediate complexes detected | 2 |
| isobutyric acid | Co(III) | 22.6 | +16 | no intermediate complexes detected | 3 |
| isobutyric acid | $\text{Mn}_{\text{aq}}^{3+}$ | 25 | +10 | no intermediate complexes detected | 4 |
| benzene | Co(III)(DH ₂) | 19 | -12 | no intermediate complexes detected | 5 |
| benzene | Co(III)(DH) | 29 | +23 | complexes detected | 5 |
| Br_2 | Co(III)(D) | 30 | +47 | inner-sphere reaction of cation + HN_3 complex | 6 |
| HN_3 | Co(III)(DH ₂) | 12.6 | -3.6 | with HN_3 reaction of cation + HN_3 complex | 7 |
| HN_3 | $\text{Mn}_{\text{aq}}^{3+}$ | 19.6 | +23 | with HN_3 | 8 |
| H_2O_2 | $\text{Co}_{\text{aq}}^{3+}$ | 17 | +55 | inner-sphere | 9, 11 |
| H_2O_2 | $\text{Fe}_{\text{aq}}^{3+}$ | 28 | +51 | inner-sphere | 10, 11 |

had an initial $[\text{Co(III)}] \lesssim 5 \times 10^{-4} \text{ M}$ where Co(III) exists mainly as a dimer^{9, 12}: if the latter is the reactive species, the order in total Co(III) will be unity, as observed. Hydrolysis of the dimer can occur: if the unhydrolyzed dimer is DH_2 , the mono-hydrolyzed dimer DH may be $(\text{Co}^{3+}\text{OH}-\text{Co}^{3+})_{\text{aq}}$ or $(\text{Co}^{3+}\text{H}_2\text{OCo}^{3+}\text{OH}^-)_{\text{aq}}$, and the dihydrolyzed dimer D is $(\text{Co}^{3+}\text{O}^{2-}-\text{Co}^{3+})_{\text{aq}}$ or $(\text{HO}-\text{Co}^{3+}\text{H}_2\text{OCo}^{3+}\text{OH}^-)_{\text{aq}}$. The reactive form of the dimer, indicated in table 1, can be identified kinetically by the variation of rate with $[\text{H}^+]$. The reaction of D with Br_2 has a high positive ΔS^* : the rate-determining step (eqn. (1))



¹ D. G. Hoare and W. A. Waters, *J. Chem. Soc.*, 1964, 2552.

² C. F. Wells and G. Davies, *Trans. Faraday Soc.*, 1967, **63**, 2737.

C. F. Wells, C. Barnes and G. Davies, *Trans. Faraday Soc.*, 1968, **64**, 3069.

³ A. A. Clifford and W. A. Waters, *J. Chem. Soc.*, 1965, 2796.

⁴ C. F. Wells and C. Barnes, to be published.

⁵ C. F. Wells, *Trans. Faraday Soc.*, 1967, **63**, 156.

⁶ C. F. Wells and D. Mays, *J. Chem. Soc. A*, 1968, 2740.

⁷ C. F. Wells and D. Mays, to be published.

⁸ C. F. Wells and D. Mays, *J. Chem. Soc. A*, 1968, 1622.

⁹ J. H. Baxendale and C. F. Wells, *Trans. Faraday Soc.*, 1957, **53**, 800.

¹⁰ W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, *Trans. Faraday Soc.*, 1951, **47**, 591.

¹¹ C. F. Wells and D. Mays, *J. Chem. Soc. A*, 1968, 665.

¹² C. E. H. Bawn and A. G. White, *J. Chem. Soc.*, 1951, 331. L. H. Sutcliffe and J. R. Weber, *J. Inorg. Nucl. Chem.*, 1960, **12**, 281. M. Anbar and I. Pecht, *J. Amer. Chem. Soc.*, 1967, **89**, 2553.

involves the simultaneous transfer of two electrons from Br_2 to the dimer with concomitant depolymerization of the cobalt as Co(II) .¹ The reaction of DH_2 with benzene has a negative ΔS^* : the rate determining step (eqn. (2))

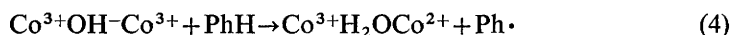


involves only a single-electron transfer to the dimer,² and hence depolymerization occurs in subsequent steps. Therefore, it is suggested that a high positive ΔS^* results from the loss of restriction due to depolymerization on conversion of both Co atoms to Co(II) in the transition state. One possible rate-determining step is suggested in eqn. (3))

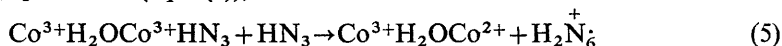


to explain the high ΔS^* for the secondary alcohols + Co(III) , and the protons are transferred to the dimer and not to the bulk solvent as in eqn. (2): the observed complex variation of rate with $[\text{H}^+]$ ³ probably results from the participation of various hydrolyzed Co dimers and from the protonation of the alcohol.

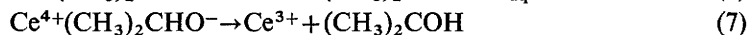
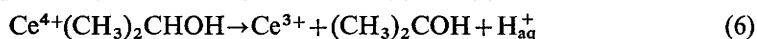
An intermediate positive ΔS^* is obtained for the reaction of DH with benzene. No depolymerization of Co occurs in the rate determining step² (eqn. (4)),



and the higher ΔS^* than obtained for eqn. (2) arises from the absence of restriction on bulk solvent by the released proton and some loss of restriction in the dimer due to a weaker bridge: the lower E for reaction (2) derives from the stabilization of H^+ in the solvent. No depolymerization of Co occurs in the rate-determining step of the $\text{Co(III)} + \text{HN}_3$ reaction (eqn. (5)),⁴



and hence the overall negative ΔS^* . The high positive value for ΔS^* for the reaction of H_2O_2 with monomeric Co^{3+} is comparable with ΔS^* for the $\text{Fe}^{3+} + \text{H}_2\text{O}_2$ reaction. Both are inner-sphere electron transfers involving⁵ a first-order reaction of intermediate species $\text{Co}^{3+}\text{HO}_2^-$ and $\text{Fe}^{3+}\text{HO}_2^-$. The high overall ΔS^* arise from the loss of restricted hydration by charge cancellation in the complex. ΔS^* for the inner-sphere electron transfer is only 8.9 cal/mole deg. for $\text{Co}^{3+}\text{HO}_2^-$ and 2.0 for $\text{Fe}^{3+}\text{HO}_2^-$,⁵ suggesting that fragmentation reactions (e.g., to Co^{2+} and $\text{HO}_2\cdot$) have low values for ΔS^* . This is supported by data for fragmentations (6) and (7):



for reaction (6) $E = 21$ kcal mole⁻¹ and $\Delta S^* \sim \text{zero}$; for reaction (7) $E = 27$ kcal mole⁻¹ and $\Delta S^* = 20$ cal/mole deg.⁶ The higher values for (7) arise from the absence of restriction imposed on the bulk solvent by the proton released from the α C—H bond, as discussed above.

I suggest, therefore, that the high positive values for ΔS^* responsible for the high redox reactivity of Co(III) with some substrates arises when depolymerization of the dimeric Co occurs in the rate-determining step and not from fragmentation of an intermediate Co(III) -substrate complex present in low concentration.

¹ C. F. Wells and D. Mays, *J. Chem. Soc. A*, 1968, 2740.

² C. F. Wells, *Trans. Faraday Soc.*, 1967, **63**, 156.

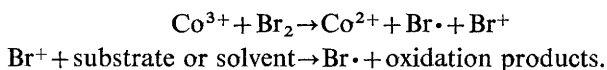
³ D. G. Hoare and W. A. Waters, *J. Chem. Soc.*, 1962, 965.

⁴ C. F. Wells and D. Mays, to be published.

⁵ C. F. Wells and D. Mays, *J. Chem. Soc. A*, 1968, 665.

⁶ C. F. Wells and S. M. Husain, to be published.

With regard to the oxidation of toluic acid at 100-130°C catalyzed by cobalt bromide discussed by Bawn and Wright, the reaction of Co(III) with molecular bromine formed in the mixtures may be a source of bromine atoms. At such high temperatures in an ionizing solvent with monomeric Co(III) the following reactions will be rapid:¹



Prof. W. A. Waters (*Oxford University*) said: With reference to the paper by Wells *et al.*, the dimerization of cobaltic ions in water undoubtedly occurs at concentrations $>10^{-2}$ M and perchloric acid concentrations below 0.4 M² but is negligible under the conditions of all our work at Oxford for we have always taken $[\text{Co}^{\text{III}}]$ ca. 10^{-3} M and $[\text{HClO}_4] = 1.5$ M (most frequently 2 M) and have checked that the extinction coefficient of the Co^{III} ion was independent of its concentration in our solvents. Again, the effects of adding acrylamide to the oxidations of alcohols and of CHBr_3 to the oxidations of acids show conclusively that we have been producing organic free radicals.

The large positive entropy of the cobaltic perchlorate oxidations has been commented on in many of our papers³ and we ascribe it to the concerted fragmentation that is involved in the breakdown of the reaction complex.⁴ In particular, the breakdown of the hexagonal d^6 structure of a cobalt (III) complex to give the d^7 configuration of Co^{II} , aq. is accompanied by a significant gain of entropy since a much less symmetrical and much more loosely co-ordinated ion is being formed. In my view, the entropy gain which is involved in the addition of one electron to the d^6 structure of co-ordinated cobalt (III) provides a major part of the driving force ΔF^* of cobaltic salt oxidations.

Dr. C. F. Wells (*Birmingham University*) (*communicated*): In reply to Waters, the evidence that Co(III) exists in perchlorate media mainly as a dimer at $[\text{Co(III)}] \sim 10^{-3}$ M may be summarized as follows. The oxidation of water by Co(III) was shown by Bawn and White to have an order between 1 and 2 in $[\text{Co(III)}]$,⁵ and they suggested concurrent reactions of monomeric and dimeric Co(III). However, Baxendale and Wells found,⁶ under conditions carefully controlled to minimize the reaction of Co(III) with trace organic impurity, that the order is 1.5 in $[\text{Co(III)}]$ in ~ 0.1 M HClO_4 , and suggested that this can only be explained if the predominant species of Co(III) is an unhydrolyzed dimer, probably $(\text{Co}^{3+}\text{H}_2\text{OCo}^{3+})_{\text{aq}}$.⁷ Sutcliffe and Weber stated⁸ that this dimer is the predominant species in the conditions used by Baxendale and Wells, viz., $[\text{Co(III)}] \sim 3 \times 10^{-3} \text{ M} - 3 \times 10^{-4} \text{ M}$. Anbar and Pecht,⁹ using water enriched in H_2O ,¹⁸ have confirmed the mechanism of Baxendale and Wells involving dimeric Co(III) even in 6 M HClO_4 . Wells has shown⁷ that the absence of an effect of oxygen on the oxidation of benzene by Co(III) can be explained if the predominant species of Co(III) is a dimer in 0.5-2.0 M HClO_4 at $[\text{Co(III)}] \sim 10^{-3}$ M,

¹ C. F. Wells and D. Mays, *J. Chem. Soc. A*, 1968, 2740.

² Sutcliffe and Weber, *J. Inorg. Nuclear Chem.*, 1960, **12**, 281.

³ see especially *Proc. Roy. Soc. A*, 1963, **274**, 480.

⁴ *Chem. Soc. Spec. Publ.* 19, 1965, p. 81.

⁵ C. E. H. Bawn and A. G. White, *J. Chem. Soc.*, 1951, 331.

⁶ J. H. Baxendale and C. F. Wells, *Trans. Faraday Soc.*, 1957, **53**, 800.

⁷ C. F. Wells, *Trans. Faraday Soc.*, 1967, **63**, 156.

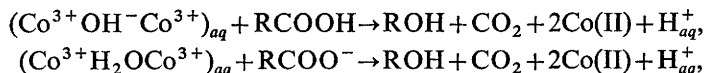
⁸ L. H. Sutcliffe and J. R. Weber, *J. Inorg. Nucl. Chem.*, 1960, **12**, 281.

⁹ M. Anbar and I. Pecht, *J. Amer. Chem. Soc.*, 1967, **89**, 2553.

and spectrophotometric measurements in this acidity range¹ suggest that this is the unhydrolyzed dimer (hydrolysis constant^{1, 2} $\sim 10^{-2}$ - 10^{-3} mole l.⁻¹). Wells and Mays found³ that the rate of reduction of Co(III) by excess molecular bromine is independent of [Co(III)] in the range 4×10^{-4} M- 2×10^{-3} M and $\propto [H^+]^{-2}$, and they concluded that this also can only be explained if most of the Co(III) (> 95 %) in this concentration range in 0.5-5.0 M HClO₄ is an unhydrolyzed dimer which has lost two protons in the transition state. The low hydrolysis constant of the dimer is confirmed by the invariance with [H⁺] of the rate of reduction of Co(III) by excess hydrazoic acid in the range 0.5-5.0 M HClO₄.⁴

Presumably the mechanism of dimerization of Co(III) is analogous to that for Fe(II)⁵ and Mn(II),⁶ but at a much lower pH: this suggests that the first hydrolysis constant of monomeric Co(III) is very high. The diamagnetism of Co(III) in perchlorate media⁷ may result from the dimerization or from a low spin t_{2g}^6 electronic arrangement for each Co atom.⁸

Although reaction (3) with an alcohol yields a ketone directly, intermediate free radicals, e.g., (CH₃)₂COH, will be produced if a small proportion of the reaction goes via successive single electron transfers with (Co³⁺H₂OCO³⁺)_{aq} or (Co³⁺OH-Co³⁺)_{aq} (e.g., cf. reaction (4)): indeed the complex variation with [H⁺] of the rate of oxidation of alcohols⁹ suggests that all these paths occur. However, to prove the presence of free radicals with the initiation of vinyl polymerization by the oxidation of substrates by Co(III), it is essential to show that the rate of polymerization is greater with than without the substrate, as Co(III) in perchlorate media itself initiates vinyl polymerization. Alternative explanations exist¹⁰ for the observed variation with [H⁺]¹¹ of the rate of oxidation of carboxylic acids by Co(III), and two possibilities involving a simultaneous double electron transfer are



Again, some participation of consecutive single electron transfers will provide free radicals.

Dr. F. R. Mayo (*Standard Research Inst., California*) said: I propose that a critical factor in Bawn's oxidation of p-toluic acid is the competition between the reactions of p-HO₂C · C₆H₄ · CH₂ · radicals with oxygen (his reaction (3)) and with bromine (reaction (11)). The reaction with oxygen is essential for his chain autoxidation (reactions (2)-(4)). Since too much reaction with bromine will retard or prevent the oxidation, a reasonable balance is essential in the competition between Br₂ and O₂ for the benzyl radicals. The required balance depends on the concentrations of bromine and oxygen, neither of which seems to be known. The retarding effects of high bromide concentrations may well be due to higher equilibrium concentrations of bromine.

¹ J. H. Baxendale and C. F. Wells, *Trans. Faraday Soc.*, 1957, **53**, 800.

² L. H. Sutcliffe and J. R. Weber, *Trans. Faraday Soc.*, 1956, **52**, 1225.

³ C. F. Wells and D. Mays, *J. Chem. Soc. A*, 1968, 2740.

⁴ C. F. Wells and D. Mays, to be published. D. Mays, *Ph.D. thesis* (University of Birmingham, 1968).

⁵ C. F. Wells and M. A. Salam, *J. Chem. Soc. A*, 1968, 24.

⁶ C. F. Wells and M. A. Salam, *J. Inorg. Nucl. Chem.*, in press.

⁷ H. L. Friedman, J. P. Hunt, R. A. Plane and H. Taube, *J. Amer. Chem. Soc.*, 1951, **73**, 4028.

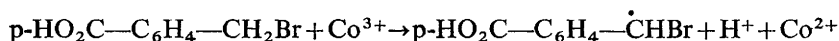
⁸ C. F. Wells, *Nature*, 1965, **205**, 693.

⁹ D. G. Hoare and W. A. Waters, *J. Chem. Soc.*, 1962, 965.

¹⁰ C. F. Wells, *Disc. Faraday Soc.*, 1960, **29**, 248.

¹¹ A. A. Clifford and W. A. Waters, *J. Chem. Soc.*, 1965, 2796.

I am uncertain whether the reaction of benzyl radicals with bromine is an undesirable diversion of bromine or an essential feature in catalysis. The answer depends partly on how badly the reaction



(proposed also by Waters) is needed either to return Co^{3+} to Co^{2+} or to release bromine from the oxidation product of the benzyl bromide, or both. The answer also depends on the relative reactivities of *p*-toluic acid and its bromo derivative toward Co^{3+} and on the availability of alternative routes for the necessary cycling of bromine and cobalt; these factors probably change with temperature.

Since the CoBr_2 -catalyzed oxidation of *p*-toluic acid is a free radical-chain reaction, another important unknown is the kinetic chain length, or the number of molecules of *p*-toluic acid reacting per initiating radical. The oxidation of this aromatic methyl group seems to require special provision for chain initiation, either because of an unfavourable ratio of propagation to termination constants, or because of a poor yield, or unusual instability of the hydroperoxides necessary for catalysis. Measurements of kinetic chain lengths should help to decide between these alternatives and perhaps others related to the bromine-oxygen competition.

Dr. E. K. Fields (*Amoco Chemicals Corp., Indiana*) said: With reference to the paper by Bawn, in the oxidation of aromatic hydrocarbons by oxygen, with cobalt acetate and bromide catalysts in acetic acid solvent, we have found evidence of attack on the aromatic nucleus. Thus, in the oxidation of toluene- α - d_3 under these conditions, after 90 min the product contained an estimated 6 % benzaldehyde- d_1 and 11 % benzyl alcohol- d_2 and benzyl acetate- d_2 . In addition, samples taken at three intervals gave the following isotopic analyses for the recovered toluene:

| time, min number of deuterium atoms | | 20 | 60 | 90 |
|---|------|------------------------------|------|------|
| | | toluene isotopic composition | | |
| d_0 | 0 | 0.1 | 0.1 | 0.4 |
| d_1 | 0.2 | 0.7 | 1.2 | 0.8 |
| d_2 | 4.7 | 6.1 | 6.6 | 12.1 |
| d_3 | 91.1 | 89.1 | 88.0 | 82.6 |
| d_4 | 3.1 | 3.1 | 3.1 | 3.3 |
| d_5 | 0.6 | 0.7 | 0.7 | 0.7 |
| d_6 | 0.3 | 0.2 | 0.2 | 0.1 |

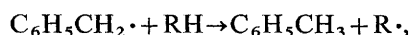
Toluene- d_4 , d_5 , and d_6 remained constant; d_3 decreased, and d_2 increased. This indicated some exchange, probably by way of benzyl radical that abstracted protium in place of the original deuterium. Toluene- α - d_3 , refluxed for 2 h in acetic acid with the same concentration of cobalt acetate and cobalt bromide, was recovered unchanged. The protium atoms, could have been furnished by the acetic acid. To determine the extent of hydrogen abstraction from the solvent, toluene was oxidized in acetic acid- d_4 .

Oxygen at 0.6 cu. ft./h was passed through a refluxing solution of 0.5 mole of acetic acid- d_4 , 0.001 mole of cobalt bromide, 0.003 mole of cobalt acetate, and 0.05 mole of toluene in a Vibramix apparatus. Aliquots were withdrawn at intervals, washed free of acetic acid, and worked up to give products boiling above 100° for analysis by low-voltage (7.5 V, uncorr.) mass spectrometry with the following results:

| mass | time, min | | | probable compound |
|------|-----------|---|-----|-------------------------------|
| | 20 | 60 relative intensities ^a | 90 | |
| 92 | 1063 | 637 | 507 | toluene |
| 93 | — | — | — | |
| 94 | — | — | — | |
| 95 | 3 | 2 | 5 | |
| 106 | 22 | 58 | 80 | benzaldehyde |
| 108 | 40 | 55 | 12 | benzyl alcohol |
| 109 | — | 13 | 15 | benzyl alcohol-d ₁ |
| 153 | — | 13 | 22 | benzyl acetate-d ₃ |
| 182 | 5 | 18 | — | bibenzyl |

(a) Total ion current was the same for all samples within 2 %.

The absence of peaks at 93 and 94 confirms that in the abstraction,



only toluene is the hydrogen donor, not acetic acid. The other products in the table and the absence of corresponding deuteriated products are consistent with the results from the oxidation of toluene- α -d₃. The small amount of benzyl alcohol-d₁ probably arises by solvolysis of benzyl acetate; the greater amount of unlabelled benzyl alcohol at 60 min shows that the benzyloxy radical that produces benzyl alcohol, presumably by $\text{C}_6\text{H}_5\text{CH}_2\text{O}\cdot + \text{RH} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{R}\cdot$, also abstracts hydrogen from toluene rather than from acetic acid, even though the latter is more abundant by a factor of 10.

Dr. N. Uri (*Ministry of Technology, Waltham Abbey*) said: I would ask the following questions of Bawn: (i) is the apparent specificity of cobalt in this system due to chelating or the magnitude of its oxidation-reduction potential? (ii) How is terephthalic acid identified and determined? (iii) Water is reported to have no effect up to concentrations of ten times that of the catalyst. Does the rate of reaction, however, decrease sharply when the water concentration exceeds 5 %, as we observed, e.g., in the cobalt acetate catalyzed oxidation of N-butylacetamide. Are there suitable solvents apart from glacial acetic acid and has any systematic study been carried out on the solvent effect in general, e.g., is an acidic solvent essential?

Prof. C. E. H. Bawn (*Liverpool University*) said: In reply to Uri, the reaction is not specific to cobalt. Other transition metal salts particularly manganese are also effective catalysts. The terephthalic acid formed is practically insoluble in the reaction medium and may be determined by cooling the system to room temperature, filtration, washing and weighing. The effect of concentrations of added water above 10^{-1} M was not studied. A decrease in rate would be expected at high water concentrations. Acetic, other aliphatic acids, and benzoic acid are suitable unreactive solvents in which both reactants and catalyst are soluble. There is no reason why other solvents fulfilling these conditions should not be useful.

I agree with Mayo's conclusion that the factors which make the cobalt-bromine combination such an effective catalyst are the nicely balanced rates of the competing radical reactions with oxygen, bromine and bromides. It has not been possible to identify with precision the exact cycle of reactions involved. The occurrence of the two distinct stages is clear and it is this complexity which makes it difficult to determine the kinetic chain length. Also, further work has shown that the reaction rates and transition points from stage (I) to stage (II) are dependent on alkali acetate, hydrogen ion concentration and solvent medium.

Prof. W. A. Waters (*Oxford University*) said: The observation by Bawn and Wright that benzyl bromide was a catalyst for the cobalt-catalyzed autoxidation of p-toluic acid reminds me of work carried out with A. Robertson.¹ We found that many organic halides, then thought of as containing "positive halogens", could dissociate homolytically to generate free radicals capable of catalyzing the autoxidation of tetralin. Benzyl bromide was definitely shown to be an autoxidation catalyst. The homolysis $\text{PhCH}_2\text{Br} \rightarrow \text{PhCH}_2\cdot + \cdot\text{Br}$ should be considered as a way for returning bromine into the reaction chain from the organic halide.

Dr. N. Uri (*Ministry of Technology, Waltham Abbey*) said: With reference to the paper of Márta *et al.*, it is rare to find quantitative data concerning Ni^{3+} . The rate constants for reactions (4a) and (5a) in their paper are interesting and I ask whether activation energies have also been determined. In this context, we found both the bis(N-butylsalicylaldimino) and bis(N-phenylsalicylaldimino) nickel chelates to be fairly efficient catalysts for the autoxidation of various hydrocarbons. The rate was approximately one tenth of that observed with similar cobalt chelates. In terms of the kinetic formula, this suggests that the overall rate of free radical formation must have been 100 times faster with cobalt chelate catalysts than that obtained in the presence of the corresponding nickel chelate catalysts at the same concentration. Inhibition which is usually second order with regard to metal was not observed with these hydrocarbons systems when the nickel chelate concentration was increased to M/200 but it cannot be ruled out at still higher concentrations. Did Márta observe, as we did, an inhibitory reaction which is second order with respect to the concentration of the transition metal compound. Does he attribute the relationship of induction period $\propto [\text{catalyst}]^{1.7}$, reported in his paper, to such a second-order termination reaction? Since I view literature reports in which precise claims are based on partially heterogeneous systems, such as hydrocarbons loaded with cobalt stearate, with scepticism, I would ask whether all the experiments were carried out in a homogeneous environment.

Prof. F. Márta (*University of Szeged*) said: In reply to Uri, the activation energy for reaction (5a) has not been measured, while for the reaction (4a) it was found to be 22.9 kcal/mole. In connection with the catalytic efficiency of nickel compared to cobalt, we observed nearly the same difference as found by Uri in his experiment. This is indicated by the values of the overall rate constants which were $5.6 \times 10^{-1} \text{ l. mole}^{-1} \text{ sec}^{-1}$ and $4.27 \times 10^{-2} \text{ l. mole}^{-1} \text{ sec}^{-1}$ under the same experimental conditions for cobalt- and nickel-acetate, respectively. We observed the inhibitory effect of cobaltous acetate to be proportional to (catalyst).^{1, 7} I agree that this indicates a second order termination with respect to the concentration of the catalyst, but both first- and second-order terminations could be taken into account. In answer to the last question, all experiments were carried out in homogeneous environment.

¹ A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1947, 492.