nates, which are both inert to oxygen by our standards, had no effect on the polymerization of styrene (see Experimental).

Experimental

Materials.—Purification of the diphenyl ether solvent, the oxygen and the preparation of the chelates have been described in previous papers.[4,6] Commercially obtained reagents were purchased from the following suppliers: benzoyl peroxide (Lucidol Division of Novadel-Agene Corp.), NNDP (Eastman, Technical grade), hydroquinone (J.T. Baker), AIBN (Eastman, White Label), phenol (Eastman, White Label), 2,4,6-tri-*t*-butylphenol (Koppers Co.). Ferrocene was contributed by Dr. Tod W. Campbell of the du Pont Co. and disalicylalethylenediamine by Dr. F. Yeoman of the Westinghouse Electric Corp.; we are most appreciative for this help. These materials were purified until their physical constants agreed with well-established literature values. Styrene was purified according to the method of Tobolsky and Johnson.[12] The vacuum distilled product was used immediately after distillation.

Kinetic Procedures.—The techniques for gasometric kinetic study of the autoxidation reaction have already been described.[4,5] In the case of AIBN-catalyzed reactions calculations showed that corrections for the volume of evolved nitrogen were for the most part negligible. The theoretical quantity from the solution containing 6 mole % AIBN would be about 2 ml., and in this case, and that of the 3 mole % solution, a volume correction for this factor was included.

Styrene Polymerization Experiments.—Samples were prepared which contained 0.32 mole % of various acetylacetonates in styrene and a similar set which also contained 0.10 weight % *t*-butyl perbenzoate. The samples were placed in narrow tubes which were connected to a manifold. As vacuum was applied the tubes were placed in a Dry Ice–acetone bath at −20°. When the styrene started to boil, the vacuum was replaced by an atmosphere of nitrogen. This process was repeated five times for each sample and then the tubes were sealed under nitrogen. Markings on the sample tubes indicated that only about 6% of the styrene was lost through evaporation. The sealed samples were heated simultaneously in an oven at 110°.

The extent of polymerization was followed qualitatively by two methods. Rates of polymerization were followed by change of volume, polystyrene being about 15% more dense than the monomer. Bubble viscosities (Gardner system) were also compared. Both methods were used only for comparative purposes between the various samples and gave the same results. All of the samples were heated for 13 hr. and inspected every 15 minutes for the first hour and every 3 hr. thereafter. There were no reversals in the rates of polymerization, the order first observed being maintained throughout the 13 hr.

The peroxide catalyzed system gave the following sequence, expressed as order of increasing polymer formation: V(III) $<$ styrene (without chelate) = Cr(III) = Al(III) $<$ Fe(III) $<$ Mn(III) $<$ Ce(IV) $\approx$ Co(III). Thus Co(III) and Ce(IV) were the best polymerization accelerators. Al(III) and Cr(III) had no apparent effect, and V(III) acted as an inhibitor. For the non-peroxide system, the order was as follows: V(III) $<$ styrene (no chelate) = Cr(III) = Al(III) $<$ Fe(III) $<$ Co(III)) $<$ Ce(IV) $<$ Mn(III). Again Cr(III) and Al(III) had no apparent effect, and V(III) inhibited the polymerization.

Several interesting color changes occurred which indicate a reduction–oxidation mechanism. The peroxide-catalyzed sample containing Ce(IV) turned from a very dark red to yellow indicating reduction to Ce(III). In the absence of peroxides the sample became brownish red, also indicating formation of some Ce(III). The peroxide-catalyzed sample containing Co(III) changed from dark green to violet, indicating formation of Co(II). This change was not so apparent in the non-peroxide sample. The other metal acetylacetonates did not show any appreciable color changes.

Dr. E. H. Gleason of the Koppers Company has subsequently made a more detailed study of the effects of Ce(IV) and Co(III)-acetylacetonates on the polymerization of styrene. This work is being prepared for publication.

Acknowledgment.—We wish to express our appreciation to Professor Henry Freiser of the University of Arizona (and formerly of the University of Pittsburgh) under whose guidance work in this area was initiated and who provided us with considerable help and encouragement. We also wish to thank Dr. J. Swiss of the Westinghouse Research and Development Center for his aid to this project.

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[12] A. V. Tobolsky and D. H. Johnson, *J. Am. Chem. Soc.*, **74**, 938 (1952).

[CONTRIBUTION NO. 1135 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, PITTSBURGH 13, PENNSYLVANIA]

Destructive Autoxidation of Metal Chelates. IV. Kinetics and Mechanism[1,2]

BY EDWARD M. ARNETT[3] AND MORRIS A. MENDELSOHN[4]

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Further evidence that the autoxidation of metal acetylacetonates does not follow a conventional chain mechanism is provided by the striking difference between the effect of certain such chelate systems on the autoxidation of tetralin (which is a chain reaction) and the destructive autoxidation of the same chelates by themselves. The autoxidation of iron(III) acetylacetonate is nearly independent of oxygen pressure and has an apparent energy of activation of about 22 kcal./mole. A mechanism is proposed for the destructive autoxidation of chelates which is in harmony with the observations in this and the preceding three papers in this series. On the basis of this mechanism and a well-accepted termination reaction it is predicted that 2,3,4-pentanetrione is an intermediate from which the major products of the reaction (water, carbon dioxide, acetic acid, and biacetyl) arise. A sample of this triketone is observed to give these products upon reaction with oxygen at the temperature used for our experiments.

In three previous papers[5–7] we have considered the effects of structural and environmental factors on the rates of decomposition of various beta-diketone chelates in the presence of pure oxygen at 100° in diphenyl ether as solvent. In this article we shall present several other kinetic results and then propose a mechanism for the representative compound iron(III) acetylacetonate. This mechanism is the only one of over fifty which we have con-

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[1] From the thesis of M. A. Mendelsohn submitted to the Department of Chemistry of the University of Pittsburgh in partial fulfillment of the requirements for the Ph.D. degree in 1960.

[2] Presented at the 140th Meeting of the American Chemical Society, Chicago, Illinois, September, 1961.

[3] University of Pittsburgh, Department of Chemistry, Pittsburgh 13, Pa.

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[5] M. Mendelsohn, E. M. Arnett and H. Freiser, *J. Phys. Chem.*, **64**, 660 (1960).

[6] E. M. Arnett, H. Freiser and M. A. Mendelsohn, *J. Am. Chem. Soc.*, **84**, 2482 (1962).

[7] E. M. Arnett and M. Mendelsohn, *ibid.*, **84**, 3821 (1962).

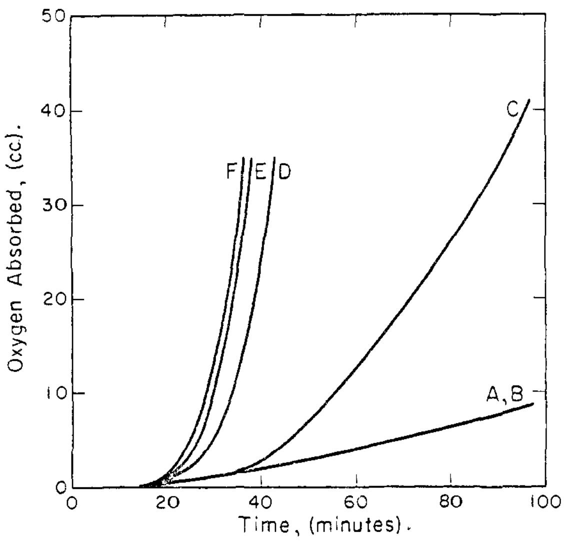

Fig. 1.—Effect of additives on the autoxidation of tetralin at 98.5°. Curves represent oxidation of 10 ml. solutions of 1.368 molal tetralin in diphenyl ether with the following additives (mole percentages are based on tetralin): A, no additive; B, 1 mole % Al(acac)$_3$; C, 1 mole % ferrocene; D, 1 mole % Fe(III) (3-phenyl acac)$_3$; E, 1 mole % Fe(III) acac$_3$; F, 0.5 mole % Fe(III) acac$_3$ + 0.5 mole % ferrocene.

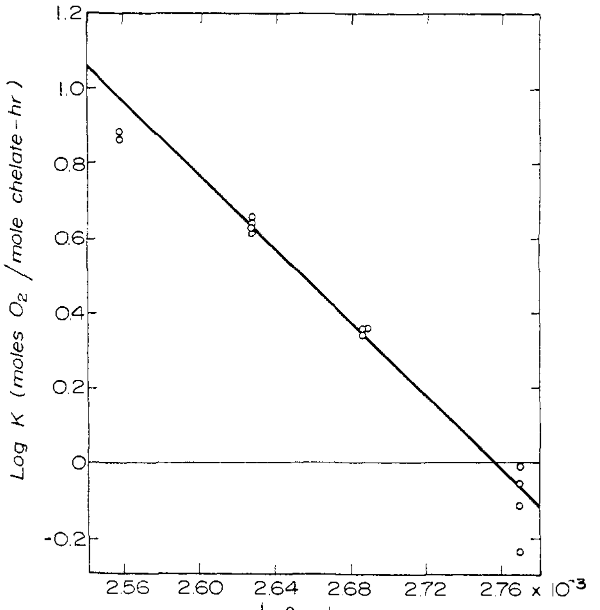

Fig. 2.—Effect of temperature on rate of oxygen consumption by iron(III) acetylacetonate, 0.129 molal solution in diphenyl ether; slope −4.83 × 10^3, *Ea* 22.1 kcal.

sidered which accommodates the facts that we have accumulated so far. On the basis of it one is led to predict that 2,3,4-pentanetrione is an intermediate in the reaction leading to the formation of biacetyl. This prediction is tested and found to be consistent with the facts.

Results

Tetralin Oxidation.—We have frequently noted contrasts between destructive autoxidation of chelates and "classical" autoxidation of organic substrates.[5–7] These will be reviewed at an appropriate point in the discussion below. As a further demonstration of the difference between the two systems and to provide additional proof that we are not dealing with metal-catalyzed autoxidation of one chelate molecule by another, we have tested the influence of a number of our key compounds on the autoxidation of tetralin, a compound whose autoxidation has been well studied[8–10] and which possesses a high enough boiling point to permit investigation under our conditions.

The results summarized in Fig. 1 reveal a number of important points. First, the over-all behavior of tetralin autoxidation is entirely different from that of the chelate autoxidations.[5,7] In the absence of additives the beta-diketone chelates that undergo decomposition in oxygen do so with little or no induction period. There is then a linear portion of the oxygen absorption curve followed by a rather sharp drop in rate until the reaction stops. In contrast, the tetralin autoxidations all showed a considerable induction period which was but little affected by the presence of the additives used (although ferrocene appears to prolong it). In the cases of the three systems which did promote autoxidation of tetralin (curves D, E, F) oxygen was consumed at such a rapid rate after the induction period that prudence prohibited our following the reactions beyond the points indicated since the rates probably would have become diffusion controlled and we were afraid of an explosion.

As might be expected, the aluminum(III) chelate gave no measurable effect on the reaction, having only one readily available oxidation state.[11] Ferrocene, a potent inhibitor for the autoxidation of iron(III) acetylacetonate[7] is seen to accelerate the rate of tetralin autoxidation despite prolonging the induction period. Of great importance is the fact that iron(III)-3-phenylacetylacetonate, which is itself almost inert to destructive autoxidation,[5,6] is as good a catalyst for the autoxidation of tetralin as is the easily oxidized standard compound iron(III) acetylacetonate. Furthermore, curve F shows that iron(III) acetylacetonate and ferrocene (which mixture was shown to be itself inert)[7] now serves as a very good catalyst.

Effect of Temperature on Rate.—Presented in Fig. 2 is an attempt to fit our results for variation of the rate between 87.2 and 117.8° to the Arrhenius equation. It is not possible using our present apparatus[5,6] to measure a large spread in autoxidation rates. Hence, there is large experimental error at the two extremes of the curve. If the data do indeed generate a straight line, its slope may be used to calculate an apparent energy of activation for the autoxidation of iron(III) acetylacetonate of about 22 kcal./mole. If this corresponds to a simple rate-determining step for the reaction, it

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(8) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.* (London), **A198**, 252 (1959).

(9) A. E. Woodward and R. B. Mesrobian, *J. Am. Chem. Soc.*, **75**, 6189 (1953).

(10) G. S. Hammond, C. E. Boozer, C. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3238 (1955).

(11) F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, pp. 338–342.

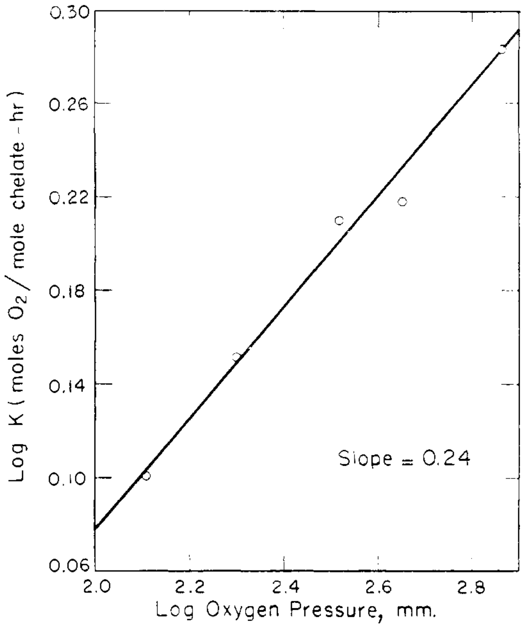

Fig. 3.—Effect of oxygen pressure on rate of oxygen uptake of Fe(III) acetylacetonate: temperature, 98.5°; solvent, diphenyl ether; concentration, 0.129 molal.

contrasts sharply with the range of 5–8 kcal./mole which has been cited[12] as customary for the rate-limiting hydrogen abstraction step in "classical" autoxidation. In view of the failure of the reaction to conform to a simple integrated rate expression and the odd units of K, we are not justified in calculating a frequency factor.

Effect of Oxygen Concentration.—We have already shown[6] that the reaction is one-half order with respect to the concentration of iron(III) acetylacetonate. The result of varying the oxygen pressure is portrayed in Fig. 3 where it is seen that the rate of oxygen consumption is relatively independent of oxygen concentration. The 0.24 order dependence for oxygen is not an exact figure in view of the inability of our apparatus to handle reactions at pressures greater than atmospheric and a multitude of difficulties that arise when a reaction in a liquid solvent is studied at rather high temperature and low pressure. There does seem to be clearly a slight dependence on oxygen pressure but it must be small.

Discussion

The important facts upon which any mechanism for the destructive autoxidation of iron(III)[13] beta diketone chelates (in particular the acetylacetonate) must be developed are

(a) The reaction is entirely different from "classical" chain autoxidation[12] in terms of the overall oxygen absorption curve (see above), the rate equation,[6] the response to additives[7] and the expected effects of ligand variation.[6]

(b) The chelate is rapidly (but only partially) converted to water, carbon dioxide and the surprising product, biacetyl. Small amounts of other materials are also formed, but the three main products appear almost at once and no intermediate can be isolated.

(c) Only the acetylacetonates of metals capable of easy oxidation–reduction changes undergo the oxidation rapidly enough for us to detect reaction within ninety minutes. The free ligands are relatively impervious to decomposition in the presence of oxygen.[6]

(d) The rate of autoxidation of iron(III) acetylacetonate is dependent on the square root of the chelate concentration[6] and is almost independent of oxygen concentration (see below).

(e) Variation of the ligand structure of iron(III) beta-diketone chelates has a marked effect on rate.[5,6] There does not appear to be any point of primary attack. Most particularly, the hydrogen in the 3-position of iron(III) acetylacetonate is not involved in the rate-determining step, although this is the site of attack in electrophilic substitution.[14]

Iron(III) dibenzoylmethide, which has no hydrogens attached to carbons in the position alpha to the chelate ring, is very rapidly autoxidized.[5] Assuming that this compound reacts by the same mechanism as iron(III) acetylacetonate, this means that the latter is not reacting by hydrogen abstraction from the quasibenzylic methyl groups which would seem to be a reasonable possibility.

(f) The reaction is strongly inhibited by compounds that usually serve as powerful initiators[7] through generation of reactive radicals. It is relatively immune to the influence of common antioxidants, but is strongly inhibited by ferrocene, a known radical trap, and is also stopped by the mixing of otherwise reactive chelates.

(g) The chelates which undergo ready autoxidation are also highly effective at initiating the polymerization of styrene both in the presence and absence of added *t*-butyl perbenzoate.[7] There is a very rough correlation between speed of autoxidation of an acetylacetonate and its ability to initiate polymerization and also with its tendency to pyrolytic decomposition. One may at least say that chelates of metals with only one stable oxidation state do not undergo any of these reactions easily. As might be expected, there is little or no correlation between rates of autoxidation and such factors as stability constants, oxidation–reduction potentials or rates of displacement reactions, all of which involve large solvation factors that are entirely different from those in the present case.

(h) Some of the chelate systems are potent catalysts for the autoxidation of tetralin, but aside from the requirement that the metal have more than one stable oxidation state, there is no relationship between the stability of a chelate system to oxygen and its ability to promote the autoxidation of tetralin.

On the basis of these facts we conclude that the mechanism describing the main course of the reaction might be a simple one (points a, b), and that it probably involves a reversible (d), unimolecular

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[12] C. Walling, "Free Radicals in Solution," John Wiley and Sons, New York, N. Y., 1957, p. 422.

[13] We have already shown[6] that corresponding chelates of some other metals must follow other mechanistic paths.

[14] J. P. Collman, R. S. Moss, H. Maltz and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961); J. P. Collman, R. P. Blair and E. T. Kittleman abstracts of the 140th Meeting of American Chemical Society, Chicago, Illinois, Sept. 1961.

(d, e, f, g) heterolysis involving intramolecular oxidation–reduction (c) to form radical species (f, g, h) which are stable enough to avoid complexing with the usual inhibitors but which are intercepted by highly reactive radicals arising from the usual initiators. Points a, b, c, d, e, f, all argue strongly against the usual type of radical chain reaction going through hydroperoxides and having hydrogen abstraction as a rate-determining step. A kinetic requirement is that the mechanism shall conform to the rate equation

$$\text{Rate} = k[\text{Chelate}]^{0.5}[\text{Oxygen}]^{0.24}$$

It would also be valuable if the mechanism should lead to an explanation of the surprising appearance of biacetyl in the products.

This mechanism meets these requirements

$$\text{Fe(III)-acac}_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{R}\cdot + \text{Fe(II)-acac}_2$$

$$\text{R}\cdot \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \text{L}\cdot$$

$$\text{L}\cdot + \text{O}_2 \xrightarrow{k_3} \text{LO}_2\cdot$$

$$2\text{LO}_2\cdot \xrightarrow{k_4} \text{P}$$

$$\text{LO}_2\cdot + \text{Fe(II)-acac}_2 \xrightarrow{k_5} \text{Q}$$

$$\text{Fe(II)-acac}_2 \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} \text{Fe(II)}_s$$

$$\text{Fe(II)}_s + \text{O}_2 \xrightarrow{k_7} \text{S}$$

If we assume that the radical R· is stable enough to avoid interception by oxygen and that both R· and L· can maintain steady-state concentrations in the early stages of the reaction effectively permitting the equilibria shown and that during the early stages of the reaction R· and Fe(II)-acac$_2$ maintain small and nearly equal concentrations through undergoing subsequent decomposition reactions at small and nearly equal rates, we may write the equations

$$-\frac{d(\text{O}_2)}{dt} = k_3(\text{L}\cdot)(\text{O}_2)$$

$$\frac{d(\text{L}\cdot)}{dt} = k_{-2}(\text{L}\cdot) + k_3(\text{L}\cdot)(\text{O}_2) - k_2(\text{R}\cdot) = 0$$

$$(\text{L}\cdot) = \frac{k_2(R\cdot)}{k_{-2} + k_3(\text{O}_2)}$$

$$K_{\text{eq}} = \frac{(\text{R}\cdot)(\text{Fe(II)-acac}_2)}{(\text{Fe(III)-acac}_3)}$$

Assuming that (R·) = (Fe(II)-acac$_2$) during the very early stages of the reaction, we have

$$(\text{R}\cdot) = [K_{\text{eq}}(\text{Fe(III)-acac}_3)]^{0.5}$$

Thus we can write

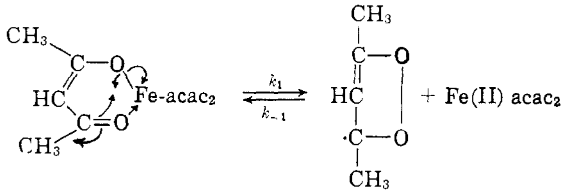
$$-\frac{d(\text{O}_2)}{dt} = \frac{k_3k_2(\text{O}_2)[K_{\text{eq}}\text{Fe(III)-acac}_3)]^{0.5}}{k_{-2} + k_3(\text{O}_2)}$$

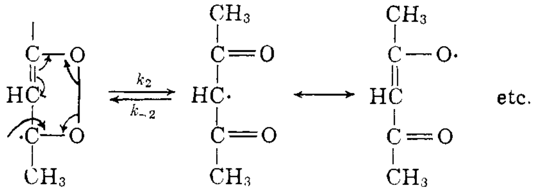
If $k_3(\text{O}_2) \gg k_{-2}$ and k_{-2} is small, then

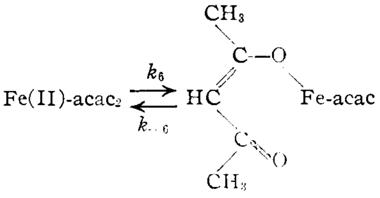
$$-\frac{d(\text{O}_2)}{dt} = k_2\,[K_{\text{eq}}(\text{Fe(III)-acac}_3)]^{0.5}$$

Within the limitations of our ingenuity this over-all scheme is the only one of some fifty which we have considered which can be reduced to the proper rate equation.[15] It is now necessary to consider reasonable structures and reactions for the chemical species demanded by the mathematical analysis.

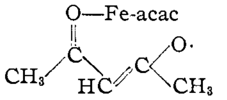
The first step might be an example of neighboring group participation in homolysis and the concerted formation of an O–O bond aids in cleavage of the O–Fe bond. While this reaction appears plausible, there are no data in the literature that would permit calculations of these energetics, although the work of Martin and Bentrude[16] provides some precedent for a neighboring group participation in homolysis. In any event the unimolecular homolytic dissociation of the chelate gives a free radical species and iron(II) acetylacetonate. Radical R· thermally decomposes or rearranges to give L·. Since we are postulating that R· is a peroxide radical, it appears reasonable that it should be relatively stable to oxygen and rearrange to give L· which then reacts with oxygen. Either R· or L· might have been responsible for promoting the polymerization of styrene. P, Q, and S represent products which can undergo further reactions during the later stages of the reaction. Step 6 might be depicted as


(R·)


(R·) (L·) (resonance form)


[Fe(II)]$_s$

It is unlikely that homolytic splitting occurs here since this would be tantamount to reducing the iron(II) to an oxidation state of unity.



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(15) This is the reason for introducing the extra complication of two rather than one stable radical intermediate and for proposing the two equilibria shown.

(16) J. C. Martin and W. G. Bentrude, *Chem. and Ind.* (London), 192 (1959).

The following reactions might occur involving the product S.

$$\mathrm{Fe(II)_s} + \mathrm{O_2} \xrightarrow{k_7} \mathrm{acac_2\text{-}FeOO\cdot}$$

$$2\ \mathrm{acac_2\text{-}FeOO\cdot} \longrightarrow \mathrm{acac_2\text{-}Fe\text{–}O\text{–}OFe\ acac_2} + \mathrm{O_2}$$

$$\mathrm{acac_2\text{-}Fe\text{–}O\text{–}O\text{–}Fe\text{-}acac_2} \longrightarrow 2\ \mathrm{acac_2\text{-}FeO\cdot}$$

A solution of the kinetics, using reactions 6 and 7 in place of 5 is presented below which leads to the expression

$$-\frac{d(O_2)}{dt} = \frac{k_3k_2(R\cdot)(O_2)}{k_{-2} + k_3(O_2)} + \frac{k_7k_6(\mathrm{Fe(II)\text{-}acac_2})(O_2)}{k_{-6} + k_7(O_2)}$$

If it is assumed that $(R.) \approx (\mathrm{Fe(II)\text{-}acac_2})$ we have

$$-\frac{d(O_2)}{dt} = [K_{eq}\,\mathrm{Fe(III)\text{-}acac_3}]^{0.5}(O_2)\left[\frac{k_3k_2}{k_{-2} + k_3(O_2)} + \frac{k_6k_7}{k_{-6} + k_7(O_2)}\right]$$

Since these reactions with oxygen are fast, $k_3(O_2) >> k_{-2}$ and $k_7(O_2) >> k_{-6}$ the expression reduces to

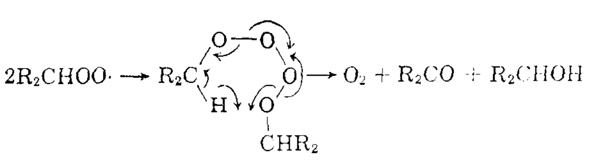
$$-\,d(O)_2/dt = [K_{eq}\mathrm{Fe(III)\text{-}acac_3}]^{0.5}[k_2 + k_6]$$

or

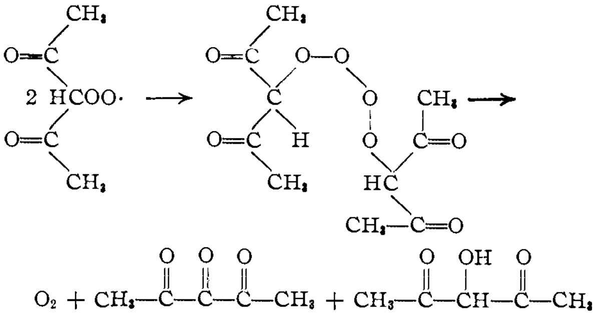
$$-\,d(O_2)/dt = k'[K_{eq}(\mathrm{Fe(III)\text{-}acac_3})]^{0.5}$$

Some direct attack of oxygen on the iron(II) acetylacetonate can explain the very slight dependence on oxygen pressure. If k_6 and k_7 are nearly equal to k_2 and k_3, respectively, we may use reactions 6 and 7 instead of (5) for termination and have more justification for setting (R·) and (Fe(II)-acac$_2$) equal to each other. Furthermore, it is known that iron(II) acetylacetonate reacts very rapidly with oxygen.[17] Even though there is an almost immediate appearance of carbon dioxide and water during this reaction, it should be pointed out that a considerable quantity of these materials could be formed from each R·, and they could also be formed simultaneously from the oxidized iron(II) acetylacetonate.

2,3,4-Pentanetrione as an Intermediate.—In a detailed study of the termination reactions of peroxy radicals containing α hydrogen atoms Russell[18] and Blanchard[19] proposed the following mechanism, which has subsequently received



elegant verification by Traylor and Bartlett.[20] Since we are also dealing with peroxy radicals containing α hydrogen atoms, the following termination step may be formulated. Under our conditions the 3-hydroxy-2,4-pentanedione would very likely be oxidized to give additional 2,3,4-pentanetrione.



$$\mathrm{O_2 + CH_3\text{—}\overset{\overset{O}{\|}}{C}\text{—}\overset{\overset{O}{\|}}{C}\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_3 + CH_3\text{—}\overset{\overset{O}{\|}}{C}\text{—}\overset{\overset{OH}{|}}{CH}\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_3}$$

It has been known for some time that 2,3,4-pentanetrione is a powerful reducing agent[21,22] and that it forms biacetyl and carbon dioxide on heating over copper sulfate. This prompted us to consider it as an unstable intermediate in the formation of the biacetyl. The latter was invariably a product of the autoxidation of acetylacetonates[5,6] and also appeared in the oxidation of 3-methyl iron(III) acetylacetonates[6] but not in the oxidation of iron(III) benzoylacetonate (a case which would have required kinetically free acetyl radicals).

Accordingly, a sample of 2,3,4-pentanetrione was prepared and subjected to attack by oxygen (see Experimental) and the products analyzed immediately by mass spectrometer. The products were found to be diacetyl, carbon dioxide, water and acetic acid, the same as are usually found in our autoxidation reactions. Unfortunately, it was necessary to perform the oxidation on the pure trione itself in order to use mass spectrometric analysis instead of doing it in the usual dilute diphenyl ether solution. Nonetheless, this result which was arrived at purely on the basis of the kinetic requirements of the mechanism is a powerful argument for the general validity of the proposed path.

It is possible to rationalize most of the effects of ligand structure[5,6] on rate in terms of the above mechanism. The rapid autoxidation of iron(III) dibenzoylmethide and benzoylacetonate can be interpreted as a result of resonance stabilization and similarly the faster rate of the 3-methyl acetylacetonate may be due to slight extra stabilization of the second radical L· by hyperconjugation which would increase its steady-state concentration. The slow rate of autoxidation of the dipivaloyl methide may be due to steric hindrance to attack of oxygen at the 3-carbon of L· and this same factor could be invoked for the slow rates of the 3-phenyl and 3-benzyl compounds.

Alternative Mechanisms.—We have presented considerable evidence against the reaction going by way of a conventional chain mechanism involving hydrogen abstraction by peroxy radicals, with or without metal catalysis. We may note further that in all such mechanisms[13,15] the order with respect to substrate would be considerably higher than we observed. There is no reason why autoxidation of suitable acetylacetonates under suitable conditions might not go by such a path. Replacement of the methyl groups of the acetyl-

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[17] R. Charles, private communication.

[18] G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

[19] H. S. Blanchard, *ibid.*, **81**, 4548 (1959).

[20] T. G. Traylor and P. D. Bartlett, *Tetrahedron Letters*, No. 24, 30 (1960).

[21] E. H. Rodd, "Chemistry of the Carbon Compounds," Vol. IB, Elsevier Publishing Company, New York, N. Y., 1952, p. 1045.

[22] A. Quilico and C. Musanti, *Gazz. chim. ital.*, **71**, 340 (1941).

acetonates by isopropyl groups would produce a quasi-aromatic analog of meta-diisopropylbenzene which might be sensitive to α-hydrogen abstraction.

Direct attack of oxygen on the chelate double bond or the metal in a rate-determining step is ruled out by the low order with respect to oxygen in the rate equation, the self-inhibition of the reaction and inhibition by radical initiators. A number of authors[23-25] have found evidence for initial attack of oxygen followed by a chain reaction in which the peroxy radicals abstract hydrogen atoms in the usual way. The arguments already cited against a chain reaction hold here again as also does the failure of the reaction to be autocatalytic, its insensitivity to special purification of the chelate by chromatography and failure of peroxide intermediates to accumulate as they usually do in these cases.

Autoxidation of an intermediate anion would be unlikely in non-polar diphenyl ether and could not explain the enormous importance of the oxidation–reduction characteristics of the metal on the reaction.

Experimental

Most of the materials and the procedure for following rate studies have already been described.[5,6] Tetralin (Eastman, Practical Grade) was further purified by the method of Woodward and Mesrobian.[9] It was stored over Drierite in a refrigerator and vacuum distilled under nitrogen just prior to use.

Oxygen pressure was varied by partial evacuation of the closed system to the pressure indicated. After determining that the apparatus was pressure-tight by means of a mercury manometer attached to the system, the reaction was begun in the usual way.[5] Since the rate was always measured at constant pressure using a highly sensitive dibutyl phthalate manometer, it was possible to follow the autoxidation down to the pressures shown in Table I. 2,3,4-Pentanetrione was prepared by the method of Sachs and Barschall.[26] About 0.5 g. of the triketone was placed in a glass tube of 100 ml. capacity attached to a mass spectometer and the material subjected to autoxidation at 105° under oxygen at 8 cm. pressure. The results are as presented in Table II.

TABLE I

EFFECT OF OXYGEN PRESSURE ON RATE OF OXYGEN UPTAKE OF IRON(III) ACETYLACETONATE (CONCENTRATION 0.936 MOLAL)

Run no.	Oxygen pressure, mm.	Rates of O_2 uptake moles O_2/mole chelate, hr.
M2-93 to M2-108*	735	1.94
M2-131	128	1.26
M2-133	198	1.42
M2-134	328	1.62
M2-136	549	1.65

TABLE II

MASS SPECTRAL ANALYSIS OF AUTOXIDATION PRODUCTS OF 2,3,4-PENTANETRIONE[a]

Time, min.	Phase	Bi-acetyl	Acetic acid	CO_2	H_2O	O_2	Unidentified
15	Gas	6.2		29.0		64.8	
30	Gas	11.3		47.1		41.6	
60	Gas	10.9		57.4		31.7	
60	Liquid	26.3	11.8	6.0	53.2		2.7

[a] During this analysis the spectroscopist had difficulty in measuring water in the gas phase. He reported the data on a water-free basis but stated that there may have been from 1 to 10% water. No difficulty was encountered in measuring the water content of the liquid phase.

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(23) L. Bateman, H. Hughes and A. L. Morris, *Discussions Faraday Soc.*, **14**, 190 (1953).

(24) A. A. Miller and F. R. Mayo, *J. Am. Chem. Soc.*, **78**, 1017 (1956).

(25) G. A. Russell, *ibid.*, **78**, 1035, 1041 (1956).

(26) F. Sachs and H. Barschall, *Ber.*, **34**, 3047 (1901).