dimethylacetamide (DMA) and triethylamine are 3.3, 4.9, 251 and 9120, respectively. These values vary considerably from the experimentally determined values reported in Table I. This demonstrates the limited application of using a log *K vs.* $\Delta\nu_{O-H}$ relationship to predict equilibrium constants.

The $\Delta S/\Delta H$ ratios contained in Table I indicate that entropy effects are causing deviations in the log *K vs.* $\Delta\nu_{O-H}$ plot. The $\Delta S/\Delta H$ ratio is 1.8–2.0 for acetone and all amides except DMTCA. The unusual entropy effect in the case of DMTCA has been explained in a previous paper[6] as being evidence for the interaction of the chlorine *cis* to the carbonyl with phenol. For the nitrogen bases (acetonitrile, triethylamine, pyridine) the $\Delta S/\Delta H$ ratio is 2.3–2.4. The organophosphorus compounds have a larger range of values for $\Delta S/\Delta H$, but all are less than 1.7. Diethyltrichloromethylphosphonate [$Cl_3C\overset{O}{P}(OEt)_2$] has a low value for the ratio $\Delta S/\Delta H$ in comparison with the other phosphorus compounds. Since this compound is similar in structure to DMTCA ($Cl_3C\overset{O}{C}NMe_2$), we propose that the chlorine of the $-CCl_3$ group in diethyltrichloromethylphosphonate interacts with phenol as reported previously for DMTCA.[6] This chelate effect produces an entropy term favoring complexation and increases the equilibrium constant.

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Destructive Autoxidation of Metal Chelates. III. Effects of Additives on the Reaction. Metal Acetylacetonates as Radical Sources[1]

BY EDWARD M. ARNETT[2] AND MORRIS A. MENDELSOHN[3]

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The autoxidative decomposition of Fe(III) acetylacetonate at 100° under pure oxygen in diphenyl ether as solvent is inhibited and slowed by benzoyl peroxide and strongly inhibited by azobisisobutyronitrile, both of which compounds usually serve as good autoxidation initiators. Conversely, the reaction is not inhibited by phenol, hydroquinone or 2,4,6-tri-*t*-butylphenol which are usually good antioxidants. N,N'-Diphenyl *p*-phenylenediamine is a fairly good inhibitor, but by far the most potent inhibiting action is produced by introducing ferrocene and the acetylacetonates of some other transition metals even though the latter chelates themselves are easily autoxidized. These results suggest that rather stable radicals are formed by thermal decomposition of the chelate and that these radicals are intercepted by the radicals produced from initiator decomposition but not by most inhibitors. It is found that the chelates which undergo facile autoxidation will initiate the polymerization of styrene.

In two previous papers[4,5] we have shown that various beta-diketone chelates decompose irreversibly in the presence of molecular oxygen at 100° in diphenyl ether as solvent.

The rate of this reaction depends to a considerable extent not only upon the structure of the organic ligand but also upon the ability of the metal to undergo valence changes. Both on the basis of the rate equation and the effect of variation of the structure of the ligand it appears likely that for the iron(III) beta-diketone chelates the organic part of the compound does not suffer direct initial attack in the reaction and that the decomposition does not occur through the complex chain reactions customary for autoxidation of hydrocarbon substrates.

In view of the conditions of the reaction and the nature of the products obtained, one would surely expect a free radical mechanism to be involved. We have therefore examined the influence of various free radical initiators and inhibitors on chelate autoxidation. It will be seen below that the effects produced by these compounds is unusual and that many of the chelates formed probably produce rather stable radicals, a supposition which is supported through the use of the same chelates to initiate and promote the polymerization of styrene.

It will be shown that not only do other organometallic compounds have a profound effect on the rate of chelate autoxidation but that mixtures of chelates frequently are insensitive to oxygen even though the component chelates are themselves quite easily oxidized.

Results

Initiators.—The rates of most kinds of autoxidation reactions are greatly affected by the presence of radical sources[6] such as benzoyl peroxide or azobisisobutyronitrile (AIBN) and indeed require some initiator for the commencement of reaction. In view of the very short or non-existent induction periods which we have usually observed for chelate

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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.

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

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

(6) C. Walling, "Free Radicals in Solution," John Wiley and Sons, New York, N. Y., 1957, Chapter 9.

autoxidation, we supposed that the main effect of radical sources would be to increase the rate of autoxidation. It is clear from the results in Table I that if benzoyl peroxide has any effect at all on the rate of autoxidation of iron(III) acetylacetonate (the compound we have studied most intensively), it is to slow the reaction and lengthen the induction period. When a small amount of disalicylalethylenediamine (a potent activator for benzoyl peroxide) is added, the induction period is lengthened to nine minutes and a sharp drop in rate is observed. Since initial rates of oxygen uptake[4] are reproducible within 1% the observed rate decrease probably is real.

TABLE I

EFFECT OF ADDITIVES ON RATES OF OXIDATION OF IRON(III) ACETYLACETONATE

Additive	Concn. (mole %)	Rate[a]	Induction period (min.)
None		2.26	0–2
Benzoyl peroxide	1.0	0.588[b]	3
Benzoyl peroxide	1.0	2.22	5
Benzoyl peroxide	1.0	1.71	9
Disalicylalethylenediamine	0.5		
AIBN[c]	.25	2.31	2
AIBN	.50	2.31	2
AIBN	.50	2.33	1–2
AIBN	1.0	2.30	42
AIBN	1.5	2.04	59
AIBN	3.0	2.46	28
AIBN	6.0	2.16	34
2,4,6-Tri-*t*-butylphenol	2.0	2.27	0-1
Phenol	0.5	2.25	1–2
Phenol	1.6	2.25	1–2
Hydroquinone	0.2	2.27	0–1
Hydroquinone	1.0	2.27	2–3
NNDPP[d]	0.25	2.35	4
NNDPP	1.0	0.62	3
NNDPP	2.2	0.26	3
Ferrocene	16.9		>90
Ferrocene	8.1		>90
Ferrocene	2.1		>90
Ferrocene	0.2	2.25	44

[a] In all runs, unless otherwise specified, conditions were: temperature, 98.5°; concentration, 0.128 molal in phenyl ether; oxygen pressure, 720–745 mm.; stirrer speed, 923–1260 r.p.m.; adsorbent, equal parts Molecular Sieves 5A and 13X. Units of rate are moles O_2/mole chelate-hr.[4] Per cent additives are based on quantity of chelate. [b] Temperature is 87.5° (average value of K for runs at 87.5° without additives is 0.807). [c] AIBN, 2,2′-azodiisobutyronitrile. [d] NNDPP, N,N′-diphenyl-*p*-phenylenediamine.

AIBN undergoes "clean" thermal decomposition to give nitrogen and butyronitrile radicals at a rate which should have a half life of about 14.5 minutes at 98.5°,[7,8] the condition we have most usually employed. To our surprise this compound greatly increased the induction period of autoxidation, the influence on rates being small and erratic. The results in Table I suggest that the effect of lengthening the induction period goes through a maximum at an AIBN concentration of 1.5 mole % or perhaps reaches a constant value.

In this paper, as in the others in this series, rates are expressed in terms of initial rates of oxygen consumption. Following the induction period (when there was one), there was always a long linear portion of the oxygen uptake curve. The slope of this line was reproducible within 1% error[4] and is used for comparison of the rates. It is expressed in moles of oxygen/moles of chelate hr. in order to make the units consistent with those used in the first paper in this series[4] which was written before the rate expression for the reaction of the iron(III) chelate had been established. Since different chelates appear to follow different mechanisms, it seems prudent to express results in terms of an empirically observable initial rate rather than through a constant which assumes a specific rate equation.

Inhibitors.—Hammond and co-workers[9] have evaluated the effectiveness of a large number of compounds for inhibiting the autoxidation of cumene and tetralin. Although phenol, hydroquinone and 2,4,6-tri-*t*-butylphenol are all potent antioxidants for these hydrocarbons, it is seen in Table I that they are without effect on the autoxidation of iron(III) acetylacetonate and do not appreciably prolong the induction period. The only inhibitor showing activity was N,N′-diphenyl-*p*-phenylenediamine. In small amounts this material appeared to produce a slight acceleration, but above that it reduced the rate sharply, although it did not have a significant effect on the induction period.

Organometallic Compounds and Mixed Chelates.—Only the acetylacetonates of metals with several common oxidation states undergo autoxidation easily. This suggested that some kind of oxidation–reduction couple might be involved in the reaction and ferrocene, a relatively non-polar compound in which iron is formally bivalent, might catalyze the reaction. Instead, this compound provided a dramatic example of inhibition. It appears that its effect is to increase the induction period since at a concentration of 0.2 mole %, the reaction proceeds at its normal rate once the induction period is reduced within the limit of ninety minutes which we have set for these experiments.

We have previously given evidence[5] that manganese(III) acetylacetonate undergoes destructive autoxidation by a different route than does the corresponding iron(III) chelate. In Table II are presented the results of adding to manganese(III) acetylacetonate some N,N′-diphenyl-*p*-phenylenediamine and ferrocene, both of which produced

TABLE II

EFFECT OF ADDITIVES ON RATES OF OXIDATION OF MANGANESE(III) ACETYLACETONATE

Additive	Concn. (mole %)	Rate[a]	Induction period (min.)
None		2.73	0–1
NNDPP	2.0	2.81	1–2
Ferrocene	2.85	3.53	0–1

[a] Expressed in moles of oxygen/moles of chelate hr. (See above.)

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(7) C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

(8) L. M. Arnett, *J. Am. Chem. Soc.*, **74**, 2027 (1952).

(9) G. S. Hammond, C. E. Boozer, C. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3233 (1955); G. S. Hammond, C. E. Boozer, C. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3238 (1955).

TABLE III

EFFECT OF METAL CHELATES AS ADDITIVES TO EACH OTHER[a]

Chelates	Concn. (molal)	Rate[b]	Induction period (min.)
Fe(III)-acac$_3$	0.128	~0.01	2
Mn(III)-acac$_3$	.0013		
Fe(III)-acac$_3$	.128	0.1	1
Mn(III)-acac$_3$	.006		
Fe(III)-acac$_3$	.096	.44	3-4
Mn(III)-acac$_3$	.032		
Fe(III)-acac$_3$	.064	.995	1-2
Mn(III)-acac$_3$	.064		
Fe(III)-acac$_3$	.032	1.51	1-2
Mn(III)-acac$_3$	.096		
Fe(III)-acac$_3$	.0013	2.74	0-1
Mn(III)-acac$_3$	.128		
Fe(III)-acac$_3$	.128	~0	>90
Co(III)-acac$_3$	.0013		
Fe(III)-acac$_3$	.128	~0	17
Co(II)-acac$_2$	.0013		
Fe(III)-acac$_3$	.128	~0	44
Ce(IV)-acac$_4$	.0013		
Fe(III)-acac$_3$	.128	2.66	1
V(III)-acac$_3$	.0013		
Fe(III)-acac$_3$	.128	2.73	2-3
Fe(III)-dibenz$_3$	.0013		
Fe(III)-acac$_3$	.128	2.32	0-1
Cr(III)-acac$_3$	.0013		
Fe(III)-acac$_3$	.128	2.23	0-1
Al(III)-acac$_3$	.0013		
Mn(III)-acac$_3$	.128	2.72	2-3
Ce(IV)-acac$_4$	.0013		
Al(III)-acac$_3$[c]	.044	~0	
Fe(III)-acac$_3$	.0006		
Al(III)-acac$_3$[c]	.044	~0	
Co(III)-acac$_3$	.0006		
Cr(III)-acac$_3$[c]	.044	~0	
Fe(III)-acac$_3$	.0006		

[a] Conditions are same as described in Table I. [b] Rates moles of chelate in rate expression refers to the total of both ingredients. Values represented as ~ 0 refer to rates which were too slow to measure. Rates are initial rates expressed in moles O_2/mole chelate-hr. [c] Performed at 125°.

potent effects on the oxidation of the iron(III) chelate. It is clear that these additives have entirely different effects on the chelates of these two metals.

The powerful inhibitory influence of ferrocene on the iron(III) chelate suggested that acetylacetonates of different metals might mutually inhibit each other's autoxidation. This is dramatically borne out by the results presented in Table III, where it is seen that a very small trace of manganese(III) is a strong antioxidant for iron(III) acetylacetonate even though the manganese chelate itself is easily autoxidized. An equally small trace of the iron(III) chelate has no corresponding effect on the autoxidation of the manganese(III) compound. Cobalt(III), cobalt(II) and cerium(IV) acetylacetonates also strongly protect iron(III) acetylacetonate from autoxidation, but the vanadium(III) chelate accelerates the reaction slightly as also does the presence of a small amount of the rapidly autoxidized[5] iron(III) dibenzoylmethide. The acetylacetonates of chromium and aluminum which are themselves resistant to autoxidation[4] are without appreciable influence on the autoxidation of the iron(III) chelate, and it has no observable effect on them. It will be noticed finally that manganese(III) acetylacetonate again distinguishes itself from the iron(III) analog by being immune to the presence of a trace of the cerium(IV) chelate.

Discussion

The autoxidation of iron(III) acetylacetonate is not inhibited by several compounds that are powerful antioxidants in other systems. More remarkable than this is the fact that benzoyl peroxide and AIBN, which are excellent sources of reactive free radicals under the conditions of the experiments, *act as powerful oxidation inhibitors* rather than serving to speed the oxidation. We know of no clear precedent for this unusual result.

We are led to the conclusion from these results (and it is supported by the kinetic analysis to be presented in the next paper in this series) that we are dealing with a thermally induced reaction which produces intermediate radical species of considerable stability. Such stable radicals would presumably have little tendency to form complexes[6] with the compounds which usually inhibit autoxidation. They should however be deactivated by coupling with the highly active radicals produced by the thermal decomposition of benzoyl peroxide or AIBN (or the peroxy radicals formed from them in a medium saturated with oxygen). Ferrocene recently has been recognized as a powerful radical scavenger[10] and may be assuming this role in the present case. We have no insight at present into the remarkable inhibitory action of mixed chelate systems, although it is clearly a phenomenon which could find practical application to improving the oxidative stability of chelate systems.

The order of stability which we have observed for chelate oxidation[4] is roughly paralleled by the order of pyrolytic stability found for many of the same compounds by Charles and Pawlikowski.[11] This would be consistent with the idea that the decomposition rate of the chelates to produce intermediate radicals is the same in the absence of oxygen as it is in its presence. These results and the conclusions drawn from them, moreover, suggest that the acetylacetonate chelates which undergo ready autoxidation and pyrolysis should serve as a source of radicals for the inducing of radical-promoted reactions. We have accordingly used a number of the chelates for the promotion of styrene polymerization both in the absence and presence of *t*-butyl-perbenzoate. It was found that under both sets of conditions a number of the acetylacetonates were polymerization promotors and that these were the same chelates which are also sensitive to attack by oxygen while the chromium(III) and aluminum(III) acetylaceto-

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(10) E. Collinson, F. S. Dainton and H. Gillis, *J. Phys. Chem.*, **65**, 695 (1961).

(11) R. G. Charles and M. A. Pawlikowski, *ibid.*, **62**, 440 (1958).

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.[4,5] 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) ≈ 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.

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

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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.

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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).