of argon and nitric acid separates the two bodies of data. At 600°K., nitric acid appears to be at least twice as effective an energy transfer agent as argon and was so accounted in fitting the data to the above equation. In Fig. 5, however, the points of both studies are shown without correction for the relative collision efficiencies of the two "M" gases.

If we wish to consider the *s*-parameter to be more than a number imposed upon the data to enforce a fit with theory and if we then identify the number of "square terms" with the internal motions of the nitric acid molecule, it is to be objected that infrared spectra[11] show that for only five of the nine vibrational modes is $h\gamma/kT$ less than or on the order of unity, a rather strict requirement for the classical RRK model. Thus even a generous model is hard put to account for the observed "low" activation energy.

Acknowledgment.—This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, Contract AF-49-(638)-306.

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[11] H. Cohn, C. K. Ingold and H. G. Poole, *J. Chem. Soc. IV*, 4272 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PITTSBURGH AND THE UNIVERSITY OF ARIZONA]

Destructive Autoxidation of Metal Chelates. II. Further Studies of the Effect of Ligand Structure on Initial Rate[1]

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Further results are presented for the destructive autoxidation of iron(III) beta-diketone chelates by molecular oxygen in diphenyl ether as solvent. The new data refute our earlier conclusion that attack occurs on the hydrogen attached to the 3-carbon. Kinetic results indicate that the the reaction does not proceed through a classical radical-chain mechanism and that not all metal acetylacetonates follow the same mechanism. Evidence is presented supporting the supposition that the diacetyl which is always formed in good quantity in the reaction cannot come from the coupling of kinetically free acetyl radicals.

In a previous paper[3] in this series we described the irreversible decomposition of a number of beta diketone chelates under attack by molecular oxygen at 100° in diphenyl ether as solvent. Comparison of the acetylacetonates of fourteen metals showed that only those of metals capable of facile oxidation–reduction underwent reaction at an easily measurable rate.

The structure of the ligand was also varied in order to cast light on the position of initial attack on the chelate molecule. By means of blocking various positions in the organic part of the molecule, it was observed that the replacement of the lone hydrogen on the 3-position of the ligand with phenyl or benzyl groups led to an inert chelate and that replacement of the two methyl groups flanking this hydrogen with large *t*-butyl groups also stabilized the chelate. From these indications it was concluded that the 3-hydrogen was the point of attack, perhaps through some variant of a classical metal-catalyzed chain reaction involving, for example, abstraction of the hydrogen by a peroxy radical.

In the present paper we shall present more observations on metal chelates of other substituted acetylacetonates. In two other papers to follow we shall present extensive new evidence which refutes our original suggestion that the reaction proceeds through a complex chain mechanism. Instead it will be seen that the reaction probably goes by a rather simple mechanism which is consistent with a large body of evidence.

Results and Discussion

We have focused our main interest on iron(III) chelates and have aimed in particular toward elucidating the mechanism of autoxidation of iron(III) acetylacetonate. There is evidence that not all of the chelates to be discussed follow the same mechanism as does this compound, but because it is convenient for study and might be considered in many ways to be typical, it will be considered as the reference compound. Accordingly, we have chosen to compare the influence of ligands on the reaction mainly through their iron(III) chelates. These are presented in Table I.

Table I

Relative Initial Rates[3] of Oxygen Uptake for Iron(III) Chelates

Ligand	Relative rate
Dibenzoylmethane	7.60
Benzoylacetone	1.70
3-Methylacetylacetone	1.07
Acetylacetone	1.00
Acetylacetone-3d	0.98
Dipivaloylmethane	Very slow
3-Phenylacetylacetone	Very slow
3-Benzylacetylacetone	Very slow

Iron(III) 3-Methylacetylacetonate.—The first clear evidence that the 3-position is probably not involved directly in a rate-controlling step was provided by the rapid autoxidation of this chelate. Although the 3-phenyl and 3-benzyl compounds are inert, the 3-methyl compound reacts even faster than the unsubstituted reference compound. In order to test the possibility that the 3-methyl chelate is not following a different mechanistic path than the other iron(III) chelates in Table I,

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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, 1960.

[2] Department of Chemistry, University of Pittsburgh, Pittsburgh 13, Pennsylvania.

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

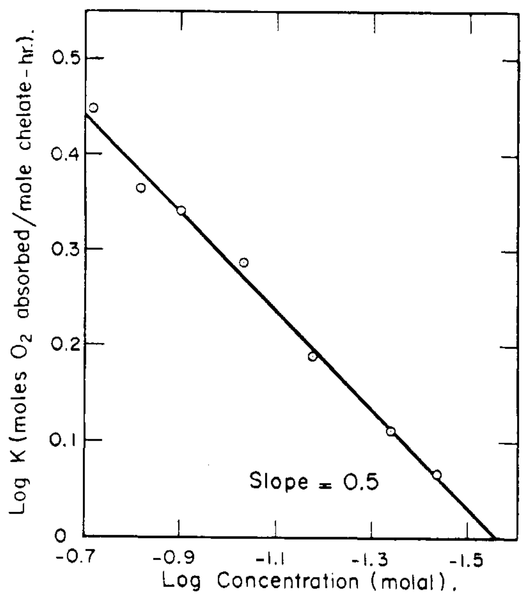

Fig. 1.—Effect of concentration on rate of oxygen uptake of Fe(III) acetylacetonate: temperature, 98.5°; solvent, diphenyl ether.

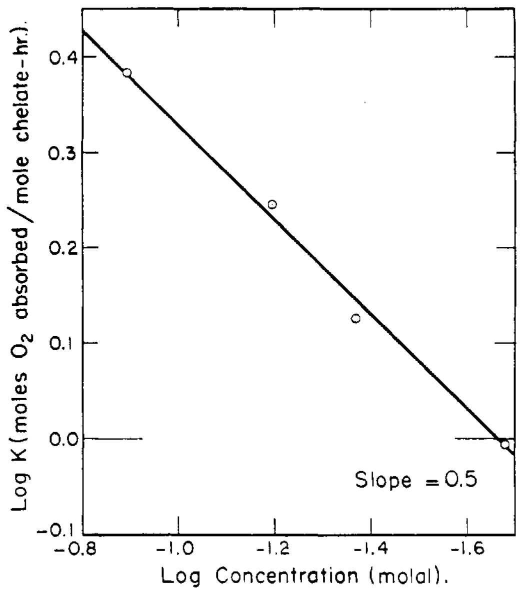

Fig. 2.—Effect of concentration on rate of oxygen uptake of Fe(III) 3-methylacetylacetonate: temperature, 98.5°; solvent, diphenyl ether.

the stoichiometry of its autoxidation was examined and the kinetic order of its reaction was determined for comparison with iron(III) acetylacetonate.

Using the method of product study already described,[3] the results may be symbolized by the equation: Fe(III) 3-methyl $acac_3 + 4.52\ O_2 \rightarrow 1.86$ diacetyl + 0.81 acetic acid + 0.98 3-methyl acetylacetone + 0.126 methyl acetate + 1.92 H_2O + 0.91 CO_2 + insoluble iron-containing products. When compared with the results of the previous study[3] of iron(III) acetylacetonate itself: Fe(III) $acac_3 + 3.86\ O_2 \rightarrow 1.26$ diacetyl + 0.64 acetic acid + 0.096 acetylacetone + 2.02 H_2O + 1.31 CO_2 + insoluble iron products, it is seen that the general pattern of product yields is quite similar, particularly in the quantities of diacetyl, water and carbon dioxide, but that considerably more of the free ligand appears to be liberated and to survive in the case of the 3-methyl compound. The appearance of methyl acetate is accompanied by a reduction in the amount of carbon dioxide formed suggesting that the methyl acetate contains what was previously the 3-carbon in the original ligand and that this appears as carbon dioxide in the autoxidation of the unsubstituted chelate.

Variation of the rate with concentration of chelates (Figs. 1 and 2) showed that the order with respect to chelate in both systems was one half. In addition to providing evidence that the two substrates are not autoxidized by different mechanisms, this result is noteworthy as powerful evidence that we are not dealing with a classical radical chain type of autoxidation in which the order with respect to substrate is usually one and is frequently greater. We shall return to this matter in more detail in a later paper concerned exclusively with kinetics and mechanism.

Iron(III) Acetylacetonate-3*d*.—As a somewhat more rigorous test of the involvement of the hydrogen at the 3-position in a rate-determining step, the effect of deuteriation on the rate was investigated. The fact that the chelate from the 3-deuteriated ligand underwent autoxidation at the same rate as did the 3-protium compound indicates that it is quite unlikely that hydrogen abstraction from this position is rate-determining.[5]

Evidence that Other Chelates May Follow Other Mechanisms.—The results presented up to this point for the iron(III) beta-diketone chelates indicate strongly that in their case reaction does not occur primarily through attack on the organic part of the molecule. Furthermore, the sensitivity of the reaction to the nature and position of substitution on the organic portion of the molecule argues against initial attack by oxygen on the iron being important, as do also the kinetic results to be described in a later paper. We should expect, however, that similar chelates of other metals might follow other pathways if they become energetically favorable.

In view of the higher oxidation states that are available to manganese, this seemed to be a likely substrate to use for testing the universality of the kinetic form. The initial rate of autoxidation of manganese(III) acetylacetonate was observed (Fig. 3) to vary as the 0.22 power of the chelate concentration instead of following the half-order dependence of the iron(III) compound.

The iron(III) chelates follow the rate sequence for their ligands: dibenzoylmethane > 3-methyl acetylacetone > acetylacetone. It will be noted from the results in Table II that, although concentrations are not comparable, Co(III) dibenzoylmethide probably undergoes autoxidation more slowly than does Co(III) 3-methyl acetylacetonate,

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

(5) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960, p. 65 ff.

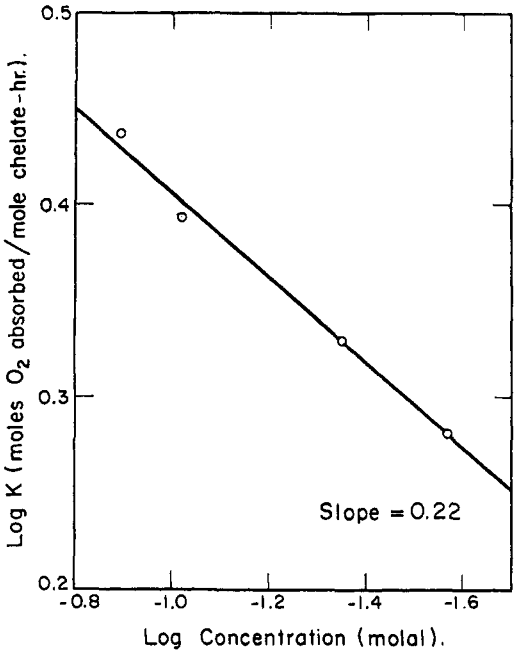

Fig. 3.—Effect of concentration on rate of oxygen uptake of Mn(III) acetylacetonate: temperature, 98.5°; solvent, d phenyl ether.

the reverse of the order for the iron(III) compounds. This is based on the assumption that these chelates follow the same rate law as that for the iron(III) chelates. The chromium(III) chelates may be following the same order as do the iron(III) ones, but more data are needed to decide this matter.

Table II

Other Ligands of Other Metals

Chelate	Concentration (molal)	Initial rate moles O_2/Mole chelate-hr.
Co(III)-dibenzoylmethide	0.022[a]	0.22
Co(III)-3-methyl $acac_3$	.128	8.9
Co(III)-$acac_3$	.128	0.28
Cr(III)-dibenzoylmethide	.023[a]	0.12
Cr(III)-$acac_3$	.128	0[b]

[a] This represents the maximum solubility possible at the experimental conditions. [b] No oxygen absorbed within 3 hr.

Iron(III) Benzoylacetone.—One of the most remarkable facts about the autoxidation of metal acetylacetonates under our conditions is that copious quantities of diacetyl are always produced. Although this product probably arises from the coupling of acetyl radicals, it would be most unlikely if these radicals were kinetically free since one would expect them to be intercepted by oxygen long before coupling could occur.[4,6] As a check on this assumption iron(III) benzoylacetonate was subjected to autoxidation. If the acetylacetone chelates produce free acetyl radicals during autoxidation which then couple to form diacetyl, one would by the same token expect the benzoylacetonates to produce acetyl and benzoyl radicals, and if these radicals survive interception by the surrounding oxygen, they should couple to yield benzoylacetyl, benzil and also diacetyl. The strong odor of the latter compound permits its detection down to about 10^{-6} mole in 10 g. of solution, a concentration which is below the limit of detection for our gas chromatographic equipment. The products of the autoxidation of iron(III)-benzoylacetonate gave no trace of diacetyl by this criterion, showing that if this chelate proceeds by the same path as does the acetylacetonate the coupling of acetyl radicals in the latter case must occur by an intramolecular or cage process rather than through the coupling of kinetically free radicals.

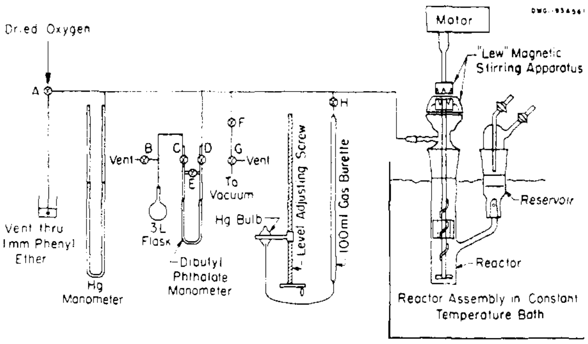

Fig. 4.—Flow diagram of oxidation apparatus.

The rate of autoxidation of iron(III)-benzoylacetonate falls partway between that for iron(III)-acetylacetonate and iron(III)-dibenzoylmethide as might be expected if the three compounds follow the same mechanism.

Stability of the Free Ligands to Autoxidation.—Acetylacetone, dibenzoylmethane and 3-phenyl acetylacetone were subjected to the attack of oxygen under the same conditions used for autoxidation of their metal chelates. All three appeared to be quite stable for protracted periods both in the presence and absence of small amounts of the corresponding iron(III) chelate. If free ligands are considered as chelates of hydrogen, they fit the pattern of stability for metals which do not undergo facile valence change. The fact that they are stable in the presence of reactive iron chelates of the same ligand shows that the autoxidation of the chelate cannot be ascribed to classical autoxidation of the organic part of the chelate catalyzed in the usual way[6] by the metal atoms of other chelate molecules in the mixture. Our results on the free ligands parallel those of Charles, Hickam and Hoene,[7] who found that acetylacetone exhibits much greater stability to pyrolysis than do many of its metal chelates.

Experimental

The techniques and materials employed for the kinetic runs have already been described[3] but for the sake of completeness a flow diagram of the apparatus is presented in Fig. 4 and a drawing of the reactor in Fig. 5. As before, the reactivity is expressed in terms of a linear rate of oxygen uptake which was reproducible with an error of less than 1%.

Synthesis.—3-Methylacetylacetone was prepared from methyl ethyl ketone and acetic anhydride according to the method of Hauser and Adams.[8]

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(6) C. A. McDowell and J. H. Thomas, *J. Chem. Soc.*, 2208, 2217 (1949); 1462 (1950).

(7) R. G. Charles, W. M. Hickam and J. Hoene, *J. Phys. Chem.*, **63**, 2084 (1959).

(8) C. R. Hauser and J. T. Adams, *J. Am. Chem. Soc.*, **66**, 345 (1944).

The iron(III)-3-methylacetylacetonate was prepared by adding a solution of 5.13 g. (0.045 mole) of 3-methylacetylacetone in 40 ml. of methanol to a solution of 1.62 g. (0.01 mole) ferric chloride (Fisher Scientific Purified Grade, anhydrous, sublimed) in 10 ml. of distilled water. To the resulting solution sodium acetate trihydrate (Fisher Scientific Certified-A.C.S. Grade) 8.16 g. (0.06 mole) dissolved in 20 ml. of distilled water was added slowly with vigorous stirring. The mixture was warmed to 50–75° for about 15 minutes and then cooled in a refrigerator for several hours. The red solid was separated on a Büchner funnel, washed with water and petroleum ether and dried over Drierite at 50° (1 mm.) for 16 hr. After two recrystallizations from benzene–petroleum ether, the chelate was dried for 24 hr. at 50° (0.005–0.01 mm.) The recrystallized product was obtained in about 50% yield.

Anal. Calcd. for $C_{18}H_{27}O_6Fe$: C, 54.7; H, 6.9; Fe, 14.15. Found: C, 54.3; H, 6.8; Fe, 14.1.

Iron(III)-acetylacetonate-3d was prepared by an exchange reaction between the activated hydrogens of the 3-carbon of acetylacetone and D_2O. Five g. iron(III)-acetylacetonate, 41.0 g. D_2O (Stuart Oxygen Division of General Dynamics Corp., D/(D + H) 0.995, and 3.60 g. acetyl chloride were placed in a 250 ml. standard taper Erlenmeyer flask. The flask was stoppered and placed in a desiccator over Drierite for 24 hr. A solution of 3.82 g. of anhydrous sodium acetate in 15.5 g. of D_2O was then added to the flask, protected by a blanket of nitrogen, while rapid stirring was maintained. The chelate formed a voluminous red precipitate during this addition. After filtration, washing with water and two recrystallizations from benzene–petroleum ether, a yield of 3.1 g. of deuteriated chelate was obtained. Analysis (Jose Nemeth Laboratories, 303 Washington Drive, Urbana, Illinois) of the products showed that the quantity 100 D/(D + H) was equal to 18.38. Since the calculated value for replacement of all of the 3-hydrogens is 14.3, it appears that a small portion of the deuterium was exchanged into the terminal methyl groups. In view of the results of Shigorin[9] and Nesmeyanov[10] on deuteriation of acetylacetonates and the fact that the hydrogen on the 3-carbon is the most acidic, it is to be expected that the 3-position was fully deuteriated.

Stoichiometry of Iron(III) 3-Methylacetylacetonate.—Oxygen was bubbled continuously through a solution of 4.750 g. (0.0120 mole) of iron(III) 3-methylacetylacetonate in 126 g. of phenyl ether for 24 hr. at 106 ± 0.5°. The procedure and apparatus were the same as those used for the continuous oxidation of iron(III)-acetylacetonate.[3] A summary of the products found is listed below.

Product	Weight (g.)
Diacetyl	1.553
Acetic acid	0.473
Carbon dioxide	.388
Water	.338
3-Methylacetylacetone	.110
Methyl acetate	.091
Insoluble residue	2.22
Unreacted chelate	0.91

An elemental analysis of the residue which was insoluble in organic solvents showed it to contain 33.20% C, 4.33% H and 24.86% iron. The soluble residue was purified by recrystallization from benzene–petroleum ether and corresponded to a 75% recovery of original chelate having, after purification, a melting point of 244° and a mixed melting point of 245° with starting material.

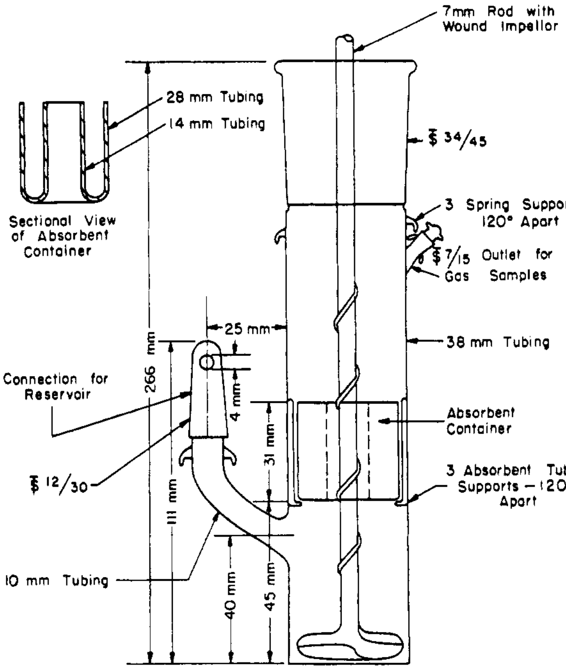

Fig. 5.—Oxidation reactor.

Material balances from mass spectral data could be made to account for 102% of the iron, 94.7% of the carbon and 91.1% of the hydrogen. The combined oxygen content of the products showed 4.52 moles of oxygen absorbed per mole of chelate.

Kinetic Results of Autoxidation of Other Materials. A. Ligands. 1. **Dibenzoylmethane.**—Dibenzoylmethane was subjected to the same oxidizing conditions as its iron(III) chelate except at triple the molal concentration since there are three ligands per mole of chelate. Unless otherwise stated, runs were performed at 98.5° under an atmosphere of pure oxygen at a concentration of 0.13 molal in phenyl ether. If no measureable rate of oxygen uptake was apparent after 90 minutes, the material was considered inert or stable towards oxidation. The ligand appeared to be inert to oxidation as opposed to the rapid oxidation of the corresponding metal chelate.

Another rate measurement was made under identical conditions except that 1.8 mole per cent of iron(III) dibenzoylmethane was added to the dibenzoylmethane. A very slow rate of oxygen uptake occurred which was attributed to the chelate alone.

2. **3-Phenyl Acetylacetone.**—3-Phenyl acetylacetone was found to be stable towards autoxidation and also was not affected by addition of iron(III)-3-phenyl acetylacetonate.

3. **Acetylacetone.**—Oxygen was bubbled through a solution of 300 g. acetylacetone and 0.20 g. iron(III)-acetylacetonate at 98° for 24 hr. Provision was made for recovery of volatile products by use of a Dean-Stark trap and a reflux condenser. Only a small quantity of acetylacetone was found in the trap, and there was no odor of biacetyl.

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[9] D. N. Shigorin and Y. K. Syrkin, *Doklady Akad. Nauk, S.S.S.R.*, **70**, 1033 (1950).

[10] A. N. Nesmeyanov *et al.*, *Izvest. Akad. Nauk, S.S.S.R., Otdel Khim., Nauk*, 598 (1949).