672. *The Kinetics of the Oxidation of Organic Compounds by Ceric Sulphate. Part II. The Reactivities of Aliphatic Ketones and Acetaldehyde.*

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The detailed study of the oxidation of acetone by ceric sulphate (*J.*, 1950, 3276) has been extended to that of seven other ketones and of acetaldehyde. A connexion between enolisation and oxidation is revealed by comparison of their respective rates. With unsymmetrical ketones the relation is between the rate of oxidation and the rate of formation of that enol which is derived from an α-CH_2 or α-CH group. Acetone and acetaldehyde, however, do not themselves obey the general rule.

The stoicheiometric relations reveal the nature of the products in each case and mechanisms are suggested for these processes.

To account for the reactivity of the enols at α-CH_2 or α-CH groups, and the unreactivity of those formed at α-CH_3 groups, it is suggested that oxidation products of the former can be stabilised by hyperconjugation. This accounts for the varying proportions in which competing reactions occur in different ketones and for various discrepancies in the relation between ease of enolisation and of oxidation.

PART I (*J.*, 1950, 3276) describes an investigation of the kinetics and stoicheiometry of the oxidation of acetone by ceric sulphate. This paper makes a comparative survey of the reactivities and stoicheiometry for acetaldehyde and a series of aliphatic ketones.

The kinetic results for acetone indicated that there is a slow oxidation of the enol which is present usually in approximately equilibrium amount. If this applies in general, the influence of structure on reactivity will express itself in effects, first, on the enol equilibrium and, secondly, on the rate of oxidation of the enol. The detailed analysis of this problem will be of considerable complexity, and relevant data are not available. However, a correlation has been discovered between the rate of oxidation and the rate of formation of that enol which is the more readily oxidised. There will almost certainly be a correlation (of the Brønsted type) between the rate of enolisation and the equilibrium constant for enol formation. The empirical result therefore probably means that the effect of structure operates chiefly through the enolisation equilibrium, the actual oxidation rates of the relevant enol forms being, in general, much less subject to variation.

Rates of Oxidation and Enolisation.—The most important measurements of oxidation rates are summarised in Table I. The oxidation of acetaldehyde and of the higher ketones is not autocatalytic. Accordingly the experiments were designed simply to give values of the initial rate, r_0, as described in Part I. All experiments were made at 70° and the rates were expressed as equivalents of ceric sulphate $\times 10^3$ reacting per l. per minute. The results in Table I refer to reaction mixtures with $[Ce^{IV}]_0 = 0{\cdot}05$N., [ketone or aldehyde]$_0 = 0{\cdot}005$M., and $[H_2SO_4] = 2{\cdot}00$N. ($[H^+] = 1{\cdot}003$). As shown in Fig. 1 the curves for ethyl methyl, diethyl, and methyl *iso*propyl ketones could be nearly superimposed over a considerable portion of their course.

TABLE I.

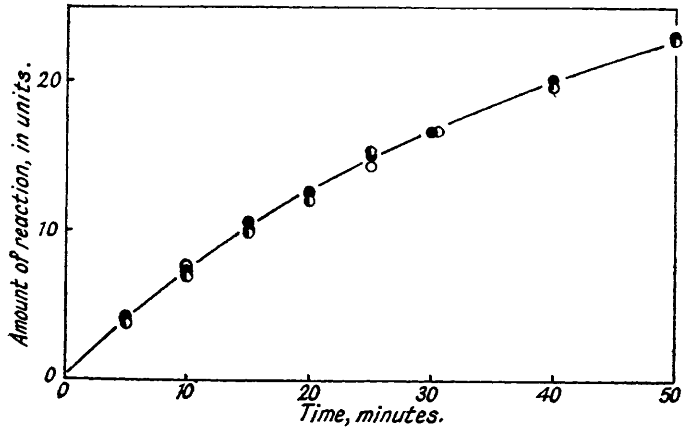
Compound.	r_0, units/min.	r_0' (relative to value for acetone).	Compound.	r_0, units/min.	r_0' (relative to value for acetone).
Me·CHO	1·50	5·55	$COMePr^n$	0·70	2·59
$COMe_2$	0·27	1·00	$COMePr^i$	0·765	2·84
COMeEt	0·85	3·15	$COMeBu^i$	0·435	1·61
$COEt_2$	0·84	3·12	$COPr^i_2$	0·202	0·748
			$COMe{\cdot}C_5H_{11}$-*n*	0·61	2·26

Most of the enolisation rates can be obtained from Dawson's work (*J.*, 1910, **97**, 2048; 1911, **99**, 1740); the values for *n*-amyl methyl ketone, di*iso*propyl ketone, and acetaldehyde were measured in the present work. The results refer to the rates of acid-catalysed enolisation, at 25°, measured by the halogenation method, and expressed relatively to the rate of enolisation of acetone. They are shown in Table III under the heading r_e. [Dawson (*J.*, 1914, **105**, 1275) showed that the reaction between acetaldehyde and iodine in acid solution was an iodination and not an oxidation to acetic acid.]

For unsymmetrical ketones there are two enols. No values are available for their specific rates of formation (to be referred to as "partial rates of enolisation ") under the conditions of kinetic measurements. For four such ketones, however, results are available for the composition of the ultimate product of bromination with bromine and potassium chlorate in aqueous solution at *ca.* 40° (the author is indebted to Dr. H. M. Cardwell for drawing his attention to this). E. R. H. Jones and his co-workers (*J.*, 1948, 272, 276), and Cardwell and Kilner (private communication), have carried out quantitative fractional distillations of the mixed bromides and have identified the components by comparison with synthetic products. The results in Table II are calculated from their results.

FIG. 1.

The oxidation of diethyl ketone, methyl ethyl ketone, and methyl iso*propyl ketone by ceric sulphate at* 70°.



○ $COEt_2$. ● COMeEt. ◐ $COMePr^i$.

$[Ketone]_0 = 0{\cdot}005$M., $[Ce^{IV}]_0 = 0{\cdot}05$N., $[H_2SO_4] = 2{\cdot}00$N. ($[H^+] = 1{\cdot}003$N.).

(*Note : Eight points are actually plotted for each ketone.*)

TABLE II.

Compound.	Bromination at α-position, %. CH_3.	CH_2.	CH.
COMeEt	28	72	—
$COMePr^n$	38	62	—
$COMePr^i$	0	—	100
$COMeBu^i$	48	52	—

These values may be assumed to show the percentages of the different enols formed and can be used to calculate partial rates of enolisation from total rates. Comparable values for the symmetrical ketones are obtained simply by dividing the total rate by two. No results are available for *n*-amyl methyl ketone; it will be assumed that they would be similar to those for methyl *n*-propyl ketone, and that 40% of the enolisation involves the methyl group. The values for the partial rates, relative to the total rate for acetone, are shown in Table III, under the heading r_e'.

TABLE III.

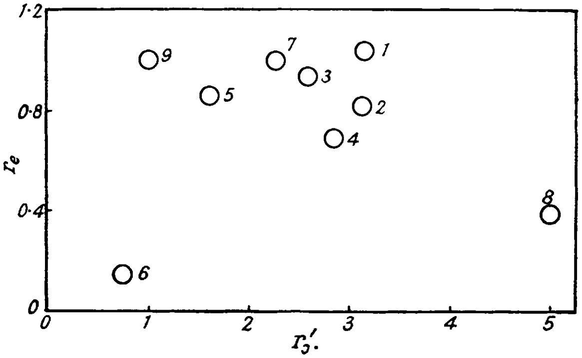
		r_e'.					r_e'.		
Compound.	r_e.	CH_3.	CH_2.	CH.	Compound.	r_e.	CH_3.	CH_2.	CH.
Me·CHO	0·388	0·388	—	—	$COMePr^n$	0·94	0·36	0·58	—
$COMe_2$	1·00	0·50	—	—	$COMePr^i$	0·695	0·00	—	0·695
COMeEt	1·04	0·29	0·75	—	$COMeBu^i$	0·86	0·415	0·445	—
$COEt_2$	0·82	—	0·41	—	$COPr^i_2$	0·14	—	—	0·07
					$COMe{\cdot}C_5H_{11}$-*n*	0·996	0·396	0·60	—

When relative values for the total rate of enolisation, r_e, at 25° are plotted against the relative rates (r_0') of oxidation by ceric sulphate at 70° no proportionality appears (Fig. 2). (The rate of oxidation of acetaldehyde is corrected for the fact that 10% of the reaction involves the aldehyde group and not the methyl group—see below.)

In Fig. 3 the points for the symmetrical ketones are plotted as before. For the five unsymmetrical ketones the partial rate of enolisation at the α-CH_2 or the α-CH group (whichever the ketone possesses) is plotted against the rate of oxidation. The total rates of enolisation for the symmetrical ketones and acetaldehyde and the above particular rates for the unsymmetrical ketones will be called the " relevant rates of enolisation." For seven of the ketones there is approximate proportionality between the relevant rate of enolisation and the rate of oxidation. In other words the oxidation rate is related to the rate at which a particular enol is produced. No such relation is apparent if rates of enolisation at the methyl group are used for the unsymmetrical ketones.

FIG. 2.

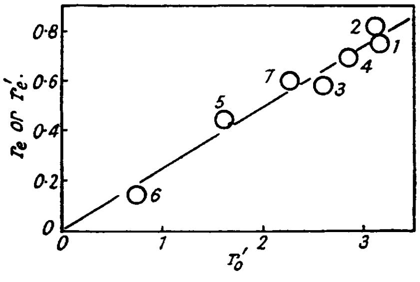
Lack of relation between total rate of enolisation at 25° and rate of oxidation at 70°.



1, COMeEt. 2, $COEt_2$. 3, $COMePr^n$. 4, $COMePr^i$. 5, $COMeBu^i$. 6, $COPr^i_2$. 7, $COMe{\cdot}C_5H_{11}$-*n*. 8, Me·CHO. 9, $COMe_2$.

FIG. 3.

The relation between relevant rate of enolisation at 25° and rate of oxidation at 70°. For key, see Fig. 2.



The two exceptions are acetone and acetaldehyde. The former oxidises very much more slowly than corresponds to its rate of enolisation, the latter very much faster. These anomalous results may be due, in part at least, to the comparison of rates of enolisation at 25° with rates of oxidation at 70°. It may also be significant, however, that acetone and acetaldehyde are the only two compounds studied which have no carbon atoms in the β-position to the carbonyl group.

The correlation of the rate of oxidation with the rate of production of a particular enol is, however, sufficient to suggest, in the first place, that the mechanism of the oxidation reaction involves enolisation; this is consistent with results for acetone (Part I), and with suggestions by other workers regarding the oxidation of ketones by various reagents. In the second place, for unsymmetrical ketones it suggests that enols formed from a methyl group are much less readily oxidised than those formed from a CH_2 or CH group; this would account for the anomalous behaviour of acetone, where only the former type is available. The effect of structure on reactivity will be discussed after consideration of the course of the oxidation reactions. The enolisation hypothesis accords with the stoicheiometric results satisfactorily.

Stoicheiometric Results for Acetaldehyde and a Series of Ketones.—The amounts of ceric sulphate required and of formic acid produced were determined. The results for acetone and acetaldehyde (Table IV) were obtained with $[Ce^{IV}]_0 = 0{\cdot}05$N., $[\text{ketone}]_0 = 0{\cdot}005$M., $[H_2SO_4] =$ 2N., and the rest with $[Ce^{IV}]_0 = 0{\cdot}0667$N., $[\text{ketone}]_0 = 0{\cdot}00333$M.

In general the reactions will be formulated as successive hydroxylations with intermediate formation of enols (cf. Part I). In the light of experiments on the fatty acids and other possible intermediate products such as diacetyl and pyruvic acid it will be assumed that the ultimate products are fatty acids, carbon dioxide, and water.

TABLE IV.

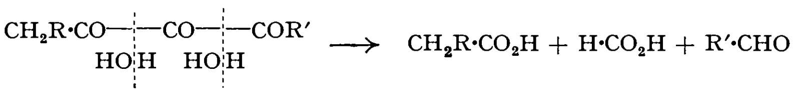
Compound.	Equivs. of Ce^{IV} used per mol. of ketone.	Mols. of $H{\cdot}CO_2H$ produced per mol. of ketone.	Compound.	Equivs. of Ce^{IV} used per mol. of ketone.	Mols. of $H{\cdot}CO_2H$ produced per mol. of ketone.
Me·CHO	5·75	1·75	COMePr^{n}	14·25	2·75
$COMe_2$	8·6	1·40	COMePr^{i}	12·4	1·35
COMeEt	11·95	2·25	COMeBu^{i}	14·75	2·15
$COEt_2$	13·4	2·85	COPr$^{i}_{2}$	12·3	1·55
			$COMe{\cdot}C_5H_{11}$-*n*	18·2	2·75

Acetaldehyde. The results (see Table IV) may be explained in terms of the reactions (i) $CH_3{\cdot}CHO + O \longrightarrow CH_3{\cdot}CO_2H$, (ii) $CH_3{\cdot}CHO + 3O \longrightarrow 2H{\cdot}CO_2H$. If 10% of the aldehyde undergoes reaction (i) and 90% undergoes reaction (ii), 5·6 equivalents of ceric sulphate will be used and 1·8 moles of formic acid will be produced, as is the case. Nothing can be said about the mechanism of reaction (i). Reaction (ii) may proceed by stages analogous to those postulated for acetone, *viz.*, $CH_3{\cdot}CHO \longrightarrow CH_2{:}CH{\cdot}OH \longrightarrow HO{\cdot}CH{:}CH{\cdot}OH \longrightarrow (CHO)_2 \longrightarrow 2H{\cdot}CO_2H$.

Methyl iso*propyl ketone.* The results may be explained by supposing that attack starts at the CH group, and that there is no reaction at the α-methyl group. This accords with the enolisation hypothesis since E. R. H. Jones (*loc. cit.*) showed that the only enol formed is that involving the CH group. (In any case the other enol would be much less reactive if the above interpretation of the kinetic results is correct.) The first major stage of the reaction may not be supposed to involve hydroxylation of the CH carbon atom followed by oxidative fission of the C–C bond : $(CH_3)_2CH{\cdot}CO{\cdot}CH_3 + 2O \longrightarrow CH_3{\cdot}CO{\cdot}CH_3 + CH_3{\cdot}CO_2H$. Acetone itself may be produced as the direct result of the fission, which seems more likely to yield acetone hydrate and then the enol by elimination of water. The acetone is assumed to be oxidised, as described in Part I, with consumption of 8·4 equivalents of ceric sulphate and the production of 1·4 moles of formic acid. Thus this ketone should require 12·4 equivalents of ceric sulphate and yield 1·4 moles of formic acid, in satisfactory agreement with experiment.

*Di*iso*propyl ketone.* The values shown in Table IV are close to those for methyl *iso*propyl ketone, and the interpretation is similar, the first stage yielding *iso*butyric instead of acetic acid. As before the ketone should use 12·4 equivalents of ceric sulphate and produce 1·4 moles of formic acid.

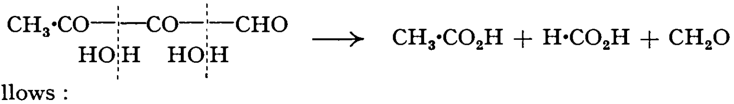
In the discussion of the remaining ketones a new principle must be used. In order to account for the high degree of oxidation that occurs, it is necessary to suppose that oxidation can proceed along the carbon chain as far as some form of triketone. This might occur by a mechanism such as : $CH_2R{\cdot}CO{\cdot}CH_2{\cdot}CH_2R' \longrightarrow CH_2R{\cdot}C(OH){:}CH{\cdot}CH_2R' \longrightarrow CH_2R{\cdot}C(OH){:}C(OH){\cdot}CH_2R' \longrightarrow CH_2R{\cdot}C(OH)_2{\cdot}C(OH)_2{\cdot}CH_2R' \longrightarrow CH_2R{\cdot}CO{\cdot}C(OH){:}CHR' \longrightarrow CH_2R{\cdot}CO{\cdot}CO{\cdot}COR'$. The individual steps can be formulated as for acetone. The diketone as such will not occur as an intermediate, experiments with diacetyl showing that rapid oxidation occurs to two molecules of acetic acid. Little is known about such triketones, but they are certainly very unstable, being powerful reducing agents and undergoing degradation by alkalis. The triketone might break down by fission with water as follows :



$$\begin{array}{c}\mathrm{CH_2R{\cdot}CO{-}\vdots{-}CO{-}\vdots{-}COR'}\\ \mathrm{HO\vdots H\quad HO\vdots H}\end{array} \longrightarrow \mathrm{CH_2R{\cdot}CO_2H + H{\cdot}CO_2H + R'{\cdot}CHO}$$

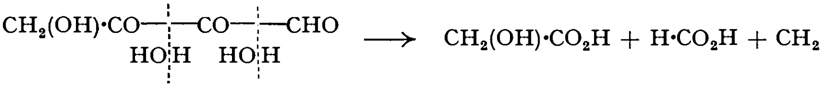
the aldehyde undergoes further oxidation. Oxidation might also proceed along the chain in the other direction and lead to $R{\cdot}CH(OH){\cdot}CO{\cdot}CO{\cdot}COR'$ or $R{\cdot}CO{\cdot}CO{\cdot}CO{\cdot}CH_2R'$.

Ethyl methyl ketone. Oxidation starts at the methylene group and proceeds along the chain until either $CH_3{\cdot}CO{\cdot}CO{\cdot}CHO$ or $CH_2(OH){\cdot}CO{\cdot}CO{\cdot}CHO$ is formed. The former might undergo fission as follows :



$$\begin{array}{c}\mathrm{CH_3{\cdot}CO{-}\vdots{-}CO{-}\vdots{-}CHO}\\ \mathrm{HO\vdots H\quad HO\vdots H}\end{array} \longrightarrow \mathrm{CH_3{\cdot}CO_2H + H{\cdot}CO_2H + CH_2O}$$

the latter as follows :



$$\begin{array}{c}\mathrm{CH_2(OH){\cdot}CO{-}\vdots{-}CO{-}\vdots{-}CHO}\\ \mathrm{HO\vdots H\quad HO\vdots H}\end{array} \longrightarrow \mathrm{CH_2(OH){\cdot}CO_2H + H{\cdot}CO_2H + CH_2O}$$

The formaldehyde would then be oxidised to formic acid. (Experiment showed that one molecule of formic acid was probably produced by each two equivalents of ceric sulphate used.) The glycollic acid would be oxidised to formic acid, carbon dioxide, and water (Willard and Young, *J. Amer. Chem. Soc.*, 1930, **52**, 132).

The two modes of oxidation are thus represented by the equations :

$$\text{(i)}\quad CH_3\cdot CO\cdot CH_2\cdot CH_3 + 5O \longrightarrow CH_3\cdot CO_2H + 2H\cdot CO_2H$$

$$\text{(ii)}\quad CH_3\cdot CO\cdot CH_2\cdot CH_3 + 8O \longrightarrow 3H\cdot CO_2H + H_2CO_3$$

If 70% of the ketone is oxidised by reaction (i) and 30% by reaction (ii), 11·8 equivalents of ceric sulphate will be required, and 2·3 moles of formic acid will be produced (cf. Table IV).

Diethyl ketone. When full oxidation has occurred at one methylene group the other will probably be attacked in preference to the methyl group, thus giving $CH_3\cdot CO\cdot CO\cdot CO\cdot CH_3$ and not $CH_3\cdot CH_2\cdot CO\cdot CO\cdot CHO$. The triketone may be supposed to undergo the fission, $CH_3\cdot CO\cdot CO\cdot CO\cdot CH_3 \longrightarrow CH_3\cdot CO_2H + H\cdot CO_2H + CH_3\cdot CHO$.

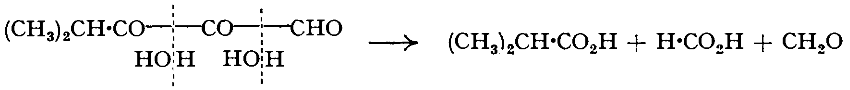
The acetaldehyde would be oxidised and according to the above discussion should require 5·6 equivalents of ceric sulphate and yield 1·8 moles of formic acid. In all, diethyl ketone should require 13·6 equivalents of ceric sulphate and yield 2·8 moles of formic acid, in agreement with experiment.

Methyl n-*propyl ketone.* The values recorded in Table IV are close to those for diethyl ketone and suggest oxidation on similar lines. From initial attack at the α-methylene group it proceeds along the chain until $CH_3\cdot CO\cdot CO\cdot CO\cdot CH_3$ is formed, and this undergoes fission as before.

This ketone, however, uses slightly more ceric sulphate than does diethyl ketone. A small amount of attack on the α-CH_3 group may occur, leading to $CH_2(OH)\cdot CO\cdot CO\cdot CO\cdot CH_3$ which then yields glycollic acid, formic acid, and acetaldehyde, the first and third of these then undergoing further oxidation. For this, 19·6 equivalents of ceric sulphate are required and 3·8 moles of formic acid are produced. If this reaction occurs to the extent of 5%, 14·0 equivalents of ceric sulphate would be used and 2·85 moles of formic acid produced, approximately as found.

n-*Amyl methyl ketone.* If the attack is assumed to start at the α-methylene group, degradation will occur when the compound $CH_3\cdot CH_2\cdot CH_2\cdot CO\cdot CO\cdot CO\cdot CH_3$ is reached, and this will suffer fission to $CH_3\cdot CH_2\cdot CH_2\cdot CHO$, $H\cdot CO_2H$, and $CH_3\cdot CO_2H$. The oxidation of *n*-butyraldehyde has not yet been examined but should be according to (i) $CH_3\cdot CH_2\cdot CH_2\cdot CHO + O \longrightarrow CH_3\cdot CH_2\cdot CH_2\cdot CO_2H$ and (ii) $CH_3\cdot CH_2\cdot CH_2\cdot CHO + 5O \longrightarrow CH_3\cdot CO_2H + 2H\cdot CO_2H$. If reaction (i) constitutes 10% of the total, *n*-butyraldehyde will require 9·2 equivalents of ceric sulphate and yield 1·8 moles of formic acid. This mode of oxidation will require 17·2 equivalents of ceric sulphate and yield 2·8 moles of formic acid. The fact that the amount of ceric sulphate used is slightly greater than this suggests some oxidation of the α-methyl group. This mode of oxidation involves the fission of the compound $CH_3\cdot CH_2\cdot CH_2\cdot CO\cdot CO\cdot CO\cdot CH_2\cdot OH$. If this yields *n*-butyraldehyde, formic acid, and glycollic acid (cf. methyl *n*-propyl ketone), in all 23·2 equivalents of ceric sulphate will be required and 3·8 moles of formic acid will be formed. If this mode of oxidation occurs to the extent of 5% (cf. methyl *n*-propyl ketone), the resultant stoicheiometry will be 17·5 equivalents of ceric sulphate used and 2·85 moles of formic acid produced.

iso*Butyl methyl ketone.* As before, attack must be supposed to start at the α-methylene group. The compound $(CH_3)_2C(OH)\cdot CO\cdot CO\cdot CH_3$ should be produced, and would be expected to undergo oxidative fission to acetone, carbon dioxide, water, and acetic acid (cf. methyl *iso*propyl ketone and di*iso*propyl ketone). Such a reaction cannot, however, be fitted into a scheme to explain the stoicheiometric results. Two modes of oxidation are indicated : (i) The compound $(CH_3)_2CH\cdot CO\cdot CO\cdot CHO$ is ultimately formed and this undergoes fission as follows :



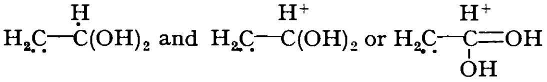
$$(CH_3)_2CH\cdot CO{-}\underset{HO\,\vdots\,H}{\vdots}{-}CO{-}\underset{HO\,\vdots\,H}{\vdots}{-}CHO \longrightarrow (CH_3)_2CH\cdot CO_2H + H\cdot CO_2H + CH_2O$$

the formaldehyde being oxidised to formic acid; 10 equivalents of ceric sulphate are required and 2 moles of formic acid produced. (ii) The compound $(CH_3)_2C(OH)\cdot CO\cdot CO\cdot CH_2\cdot OH$ is ultimately formed and undergoes the oxidative fission, $(CH_3)_2C(OH)\cdot CO\cdot CO\cdot CH_2\cdot OH + 6O \longrightarrow CH_3\cdot CO\cdot CH_3 + H_2CO_3 + CH_2(OH)\cdot CO_2H$, the acetone and glycollic acid being subsequently oxidised in the usual way. In all 24·4 equivalents of ceric sulphate are required and 2·4 moles of formic acid are produced. If 67% is oxidised by reaction (i) and the rest by reaction (ii), 14·75 equivalents of ceric sulphate will be used and 2·15 moles of formic acid produced, as required (see Table IV). Considerable oxidation of the methyl group evidently occurs and this would not be expected from the behaviour of other ketones. The matter will be considered further in the next section.

Effect of Structure on Reactivity.—The oxidation of ketones has been correlated with enolisation followed by oxidation of the enol, and the effect of structure on the ease of oxidation of enols will now be discussed. It will be necessary to account for the anamolous behaviour of acetone and acetaldehyde, for the greater ease of oxidation of the " relevant enol " of an unsymmetrical ketone, for the varying proportions of competing reactions in different ketones, and for various discrepancies in the relation between enolisation and oxidation rates.

The proportionality between relevant enolisation rate and the rate of oxidation indicates that all enols which are actually oxidised are about equally reactive, with the exception of those from acetone and acetaldehyde. Such enols all possess β-hydrogen atoms [*i.e.*, at a position as in CH·C⁚C(OH)]. In these cases it would be possible for intermediate products of oxidation (see discussion on acetone in Part I) to be stabilised by hyperconjugation from the β-hydrogen atoms. For the neutral radical formed by the loss of one electron and addition of a hydroxyl ion, the hyperconjugation would be of the type $\mathrm{R{-}\overset{H}{\dot{C}}H{-}\underset{\cdot\cdot}{C}H{-}CR(OH)_2}$. For the positive ion formed by the loss of a further electron the hyperconjugation would be $\mathrm{R{-}\overset{H^+}{C}H{=}CH{-}CR(OH)_2}$. Such an effect might facilitate reaction and be a major factor governing the reactivity of the enol towards ceric sulphate. No such hyperconjugation could occur in the products of oxidation of an enol of the type $\mathrm{CH_2R{-}C(OH){=}CH_2}$. The application of this hypothesis to various compounds and series will now be examined.

Acetaldehyde. This is oxidised much faster than corresponds to its enolisation rate. It is unique among the compounds studied in that its oxidation products could be stabilised by hyperconjugation of the type



$$\mathrm{H_2\underset{\cdot\,\cdot}{C}{-}\overset{H}{\dot{C}}(OH)_2} \text{ and } \mathrm{H_2\underset{\cdot\,\cdot}{C}{-}\overset{H^+}{C}(OH)_2} \text{ or } \mathrm{H_2\underset{\cdot\,\cdot}{C}{-}\overset{H^+}{\underset{OH}{C}}{=}OH}$$

This would appear to be a very important process and to enhance greatly the reactivity of the enol.

Acetone. This is oxidised much more slowly than corresponds to the rate of enolisation. The oxidation products of the enol lack the possibilities for hyperconjugation of those from acetaldehyde and of those from ethyl methyl ketone. The reactivity of the enol is greatly diminished. The absence of this effect might also hinder certain subsequent stages in the oxidation, which in other ketones are fast, and lead to an autocatalytic form of reaction–time curve (see Part I). The anomalous result for acetone may thus be due in part to a low consumption of ceric sulphate in the stages contributing to r_0.

Effect of chain length in the series, COMeR, *where* R = Et, Pr^n, *or* n-*amyl.* Fig. 3 shows that the rates of oxidation in this series are in accord with the view that the oxidisable enol is of the type Me·C(OH)⁚CHR′. Reactivity decreases with the chain length; similarly, in oxidation by selenious acid Mel'nikov and Rokitskaya (*J. Gen. Chem. Russia*, 1938, **8**, 1369) found that the rate diminished continuously from acetone to *n*-hexyl methyl ketone, but for oxidation by dichromate Petit (*Bull. Soc. chim.*, 1945, **12**, 568) found that reactivity increased with chain length. The drop from R = Et to R = Pr^n corresponds to the diminution in the relevant rate of enolisation, but the compound with R = *n*-amyl is oxidised rather more slowly than might have been expected. Possibly the methyl group in Pr^n promotes the stabilisation of the products by hyperconjugation, and this influence is damped by the interposition of additional methylene groups (compare the views on the electron release of alkyl groups put forward in *J.*, 1949, 2412).

In the interpretation of the stoicheiometric measurements it was shown that about 30% of the ethyl methyl ketone but only about 5% of the higher straight-chain ketones ultimately suffered attack at the methyl group. This is in accordance with the hypothesis that products are stabilised by hyperconjugation in suitable cases. In ethyl methyl ketone the possibility of such stabilisation ceases when the α-methylene group has been fully attacked; further oxidation involves the methyl groups and there is no reason why the β-methyl group should be attacked in preference to the α-group. With the longer chains, however, there will be a bias in favour of oxidation proceeding along the chain, since in that direction continued stabilisation of the products can be obtained.

Methyl iso*propyl ketone.* Enolisation is said to occur entirely on the CH group, and this enol is the one whose oxidation products could be stabilised by hyperconjugation. The rates of enolisation and oxidation are both slightly lower than those of ethyl methyl ketone; the oxidation curves are nearly coincident (Fig. 1). No explanation can be offered, since the reaction mechanisms for the two compounds should be very different. The additional hydrogen atoms in methyl *iso*propyl ketone appear to make no difference to the reactivity of the enol, compared with that of ethyl methyl ketone.

iso*Butyl methyl ketone*. Fig. 3 shows that the rate of oxidation is in accord with the view that the oxidisable enol is $Me_2CH{\cdot}CH{:}CMe(OH)$. The results of the stoicheiometric measurements showed that a great deal of attack at the α-methyl group ultimately occurred. The advantages possessed by the α-methylene group over the α-methyl group are apparently much reduced when there is only one β-hydrogen atom, resulting in diminution in the stabilisation effect. (In the compound $Me_3C{\cdot}CH_2{\cdot}COMe$, hyperconjugation could play no part in the stabilisation of the oxidation products.)

Diethyl ketone. The total rate of enolisation of this compound is approximately the same as the relevant rate of enolisation of ethyl methyl ketone. The rates of oxidation are almost identical (Fig. 1). The rate of oxidation is perhaps slightly lower, in comparison with that of ethyl methyl ketone, than would have been expected from the enolisation rates. Possibly the greater electron release from the other alkyl group hinders the stabilisation of the products by hyperconjugation. The interpretation of the stoicheiometry requires that both methylene groups are attacked and that no attack on methyl groups occurs. This is in accordance with the view that the products of attack on methylene, but not on methyl, groups can be stabilised by hyperconjugation.

*Di*iso*propyl ketone*. The 1ate of oxidation is roughly in accord with its rate of enolisation. Possibly, compared with that of methyl *iso*propyl ketone, it is a little slower than would be expected. This might be due to a steric effect or to opposition to the stabilisation of the products caused by electron release from the other alkyl group.

EXPERIMENTAL.

The ketones were fractionated from commercial specimens; purity was checked by boiling points and refractive indices.

Details about solvent and reagents are given in Part I, where the experimental methods for measuring rate of oxidation and investigating stoicheiometry are described.

The rates of enolisation of acetaldehyde, *n*-amyl methyl ketone, and di*iso*propyl ketone at 25° were measured by the iodination method. Acetaldehyde was examined in aqueous solution, and the ketones in 63% alcohol (by volume). Measurements with acetone for purposes of comparison were made with both solvents.

With di*iso*propyl ketone a reaction between iodide ions and the ketone made it necessary to work in the initial absence of iodide, and to make allowance for the effect of that produced in the iodination of the ketone, when calculating the rate of enolisation from the rate of removal of iodine.

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