

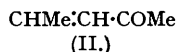
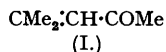
143. *The Oxidation of $\alpha\beta$ -Unsaturated Ketones with Alkaline Hydrogen Peroxide.*

By C. A. BUNTON and G. J. MINKOFF.

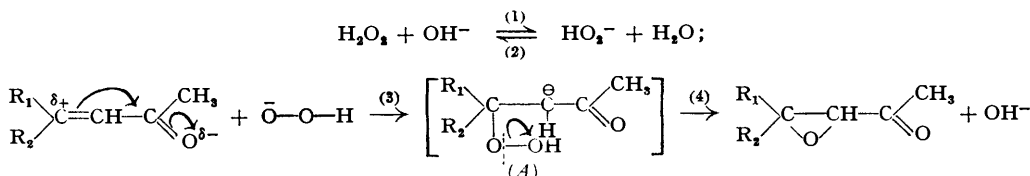
The kinetic course of the oxidation of mesityl oxide and of ethylideneacetone by hydrogen peroxide in an aqueous alkaline medium has been studied at 0°. The evidence shows clearly that the rate-determining stage is the attack of the hydroperoxide ion HO₂⁻ on the olefinic double bond.

THE reaction between hydrogen peroxide (in alkaline media) and unsaturated ketones was first studied by Weitz and Scheffer (*Ber.*, 1921, **54**, 2327), who found that epoxides were the main product. Fieser and his co-workers have prepared naphthaquinone oxides by the action of

alkaline hydrogen peroxide on 1:4-naphthaquinones (*J. Amer. Chem. Soc.*, 1939, **61**, 3219; 1940, **62**, 2866). A study of the kinetic course of the reaction of alkaline hydrogen peroxide with mesityl oxide (I) and with ethylideneacetone (II) shows that the reaction is of first order with



respect to both the unsaturated ketone and the hydroperoxide ion HO_2^- . This experimental order is in accord with the supposition that the rate-determining step of the reaction involves an attack by the ion HO_2^- on the β -carbon atom (cf. the attack of this ion on a carbonyl carbon; Bunton, Everett, Halberstadt, and Minkoff, *Nature*, 1948, **161**, 172). The reaction therefore falls into the general Michael class, involving attack by a nucleophilic reagent on a carbon-carbon double bond conjugated to an unsaturated electron-withdrawing group. We suggest that the reaction mechanism follows the general scheme:



Our kinetic study can of itself give no information on the nature of the intermediate (A); the formation of the new C-O bond (step 3) may be synchronous with the breaking of the O-O bond (step 4). No evidence was found which indicated the attack of HO_2^- on the carbonyl carbon atom.

The nucleophilic attack on the ketone should be hindered by electron accession to the reaction centre, and in fact the substitution of a methyl group for a hydrogen atom on the β -carbon atom decreases the rate by a factor of 5.6. This marked effect of alkyl groups in decreasing the rate is in contrast to the reaction between olefins and per-acids; this latter reaction involves electrophilic attack and is facilitated by alkyl substituents (Meerwein, *J. pr. Chem.*, 1926, **113**, 9; Swern *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 1692). A distinction must also be drawn between these reactions and those of hydroxyl radicals, which can be formed from hydrogen peroxide by irradiation with ultra-violet light or by the action of multivalent metal ions (Treibs, *Ber.*, 1939, **72**, 7, 1194; Haber and Weiss, *Proc. Roy. Soc.*, 1934, **147**, A, 333; Waters, *Ann. Reports*, 1945, **42**, 148; Baxendale, M. G. Evans, and Park, *Trans. Faraday Soc.*, 1946, **42**, 155).

EXPERIMENTAL.

Kinetic Measurements.—The reactions were carried out at 0° in a blackened flask. Hydrogen peroxide (100-vol.) was added to a solution of a known weight of the ketone in aqueous alkali (free from carbon dioxide) at 0°. The zero time of the reaction was taken as the time of mixing of the reagents and the initial concentration of hydrogen peroxide was obtained by an extrapolation back to zero time. The concentration of hydrogen peroxide at a given time was estimated by titrating the iodine liberated from acid potassium iodide in the presence of ammonium molybdate. Calibrated volumetric glassware was used. The hydroxide-ion concentration was determined by titration with standard acid, with bromophenol-blue indicator; no change of alkali concentration occurred in the course of reaction.

Blank experiments showed that, although there was no sensible decomposition of the alkaline hydrogen peroxide under our conditions, there was a very slow reaction between the hydrogen peroxide and the epoxide formed in the course of the reaction. The decrease in the concentration of hydrogen peroxide after a time equal to 10 times the half-life period of the reaction was up to 5% greater than that corresponding to the amount of unsaturated ketone originally present. This side reaction should, however, have a negligible effect on the rate in the early stages of the reaction. The reaction of ethylideneacetone was not investigated as fully as that of mesityl oxide as the rates became too fast for accurate determination. The plot of titre against time for a typical run of mesityl oxide is shown in Fig. 1.

The reaction of alkaline hydrogen peroxide both with mesityl oxide and with ethylideneacetone shows no definite kinetic order with respect to either hydrogen peroxide or hydroxide-ion concentration; it is therefore not possible to quote integrated rate constants. Initial rates were, however, obtained by fitting the experimental results to an empirical equation of the form

$$\log_{10} [\text{ketone}] = A + Bt + Ct^2$$

— B is then equal to the first-order rate constant with respect to the ketone concentration, *i.e.*, $k_1 = -B$.

Since the values of (initial) k_1 showed no obvious correlation with the concentrations of either H_2O_2 or OH^- , the influence of the concentration of hydroperoxide ion was investigated. This concentration was obtained from the equation

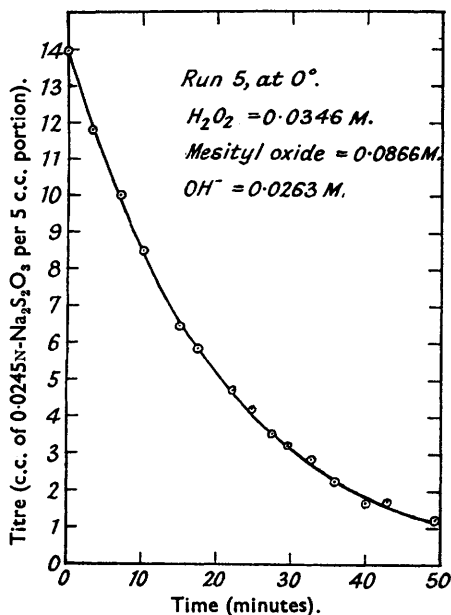
$$[\text{HO}_2^-]/([\text{H}_2\text{O}_2][\text{OH}^-]) = K_{\text{H}}/K_{\text{W}} = K$$

in which K_H is the dissociation constant of hydrogen peroxide at 0° , and K_W that of water. Then

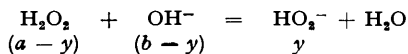
$$K = 0.67 \times 10^{-12} / 0.114 \times 10^{-14} \text{ (International Critical Tables) } = 600.$$

This value of K being used, the concentrations of HO_2^- were calculated as follows: Let a be the total concentration of H_2O_2 , as found by titration at a given time. Let b be the initial concentration of

FIG. 1.



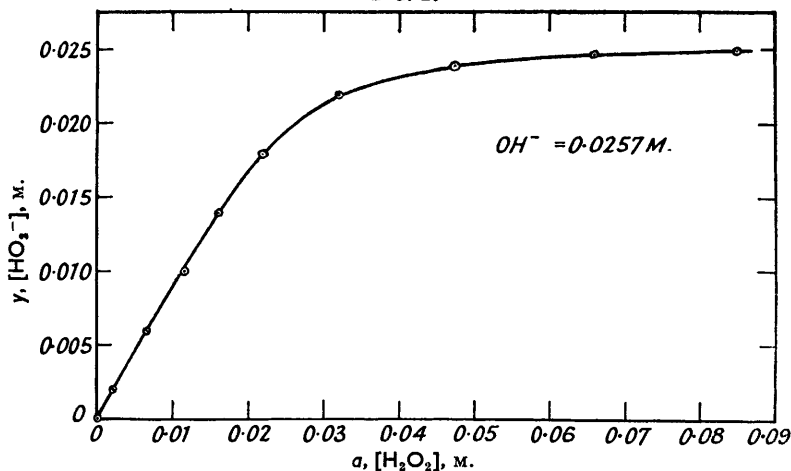
hydroxyl ions. Let y be the concentration of HO_2^- when total $[\text{H}_2\text{O}_2] = a$. The actual concentrations are then



and they are related by the expression

$$y/(a - y)(b - y) = 600$$

FIG. 2.

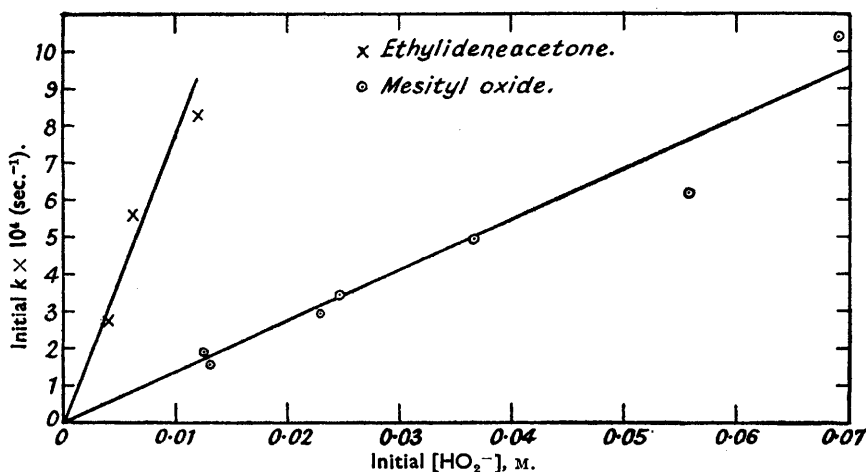


Graphs were plotted for the various values of b which were used, of y against a , and from these, the required values of $[\text{HO}_2^-]$ were obtained. Such a graph is shown in Fig. 2; it shows that for concentrations of hydrogen peroxide greater than that of the hydroxyl ion, the concentration of hydroperoxide ion is sensibly constant, and slightly below the concentration of hydroxyl ions; when the concentration of

hydrogen peroxide is less than that of the OH^- , $[\text{HO}_2^-]$ decreases with decreasing H_2O_2 . It seems not unreasonable to connect the extensive ionisation of hydrogen peroxide to HO_2^- and H^+ in alkaline media with the experimental observation that it is a strongly oxidising agent in such circumstances.

When the initial values of k_1 , calculated as above, were plotted against initial $[\text{HO}_2^-]$, both for mesityl oxide and for ethylideneacetone, straight lines were obtained, as shown in Fig. 3. The slopes of these lines gave the values of the initial second-order constants k_2 , which were respectively 1.37×10^{-2} and 7.70×10^{-2} sec^{-1} l.g.-mol.⁻¹.

FIG. 3.



Initial k_2 for mesityl oxide = 1.37×10^{-2} .

Initial k_2 for ethylideneacetone = 7.70×10^{-2} .

The experimental conditions (concentrations in mols./l.) were:—

Run no.	$[\text{H}_2\text{O}_2]$, M.	[Ketone].	$[\text{OH}^-]$.	Initial k_1 , (sec^{-1}) $\times 10^4$.	Initial $[\text{HO}_2^-]$.
Mesityl oxide.					
1	0.0717	0.0423	0.0134	1.55	0.0131
2	0.0735	0.0821	0.0130	1.90	0.0126
3	0.0655	0.0843	0.0384	4.96	0.0367
4	0.0698	0.0842	0.0257	3.44	0.0247
5	0.0346	0.0866	0.0263	2.92	0.0230
6	0.0678	0.0856	0.0646	6.19	0.0558
7	0.0154	0.0547	0.0740	10.40	0.0690
Ethylideneacetone.					
9	0.0610	0.0289	0.0121	8.32	0.0122
10	0.0462	0.0283	0.0042	2.76	0.004
11	0.0508	0.0335	0.0068	5.61	0.0062

These results show that the initial rate is proportional to the concentrations of the ketone and of the hydroperoxide ion.

In the case of mesityl oxide, the proposed kinetic order was further tested by estimating graphically the instantaneous rates from the slopes of the graphs of titre against time, and plotting these, for reactions 1—7, against the product of the concentrations of ketone and hydroperoxide ion on the same graph. The points all lay close to a common straight line, the slope of which gave the mean value of k_2 , with an accuracy limited by the accuracy of the determination of the slopes. For the sake of clarity, the points of runs nos. 1, 3, 4, and 5 only are shown in Fig. 4. By contrast, the instantaneous rates are also plotted against the products $[\text{Ketone}][\text{H}_2\text{O}_2][\text{OH}^-]$ in Fig. 5; it is obvious that no simple relationship exists between these quantities. A further confirmation lies in the fact that the initial second-order constants (based on $[\text{HO}_2^-]$) obtained by the two methods agree closely, the values being 1.37×10^{-2} sec^{-1} l.g.-mol.⁻¹ in both cases.

Preparation of Materials.—*Ethylideneacetone.* Acetaldehyde and acetone were condensed in the presence of alkali, and the products were dehydrated by distillation from iodine. The ethylideneacetone was purified by fractionation through a ten-plate column; b. p. 122—123°.

Mesityl oxide. This was prepared by the iodine-catalysed dehydration of B.D.H. diacetone alcohol, and purified by fractionating through a similar column; b. p. 129—129.5°.

Isolation of the Oxide of Mesityl Oxide.—The end-products were isolated as follows from 500 c.c. of a solution in which mesityl oxide (10 g.) reacted with hydrogen peroxide (M/4), $[\text{OH}^-]$ being M/8, after 6 hours at 0°. The solution was extracted with ether, and the extract dried with potassium carbonate and calcium sulphate. After evaporation of the ether, the products were fractionated in a vacuum;

FIG. 4.

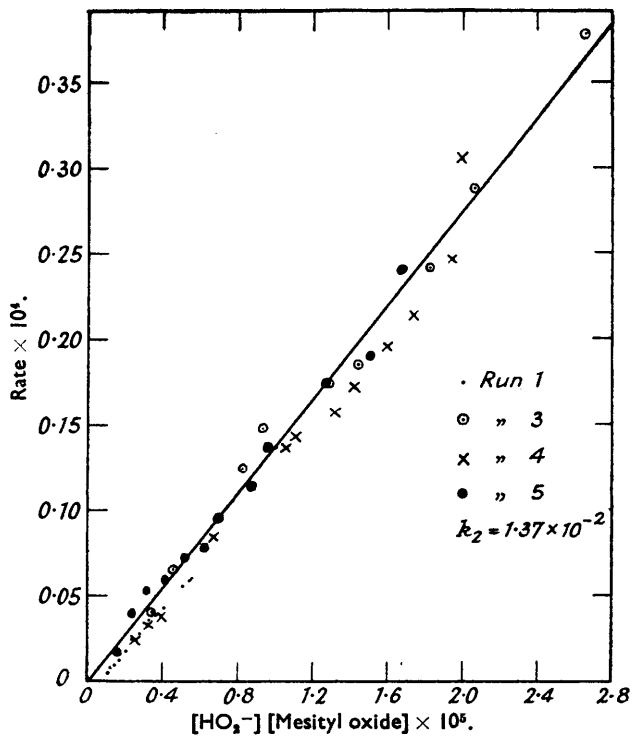
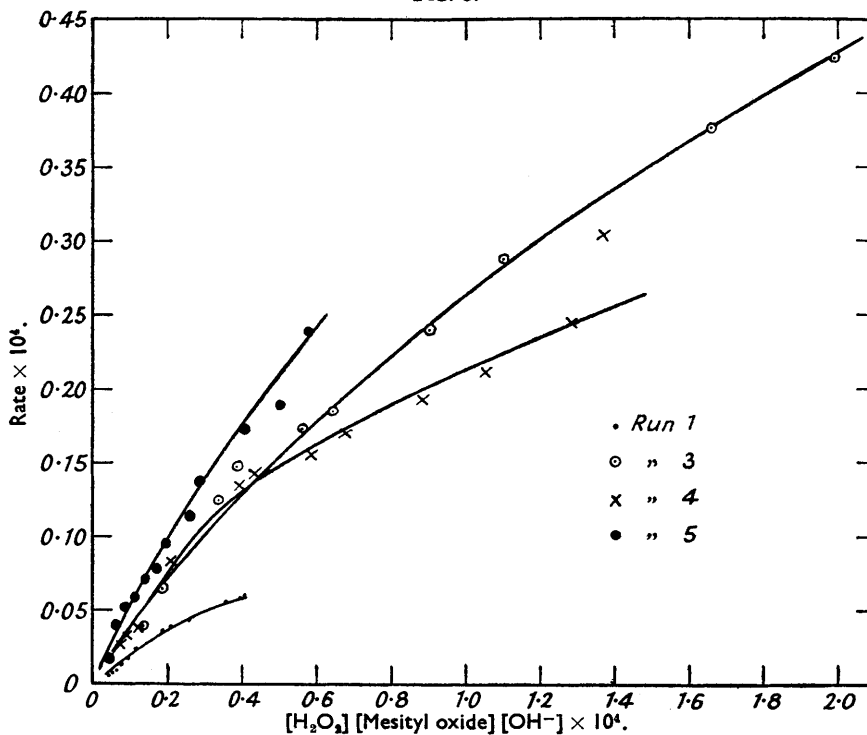


FIG. 5.



7.5 g. of product boiled at 59—60°/17 mm. (Found : C, 62.2; H, 8.6. Calc. for $C_6H_{10}O_2$: C, 63.0; H, 8.8%), and an unidentified residue distilled between 60° and 80°. The low value of the carbon in the oxide of mesityl oxide may be due to the presence of a small quantity of glycol.

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