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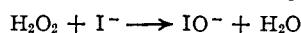
Mechanisms of Reduction of Cumene Hydroperoxide. II. Nucleophilic Displacement of Hydroxyl Ion by Iodide Ion

BY HAROLD BOARDMAN AND G. E. HULSE

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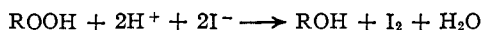
The kinetics of the reaction of iodide ion with cumene hydroperoxide is consistent with a mechanism in which the rate-controlling step consists of a nucleophilic displacement of the hydroxyl ion from the hydroperoxy group by the iodide ion. The intermediate tertiary hypoiodite then reacts with iodide ion to liberate iodine.

Sodium or potassium iodide has been used for a long time in the analysis of certain peroxides. As early as 1895 it was concluded by Noyes¹ that hydrogen peroxide reacts with iodide ion by what would now be interpreted as a two-electron transfer process, the rate-controlling step being



McAlpine² has shown that this reaction is first order with respect to each of the hydrogen peroxide and iodide ion concentrations and less than first order with respect to the hydrogen ion concentration. Taube³ has developed a method which can be used to determine whether a given peroxide reacts with iodide ion by a two-electron or a one-electron transfer process. The method relies upon the fact that oxalate ion will react with iodine by a chain process, if iodine radicals are present. It was concluded that hydrogen peroxide reacts by a two-electron transfer, persulfate reacts largely by a one-electron transfer, while some peroxides react by the two processes simultaneously.

The object of this work was to determine the course of the reaction of cumene hydroperoxide with iodide ion. The over-all reaction is



where R is the α,α -dimethylbenzyl radical. If the reduction takes place *via* a one-electron transfer this would necessitate the formation of the α,α -dimethylbenzyloxy radical, which is known to decompose readily to acetophenone and methyl radical.⁴ The quantitative reduction of cumene hydroperoxide to α,α -dimethylbenzyl alcohol under the conditions of these experiments suggests a two-electron transfer, but does not eliminate the possibility of two successive one-electron transfers. Taube's oxalate³ reaction was applied in order to decide this. The data given in Table I exclude the possibility of the reaction proceeding by two successive one-electron transfers, since the number of equivalents (expressed as ml. of 0.0102 *N* sodium thiosulfate required in a 25-ml. sample) of oxalate ion consumed up to time "*t*" (in hours) by a free-radical initiated reaction, calculated by

$$(\text{C}_2\text{O}_4^{2-}) = I_0 + I_{\text{ROOH}} - I_t - I_h \times t$$

is essentially zero. The symbols have the following meanings

I_0 = initial number of equivalents of iodine.
 I_{ROOH} = equivalents of iodine liberated by all the hydroperoxide

I_t = equivalents of iodine at time "*t*" some time after all the hydroperoxide has reacted.
 I_h = equivalents of iodine used up in unit time by thermal reaction with oxalate ion, determined after all the hydroperoxide has reacted.

TABLE I

$(\text{C}_2\text{O}_4^{2-})_0$	$[\text{HC}_2\text{O}_4^-]_0 \times 10^2$	I_0	I_{ROOH}	I_t	I_h	t (hours)	$(\text{C}_2\text{O}_4^{2-})$
0.15	0.78	1.73	1.08	2.38	0.0195	23.8	-0.03
.16	.84	1.86	0.46	1.97	.017	23.8	.05

Since the rate of the reaction under the conditions of these experiments was quite slow, only initial rates (determined by a colorimetric method over a period of one-hour reaction time) were determined. The order of the reaction with respect to each of the cumene hydroperoxide, iodide ion and hydrogen ion concentrations was obtained by maintaining two of the constituents at a constant concentration and determining the rate dependence of the iodine liberation upon the third component. The data are tabulated in Table II, from which it is evident that the reaction is first order with respect to each of the cumene hydroperoxide and iodide ion concentrations and independent of the hydrogen ion concentration.

TABLE II

DETERMINATION OF ORDER OF REACTION AT 25°

pH	$\left(\frac{dI_2}{dt}\right)_0 \times 10^4$, mole l. ⁻¹ min. ⁻¹	$(\text{I}^-)_0 \times 10^3$, mole l. ⁻¹	$(\text{ROOH})_0 \times 10^3$, mole l. ⁻¹	$k \times 10^{22}$
6.0	0.58	1.81	7.59	4.2
6.0	0.88	2.70	7.59	4.3
6.0	1.19	3.62	7.59	4.3
6.0	0.98	1.81	11.4	4.7
6.0	1.20	1.81	13.9	4.8
5.0	0.58	1.81	7.59	4.2
4.0	0.58	1.81	7.59	4.2

^a k determined by dividing $\left(\frac{dI_2}{dt}\right)_0$ by $(\text{I}^-)_0(\text{ROOH})_0$.

Discussion

The kinetics suggests that the iodide ion reacts with the hydroperoxide in a rate-controlling step which is most easily explained as a nucleophilic attack of the iodide ion on the oxygen atom adjacent to the tertiary carbon atom to give a tertiary hypoiodite as the intermediate. Under certain conditions the tertiary hypohalites are relatively stable compounds in comparison to the primary or secondary hypohalites,⁵ but they react rapidly with iodide ion. Hence it is possible that the intermediate hypoiodite formed in the rate-determining step

(5) F. D. Chattaway and O. G. Backeberg, *J. Chem. Soc.*, **193** 2999 (1923).

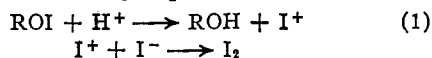
(1) A. A. Noyes and W. O. Scott, *Z. physik. Chem.*, **18**, 131 (1895).

(2) R. K. McAlpine, *J. Chem. Educ.*, **22**, 387 (1945).

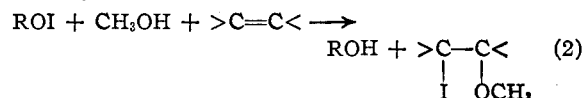
(3) H. Taube, *THIS JOURNAL*, **64**, 161 (1942).

(4) H. Boardman, *ibid.*, **75**, 4268 (1953).

undergoes the following sequence of rapid reactions



Evidence for the existence of the intermediate hypoiodite was sought for by attempted reaction with cyclohexene in methanol



A solution of sodium iodide in methanol was added dropwise to a solution of cumene hydroperoxide and cyclohexene in methanol. Considerable iodine was liberated, indicating that reaction (1) was taking place. However, a small amount of material was isolated that contained iodine and methoxyl group which is presumptive evidence that a hypoiodite was formed in the reaction.

Experimental

The rate of iodine formation was followed with a Klett-Summerson photoelectric colorimeter, fitted with a Corning

5112 glass filter between the light source and the cell; a voltage stabilizer was utilized to supply the light source with a constant voltage. A series of standard iodine solutions were used to calibrate the colorimeter. The procedure was: 27 ml. of a buffered cumene hydroperoxide solution was placed in the absorption cell and a slow stream of nitrogen was passed through the solution for 15 minutes, then 3 ml. of a potassium iodide solution was added at zero time, the nitrogen sparge tube was removed, and the cell was capped to exclude air. The cell was maintained at $25 \pm 0.1^\circ$ in a constant-temperature bath, from which it was removed at periodic intervals to determine the optical density.

The cumene hydroperoxide used was of 96% purity and the hydroperoxide solutions were buffered with recrystallized monopotassium phosphate and carbonate-free 0.1 *N* sodium hydroxide.

Solutions of sodium oxalate, oxalic acid, potassium iodide, iodine and cumene hydroperoxide were made as shown in Table I for detecting free-radical intermediates according to Taube's method.³ Oxygen was excluded from the solutions by flushing the flasks (regular iodine flasks) with nitrogen whenever they were opened. After the cumene hydroperoxide had reacted completely, 25-ml. samples were titrated periodically with 0.0102 *N* sodium thiosulfate to determine the rate of iodine consumption by the thermal reaction with oxalate ion.

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[CONTRIBUTION FROM THE NATIONAL INSTITUTES OF HEALTH]

Crystalline Ozonides from *cis-trans*-Ethylene Derivatives¹

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Ozonolysis of the methyl, ethyl and phenyl esters of fumaric and maleic acids leads only to one type of crystalline ozonide presumably the (resolvable) *trans* structure (Ia, Ib, Ic).

Whereas fumaric acid is practically inert to the action of ozone,² ethyl fumarate yields a crystalline ozonide, m.p. 42–43°, in moderate yield,³ the significant infrared bands of which are shown in Table I. The crystalline ozonide from diethyl *maleate*

melted at 37–42°, gave no significant depression on admixture and showed an infrared spectrum (main bands, see Table I) identical with the ozonide from diethyl fumarate. This identity of the infrared spectra of the ozonides from diethyl as well as di-

TABLE I
INFRARED SPECTRA IN CHLOROFORM

Compound	Ester carbonyl	Infrared absorption in chloroform	
		>C=C< and phenyl	C-O-C region ^a
Dimethyl fumarate	5.82	6.08
Dimethyl maleate	5.80	6.07
Diethyl fumarate	5.83	6.08
Diethyl maleate	5.79	6.08
Dimethyl { fumarate maleate } ozonide	5.68	..	9.0-9.15 ^b ; 10.0-10.2
Diethyl { fumarate maleate } ozonide	5.68	..	9.08, 9.82, 10.08
Diphenyl fumarate	5.75	6.12, 6.26	9.37, 9.79
Diphenyl fumarate ozonide	5.60	6.27	9.08-9.15 ^a ; 9.80 (w), 10.06-10.12 ^b
Diethyl diphenyl maleate	5.80 ^b	6.18 ^w	9.14 ^w ; 9.24 ^w ; 9.30 ^m ; 9.49 ^s ; 9.77 ^m
Diethyl diphenyl maleate	5.76	..	9.21 ^s ; 9.84 ^s ; 10.20

^a Cf. O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **23**, 277 (1951); G. M. Barrow and S. Searles, *THIS JOURNAL*, **75**, 1175 (1953). ^b In the region near 9 μ , the rather broad band is at 9.125 μ which corresponds with the value of Briner (1097 cm.⁻¹).⁴ In the 10 μ region a band at 10.08 μ is found which in the ozonides from the methyl esters shifted to 10.18 μ .

(1) Oxidation Mechanisms. XI. Preceding paper in this series: B. Witkop and S. Goodwin, *THIS JOURNAL*, **75**, 3371 (1953).

(2) C. D. Harris, *Ber.*, **65**, 1471 (1932).

(3) R. Pummerer and H. Richtzenhain, *Ann.*, **529**, 53 (1937). The stable "ozonide" from dihydrodicyclopentadiene, m.p. 116–120°, [cf. H. Staudinger, *Ber.*, **58**, 1095 (1925)] mentioned subsequent to the description of the ozonolysis of diethyl fumarate, is no true ozonide, since it shows a strong carbonyl band at 5.76 μ .

methyl maleate and fumarate has not been observed by Briner⁴ because only solutions of ozonized compounds, but not the crystalline ozonides, were employed for the infrared measurements. As

(4) E. Dallwigk, B. Susz and E. Briner, *Helv. Chim. Acta*, **35**, 353 (1952).