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MECHANISM OF THE ACID CATALYSED REARRANGEMENT OF ORGANIC HYDROPEROXIDES

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ALTHOUGH the mechanism of the acid-catalysed decomposition of cumene hydroperoxide to phenol and acetone has been studied by a variety of workers,[1-3] it is now apparent that a most important point has been overlooked in kinetic analyses of this reaction. Specifically, we have found that the organic hydroperoxide dissociates to a considerable degree in a partially aqueous acidic medium to form the carbinol and hydrogen peroxide, undoubtedly by way of one of the conjugate acids of the hydroperoxide and the dimethylphenylmethyl cation, respectively. Thus, the extensive kinetic data reported by Shlyapnikov and coworkers[3-6] needs to be reinterpreted on the basis of this new finding. However, before the new data with regard to the acid-catalysed decomposition of cumene hydroperoxide are presented, we wish to report the results of a less complicated series of reactions, *viz.*, those of the acid-catalysed decomposition reactions of certain triarylmethyl hydroperoxides.

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[1] M.S. Kharasch, A. Fono, W. Nudenberg and B. Bischof, *J. Org. Chem.* **17**, 207 (1952).

[2] F.H. Seubold and V.E. Vaughan, *J. Amer. Chem. Soc.* **75**, 3790 (1953).

[3] Yu.A. Shlyapnikov, *Kinetika i Kataliz.* **1**, (3), 365 (1960).

[4] V.A. Shushunov and Yu.A. Shlyapnikov, *Works on Chemistry and Chemical Technology* p. 50. Gorkii (1958).

[5] V.A. Shushunov, Yu.A. Shlyapnikov and A.A. Kvasov, *Works on Chemistry and Chemical Technology* p. 102. Gorkii (1959).

[6] V.A. Shushunov and Yu.A. Shlyapnikov, *Dokl. Akad. Nauk., SSSR* **128**, 341 (1959).

Evidence for the acid-catalysed dissociation in partially aqueous medium of triarylmethyl hydroperoxides to triarylcarbinols and hydrogen peroxide was obtained by exchange, kinetic and equilibrium studies. The exchange data in Table 1 indicate that complete equilibration among triarylcarbinol, hydrogen peroxide, triarylmethyl hydroperoxide and water occurs prior to any appreciable rearrangement of the hydroperoxide. The mixtures of phenols were isolated in 85-100 per cent yield and were analysed by vapor phase chromatography.

TABLE 1

Exchange and Product Ratio Data for Experiments Carried Out in 60 per cent Dioxane at 45.0°

Reactants (equimolar quantities)	Conc. of perchloric acid (M)	Mole % phenols	
		phenol	p-cresol
Triphenylmethyl hydroperoxide + diphenyl-p-tolylcarbinol	0.967	34.7	65.3
Triphenylcarbinol + diphenyl-p-tolylcarbinyl hydroperoxide	0.967	35.0	65.0
Triphenylcarbinol + diphenyl-p-tolylcarbinol + hydrogen peroxide	0.967	34.0	66.0
Diphenyl-p-tolylcarbinyl hydroperoxide (alone)	0.967	18.4	81.6
Diphenyl-p-tolylcarbinol + hydrogen peroxide	0.967	18.0	82.0
Triphenylmethyl hydroperoxide + diphenyl-p-tolylcarbinol	0.696	31.0	69.0
Triphenylcarbinol + diphenyl-p-tolylcarbinyl hydroperoxide	0.696	31.0	69.0
Triphenylcarbinol + diphenyl-p-tolylcarbinol + hydrogen peroxide	0.696	31.4	68.6

Kinetic data confirm the fact that the above stated equilibrium occurs prior to the rearrangement step since the rearrangement of triarylmethyl hydroperoxide proceeds at the same rate as the reaction of triarylcarbinol with hydrogen peroxide. An iodometric analysis for unreacted peroxide was used in the rate studies. The pseudo-second order rate constants in Table 2

TABLE 2

Rate Data for Rearrangement of Triarylmethyl Hydroperoxides in 60 per cent Dioxane at 45.0°

Initial concentration (moles/l.)					Rate constant
Triphenylmethyl hydroperoxide	Triphenylcarbinol	Hydrogen peroxide	Diphenyl-p-tolylcarbinyl hydroperoxide	Diphenyl-p-tolylcarbinol	$k_2^1 \times 10^3$ (l./mole-sec)
0.0222	-	-	-	-	1.64 ± 0.02[a]
-	0.0250	0.0251	-	-	1.61 ± 0.00[a]
-	-	-	0.0332	-	10.40 ± 0.10[a]
-	-	0.0287	-	0.0285	10.30 ± 0.05[a]
0.0272	-	-	-	-	1.57[b]
-	0.0269	0.0263	-	-	1.53[b]
-	0.0265	0.0158	-	-	1.51[b]
0.0319	-	-	-	-	0.602 ± 0.14[c]
-	0.0310	0.0313	-	-	0.587 ± 0.12[c]
-	0.0274	0.0128	-	-	0.577[c]

[a] 0.967 M $HClO_4$; [b] 0.934 M $HClO_4$; [c] 0.696 M $HClO_4$.

are the constants k_2' in the equation $d(P)/dt = k_2'(Ar_3COH)(H_2O_2)$. A plot of log k_2' vs. $-Ho$ was linear with the slope equal to 1.17.

The position of equilibrium was determined by selective titration of hydrogen peroxide with standard ceric sulfate solution.[7] The value of the equilibrium constant, $K' = K/(H_2O)$, is approximately 7.1 in 60 per cent aqueous dioxane and is independent of the direction of approach. The rate of equilibration was found to be about one fortieth of the rate of the rearrangement reaction.

With these data in mind, the following reaction sequence is proposed:

$$(C_6H_5)_3COH + H_2O_2 \overset{\overset{H^+}{k_1}}{\underset{k_{-1}}{=}} (C_6H_5)_3COOH + H_2O \qquad (1)$$

$$(C_6H_5)_3COOH + H^+ \overset{k_2}{\underset{k_{-2}}{=}} \underset{(I)}{(C_6H_5)_3COOH_2{}^+} \qquad (2)$$

$$\underset{(I)}{(C_6H_5)_3COOH_2{}^+} \xrightarrow[\text{slow}]{k_3} \text{Products (P)} \qquad (3)$$

When the steady state approximation for the concentration of I is employed, the following rate expression can be derived.

$$\frac{dP}{dt} = \frac{k_2K(\text{triphenylcarbinol})(H_2O_2)(H^+)}{\left[1 + \frac{k_{-2}}{k_3}\right](H_2O)} \qquad (4)$$

$$K = \frac{(\text{triphenylmethyl hydroperoxide})(H_2O)}{(\text{triphenylcarbinol})(H_2O_2)} \qquad (5)$$

In accord with equation (4), which indicates that a decrease in the concentration of water will cause an increase in the rate of reaction, it was found that in 80 per cent dioxane the rate of rearrangement of triphenylmethyl hydroperoxide is about twice that observed in 60 per cent dioxane. Similar data to those given in Tables 1 and 2 indicate that

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[7] F.P. Greenspan and D.G. MacKellar, *Analyt. Chem.* **20**, 1061 (1948).

complete equilibration precedes rearrangement in 80 per cent dioxane as in 60 per cent dioxane. Shlyapnikov has also reported[3] that there is an inverse dependence of the rate of the acid-catalysed rearrangement of cumene hydroperoxide on the concentration of water, but he has attributed this effect to an entirely different and, in our opinion, tenuous interpretation of the mechanism of the reaction.

The acid-catalysed rearrangement of cumene hydroperoxide is more complex, from the standpoint of a kinetics investigation, than that of the triarylmethyl hydroperoxides. This stems from the fact that a reaction of the type shown in equation (1) occurs, but equilibrium concentrations of the various reactants are not attained before a significant amount of rearrangement has taken place. The rearrangement of cumene hydroperoxide, as reported by Seubold and Vaughan[2] and confirmed by us, is pseudo-first-order in a medium of given acidity. We have now found that the reaction of α-cumyl alcohol with hydrogen peroxide is a pseudo-second-order reaction. The half life of the reaction between the alcohol and hydrogen peroxide is about six times that of the rearrangement of the preformed hydroperoxide. However, exchange experiments show that a significant degree of dissociation of one of the conjugate acids of cumene hydroperoxide to the dimethylphenylmethyl cation and hydrogen peroxide occurs in competition with the rearrangement reaction. As a specific example, when equimolar quantities of cumene hydroperoxide and dimethyl-p-tolylcarbinol were treated with a 0.967 M solution of perchloric acid in 60 per cent dioxane at 45.0°, the phenols, isolated in 85 per cent yield, consisted of 42.5 mole per cent of p-cresol and 57.5 mole per cent of phenol. Further studies are being carried out on this system.

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