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The kinetics of hydrolysis of aliphatic ketone di-tert-butylperoxyketals $R^1R^2C=0$, R^1 , $R^2=CH_3$, CH_3 ; CH_3 , C_2H_5 ; CH_3 , $n-C_3H_7$; CH_3 , $n-C_6H_{13}$; CH_3 , $i-C_5H_{10}$; CH_3 , $i-C_4H_9$; C_2H_5 , $i-C_3H_7$; $n-C_4H_9$; CH_3 , $C_6H_5=CH_2$, in dioxane in the presence of H_2SO_4 were investigated by IR spectroscopy. It was found that the reaction is reversible and takes place according to the equation $R^1R^2C \cdot (OOC(CH_3)_3)_2 + H_2O \xrightarrow{H_4} R^1R^2C=0 + 2HOOC(CH_3)_3$. The proposed mechanism of

hydrolysis includes the fast, quasiequilibrium formation of protonated peroxyketal and subsequent formation of the alkylperoxycarbenium ion. A three-parameter correlation equation is proposed for describing the initial rates of hydrolysis of $R^1R^2C(00-t-Bu)_2$ peroxyketals.

The reaction of acid-catalytic hydrolysis of acetals has been widely investigated [1-4]. The generally accepted mechanism of the reaction Al includes fast pre-equilibrium protonation of acetal with the subsequent formation of the alkoxycarbenium ion and fast decomposition of hemiacetal in the limiting stage.

Some characteristics of hydrolysis of peroxyketals (gem-diperoxides), the peroxide analogs of acetals, in dioxane medium in the presence of H_2SO_4 were investigated in the present study

 $\begin{array}{c}
 R^{1} & OOR \\
 C & + H_{2}O & \stackrel{H^{+}}{\longleftrightarrow} & C = O + 2ROOH \\
 R^{2} & OOR & R^{2}
\end{array}$ (1)

On the example of the reaction of cyclohexanone with tert-butyl hydroperoxide, it was previously shown that the ketone \neq hemiperoxyketal equilibrium is established rapidly in the presence of an acid catalyst [5] similar to what is observed for acid hydrolysis of acetals. This stage of the reaction with tert-butyl hydroperoxide cannot be observed for aliphatic ketones due to the low degree of its occurrence.

It is important to note that hydrolysis of gem-diperoxides in dioxane takes place selectively with preservation of the concentration of active oxygen O_{act} according to [1] only in the presence of a fivefold molar excess of water or hydroperoxide with respect to the peroxyketal at the minimum. Otherwise, the diperoxide undergoes acid-catalytic decomposition, accompanied by a decrease in the concentration of O_{act} in the reaction system. For this reason, tert-butyl hydroperoxide was present in all cases in conducting hydrolysis in a system containing small amounts of water with respect to the peroxyketal.

The basic kinetic characteristics of hydrolysis of gem-diperoxides were investigated on the example of acetone di-tert-butylperoxyketal. The reaction is first-order in the peroxyketal both in the presence of an excess of water and hydroperoxide. When the concentration of H_2SO_4 in the reaction system changed, the change in the initial reaction rate W_0 formally corresponded to a second-order reaction in the acid. The dependence of $\log W_0$ on the logarithm of the indicator ratio (I), measured at each point with respect to p-nitroaniline, had the shape of a straight line with a slope equal to one. Since the composition of the reaction medium was established when the concentration of acid changed, such a dependence indicates that fast ionization of the peroxyketal molecule precedes the limiting stage.

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Fig. 1. Dependence of the initial rate of hydrolysis of acetone di-tert-butylperoxyketal (I) (a), indicator ratio I on the concentration of water (b) at 21°C, and C, mole/liter: $C(I)_0 = 0.2$, $C(ROOH)_0 = 2.33$, $C_{H_2SO_4} = 0.035$.

Fig. 2. Dependence of $(\log W_0 - \log I)$ on $\log [C_{H_20}]_0$ at 18°C and C, mole/liter: $C(I)_0 = 0.2$, $C_{(ROOH)_0} = 2.33$, $C_{H_2SO_4} = 0.035$.

TABLE 1. Initial Rates of Hydrolysis of Peroxyketals W, Parameters $\sigma_1^* + \sigma_2^*$, $E_{s,1}^0 + E_{s,2}^0$, and Δn of Substituents R¹ and R² in Dioxane, 25°C {C[R¹R²C(OOR)₂]₀ = 0.2, C(ROOH)₀ = 2.32, C(H₂O)₀ = 0.097, C_{H₂SO₄ = 0.035 M}}

Compound	R	R²	W·10 ³ mole·li- ter ⁻¹ ·min ⁻¹	$\sigma_1^* + \sigma_2^*$	$\left E_{s,1}^0 + E_{s,2}^0 \right $	Δn
(I) (I1) (III) (IV) (V) (V1) (V11) (V11) (IX)	$\begin{array}{ c c } CH_3 \\ CH_3 \\ CH_3 \\ CH_3 \\ CH_3 \\ CH_3 \\ CH_4 \\ C_2H_5 \\ \textbf{n-} C_4H_9 \\ CH_3 \end{array}$	$ \begin{vmatrix} CH_{2} \\ C_{2}H_{5} \\ n-C_{3}H_{7} \\ n-C_{6}H_{1,3} \\ i-C_{5}H_{11} \\ i-C_{4}H_{9} \\ i-C_{3}H_{7} \\ n-C_{4}H_{9} \\ CH_{2}-C_{6}H_{5} \end{vmatrix} $	3,7 5,8 10,7 9,5 9,8 52 44 20 0,75	$\begin{array}{c} 0 \\ -0.1 \\ -0.12 \\ -0.13 \\ -0.126 \\ -0.13 \\ -0.29 \\ -0.26 \\ +0.25 \end{array}$	$ \begin{vmatrix} 0 \\ -0.27 \\ -0.56 \\ -0.45 \\ -0.55 \\ -1.13 \\ -1.12 \\ -1.18 \\ -0.72 \end{vmatrix} $	$ \begin{array}{c c} 0 \\ -1 \\ -1 \\ -1 \\ -1 \\ -3 \\ -2 \\ -1 \\ \end{array} $

The order of the reaction of hydrolysis of acetone di-tert-butylperoxyketal in water was determined in a solution of 2.33 M tert-butyl hydroperoxide. However, it is known that even an insignificant change in the concentration of water with low concentrations of water in an organic solvent strongly affects the acid properties of the medium [6, 7] and, consequently, the rate of reaction (1), which includes pre-equilibrium protonation of the perketal. For this reason, the indicator ratio with respect to p-nitroaniline was measured parallel with determination of the dependence of the initial rate of hydrolysis of the peroxyketal on the concentration of water in the starting reaction mixture in each experiment. The dependence of both the initial rate of hydrolysis of the peroxyketal W_0 and the indicator ratio (I) on the concentration of water in the system is bell-shaped (Fig. 1). It is logical to assume that the change in log I reflects a change in the catalytic activity of the system. For this reason, we attempted to estimate the order of reaction (1) in water from a comparison of the values of (log $W_0 - \log I$) and $\log C_{H_2O}$. The dependence of (log $W_0 - \log I$) log I) on log $C_{\rm H_{2}O}$ is a line with a slope of 0.91 (Fig. 2). However, it is necessary to keep in mind that the stoichiometric concentration of water participating in the nucleophilic event differs slightly from the total concentration of water in the reaction system due to proton hydration. It is not very probable that the acid will be totally dissociated in



the reaction medium with low concentrations of water [8] and there will be one molecule of water bound with it for each molecule of acid. Introduction of this correction causes a change in the slope of the graph of the dependence of $(\log W_0 - \log I)$ on $\log [C_{H_2O}]$, where $C_{H_2O} = C_{H_2O_{added}} - C_{H_2SO_4}$ (tan $\alpha = 0.77$). However, it is also possible that the degree of association of the acid increases as the concentration of water in the nonaqueous solvent increases [9] and the fraction of water bound with the proton increases correspondingly, resulting in a change in tan α . In view of the above, it is difficult to introduce the correction for proton hydration. However, it is possible to assume that the order of the reaction in water in the presence of an excess of hydroperoxide is close to one.

A similar relationship can be observed either when the hydrolysis reaction takes place according to a mechanism of bimolecular nucleophilic substitution, which is not characteristic of substrates with a tertiary C atom, or when addition of water to the previously formed alkylperoxycarbenium ion is not the fast stage, which can be explained by the reversibility of its formation

 $\begin{array}{c} CH_{3} & + \overset{H}{OOR} & CH_{3} \\ C & \stackrel{k_{1}}{\underset{K_{-1}}{\longleftarrow}} & \overset{C}{C} - OOR + ROOH \\ CH_{3} & OOR & CH_{3} \end{array}$

$$\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \end{array} \xrightarrow{C^{+} - OOR + H_{2}O} \xrightarrow{k_{2}} \\ CH_{3} \\ CH_{3} \end{array} \xrightarrow{CH_{3}} CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \end{array} \xrightarrow{CH_{3}} CH_{3} \\ CH_{$$

The hydroperoxide present in the reaction medium in a large excess competes with the water in the reaction with the cation, and the initial reaction rate is a function of both the concentration of protonated peroxyketal and the concentration of water.

$$W_{0} = \frac{k_{1}k_{2}C_{A}C_{H_{2}O}}{k_{-1}C_{ROOH} + k_{2}C_{H_{2}O}}$$

The mechanism which includes intermediate formation of an alkylperoxycarbenium ion is the most probable in view of the presence of a polarized peroxide group capable of delocalization of the positive charge next to the central carbon atom.

The data obtained in studying the effect of substituents R^1 and R^2 at the carbonyl group of the ketones on the rate of hydrolysis of the corresponding peroxyketals are in good agreement with the mechanism of reaction (2). The initial rates W of hydrolysis of the peroxyketals of a series of aliphatic ketones, the induction and steric parameters of substituents R^1 and R^2 , and parameter Δn , calculated with the equation (n - 6), where 6 is the number of α -C-H bonds at the carbonyl carbon in the acetone, and n is the number in the R^1R^2CO ketone, are reported in Table 1.

In the series of methyl ketone peroxyketals (II)-(VI), which have the same values of Δn and similar values of $\sigma_1^* + \sigma_2^*$, the value of $\log W/W_0$, where W_0 is the initial rate of hydrolysis of the acetone peroxyketal, is proportional to $E_{s,1}^0 + E_{s,2}^0$ (Fig. 3).

(2)

TABLE 2. Frequencies of Stretching Vibrations and Absorption Coefficients of the Carbonyl Group of $R^1C(0)R^2$ Ketones in the Reaction Medium at 25°C

Ketone	$v_{C=O}$, cm ⁻¹	ε, liter· mole ⁻¹ · cm ⁻¹	Ketone	v _{C=0} .cm ⁻¹	<pre>E. liter' mole⁻¹.cm⁻¹</pre>
(I) (II) (III) (IV) (V)	1715 1716 1716 1716 1716 1716	448 356 370 395 388	(V1) (VII) (VIII) (VIII) (IX)	1715 1712 1714 1720	331 375 358 307

The fact that the rate of hydrolysis of the peroxyketals increases with an increase in the bulk of substituents R^1 and R^2 permits totally excluding the possibility of the reaction according to the mechanism of S_N^2 bimolecular nucleophilic substitution, since there are steric hindrances for nucleophilic attack. Such a dependence can be explained by removal of the B-stress caused by the steric reaction of the substituents at the central carbon atom of the peroxyketal during formation of the alkylperoxycarbenium ion. The presence of two bulky tert-butyl peroxide substituents in the peroxyketal molecule results in a marked increase in the rate of hydrolysis even with an insignificant increase in the bulk of R^1 and R^2 , to which the reaction of the diethylketals of aliphatic methyl ketones RC· $(OC_2H_5)_2CH_3$ in a medium of 49.6% aqueous dioxane is not sensitive [10]. The rate of hydrolysis of these compounds is determined by the induction constants o* of substituent R and the parameter Δn in the Taft equation

$$\lg k/k_0 = \rho\sigma^* + h\Delta n, \ \rho = -3.6, \ h = 0.54$$

which is due to electronic stabilization of the alkoxycarbenium ion formed in the limiting stage. However, the incorporation of bulky substituents in the ketal molecule results in a sharp deviation from the dependence obtained: the rates of hydrolysis of the compounds $(CH_3)_3C(CH_2)C(0C_2H_5)_2CH_3$ and $(CH_3)_3C-C(0C_2H_5)_2CH_3$ are one and two orders of magnitude higher than the calculated rates, respectively [11]. This is due to the removal of the spatial overload in the tetrahedral ground state in ionization, similar to our case.

A correlation analysis of the kinetic data was conducted for simultaneous consideration of both the steric and the electronic characteristics of substituents R^1 and R^2 . A three-parameter equation was obtained for compounds (I)-(VIII)

$$\lg (W/W_0) = 0.8 (\sigma_1^* + \sigma_2^*) - 1.20 (E_{s,1}^0 + E_{s,2}^0) - 0.52\Delta n, \quad r = 0.984$$

The inverse dependence of the rate of hydrolysis on the factors that result in electronic stabilization of the carbenium ions is apparently due to the fact that an increase in the charge density on the carbon atom of the alkylperoxycarbenium ion decreases the selectivity of its reaction with the hydroperoxide, which is a stronger nucleophile than water.

The equality which is satisfied for reactions in the presence of a large excess of hydroperoxide with respect to water is

$$k_2 C_{\mathrm{H}_2\mathrm{O}} \ll k_1 C_{\mathrm{ROOH}}$$

becomes the opposite for hydrolysis of ketals in water-dioxane medium [10]

$$k_2 C_{\rm H,O} \gg k_{-1} C_{\rm ROOH}$$

and the reaction rate is only determined by the ionization stage.

A case of limitation of the rate of hydrolysis of ketals by the stage of the reaction of the alkoxycarbenium ion with water similar to ours is described in [12] for hydrolysis of dimethylketals of substituted acetophenones in methanol containing small amounts of water (0.01-0.3 M).

The low rate of hydrolysis of methyl benzyl ketone peroxyketal is apparently due to the pronounced destabilization of the peroxycarbenium ion because of the high positive value of o^* for the benzyl substituent, and the stage of its formation becomes rate-determining as a consequence.

EXPERIMENTAL

Dioxane was purified by standard methods and the concentration of water in it was determined by Fischer titration. Tert-butyl hydroperoxide (98.5%) was prepared according to [13, 14] and the concentration of water in it was determined according to [14]. All ketones were used after preliminary distillation. The peroxyketals were synthesized from the corresponding ketones and tert-butyl peroxide in a hexane medium in the presence of H_2SO_4 .

The course of hydrolysis of the peroxyketals was followed based on accumulation of ketone. The reaction took place directly in the thermostated cuvette of a Specord IR-75 spectrophotometer. The frequencies of stretching vibrations and the absorption coefficients of ketone C=O groups in the reaction medium are reported in Table 2.

The initial rates of hydrolysis of the peroxyketals were determined with the slope of the tangent to the initial segment of the kinetic curve. A correction was made for the concentration of acetone di-tert-butylperoxyketal formed as a by-product and determined by GLC on a LKhM-80 chromatograph with an FID under the following conditions: $600 \times 3 \text{ mm}$ column, 15% diisododecyl phthalate stationary phase with temperature programming from 50 to 100°C.

The indicator ratio was measured with respect to p-nitroaniline (0.0005 M). The absorption spectra were recorded on a Specord M-40 spectrophotometer in thermostated quartz cuvettes. The measurements were performed at $\lambda = 354$ nm, characterizing the basic form of the indicator. The absorption maximum of the acid form of the indicator is located in the shorter wave region ($\lambda = 254$ nm) inaccessible for measurement due to the complete absorption of light by the reaction mass.

The indicator ratio was calculated with the equation

$$I = \frac{(D^{\mathrm{A}} - D)}{(D - D^{\mathrm{H}})}$$

where D^A and D^H are the optical densities of the basic and acid forms of the indicator at 354 nm, and D is the optical density in the medium analyzed.

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