KINETICS OF THE ACID-CATALYZED ACYLATION OF tert-BUTYL HYDROPEROXIDE BY ACETIC AND CAPROIC ACIDS

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Hydroperoxide acylation, the analog of the method of synthesizing esters proposed in [1], leads to the formation of peroxy esters [2] and is the basis for certain procedures used in preparing these compounds [3-]. The present paper will describe the results of a study of the kinetics of the reactions of tert-butyl hydroperoxide (TBH) with acetic and caproic acids.

EXPERIMENTAL

The tert-butyl hydroperoxide (TBH) used in this work was synthesized from tert-butanol and H_2O_2 ([2], p. 13), and purified by fractionation under vacuum. The compound had a purity of 97-98%, the principal contaminant being tert-butyl peroxide. The glacial CH_3COOH was repeatedly frozen, heated with a previously calculated amount of $(CH_3CO)_2O$, and then subjected to fractionation; the reaction with iron perchlorate was used to confirm the absence of $(CH_3CO)_2O$ in the principal fraction [6]. The caproic acid was purified by vacuum fractionation.

The kinetic experiments were carried out in the same caproic acid as was used in the esterification. The fact that the TBH was quantitatively converted to the peroxy ester was demonstrated by two different methods: The total peroxide group concentration, determined by iodometric titration in the presence of $FeCl_3$ ([7], p. 44), was shown to remain constant in the reaction mixture, and the reaction mixture was shown by TLC methods to contain just two peroxides ([7], p. 225).

The reaction kinetics were studied through TBH consumption and peroxy ester build-up, each determined polarographically ([7], p. 165). Calculations were based on measured values of W_0, the initial reaction rate, since the water eliminated in acylation tended to retard the reaction. The effective acylation rate constant was calculated from the equation

$$k_2 = W_0/[\mathrm{TBH}]_0[\mathrm{RCOOH}]_0$$

TABLE 1. Synthesis of tert-Butyl Peroxyacetate from tert-Butyl Hydroperoxide (TBH) and CH_3COOH at 20°C and in the Presence of $HClO_4$ and H_2SO_4

Composition of original solution, moles/liter				$-H_0$	$k_2 \cdot 10^5$, liters/mole · sec
TBH	CH_3COOH	$HClO_4$	H_2O		
1,39	13,9	0,0139	1,39	0,546	0,016
1,48	14,8	0,0052	0,36	0,677	0,025
1,46	14,6	0,0050	0,226	0,840	0,040
1,41	14,1	0,0141	0,706	0,838	0,032
1,48	14,8	0,0052	0,192	0,916	0,040
1,46	14,6	0,0050	0,146	0,998	0,056
1,48	14,8	0,0052	0,109	1,114	0,053
1,42	14,2	0,0104	0,236	1,178	0,083
1,42	14,2	0,0048	0,053	1,186	0,073
1,42	14,2	0,0104	0,145	1,354	0,110
1,46	14,6	0,0073	0,052	1,476	0,120
1,43	14,3	0,0143	0,086	1,633	0,247
1,42	15,0	0,0025	0,0024	1,372	0,092
1,50	15,0	0,0050	0,0024	1,674	0,265
1,50	15,0	0,0100	0,0026	1,972	0,363
1,53	15,3	0,0051 *	0,051	0,344	0,0023
1,53	15,3	0,0082 *	0,052	0,654	0,023
1,53	15,3	0,0164 *	0,052	0,952	0,059

* H_2SO_4.

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TABLE 2. Synthesis of tert-Butyl Peroxycaproate from tert-Butyl Hydroperoxide (TBH) and Caproic Acid at 20°C and in the Presence of H_2SO_4

Composition of original solution, moles/liter				$-H_0$	$k_2 \cdot 10^7$, liter/mole·sec
TBH	n-$C_5H_{11}COOH$	H_2SO_4	H_2O		
0,72	7,3	0,073	0,049	1,37	25
0,72	7,3	0,037	0,049	1,23	14
0,38	7,3	0,0082	0,049	0,585	3,5
0,72	7,3	0,0073	0,049	0,50	3,0
0,72	7,3	0,0037	0,049	0,195	1,5
0,72	7,3	0,037	0,134	0,74	4,9
0,72	7,3	0,037	0,22	Heterogeneous system	

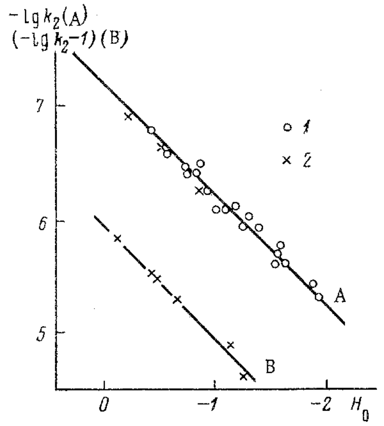

Fig. 1. Variation of the effective rate constants (k_2) for acylation of tert-butyl hydroperoxide by acetic (A) and by caproic (B) acids with the acidity function in $HClO_4$ (1) and in H_2SO_4 (2) solutions of the carboxylic acids at 20°C. Values of $-\log k_2 - 1$ are plotted on the ordinate in the case of caproic acid.

The values of k_2 shown in Tables 1 and 2 were determined from mean W_0 values obtained in parallel experiments; they differed from one another by no more than 10%. In acetic and caproic acid solutions containing mineral acids, 4-5 h were required for peroxy-ester conversion to TBH at 50°C. The indication here was that the reverse reaction could be neglected in kinetic experiments of 2-3 h duration at 20°C.

The acidity function H_0 was determined spectrophotometrically, using o-nitroaniline as indicator [8], in the aqueous solutions of caproic and mineral acids used for studying the kinetics of peroxy-ester formation. The indicator concentration in these solutions was $8.5 \cdot 10^{-5}$ M. Optical densities were measured at 395 nm. The acidity function was calculated from the equation $H_0 = -\log(C_{BH^+}/C_B) + pK_{BH^+}$, C_B and C_{BH^+} being the respective concentrations of the un-ionized and ionized forms of the indicator, and $pK_{BH^+} = -0.29$, the equilibrium constant for BH^+ deprotonation [9]. The water content of each solution was determined, by the Fischer method, prior to the introduction of the TBH.

DISCUSSION OF RESULTS

The fact that acid hydrolysis of the peroxy ester proceeded through the same transition state as the forward reaction was taken as an indication that the O—O grouping remained intact in peroxy-ester formation from the carboxylic acid and the hydroperoxide. The hydrolysis of tert-butyl peroxyacetate and peroxycaproate resulted in the quantitative formation of the hydroperoxide and carboxylic acid, but only at temperatures and mineral acid concentrations higher than those used in the kinetic studies. Hydrolytic splitting and reformation of the O—O bond could not have taken place in peroxy-ester formation and hydrolysis. The reaction in question here was therefore to be considered as a special case of O-acylation in which a hydroxyl splits off from the carboxyl group, and a H atom splits off from the hydroperoxide group: $\mathrm{RC(O)}\overset{|}{\underset{|}{-}}\mathrm{OH} + \mathrm{H}\overset{|}{\underset{|}{-}}\mathrm{OOR^1}$

The fact that log k_2 proved to be a linear function of H_0 (Fig. 1), with slope close to unity in both the synthesis of tert-butyl peroxyacetate (0.97 ± 0.05) and the synthesis of tert-butyl peroxycaproate (1.0 ± 0.05), suggested that the reactive and activated complexes both involved the molecular form of the one reactant and the ionic form of the other. The carboxylic acids are only weakly ionized; because of their low dielectric constants ($\varepsilon^{25}_{CH_3COOH} = 6.19$), mineral acids dissolved in carboxylic acid solutions tend to exist as poorly dissociated ion pairs [10].

Since the Hammett indicator base could undergo protonation from both the ion pair protons and the protons present in solution, the linear log k_2 vs H_0 plots were interpreted as showing the variation of the rate constant with the proton strength of the medium.

Although the acidity function was varied by altering the mineral acid concentration, in some solutions, and by changing the water content, in others (see Tables 1 and 2), the plotted points all fell on the same log k_2 vs H_0 line. This confirmed the belief that reaction proceeded through protonation of one reactant rather than by the association of this reactant with the mineral acid. Study of the mechanism of acid-catalyzed esterification of carboxylic acids by alcohols, and of ester hydrolysis, has shown that water can be split off when a proton adds to a carboxyl group [1, 11, 12]. Thus, in our own systems, catalysis was assured by protonation of the carboxylic acid

$$RC(O)OH_2^+ + HOOC(CH_3)_3 \rightarrow RCOOOC(CH_3)_3 + H^+(H_2O)$$

Since the consumption of carboxylic acid in protonation could be neglected in dilute mineral acid solutions containing excess of the carboxylic acid

$$RC(O)OH_2^+ = Kh_0[RC(O)OH]$$

h_0 being the acidity of the solution and K the equilibrium constant for protonation. From this is followed that W_0, the initial rate of peroxy-ester formation, would be given by an equation of the form

$$W_0 = kKh_0[(CH_3)_3COOH]_0[RC(O)OH]_0$$

in which the rate is related to the acidity of the medium and the reactant concentrations.

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CONCLUSIONS

1. Formation of a peroxy ester from tert-butyl hydroperoxide and caproic acid proceeds through rupture of the H—OO bond.

2. Rate constants for the formation of peroxy exters from tert-butyl hydroperoxide and acetic and caproic acids in the presence of mineral acids have been determined as a function of the acidity. These relations are explained in terms of the limiting step in the interaction of the protonated carboxylic acid and hydroperoxide.

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COMPLEXING OF OZONE WITH AROMATIC COMPOUNDS

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It is a well-known fact that O_3 forms π-complexes with allylaromatic hydrocarbons [1-3]. Spectrophotometric methods have been used to study the stoichiometry and equilibria of the ozone–cumene complexes [4]. The present work was an investigation of the effect of the aromatic ring substituent on the stability constants of the complexes of ozone with monosubstituted benzenes, in n-hexane solution and at temperatures ranging from −57 to −10°C.

EXPERIMENTAL

The stability constants of the various complexes of ozone with monosubstituted benzenes (ArX) were determined through spectrophotometric measurements over the interval from 377 to 390 nm [5]. The contribution of ArX and O_3 to the total optical density was neglected here. Measurements were carried out in a thermostated cell, 2 ml in volume (l = 1 cm). The O_3 solutions, approximately 2 ml in volume, were prepared in the cell itself. The ozone concentration of the liquid phase $[O_3]_0$, was first determined spectrophotometrically [6], the substrate solution (~ 0.1 ml) then introduced into the cell, and the initial optical density of the reaction mixture, D_0, recorded automatically. Preliminary measurements on substrate-free systems showed that O_3 would not react to measurable degree with the solvent under these conditions.

The benzene, fluorobenzene, chlorobenzene, toluene, bromobenzene, ethyl benzene, benzyl chloride, and hexane had been purified by standard methods [7].

DISCUSSION OF RESULTS

The value of λ_{max} fell within the interval from 340 to 540 nm in the electronic absorption spectra of the complexes of ozone with the various substituted benzenes (Table 1). According to [3], this absorption was due to the formation of charge-transfer complexes between the acceptor ozone and the π-donor aromatic compounds.

TABLE 1. Electronic Absorption Spectra of the π-Complexes of Ozone with Aromatic Compounds

Compound	λ_{max}, nm	Compound	λ_{max}, nm
Benzene	340	Cumene	377
Toluene	383	m-Xylene	390
Ethyl benzene	382*	Mesitylene	441*
tert-Butyl benzene	375*	Pentamethylbenzene	541*

* Data from [3].

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