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Features of Hydrolysis of Phthalic Acid Chlorides

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Abstract—The experimentally measured rate constants of phthaloyl and terephthaloyl chlorides hydrolysis vary at the variable reagents ratio. This change obeys the Michaelis–Menten equation suggesting the intermediate formation by the reactants of the charge-transfer complex.

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The mechanism of hydrolysis of carboxylic acid chlorides is still not entirely clear, despite a numerous studies on this subject [1–3]. It is known that the observed rate constants of pseudo-first or second order of this reaction, obtained in mixtures of water–hydrophilic solvent (dioxane, acetone, etc.) can vary greatly depending on the water concentration [4–6]. The same drift of the rate constant depending on the ratio of reactants is observed in the reactions of alcoholysis of acid chlorides. In some cases it has been found that the kinetics of alcoholysis obeys Michaelis–Menten equation, i.e., the reaction occurs through an intermediate stage of formation of a complex by the reactants [7–10]. In particular, in the reaction of benzoyl chloride with methanol the complex formation was confirmed by spectroscopic methods and physicochemical analysis [9]. Consequently, the reaction proceeds along the scheme:

$$\mathrm{RCOCl + R'OH} \overset{K_{\mathrm{eq}}}{\rightleftarrows} \mathrm{[RCOCl{\cdot}R'OH]} \xrightarrow{k_{\mathrm{tr}}} \mathrm{RCOOR' + HCl}.$$

Accordingly, the experimentally determined rate k_2 equals the product $K_{\mathrm{eq}}\times k_{\mathrm{tr}}$. The nature of the intermediate complex formed by the reactants is a charge transfer complex.

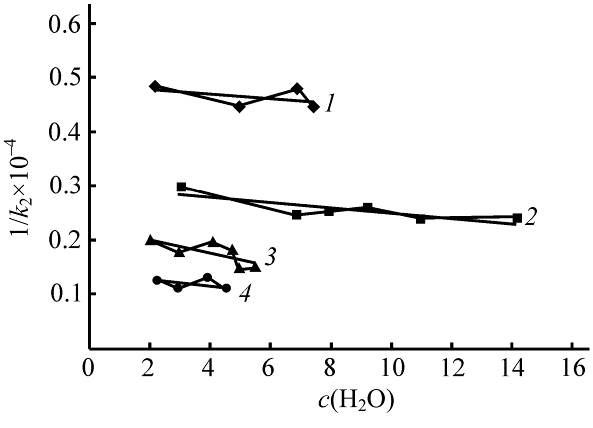

Fig. 1. Hydrolysis of phthaloyl chloride. Determination of k_{tr} of the transformation of intermediate complex to the products is carried out on the basis of the dependence of $1/k_2$ on the water concentration at the following temperatures: (*1*) 298K, R = 0.537, $k_{\mathrm{tr}} = 222\times10^{-4}$; (*2*) 308K, R = 0.822, $k_{\mathrm{tr}} = 217\times10^{-4}$; (*3*) 318K, R = 0.756, $k_{\mathrm{tr}} = 79\times10^{-4}$; (*4*) 328K, R = 0.369, $k_{\mathrm{tr}} = 250\times10^{-4}$.

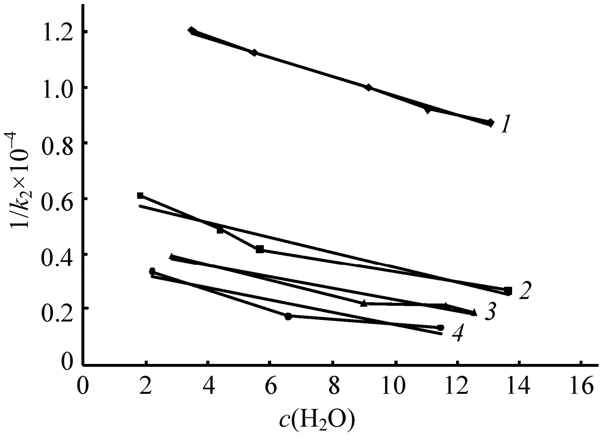

Fig. 2. Hydrolysis of terephthaloyl chloride. Determination of k_{tr} of the transformation of intermediate complex to the products is carried out on the basis of the dependence of $1/k_2$ on the water concentration at the following temperatures: (*1*) 288K, R = 0.998, $k_{\mathrm{tr}} = 29\times10^{-4}$; (*2*) 308K, R = 0.958, $k_{\mathrm{tr}} = 37\times10^{-4}$; (*3*) 322K, R = 0.974, $k_{\mathrm{tr}} = 48\times10^{-4}$; (*4*) 338K, R = 0.931, $k_{\mathrm{tr}}= 46\times10^{-4}$.

The dependence of the rate constants $k_2\times10^{-4}$ (l mol^{-1} s^{-1}) of the phthaloyl chloride and terephthaloyl chloride hydrolysis on the water concentration c (M) in dioxane [14, 15]

Phthaloyl chloride				Terephthaloyl chloride			
T, K	$c(H_2O)$	$k_2\times10^4$	$10^{-4}/k_2$	T, K	$c(H_2O)$	$k_2\times10^4$	$10^{-4}/k_2$
298	2.13	2.06	0.485	288	3.43	0.90	1.111
	3.83	1.85[a]	0.541		5.40	0.97	1.031
	4.80	2.95[a]	0.339		9.05	1.10	0.909
	4.93	2.23	0.448		10.93	1.20	0.833
	6.89	2.09	0.478		12.90	1.27	0.787
	7.45	2.24	0.446	308	0.610	1.05[a]	0.952
308	2.99	3.24[a]	0.309		0.690	1.05[a]	0.952
	3.05	3.38	0.296		0.810	1.10[a]	0.909
	3.25	3.11[a]	0.322		1.800	1.90	0.526
	4.40	4.12[a]	0.243		4.350	2.45	0.408
	4.74	4.41[a]	0.227		5.600	2.98	0.336
	5.42	4.34[a]	0.230		13.500	5.30	0.189
	6.83	4.07	0.246	322	2.80	3.23	0.310
	7.95	3.94	0.254		8.90	7.00	0.143
	9.17	3.84	0.260		11.50	7.45	0.134
	10.95	4.16	0.140		12.40	9.05	0.110
	14.15	4.16	0.240	338	2.20	3.90	0.256
318	2.01	5.0	0.200		6.50	10.30	0.097
	2.96	5.64	0.177		11.34	18.28	0.055
	4.05	5.14	0.195				
	4.71	5.52	0.181				
	4.95	6.75	0.148				
	5.49	6.65	0.150				
328	1.29	5.50[a]	0.182				
	2.25	7.79	0.128				
	2.95	8.92	0.112				
	3.92	7.65	0.131				
	4.55	9.16	0.109				

[a] These data are excluded from the calculation because of significant deviations from the linear dependence of $1/k_2$ on the water concentration.

Systematic increase in the experimental values of k_2 with increasing concentrations of glycol at its interaction with terephthaloyl chloride was observed in the studies performed by Entelis et al. [11]. Recently, analyzing these data we revealed that they also obey the Michaelis–Menten kinetics, therefore, this reaction probably also proceeds through a stage of formation of a charge-transfer complex [12].

In view of the fact that, as shown in [13, 14], the same systematic increase in the k_2 values with increasing concentrations of water was observed in the study of hydrolysis of phthaloyl and terephthaloyl chlorides in the medium of dioxane, it seems reasonable to test whether the kinetics observed in this case obeys the Michaelis–Menten equation. The table lists the corresponding values of k_2 for various temperatures and reactant ratios based on the data of [13, 14]. The reaction was carried out in an environment of dioxane, the concentration of chloride was $(0.5–1)\times10^{-5}$ M. When the results are presented in the coordinates $1/k_2 - c(H_2O)$ a clear tendency to a linear dependence is observed, despite some deviations, especially in the case of phthaloyl chloride at 298 and 308 K. The deviations are due, probably, to inaccurate UV spectral measurements at low water concentrations.

As Figs. 1 and 2 show, there is a clear trend to a linear dependence between $1/k_2$ and $c(H_2O)$. According to the approach outlined in [7, 8], the intercept on the ordinate axis is equal to $1/K_{eq}\times k_{tr}$. The slope gives the k_{tr} value. However, the correlation between these values is low, which does not allow a sufficiently reliable determination of the exact value of the rate constants of conversion of the intermediate complex in the reaction product, especially in the case of phthaloyl chloride, but gives only the order of magnitude: for phthaloyl chloride about 230×10^{-4}, and for terephthaloyl chloride, 45×10^{-4} l m^{-1} s^{-1}.

Accordingly, the calculated equilibrium constants K are even more approximate. The estimated K values are 0.03 and 0.05 l mol^{-1}, respectively. When comparing these values with those measured in [12] for the terephthaloyl chloride glycolysis, it may be noted that although the experimental values of k_2 in both cases are similar, namely, at 35°C $2–5\times10^{-4}$ and $1–3.5\times10^{-4}$ l m^{-1} s^{-1}, respectively, nevertheless, the values of k_{tr} for hydrolysis are several times higher, suggesting a much smaller stability of the intermediate charge transfer complex of terephthalic acid chloride with water. At the same time, the values of equilibrium constants in both cases are similar, about 0.05 l mol^{-1} at 35°C. The complex of water with phthaloyl chloride decomposes even faster.

In favor of the probable formation of a charge transfer complex by the reactants may be cited also the fact that the acid chlorides are known to be electron acceptors forming charge–transfer complexes with amines [15], esters [16], and other compounds possessing an unshared electron pair. At the same time, alcohols and water are electron donors of medium strength owing to the unshared electron pairs of oxygen: their basicity values are, according to Palm, 224 for ethylene glycol and 156 for water [17]. The picture here may be complicated by competitive interaction of the reactants with the environment: the basicity of dioxane is 236, so that the reactants interact obviously in a solvated form.

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