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Reaction Kinetics of Terephthalylchloride with Ethylene Glycol

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Abstract—The change in the second-order rate constants in the reaction of terephthalyl chloride with ethylene glycol obeys the Michaelis–Menten equation, suggesting that in the first stage a donor–acceptor complex is formed.

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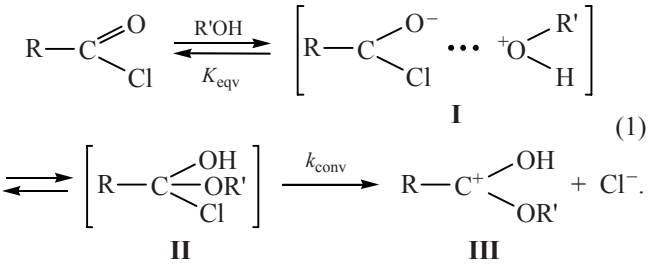
The mechanism of acid chloride alcoholysis has been the subject of numerous investigations [1–7]. Hudson and Stelzer [1] found that the reaction rate was proportional to the concentration of the associated dimeric alcohol molecules. The authors assumed that this process proceeds through the stage of formation of carbocation. The opinion more common now presumes that this is a bimolecular reaction including formation of the donor–acceptor complex **I**. The latter suffers further transformation into tetrahedral complex **II** and protonated ester **III** [2–4].



I **II** **III** (1)

All the proposed mechanisms are based on the analysis of kinetic data. Only in [6] for the reaction of acetyl chloride with benzyl alcohol was established by IR spectroscopy a reversible formation of an intermediate compound of 1:1 composition, to which 1-hydroxy-1-methyloxyalkyl halide structure was ascribed.

In some cases the kinetics of this reaction was observed to deviate from the formal second order. This fact was rationalized as a proceeding of parallel first and second order reactions or as the participation of alcohol in the alcoholysis as a dimer. In [5] attention was drawn to the fact that solvation of both the reaction complex and the initial acyl chloride molecules by excess alcohol was important for this reaction. This feature corresponds to the formation of associate **I**. Based on the analysis of IR spectra it was presumed that also the reaction of acetyl chloride with acetic acid proceeded through the formation of the donor–acceptor complexes of 1:1 or 1:2 composition [7].

However, if this reaction actually proceeds through formation of an associate, then the reaction rate constant observed experimentally (effective) would not remain constant at the change in the reagents ratio, as it was established for the reaction of dinitrochlorobenzene with aniline [8] where initially a charge transfer complex (CTC) was formed. The change in the value of the rate constant should obey the Michaelis–Menten equation [9]:

$$\frac{1}{k_{exp}} = \frac{1}{k_{conv}K_{eqv}} + \frac{C_A + C_B}{k_{conv}}, \qquad (2)$$

where K_{eqv} is the equilibrium constant of CTC formation and k_{conv} is the rate constant of its further conversion into the reaction products. For the reactions proceeding through the associative equilibrium stage the linear dependence between $1/k_{exp}$ and the concentration of the reagent taken in excess or the sum of the reagents concentrations is observed. Then the graphical determination of K_{eqv} and k_{conv} is possible

Experimental values of the second-order rate constants for reaction of terephthalyl chloride with ethylene glycol k_{exp} [12, 13] and of the rate constant for CTC conversion

$C_{ethylene\ glycol}$, mol l^{-1}	$k\times10^4$, l mol^{-1} s^{-1}	$1/k_{exp}\times10^{-4}$	$k_{conv}\times10^4$, l mol^{-1} s^{-1}
	25°C		
5.77	0.80	1.25	9.54
5.88	0.94	1.06	
7.42	1.03	0.97	
8.90	1.22	0.82	
	1.66	0.60	
10.53	1.69	0.59	
11.61			
	35.5°C		
4.51	1.26	0.79	14.88
5.52	1.52	0.65	
5.81	1.72	0.58	
6.30	1.67	0.60	
7.19	2.12	0.47	
8.76	2.50	0.40	
9.20	2.88	0.35	
	2.74	0.37	
10.50	3.48	0.29	
11.38			
	42.5°C		
5.82	2.32	0.42	25.00
7.13	3.04	0.33	
	4.58	0.22	
10.63	5.51	0.18	
11.45			
	51°C		
5.75	4.06	0.246	40.00
6.30	4.45	0.225	
6.53	4.56	0.219	
8.82	6.95	0.144	
	8.16	0.123	
10.57	9.19	0.109	
11.26			

[8, 9]. We established this relationship in studies of benzoyl chloride methanolysis with alcohol excess at 45°C in toluene [10]. By this way the values of K_{eqv} (1.09 l mol^{-1}) and k_{conv} (0.73×10^{-4} l mol^{-1} s^{-1}) were determined, the latter was twice larger than the k_{exp} value. Formation of the charge transfer complex (CTC) in C_6H_5COCl–CH_3OH system was confirmed also by the methods of phase equilibrium and UV spectroscopy. The similar results were obtained in studies of methacryloyl chloride alcoholysis [11]. Therefore it was interesting to verify the validity of this approach also for the others acids, in particular, for polyhydric acids.

In [12, 13] the reaction kinetics of terephthalyl chloride ($2–5\times10^{-5}$ mol l^{-1}) with excess ethylene glycol in dioxane solution in the temperature range of 25–51°C was studied. It was established that the observed second-order rate constant changes by the factor of 2–3 when the glycol concentration was changed. This phenomenon was attributed to the change in the medium polarity. Actually, the values of log k_{exp} increased linearly with the increase in the solution Kirkwood function. However, taking into account the above-mentioned mechanism, it is appropriate to consider a possibility for the data of these works [12, 13] to obey Eq. (2).

The corresponding data on k_{exp} from [13] are given in the table.

The data obtained were found to fit to the Michaelis–Menten equation (Fig.1) that allowed to determine the value of the CTC formation equilibrium constant and the rate constant k of its further transformation into the products using the least-squares method.

The equilibrium constants of CTC formation by terephthalyl chloride and glycol determined on the basis of kinetics scarcely changed with temperature. They all fall into the range of 0.06–0.065 l mol^{-1} that is by one and a half order of magnitude less than in the

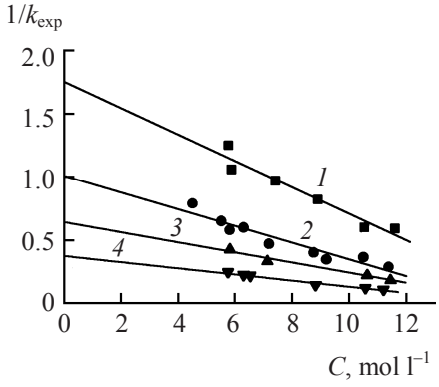


Fig. 1. Relationship between experimental rate constant and ethylene glycol concentration at: (*1*) 25°C; (2) 35.5°C ; (*3*) 42.5°C ; and (*4*) 51°C .

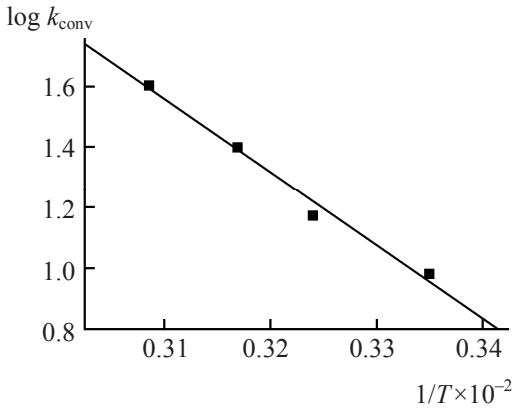


Fig. 2. The rate constant of CTC conversion into the products k (l mol^{-1} s^{-1}) as a function of reciprocal temperature.

case of methanol and benzoyl chloride CTC at 45°C (K_{eq}=1.09 l mol^{-1}, [10]), and is comparable with K_{eq} at 40°C in methacryloyl chloride–methanol system (0.14 l mol^{-1}, [11]). Since the basicities B by Koppel–Palm of both alcohols are close (224 for glycol and 218 for methanol), a significantly higher degree of glycol association probably causes this difference.

As expectable, the values of k_{conv} of glycol–terephthalyl chloride CTC vary linearly with the reverse temperature function (Fig. 2), and this allowed the calculation of the activation energy for CTC conversion into the products, which was found equal to 17.3 kJ mol^{-1}, i.e. it was of the same order of magnitude as for the reaction of methacryloyl chloride with methanol (72 kJ mol^{-1}) [11].

The results obtained are in accordance with the assumption that in this system the CTC formation is the first stage of the reaction. The suggestion in [11, 12] that the change in the medium polarity causes the observed change in the rate constant is less probable, considering that in the concentration range studied the variation of its Kirkwood function occurs only within some hundredth parts. It must be emphasized that variation in the experimental values of bimolecular reaction rate constant with the change in the reagents ratio was found also for the alcoholysis of acetyl chloride [14]. However in this case the concentration dependence of log $1/k_{eff}$ is not linear.

The statement that CTC formation is the first stage of acyl chlorides alcoholysis is indirectly confirmed by the known fact of substantial decrease in the rate of this reaction in basic solvents, in comparison with hydrocarbons, evidently due to a certain competition between alcohol reagent and basic solvent for the electron-acceptor molecule of the acyl chloride. Acyl chlorides were found [16, 17] to enter into the donor-acceptor interaction as acceptors to form CTC. The like rate decrease was established for the reactions of crotonoyl chloride with allyl alcohol [15], methacryloyl chloride with methanol [11], and propionyl chloride with menthol [4]. The rate constants values decrease in parallel with the increase in the Palm solvent basicity B. However, in this case the linearity is not observed since the other factors such as solvent polarity also affect k_{eff}.

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