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Effect of the Reactant Ratio on the Kinetics of Methanolysis of Acyl Chlorides

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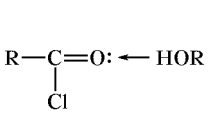
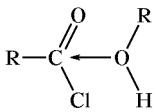
Abstract—The apparent second-order rate constants for the reaction of methacryloyl chloride with methanol regularly increase on raising the acyl chloride-to-alcohol ratio. The variation of the rate constants is described by the Michaelis–Menten equation, indicating that the process involves initial formation of an associate with a probable structure of charge-transfer complex (CTC). Thermodynamic parameters of the CTC formation and rate constants and activation parameters for the transformation of CTC into the products have been determined.

Kinetic parameters of the reaction of carboxylic acid chlorides with alcohols are quite sensitive to both solvent nature [1–3] and alcohol structure [4, 5]. The rates and activation parameters of the examined processes cannot be determined unambiguously by some single parameter but are a complex function of several factors which may be summarized via multiparameter equations based on the linear free-energy relation. Here, the main factor affecting the process is the basicity of the medium, which slows down the reaction [3]. It should also be noted that the effect of alcohol structure is characterized not only by Hammett–Taft constants σ^* and E_s but also by its solvation properties according to Koppel'–Pal'm since alcohol acts as both reagent and solvent in the alcoholysis of acyl chlorides. The dependence on solvation parameters is observed when the reaction is carried out with excess alcohol, as well as with an equimolar amount of alcohol in an inert solvent [1, 5], regardless of the structure assigned to primary reaction complex: whether it is a charge-transfer complex (CTC) **B** [6] or an H-complex **A** which then rearranges into CTC:



A



B

The formation of CTC between RCOCl and ROH is quite feasible, for carboxylic acid chlorides are electron acceptors capable of forming CTCs with electron-donor species. This is confirmed by both extremely low donor numbers of acyl chlorides (e.g., 1.0 for CH_3COCl and 2.3 for C_6H_5COCl [7]) and identification of individual CTC derived from acyl chlorides with such compounds as dioxane [8, 9], acetone (by refractometry) [10] and DMF (by conductometry [11] and spectrophotometry [12]) but primarily with pyridine [13, 14] and other tertiary amines [15, 16]. In the case of amines, the structure of CTCs was also proved, specifically the presence of a bond at the carbon atom with possible charge transfer from the amino nitrogen atom to the oxygen [15, 17]. In solvents with high dielectric constants, charge-transfer complexes can dissociate into radical ions [15].

On the other hand, alcohols exist mainly as cyclic dimers (especially in weakly polar media); therefore, they possess an appreciable basicity. Their basicities *B* according to Pal'm (i.e., shift of the OH band of phenol in the IR spectrum in the presence of a given compound in carbon tetrachloride) range from 208 (benzyl alcohol) to 260 (*tert*-pentyl alcohol) and are comparable with the basicities of other electron-donor compounds, such as diethyl ether (280), dioxane (237), DMF (291), acetone (224), pyridine (472), and DMSO (362) [18].

Unfortunately, the available scales of electron-acceptor power [19] (Gutmann acceptor numbers AN, Reichardt parameter E_T, and Kamlet–Taft parameter α) lack data for acyl chlorides, so that we cannot compare them with alcohols. However, it is known that the enthalpies of mixing of strong electron-donors,

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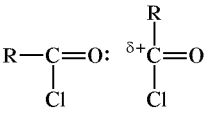
Table 1. Enthalpies of mixing of electron-donor solvents with PhCOCl, MeOH, and EtOH at 25°C according to [21] (the amount of the second component is given in parentheses)

Solvent	ΔH, kcal/mol		
	PhCOCl	MeOH	EtOH
Acetone	31.2 (19.6)	129 (24.3)	168 (17.1)
Acetonitrile	108 (19.0)	160 (77.9)	208 (18.2)
Benzene	39.6 (64.9)	112 (65.4)	136 (65.2)
	30.4 (17.5)	172 (35.0)	216 (34.0)
Dioxane	6.3 (16.0)	148 (18.0) [22]	87.9 (11.0)
Anisole	8.2 (33.0)	–	–

e.g., ethylenediamine, with organic substances are roughly proportional to the electron-acceptor parameters (AN or E_T) of the latter [20]. Therefore, comparison of the enthalpies of mixing of some strong electron donor with alcohols and with acyl chlorides should make it possible to estimate, at least roughly, the relative electron-acceptor power of these substances and hence to determine the preferential way of solvation, RCOCl : B or ROH : B. Table 1 gives the corresponding enthalpies of mixing taken from [21, 22]. Although the available data on the enthalpies of mixing with PhCOCl are few in number and were obtained at a different component ratio than the desired 1 : 1, their comparison with the repsective values for alcohols provides at least qualitative estimation of their acceptor power. It is seen that in all cases the enthalpies are positive; however, processes of mixing of the above substances with alcohols are considerably more endothermic than with PhCOCl. Obviously, the energy of hydrogen bond formation with alcohols does not compensate the energy consumed for decomposition of the dimer. On the other hand, in most cases the enthalpies of mixing of alcohols with PhCOCl are close to zero; therefore, in some media solvation of PhCOCl with the solvent should predominate over formation of CTC PhCOCl–ROH or hydrogen bond ROH···B. This explains both appreciable deceleration of the process in basic solvents and fairly large positive values of $\Delta H^{\neq}$ and $\Delta G^{\neq}$; the latter were estimated by us at 80–90 kJ/mol. The enthalpies of mixing with PhCOCl are also positive but are small, which may be due to some dimerization of acyl chloride molecules as shown below. However, there are no published data on the existence of such dimers.



We previously found [23] that the melting diagrams for the systems PhCOCl–alcohol considerably deviate from the Schroeder equation and that even a peritectic point is observed in the system PhCOCl–cyclohexanol. This indicates formation of compounds with an incongruent melting point in such systems. Moreover, in the presence of alcohols the UV absorption maximum of PhCOCl (λ 241 nm) shifts to the short-wave region with simultaneous increase in intensity, which is typical of charge-transfer complexes.

Study of the kinetics of PhCOCl reaction with methanol in toluene at 45°C showed that the apparent second-order rate constants change on variation of the reactant ratio and that their behavior is described by the Michaelis–Menten equation for reactions involving association equilibria [24, 25]:

Here, $k_{ap} = K_{eq} k_{tr}$, where k_{ap} is the experimental second-order rate constant, K_{eq} is the equilibrium constant for formation of CTC by initial reactants, and k_{tr} is the rate constant for the transformation of CTC into the products. Then we have

$$\frac{1}{k_{ap}} = \frac{1}{k_{tr} K_{eq}} + \frac{C_A + C_B}{k_{tr}}.$$

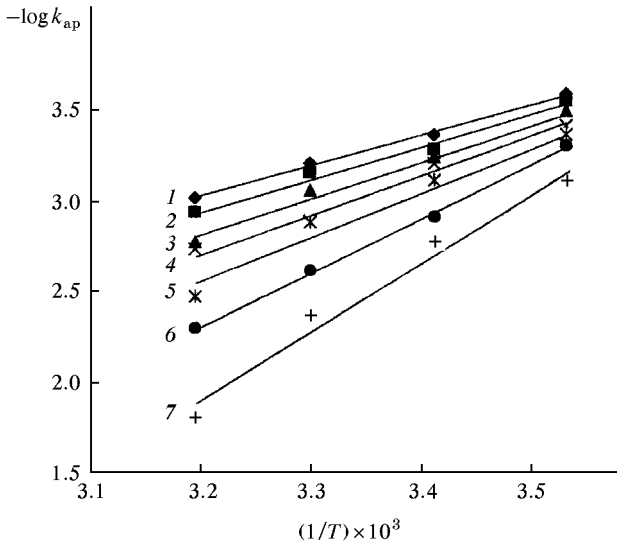


Fig. 1. Temperature dependences of the apparent rate constants for the methanolysis of methacryloyl chloride in benzene at different molar ratios RCOCl : MeOH: (*1*) 1 : 1, (*2*) 2 : 1, (*3*) 3 : 1, (*4*) 4 : 1, (*5*) 5 : 1, (*6*) 6 : 1, (*7*) 7 : 1.

Table 2. Apparent rate constants of methanolysis of methacryloyl chloride in benzene at different reactant ratios and activation parameters of the process at 303 K

Ratio XA : MeOH	$k_{ap} \times 10^3$, l mol^{-1} s^{-1}				E_{ap}, kJ/mol	$\Delta H^{\neq}_{ap}$, kJ/mol	$-\Delta S^{\neq}_{ap}$, J mol^{-1} K^{-1}	$\Delta G^{\neq}_{ap}$, kJ/mol	$1/k_{ap}$			
	283 K	293 K	303 K	313 K					283 K	293 K	303 K	313 K
1 : 1	0.25	0.42	0.60	0.94	32.3	29.7	208.6	92.9	4050	2381	1658	1060
2 : 1	0.27	0.50	0.69	1.14	34.0	31.5	201.7	92.6	3700	1990	1460	880
3 : 1	0.31	0.55	0.85	1.67	40.5	38.0	178.4	92.1	3270	1810	1174	600
4 : 1	0.37	0.60	1.03	1.82	40.9	38.4	175.6	91.6	2730	1664	976	549
5 : 1	0.41	0.74	1.28	3.33	50.1	47.6	143.3	91.0	2450	1353	783	300
6 : 1	0.47	1.18	2.36	5.00	57.2	54.7	114.8	89.5	2120	849	424	200
7 : 1	0.74	1.61	4.37	15.39	74.2	71.6	53.8	87.9	1360	621	229	65

The data of [23] refer to an aromatic carboxylic acid chloride; moreover, the reaction was studied at a single temperature and with a relatively small excess of benzoyl chloride over methanol (from 1 : 1 to 3 : 1). According to [24, 25], in order to obtain reliable data on the formation of intermediate compound, the reaction should be carried out with a considerable excess of reagent B with respect to substrate A. Therefore, we performed a more detailed study of carboxylic acid chloride alcoholysis using methacryloyl chloride and methanol as reactants and benzene as solvent.

Table 2 contains the apparent second-order rate constants obtained in the temperature range from 283 to 313 K; the acyl chloride-to-alcohol molar ratio was varied from 1 : 1 to 7 : 1. As expected, the rate constant regularly increases as the above ratio rises. This tendency becomes stronger on raising the temperature. On the other hand, at each reactant ratio, second-order kinetic relations are fulfilled with a satisfactory accuracy up to a conversion of 60–70%.

The temperature dependence of the apparent rate constants fits the Arrhenius equation (Fig. 1); therefore, the energies of activation and the other activation parameters of the overall process may be calculated with a high accuracy ($r > 0.99$; Table 2). These data indicate regular increase of the apparent energy of activation and hence of the apparent enthalpy of activation with increase in excess of RCOCl and concomitant increase of k_{ap}. In the first case, the correlation coefficient R is 0.95; exclusion of the most deviating data for the acyl chloride-to-alcohol ratio equal to 7 : 1 gives $r = 0.97$.

In the entire series of experiments, an excellent linear correlation ($r = 0.99$) is observed between the apparent entropy and enthalpy of activation, i.e., an isokinetic relation exists (Fig. 2). The Gibbs energies of activation $\Delta G^{\neq}_{ap}$ remain essentially constant at all reactant ratios and are within the range 91.6–92.9 kJ/mol. Some reduction of $\Delta G^{\neq}_{ap}$ to 88–89 kJ/mol is observed only for large escess of RCOCl (6 : 1, 7 : 1). Therefore, we can presume a common reaction mechanism throughout the examined range of reactant ratios. However, the facts that the reaction is a two-step process and that k_{ap} increases with rise in the RCOCl : MeOH ratio indicate formal character of the activation parameters determined in such a way. Furthermore, the value of $\Delta G^{\neq}_{ap}$ determined at a reactant ratio of 1 : 1 (92.9 kJ/mol) is close to those found for the reaction of crotonoyl chloride with methanol in toluene (91 kJ/mol) [26] or of β,β-dimethylacryloyl chloride with methanol in benzene (83.2 kJ/mol) [3]. On the other hand, the energy of activation, $E^{\neq}_{ap}$ =

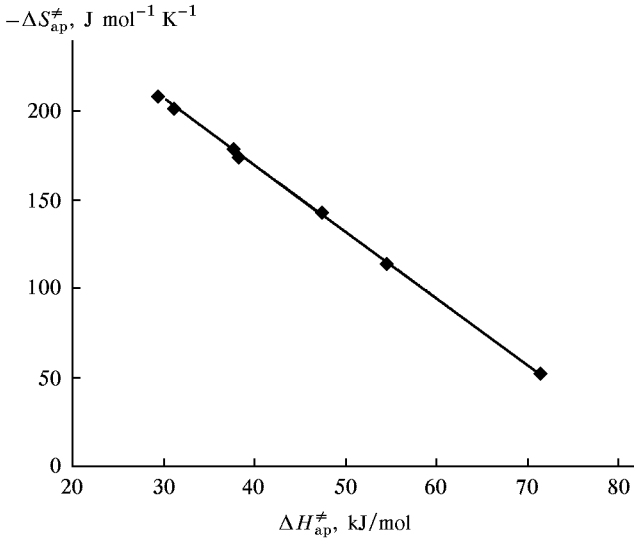


Fig. 2. Correlation between the apparent entropy and enthalpy of activation in the methanolysis of methacryloyl chloride in benzene at 303 K; RCOCl–MeOH molar ratio 1 : 1 to 7 : 1.

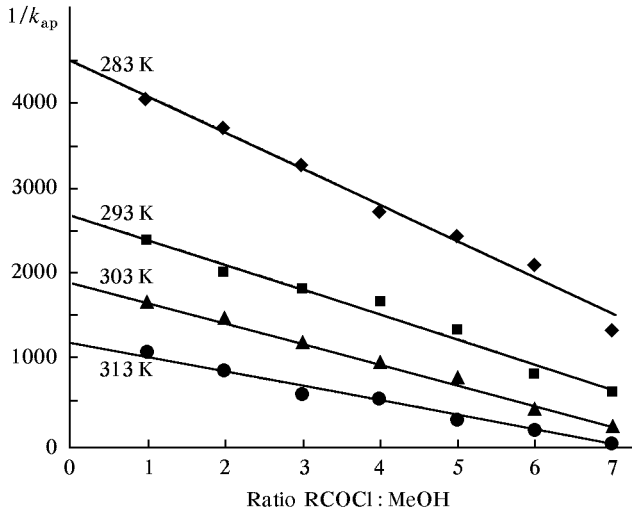


Fig. 3. Plots of the apparent rate constants for the methanolysis of methacryloyl chloride in benzene versus reactant molar ratio in the temperature range from 283 to 313 K.

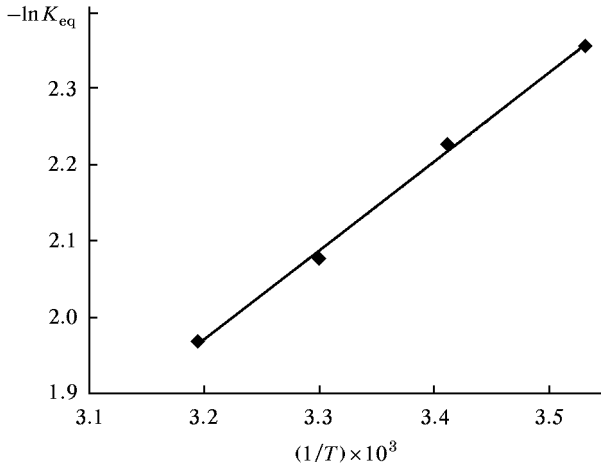


Fig. 4. Temperature dependence of the equilibrium constant for complex formation in the reaction of methacryloyl chloride with methanol in benzene.

32.3 kJ/mol, is considerably lower than the values reported in [3] and [26], 51.8 and 64.5 kJ/mol, respectively.

The variation of the apparent rate constants versus reactant ratio is excellently described in terms of the Michaelis–Menten equation (Fig. 3). The following linear relations ($r > 0.99$) were obtained:

$$283\ \text{K}: \quad 1/k_{ap} = -430.4\,C_A + 4533;$$

$$293\ \text{K}: \quad 1/k_{ap} = -286.4\,C_A + 2670;$$

$$303\ \text{K}: \quad 1/k_{ap} = -241.1\,C_A + 1922;$$

$$313\ \text{K}: \quad 1/k_{ap} = -165.9\,C_A + 1180.$$

From the slopes of these relations we can determine the rate constants k_{tr} for the transformation of intermediate H-complex or CTC into the products (ester and HCl), and from the intercepts on the *y* axis, which are equal to $K_{eq}^{-1} k_{tr}^{-1}$, the equilibrium constants for formation of CTC (K_{eq}) can be found (Table 3). It should be noted that, unlike the data of [23], k_{ap} values increase rather than decrease with rise in RCOCl excess.

The equilibrium constant for formation of charge-transfer complex RCOCl–MeOH are of a 10^{-1} order of magnitude, and (what is surprising) they increase as the temperature rises (Fig. 3). The most probable reason is that the process of decomposition of methanol dimer into monomeric molecules is energetically more favorable than decomposition of the RCOCl–MeOH charge-transfer complex, and the equilibrium is displaced to the right. On the other hand, the dependence of $\ln K_{ap}$ on $1/T$ is strictly linear ($r = 0.998$, Fig. 4), and the positive values of ΔG_{eq}, ΔH_{eq}, and ΔS_{eq} found for the complex formation and the low values of K_{eq} suggest that the formation of CTC is not favorable from the viewpoint of energy. In addition, the constant K_{eq} for formation of charge-transfer complex between methanol and benzoyl chloride [23] is higher by an order of magnitude, presumably due to greater electron-acceptor power of PhCOCl as compared to methacryloyl chloride.

The rate constants for the subsequent transformation of intermediate complex into the products are greater, on the average, by an order of magnitude than the apparent rate constants of the overall process at the same temperature (Tables 2, 3). This means that intermediate charge-transfer complex is unstable, which is consistent with the low energy of activation for its transformation into the products (–0.02 kJ/mol) and with the negative value of the enthalpy of activation (–2.5 kJ/mol). The negative $\Delta H_{tr}^{\neq}$ value originates from formation of stable HCl molecule. We shall not presume whether the transformation of CTC into the products is a one- or multistep process. The negative entropy of activation, $\Delta S_{tr}^{\neq} = -0.3$ kJ mol^{-1} K^{-1}, suggests that the rate-determining stage of the process is decomposition of CTC. It should also be noted that the overall Gibbs energy variation at both stages, formation of CTC ($\Delta G_{eq} = 5.3$ kJ/mol) and its decomposition ($\Delta G_{tr}^{\neq} = 88.1$ kJ/mol), is close to the apparent Gibbs energy of activation of the overall process, $\Delta G_{ap}^{\neq} = 92.9$ kJ/mol.

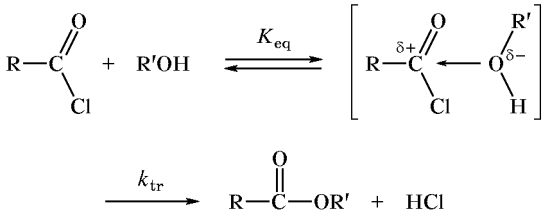
Thus the results of our study are consistent with the existing views on alcoholysis of acyl chlorides,

Table 3. Equilibrium constants K_{eq} and energy parameters for the formation of charge-transfer complex and rate constants k_{tr} and activation parameters for the transformation of charge-transfer complex into the products at 303 K[a]

Parameter	283 K	293 K	303 K	313 K	E_{tr}, kJ/mol	ΔH ($\Delta H^{\neq}$), kJ/mol	ΔS ($\Delta S^{\neq}$), J mol^{-1} K^{-1}	ΔG ($\Delta G^{\neq}$), kJ/mol
K_{eq}, l/mol	0.0949	0.1073	0.1254	0.1399	–	9.709	14.7	5.255
$-\ln K_{eq}$	2.355	2.232	2.076	1.967	–	–	–	–
k_{tr}, 10^3 s^{-1}	2.324	3.492	4.148	6.028	0.022	–2.497	–299	88.1
$-\log k_{tr}$	2.634	2.457	2.382	2.220	–	–	–	–

[a] For PhCOCl and MeOH at 318 K: $k_{tr} \times 10^3$ = 0.073 l mol^{-1} s^{-1}, K_{eq} = 1.09 l/mol [23].

which is assumed to proceed in two steps with initial formation of a charge-transfer complex between the reactants:



EXPERIMENTAL

Benzene, methanol, and methacryloyl chloride were reagent-grade products which were purified by thorough fractional distillation. Their physical constants coincided with published data.

The kinetics of the reaction of methacryloyl chloride with methanol were studied at acyl chloride–alcohol ratios of 1 : 1 to 7 : 1 using benzene as solvent (1 mol of methanol per 20 mol of benzene). A three-necked 100-ml reactor equipped with a reflux condenser, thermometer, and magnetic stirrer was charged with 64.6 ml (0.728 mol) of benzene and 1.47 ml (0.0364 mol) of methanol. The mixture was adjusted to a required temperature with an accuracy of ±0.5°C, and an appropriate amount of methacryloyl chloride, preliminarily adjusted to the same temperature, was added. This moment was taken as reaction start. The progress of the reaction was monitored following the amount of unreacted methacryloyl chloride, which was determined by potentiometric titration of a mixture of methacrylic and hydrochloric acids obtained after hydrolysis of the reaction mixture [27].

The reaction was carried out until 60–70% conversion of methacryloyl chloride. The apparent rate constants were calculated by the second-order equation from the data of 3–5 parallel runs (average values were taken). The accuracy of determination of the kinetic and activation parameters was estimated by the least-squares procedure with a confidence probability α of 0.95.

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