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Spectroscopic and Dielcometric Study of the Kinetics of Alcoholysis of Trichloroacetyl Chloride with Butanol

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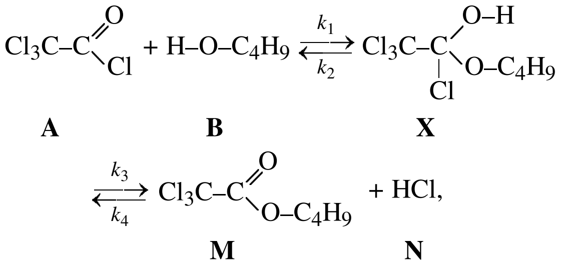
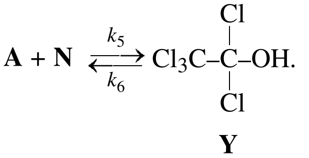
Abstract—The kinetics of alcoholysis of trichloroacetyl chloride with butanol in carbon tetrachloride were studied by dielcometry and IR spectroscopy. The reaction is reversible, and it involves intermediate formation of 1-butoxy-1,2,2,2-tetrachloroethanol and 1,1,2,2,2-pentachloroethanol.

We previously [1] studied the reaction of butyryl chloride with *n*-butanol in carbon tetrachloride and found that, in dilute solution, the alcoholysis is reversible and is accompanied by formation of two intermediates in detectable amounts. We thought it reasonable to continue our studies on the alcoholysis of acyl chlorides with examination of the effect of a strong electron-acceptor substituent in the substrate molecule on the formation and accumulation of intermediate products. The kinetics of the reaction of trichloroacetyl chloride with *n*-butanol in carbon tetrachloride were not studied previously. Our results showed that the reaction follows the scheme proposed in [1].



(1)



(2)

As in [1], the reaction kinetics were studied by IR spectroscopy and dielcometry. The carbonyl group of trichloroacetyl chloride in the initial solution absorbs at 1812 cm^{-1}; whereas the product, butyl trichloroacetate, gives rise to a carbonyl absorption band located at 1749 cm^{-1} (Fig. 1). The consumption of substrate **A** and accumulation of product **M** were quantitated from the optical densities *D* at the corresponding frequencies. Stretching vibrations of free hydroxy group in butanol in CCl$_4$ appear at 3644 cm^{-1} (Fig. 2), and absorption band belonging to the hydroxy group involved in hydrogen bonding is located at 3300 cm^{-1} [2].

Both IR spectrometric and dielcometric data revealed the same relations as those found previously in the system butyryl chloride–*n*-butanol–CCl$_4$. First, the reaction of trichloroacetyl chloride with *n*-butanol is reversible: in strongly dilute solution, the substrate conversion is as low as 17% (see table). Second, a significant imbalance is observed (Fig. 3, see table) between the amounts of the reacted trichloroacetyl

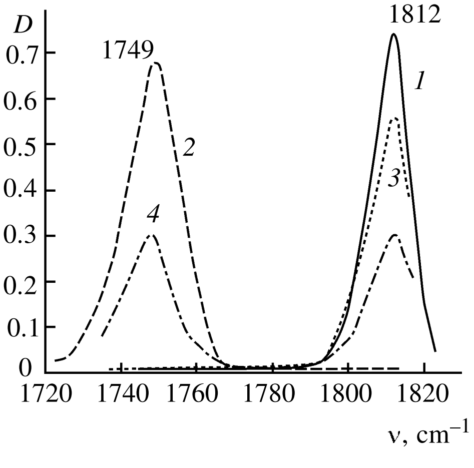


Fig. 1. IR spectra in the region of carbonyl group absorption of solutions in carbon tetrachloride (20°C) containing (*1*) 0.010 M of trichloroacetyl chloride, (*2*) 0.010 M of butyl trichloroacetate, (*3*) equilibrium mixture of 0.010 M of trichloroacetyl chloride and 0.010 M of *n*-butanol, and (*4*) equilibrium mixture of 0.045 M of trichloroacetyl chloride and 0.045 M of *n*-butanol (the thickness of the absorbing layer was correspondigly reduced).

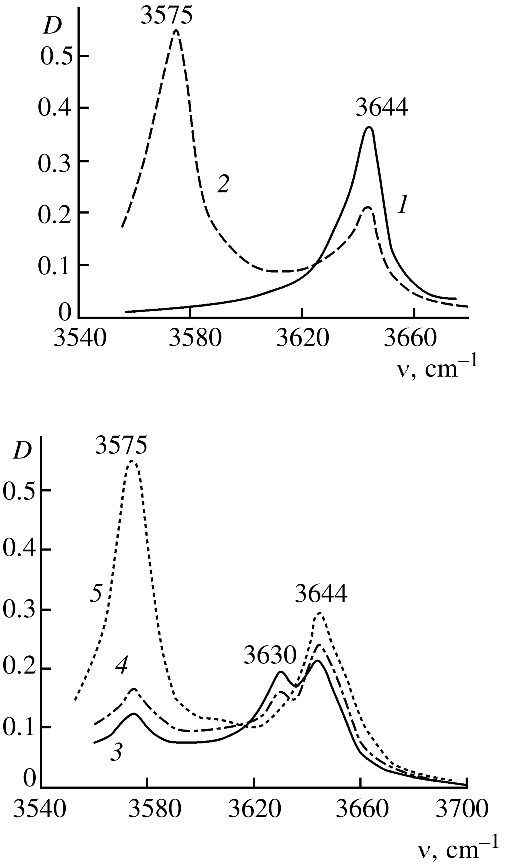


Fig. 2. IR spectra in the region of free hydroxy group absorption of solutions in carbon tetrachloride (20°C) containing (*1*) 0.010 M of *n*-butanol, (*2*) equilibrium mixture of 0.010 M of trichloroacetyl chloride and 0.010 M of *n*-butanol, (*3*) mixture of 0.470 M of trichloroacetyl chloride and 0.470 M of *n*-butanol, diluted with CCl_4 by a factor of 47 in 15 s after mixing the reactants (the spectrum was recorded in 45 s after dilution), (*4*) the same as (*3*) in 1.5 min after dilution; and (*5*) the same as (*3*) after 1 h.

chloride ($\Delta a = a_0 - a_\tau$) and final ester (m) by a time moment τ. The kinetic curves obtained by dielcometry (Fig. 4), $C = f(\tau)$, have a clearly defined maximum (C_M), indicating formation of a second intermediate product **Y**. Unlike butyryl chloride [1], the alcoholysis of trichloroacetyl chloride occurs at a higher rate, and the capacity maxima on the $C = f(\tau)$ curves are located appreciably closer to the y axis. In solutions with the initial reactant concentrations $a_0 = b_0 = 0.18$, 0.36, and 0.47 M, the time corresponding to the capacity maximum was 90, 30, and 20 s, respectively. In the system with $a_0 = b_0 = 0.70$ M, the capacity maximum was reached in less than 15 s (Fig. 4, curve *1*). In this case, the greatest relative gain in the capacity of the system ($\Delta C/C_0$) was observed; the C_0

Kinetic parameters of the reaction of trichloroacetyl chloride (*a*) with *n*-butanol (*b*) in carbon tetrachloride at 20C

Parameter[a]	Run no.				
	1	2	3	4	5
$a_0 = b_0$, M	0.010	0.045	0.180	0.360	0.470
Reaction time, min	120	100	50	40	35
C_0, pF	30	31	32	33	34
C_M, pF	30	31	36	59	110
$\Delta C = C_M - C_0$, pF	0	0	4	26	76
C_p, pF	30	32	33	42	53
$\Delta a_P = a_0 - a_P$, M	0.0017	0.0290	0.1430	0.3430	0.4630
m_P, M	0	0.0222	0.1210	0.3350	0.4460
x_P, M	0.0017	0.0068	0.0220	0	0
y_P, M	0	0	0.001	0.008	0.017
$(\Delta a_P/a_0) \times 100$	17	64	79	95	97
$(x_P/\Delta a_P) \times 100$	100	23	15	0	0
$(y_P/\Delta a_P) \times 100$	0	0	1	2	3.7
τ_{M1}, min	120	20	1	0.25	>0.25
Δa_{M1}, M	0.0017	0.0135	0.0700	0.0540	[b]
m_{M1}, M	0	0.0035	0.0390	0.0440	[b]
x_{M1}, M	0.0017	0.0100	0.0310	0	[b]
y_{M1}, M	0	0	0.001	0.010	[b]
$(x_{M1}/\Delta a_{M1}) \times 100$	100	74	44	0	[b]
$(y_{M1}/\Delta a_{M1}) \times 100$	0	0	2	18	[b]
τ_{M2}, min	[b]	[b]	1.50	0.50	0.33
Δa_{M2}, M	[b]	[b]	0.068	0.095	0.149
m_{M2}, M	[b]	[b]	0.037	0.073	0.085
x_{M2}, M	[b]	[b]	0.029	0	0
y_{M2}, M	[b]	[b]	0.002	0.022	0.064
$(x_{M2}/\Delta a_{M2}) \times 100$	[b]	[b]	43	0	0
$(y_{M2}/\Delta a_{M2}) \times 100$	[b]	[b]	3	23	43
k_1, mol^{-1} l min^{-1}	1.4 (3.0)[c]	1.9 (3.9)[c]	2.5	2.1	1.7
k_4, mol^{-1} l min^{-1}	–	0.8 (2.2)[c]	1.3	–	–
k_5, mol^{-1} l min^{-1}	–	–	–	14	–
k_2, min^{-1}	0.06 (0.12)[c]	0.09 (0.17)[c]	0.15	–	–
k_3, min^{-1}	–	0.08 (0.17)[c]	0.9	–	–
k_6, min^{-1}	–	–	–	8	–

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[a] $(a_P/a_0) \times 100$ (%) is the conversion of **A**. The quantities $(x_P/\Delta a_P) \times 100$, $(y_P/\Delta a_P) \times 100$, $(x_{M1}/\Delta a_{M1}) \times 100$, $(y_{M1}/\Delta a_{M1}) \times 100$, $(x_{M2}/\Delta a_{M2}) \times 100$, and $(y_{M2}/\Delta a_{M2}) \times 100$ (%) are the yields of products **X** and **Y** when the corresponding concentrations x_P, y_P, x_{M1}, y_{M1}, x_{M2}, and y_{M2} are reached.

[b] No maximum.

[c] In parentheses are given the rate constants measured at 48°C.

value was determined by extrapolation of the linear relation $C_0 = f(a_0)$ to the initial concentration $a_0 = b_0 = 0.70$ M. The smallest gain in the capacity of the system was observed at $a_0 = b_0 = 0.18$ M (Fig. 4, *4*). No capacity gain was detected at all for more dilute solutions (see table), whereas the concentration disbalance ($\Delta a - m$) was the greatest. Thus, the kinetic relations holding in the reaction under study are identical to those observed in the alcoholysis of butyryl chloride in the same solvent. In the two systems, accumulation of two intermediate products **X** and **Y** occurs; the former prevails in dilute solutions, and the latter, in concentrated.

In order to elucidate the structure of intermediates **X** and **Y** [reactions (1) and (2)], the IR spectra of dilute samples were recorded. In the IR spectrum of a solution with the initial reactant concentrations $a_0 = b_0 = 0.01$ M, we observed a broad absorption band at 3300 cm^{-1} and two bands in the region corresponding to stretching vibrations of a free hydroxy group, at 3644 and 3575 cm^{-1} (Fig. 2; the band at 3300 cm^{-1} is not shown). The bands at 3300 and 3644 cm^{-1} belong to *n*-butanol, and the band at 3575 cm^{-1}, to intermediate **X**, as far as just that intermediate accumulates in dilute solutions.

In the IR spectrum of the reaction mixture with $a_0 = b_0 = 0.47$ M, diluted by a factor of 47 (to a concentration of 0.01 M) with carbon tetrachloride, at a moment corresponding to the maximal capacity, we observed a broad band at 3300 cm^{-1}, corresponding to residual absorption of H-bonded hydroxy group, and three bands in the region of stretching vibrations of free hydroxy group at 3644, 3630, and 3575 cm^{-1}. The band at 3644 cm^{-1} belongs to unchanged *n*-butanol. The band at 3575 cm^{-1} was assigned to intermediate **X**, and the third band (3630 cm^{-1}), which was not observed previously for this system, is likely to arise from the second intermediate (**Y**). The stretching vibration frequency of the O–H bond is reduced due to the presence of CCl_3 group in the α-position [3–6]. The OH group can be involved in intramolecular hydrogen bond with chlorine atom of the CCl_3 group in **X**, thus forming a five-membered H-chelate ring [6, 7]. This also reduces the OH stretching vibration frequency. According to theoretical calculations [8] (no experimental spectra of compounds **X** and **Y** are available from the literature, except for our data [1]), the OH stretching vibration frequency increases as hydrogen atoms in the α-positions are replaced by chlorine. As a result, we have a frequency of 3575 cm^{-1} which is observed experimentally for intermediate **X**. The OH vibration frequency in molecule **Y**, which contains two chlorine atoms in the α-position with respect to the hydroxy group, is larger (3630 cm^{-1}).

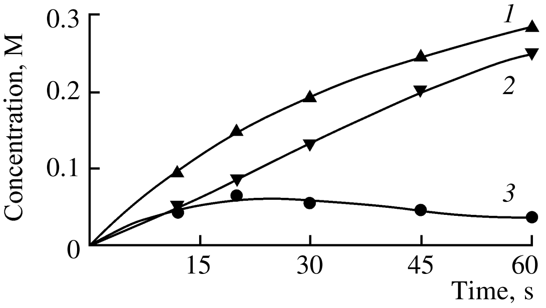

Fig. 3. Kinetic curves for (*1*) consumption of trichloroacetyl chloride, (*2*) accumulation of butyl trichloroacetate, and (*3*) accumulation of intermediate **Y**; $a_0 = b_0 = 0.470$ M (CCl_4, 20°C).

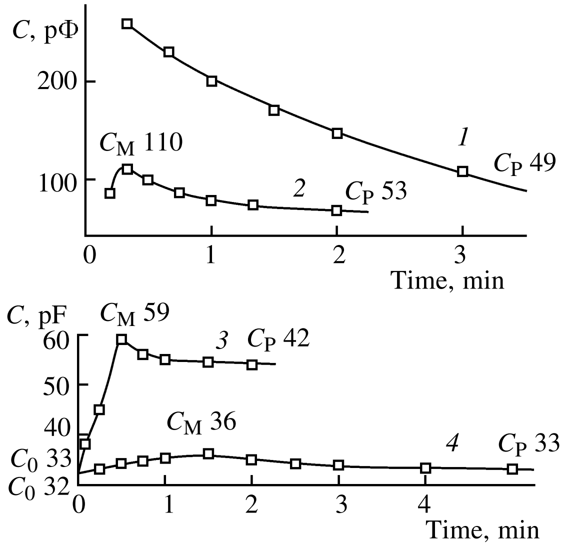

Fig. 4. Plots of the electric capacity vs. time for solutions with various initial concentrations of trichloroacetyl chloride and *n*-butanol (CCl_4, 20°C); concentration, M: (*1*) 0.700, (*2*) 0.470, (*3*) 0.360, and (*4*) 0.180.

The formation in the system of two intermediate products **X** and **Y** is confirmed by the variation of the IR spectra of a dilute sample of the reaction mixture with time (Figs. 2, curves *3* and *4*): the intensity of the band at 3630 cm^{-1} decreases, while the band at 3575 cm^{-1} becomes stronger. The former completely disappears in 1 h after dilution, while the latter reaches its maximal intensity (Fig. 2, curve *5*). Curve *5* in Fig. 2 coincides with curve *2* obtained for the system with $a_0 = b_0 = 0.01$ M. In such a way, the system comes again to the equilibrium state via accumulation of intermediate **X**, which is typical of dilute solution.

Thus, the kinetic, spectroscopic, and dielcometric data confirm the validity of the proposed scheme for alcoholysis of trichloroacetyl chloride with *n*-butanol in carbon tetrachloride, which involves formation of two intermediate products **X** and **Y** (1-butoxy-1,2,2,2-tetrachloroethanol and 1,1,2,2,2-pentachloroethanol, respectively).

The rate constants for alcoholysis of trichloroacetyl chloride with *n*-butanol were calculated with the use of differential equations, material balance equations, and calibration curve for converting the capacity ΔC into concentration of **Y**, proposed in [1]. The calculated values are given in table. The rate constants for the system under study were higher by a factor of 3–5 (and in some cases by an order of magnitude) than the corresponding rate constantrs for the alcoholysis of butyryl chloride [1]. These data suggest that the electron-acceptor CCl_3 group considerably increases the reactivity of both the carbonyl group in the substrate and intramolecularly reacting groups in intermediates **X** and **Y**. All rate constants depend on the initial reactant concentrations due to effect of intermolecular hydrogen bonding [9, 10].

EXPERIMENTAL

Dielcometric measurements were performed on an E 8-4 digital capacitometer at a frequency of 1000 s^{-1}. The IR spectra were recorded on a Specord M-80 spectrometer. All reagents were of analytical grade. The concentration dependences of the capacity and optical density *D* of the examined solutions were linear. The concentration of trichloroacetyl chloride was determined by the internal standard technique (following the decrease in the optical density *D*), and the concentration of *n*-butyl trichloroacetate was determined from the increase in *D* using a calibration curve plotted for 100% conversion. The rate constants were determined with an accuracy of ±7% (k_1–k_4) and ±20% (k_5, k_6).

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