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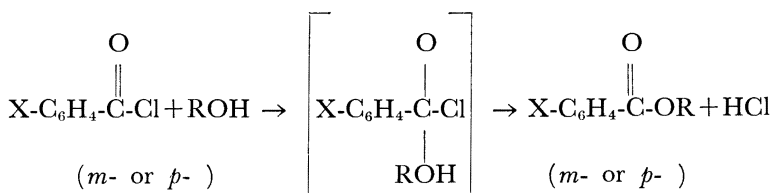
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Reaction Kinetics of the Alcoholysis of Substituted Benzoyl Chlorides

By B. R. BLUESTEIN, ALBERT HYBL* AND YOSHIMI AL NISHIOKA

INTRODUCTION

The reaction kinetics of the alcoholysis of substituted benzoyl chlorides was studied. The mechanism of the alcoholysis reaction, which is most generally accepted (1), shows that the overall reaction should be second-order and that the reaction should be first-order with respect to the acid chloride and first-order with respect to the alcohol. This rate study was carried out using a large excess of alcohol as the solvent, thus obtaining pseudo-first order rate constants, first-order with respect to the acid chloride only.



The rate of product formation was followed by conductance measurements. Since the hydrochloric acid is the only conducting species among the reactants and products, an increase in the conductance corresponds to an increase in hydrochloric acid concentration.

A few preliminary experiments using benzoyl chloride with absolute ethanol and with 95% ethanol were carried out to check the conductance cell and apparatus and to compare results from this work with other published experimental values.

The rate constants of the reaction of substituted benzoyl chlorides with *n*-propanol were determined at 25°. Hammett's equation (2) was found to be applicable to the rate values obtained from this study. This result is consistent with the general alcoholysis equation.

EXPERIMENTAL

The conductivity of the alcohol solution was determined through the measurement of the resistance of the solution with the usual

*From the Major Honors Thesis of Albert Hybl, Coe College, 1954.

type of Wheatstone bridge. The apparatus is schematically diagrammed in Fig. 1. A 1000 cycle per second audio-frequency oscillator was used as the signal generator.

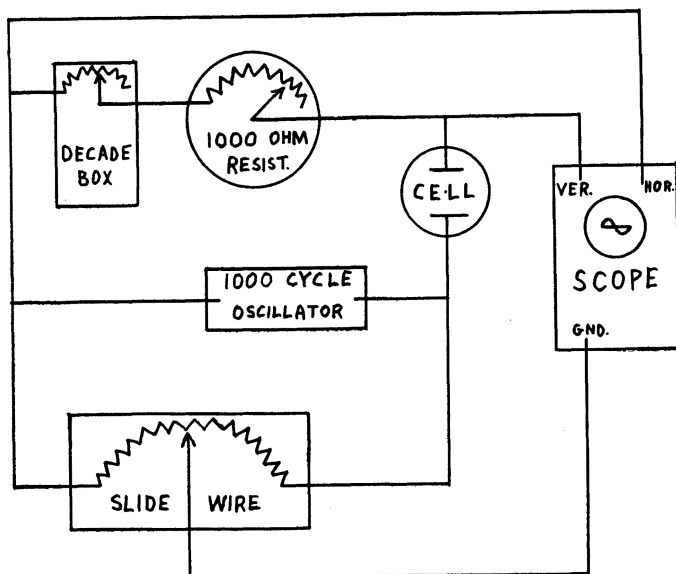


Fig. 1. Diagram of Bridge Circuit

The slide wire was set at the 50-50 mark as soon as the resistance of the solution decreased to 2000 ohms. This took from 2-5 minutes. Then the decade resistance boxes (0.1% accuracy) were used to balance the bridge, which in effect was a direct reading equal-arm bridge. A Heath-kit oscilloscope was used as the signal detector.

The conductivity cell* was made from a 50-ml. 3-necked standard taper Grignard flask. The platinized platinum electrodes were sealed into male standard taper joints and placed in the two outside necks of the flask. The middle neck was closed with a standard taper glass stopper. The cell constant was 0.665 ± 0.003 , although the value was not needed for the calculations in this research study.

A constant temperature bath was used to keep the conductivity cell at a constant reaction temperature of $25.02 \pm 0.02^\circ$.

The following general procedure was used in all of the reaction rate runs. From a 50-ml. buret 34.80 ± 0.05 ml. of alcohol was added to the conductivity cell. The cell and alcohol was thermostated in the constant temperature bath at $25.02 \pm 0.02^\circ$. Then

*The authors are grateful to Collins Radio Co., Cedar Rapids, Iowa, for the construction of the cell and the use of the platinum electrodes.

the acid chloride was added to the cell and the time readings were started. The contents of the cell were mixed together immediately. The bridge was kept in balance by adjusting the decade resistance boxes. The resistance of the alcohol solution was recorded each minute until about 95% of the reaction had been completed. The infinite resistance value was obtained by allowing the reaction to go to completion, or until there was no further change in the resistance value. After each rate run, the amount of acid present was determined by titration with standard base.

The resistance of the *n*-propanol reaction solution was inversely proportional to the concentration of hydrochloric acid in the alcohol above 0.0347 *M*. This relationship was obtained by adding known amounts of benzoyl chloride to 34.80 ± 0.05 ml. samples of *n*-propanol and allowing the reaction to go to completion. The infinite resistance was measured using the conductivity cell. Then the reciprocal of the infinite resistance for each sample was plotted against the molar concentration of benzoyl chloride in *n*-propanol, which is equivalent to the molar concentration of hydrochloric acid in *n*-propanol. The reciprocal of the resistance was linear with the concentration within experimental error above 0.0347 *M*.

The rate equation which applies to the pseudo-first order chem-

ical reaction is $k = \frac{2.303}{t} \log \frac{a}{a-x}$. Since there is a linear relationship between the concentration of the product and the conductance

above 0.0347 *M*, $\frac{a}{a-x} = \frac{L_{\infty} - L_0}{L_{\infty} - L}$ (3). Then $\frac{a}{a-x} =$

$$\left(\frac{1}{R_{\infty}} - \frac{1}{R_0} \right) \bigg/ \left(\frac{1}{R_{\infty}} - \frac{1}{R} \right) = \frac{(R_0 - R_{\infty}) R}{R_0 (R - R_{\infty})}; \text{ where } R_0 \text{ is}$$

the resistance at the initial time obtained by extrapolation of the concentration-conductance curve, R_{∞} is the resistance of the solution at the completion of the reaction, and R is the resistance at

time t . Therefore, $k = - \frac{2.303}{t} \left[\log \frac{R - R_{\infty}}{R} - \log \frac{R_0 - R_{\infty}}{R_0} \right]$

The plotting of t against $\log \frac{R - R_{\infty}}{R}$ should and did give a straight line.

The substituted benzoyl chlorides were purified by vacuum distillation. Their properties are listed in Table I. The acid chlorides were prepared from the purified benzoic acids by reacting them with excess thionyl chloride.

Table 1
Properties of Substituted Benzoyl Chlorides (X-C₆H₄COCl)

Substit. Group <i>X</i>	M.P.	B.P. (4mm.)	Neutr. Equiv.	
			Calcd.	Found
H	36-9°	70.30	70.31
<i>m</i> -CH ₃ O	65°	85.30	86.35
<i>p</i> -Br	40-1.8°	80°	109.7	106.7
<i>p</i> -I	70-1°	90°	133.2	134.8
<i>m</i> -I	85°	133.2	134.5

The commercial 95% ethanol was used without purification. Absolute ethanol was prepared according to the procedure described by Fieser(4); b.p. 78.5°. *n*-Propanol was purified by rectification of Eastman Kodak white label grade; b.p. 97°.

DISCUSSION

The reaction rate constant of benzoyl chloride with excess commercial 95% ethanol at 25.02 ± 0.02° was found to be 0.0852 min⁻¹. Titration of the reaction mixture after the reaction had been completed showed an excess of 11.14% of acid above the amount of acid expected from the alcoholysis reaction. These results are listed in Table 2. Most likely this excess of acid is due to the formation of benzoic acid by part of the benzoyl chloride undergoing hydrolysis with the water.

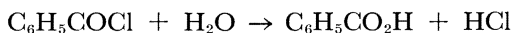


Table 2
Reaction of Benzoyl Chloride with 95% Ethanol at 25°

Molarity (m./l.)	<i>k</i> (min ⁻¹)	Titration (excess acid)
0.0398	0.0848	+11.87%
.0478	.0842	+10.32
.0626	.0855	+11.24
.0815	.0822	
.1463	.0895	Av. +11.14%
Av. 0.0852 ± .0018		

The reaction rates of these two simultaneous reactions can be calculated from the amount of benzoic acid, 11.14%, which formed and from the overall rate constant. The reaction rate of the hydrolysis reaction is 0.00949 min⁻¹ (11.14% x 0.0852 min⁻¹). The reac-

tion rate of the alcoholysis reaction is $0.0757 \text{ min}^{-1}\{(100 - 11.14\%) \times 0.0852\}$. These rate constants were compared with literature values.

Archer and Hudson(5) reported rate constants for the hydrolysis of benzoyl chloride with water in acetone solutions of varying concentrations at 25° . By graphical interpolation at a concentration of 6.22% water by volume, the value of 0.0042 min^{-1} was obtained for the rate constant of hydrolysis of benzoyl chloride in the water-acetone solution. The 6.22% figure is equivalent to the amount of water in commercial 95% ethanol.

The rate of alcoholysis of benzoyl chloride in the absolute ethanol at 25° was found to be 0.047 min^{-1} by Norris, Fasce and Staud(6). This value is in good agreement with the value of 0.0492 min^{-1} obtained in this research. Titration of the completed reaction mixtures showed that no excess acid had formed. This is expected, since there is no water present for the hydrolysis side-reaction to occur. These rate runs are shown in Table 3.

Table 3

Reaction of Benzoyl Chloride with Abs. Ethanol at 25°

<i>Molarity (m./l.)</i>	<i>k(min⁻¹)</i>	<i>Titration (excess acid)</i>
0.0601	0.0478	
.0661	.0493	
.0672	.0505	+0.09%

The values for alcoholysis with absolute ethanol and for hydrolysis with 6.22% water in acetone, 0.0492 min^{-1} and 0.0042 min^{-1} respectively, are of the same order of magnitude as the calculated values for alcoholysis and for hydrolysis from the competitive reactions with 95% ethanol, 0.0757 min^{-1} and 0.00949 min^{-1} , respectively. The latter values should be somewhat larger since the 95% ethanol is more polar than the absolute ethanol or 6.22% water-acetone, and thus the reaction velocities are increased.

n-Propanol was used as the alcohol reactant for the major portion of this research. It is interesting to note that fairly consistent rate constant values were obtained using different samples of *n*-propanol. Five different samples of *n*-propanol were purified, from five different stock samples of *n*-propanol. An average value of 0.0327 min^{-1} was obtained with only a slight deviation. This shows that the use of one stock sample of alcohol would introduce only a very slight systematic error. These rate runs are summarized in Table 4.

The rate constants for the reactions of the substituted benzoyl chlorides with *n*-propanol at $25.02 \pm 0.02^\circ$ were obtained using

Table 4
Reaction of Benzoyl Chloride with Different Samples of n-Propanol at 25°

Sample	Molarity (<i>m./l.</i>)	$k(\text{min}^{-1})$	Titration (<i>excess acid</i>)
A	0.1225	0.0354	+1.22%
A	.1521	.0331	-0.36
B	.0753	.0342	+0.65
B	.1327	.0319	+0.09
B	.1391	.0314	-0.10
C	.0929	.0300	-0.90
C	.0963	.0313	-0.68
D	.1728	.0353	-2.40
E	.1318	.0322	+0.12
E	.1548	.0321	-0.61
Av. 0.0327 ± 0.0012			Av. -0.30

one stock sample of *n*-propanol. The compounds used were benzoyl chloride, *m*-methoxybenzoyl chloride, *p*-bromobenzoyl chloride, *p*-iodobenzoyl chloride, and *m*-iodobenzoyl chloride. The rate constants, which are summarized in Table 5, were in the same order

Table 5
Rate Constants for the Reaction of X-C₆H₄COCl with n-Propanol at 25.02 ± 0.02°

Substit. X	Molarity (<i>m./l.</i>)	$k(\text{min}^{-1})$	Titration (<i>excess acid</i>)
H	0.1318	0.0322	+0.12%
H	.1548	.0321	-0.61
		Av. 0.0321	
<i>m</i> -CH ₃ O	0.1057	0.0339	-0.92%
<i>m</i> -CH ₃ O	.1112	.0341	-0.37
		Av. 0.0340	
<i>p</i> -Br	0.1156	0.0585	-2.12%
<i>p</i> -Br	.1497	.0595	-3.24
		Av. 0.0590	
<i>p</i> -I	0.1071	0.0620	-0.43%
<i>p</i> -I	.1229	.0614	-0.04
		Av. 0.0617	
<i>m</i> -I	0.0622	0.1027	+3.23%
<i>m</i> -I	.0983	.1061	+0.77
		Av. 0.1044	

of correspondence as the values of Norris, Fasce and Staud(6) and Norris and Young(7) for the reactions of substituted benzoyl chlorides with absolute ethanol at 0°. Also, the values are consistent for the mechanism of the acid chloride - alcohol reaction, as expected by the effect of the substituents in the benzene ring. This effect is shown mathematically by the use of Hammett's equation (2). The rate constants for the different substituted benzoyl chlorides were plotted against Hammett's sigma values (Fig. 2). The values of

Norris, et al. (6, 7) were also plotted on the same graph. The rho values were similar for the reactions of substituted benzoyl chlorides with absolute ethanol at 0° (6, 7) and with *n*-propanol at 25°.

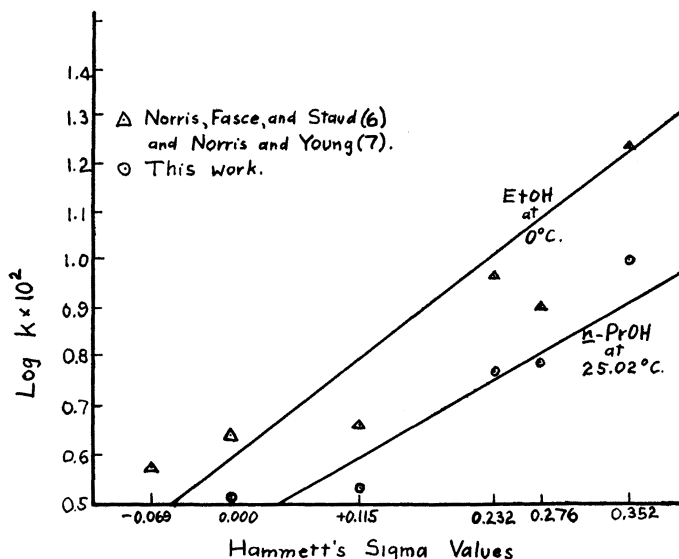


Fig. 2. Application of Hammett's Equation

SUMMARY

A study of the reaction rate of benzoyl chloride with excess 95% ethanol at 25° has been made. Apparently, two simultaneous reactions occur, a hydrolysis reaction with the water ($k=0.00949 \text{ min}^{-1}$) and an alcoholysis reaction with the ethanol ($k=0.0757 \text{ min}^{-1}$).

The effect of different substituents in the benzene ring on the pseudo-first order rate constants of the reaction of substituted benzoyl chlorides with excess *n*-propanol at 25° has been studied. The following results were obtained: benzoyl chloride, $k = 0.0321 \text{ min}^{-1}$; *m*-methoxybenzoyl chloride, $k = 0.0340 \text{ min}^{-1}$; *p*-bromobenzoyl chloride, $k = 0.0590 \text{ min}^{-1}$; *p*-iodobenzoyl chloride, $k = 0.0617 \text{ min}^{-1}$; and *m*-iodobenzoyl chloride, $k = 0.1044 \text{ min}^{-1}$.

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