

pressure. This function could be best expressed as $K_0 - 1/(a + bP_{O_2})$, in which K_0 , a and b are constants.

The character of this function was explained on the assumption that there are two mechanisms, for the reaction. One of these is a dissociation into free radicals followed by a very rapid oxidation. The other is a direct oxidation. On these assumptions alone the function would be $a + bP_{O_2}$; its more complicated form was assumed to be due either to a consistent error, or to the formation of an active intermediate which is held in a steady state other than its true equilibrium ratio with normal hexaphenyl-ethane.

The logarithm of the rate constant was found not to be a linear function of $1/T$. The calculated heats of activation increase with temperature, but are approximately constant to change of the oxygen pressure.

The reaction was not inhibited by diphenylamine, anthracene nor phenol. The last substance increased the rate.

BERKELEY, CALIFORNIA

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 49]

THE RATE OF REACTION OF CERTAIN ALCOHOLS WITH PARA-NITROBENZOYL CHLORIDE IN ANHYDROUS ETHER SOLUTION

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The speed of ester formation from alcohols and *p*-nitrobenzoyl chloride, in ether solution, has been studied in this Laboratory as a means for measuring the relative reactivity of the hydroxyl hydrogen of the alcohols. In two earlier papers,² the influence of the structure of the alcohols on the rate of the reaction has been discussed.

Although the net result of the reaction consists in the formation of a molecule of hydrogen chloride and one of an ester, from one molecule each of alcohol and acid chloride, the second-order velocity constants decrease steadily as the reaction proceeds. This peculiarity was observed with all of the twenty-nine alcohols studied, and it is not dependent on the type of alcohol, whether primary, secondary or tertiary. Furthermore, if the original molal solutions are replaced by half-molal ones, the second-order constants are much smaller and, as before, decrease with the progress of the reaction. If the drop in the value of the second-order reaction constants were attributable to the non-ideality of solution alone,

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² (a) Norris and Ashdown, *THIS JOURNAL*, **47**, 837 (1925); (b) Norris and Cortese, *ibid.*, **49**, 2640 (1927).

then the half-molal solutions would be expected to give both a higher and a more steady value for the constant. The very reverse of this, found by experiment, led to a study of the law of the reaction rate as a possible means of throwing light on the mechanism involved.

At the outset, a graphical analysis of the data for methyl and ethyl alcohols showed that the reaction was of an order higher than second, probably of the third order. The integrated form of the second-order equation for equal molal concentrations, $KtC_0 = x/(1-x)$, in terms of the fraction, x , of reactant transformed, is linear. Plotting values of $x/(1-x)$ against t should give a straight line. In all cases, however, the data led to a smooth curve, bending toward the t -axis (Fig. 1, Curve A, *n*-butyl alcohol). The slopes of this curve, corresponding to values of the constant, K , are steadily decreasing. The following considerations show how the graphically observed change in K indicates a third-order reaction. For a second-order reaction between two compounds at equal concentrations

$$dx/dt = k(1-x)^2 \text{ or } dx/(1-x)^2 = kdt$$

but

$$d\left(\frac{x}{1-x}\right) = dx/(1-x)^2 = kdt$$

In the case of a third-order reaction (equal concentrations), however

$$dx/dt = k(1-x)^3 = k(1-x)^2(1-x)$$

In other words, for a third-order reaction

$$d(x/1-x) = k(1-x)dt$$

This equation obviously satisfies the condition observed graphically and strongly suggests a reaction of the third order.

In the light of this indication, the data on all twenty-nine alcohols were calculated using the third-order equation for equal molal concentra-

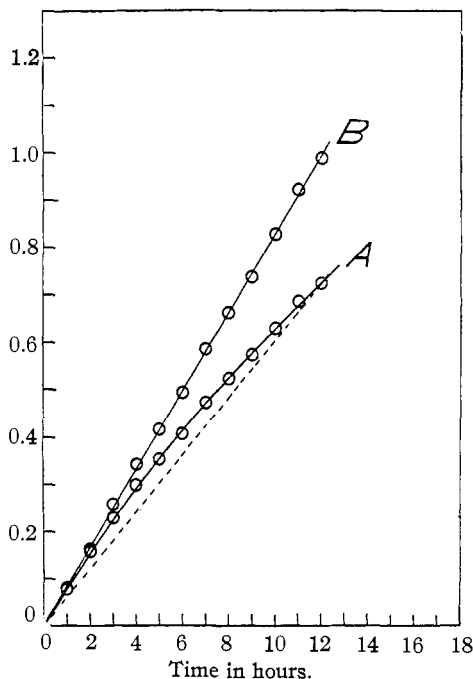


Fig. 1.—Rate of reaction of *n*-butyl alcohol with *p*-nitrobenzoyl chloride. Curve A, data calculated as a second-order reaction. $x/(1-x)$ plotted against t in hours. Curve B, data calculated as a third-order reaction. $x(2-x)/2(1-x)^2$ plotted against t in hours.

tions. For all cases throughout a given run the constants thus obtained were steady, not decreasing as did the second-order constants. Furthermore, the half-molal solutions yielded third-order constants which were higher than those for molal solutions, a consequence to be expected if the reactions were of the third order, and the solutions not ideal. In Table I the second- and third-order constants for *n*-butyl alcohol are given as an example.

TABLE I

n-BUTYL ALCOHOL AND *p*-NITROBENZOYL CHLORIDE AT EQUAL MOLAL CONCENTRATIONS

Molal					Half molal				
<i>t</i>	<i>x</i>	K_2^1	K_3^1	K_3^0	<i>t</i>	<i>x</i>	$K_2^{0.5}$	$K_3^{0.5}$	K_3^0
1	0.0717	0.0772	0.080	0.119	1	0.0266	0.055	0.110	0.138
2	.1366	.0791	.085	.125	2	.0452	.047	.097	.121
3	.1877	.0770	.086	.124	3	.0727	.052	.107	.134
4	.2302	.0747	.086	.123	4	.0854	.047	.098	.121
5	.2614	.0708	.083	.119	5	.1035	.046	.098	.121
6	.2895	.0679	.082	.116	6	.1146	.043	.092	.114
7	.3212	.0675	.084	.117	7	.1366	.045	.098	.120
8	.3439	.0654	.083	.115	8	.1506	.044	.097	.117
9	.3663	.0638	.082	.113	9	.1632	.043	.095	.115
10	.3862	.0630	.083	.114	10	.1736	.042	.093	.114
11	.4071	.0624	.084	.115	11	.1840	.041	.091	.112
					12	.1963	.041	.091	.112

K_2^1 and $K_2^{0.5}$ are second-order and K_3^1 and $K_3^{0.5}$ are third-order constants at molal- and half-molal concentrations. K_3^0 is the third-order constant at infinite dilution, computed analytically. *t* = time in hours.

Curve B, Fig. 1, also shows how the data from *n*-butyl alcohol conform to a third-order reaction. The integrated form of the third-order equation, equal molal concentrations, in terms of the fraction, *x*, of reactant used is

$$KtC_0^2 = \frac{x(2-x)}{2(1-x)^2}$$

It should yield a straight line if the numerical value of the right-hand member of the equation be plotted against *t*.

Description of Experiments

When the calculation of the third-order constants was completed, the reaction rate was tested by a series of experiments. The method for measuring the rates and the details for purifying the compounds have been described rather completely in two previous papers.² The procedure consisted in dissolving the acid chloride in anhydrous ether contained in a glass-stoppered Erlenmeyer flask, placing the flask in a thermostat at 25°, adding alcohol equivalent to the acid chloride and following the rate by titrating the hydrogen chloride produced. All concentrations were in moles per thousand grams of ether.

In a modification of the method, equal volumes of the reaction mixture, measured from a buret, were sealed in small glass vials. These were placed in the thermostat and at appropriate intervals a vial was taken out and the entire contents titrated for hydrogen chloride. This modified method was tested with *n*-butyl alcohol and found to give re-

sults like those obtained in the earlier procedure. The sealed vials were particularly advantageous where dry hydrogen chloride was added to the reaction mixture at the start.

The reversibility of the reaction was tested by dissolving equal molal quantities of ethyl *p*-nitrobenzoate and dry hydrogen chloride in anhydrous ether. The mixture was kept at 25° in the thermostat for forty-three hours. The hydrogen chloride was not absorbed, showing that the tendency to reverse must be very small under the conditions at which the reaction rates were measured. Dry hydrogen chloride was prepared by dropping pure concentrated sulfuric acid onto c. p. sodium chloride, passing the gas through two wash bottles containing pure concentrated sulfuric acid and finally through a 50-cm. column of phosphorus pentoxide.

In two trials the products of the reaction were shown to have no effect on the rate. Equal molal quantities of *n*-butyl alcohol, the acid chloride and dry hydrogen chloride were dissolved in anhydrous ether. The usual rate for *n*-butyl alcohol was observed, showing, in this case, that the decrease in the second-order constants could not be due to the influence of the hydrogen chloride evolved. A similar result was obtained for ethyl alcohol when a mole of ethyl *p*-nitrobenzoate was added to the reaction mixture at the start. The rate was unaffected by the presence of the ester in this instance.

Two experiments were carried out with *n*-butyl alcohol to test the effect on the rate of changing the concentrations of the reactants with respect to each other. If the reactions were of the second order, then the same rate would be observed whether the alcohol concentration were twice that of the acid chloride or *vice versa*. If, however, the reactions were of the third order, then the rate would be much greater in one case than in the other.³

It was found that the speed of the reaction was much faster when the concentration of the alcohol was twice that of the acid chloride than when the reverse relations were tried. Table II shows these differences. After ten hours 0.23 mole of the acid chloride had reacted when the concentrations were one mole of alcohol to half a mole of acid chloride. With the conditions reversed, however, only 0.16 mole of the acid chloride had reacted after ten hours

TABLE II

n-BUTYL ALCOHOL WITH *p*-NITROBENZOYL CHLORIDE IN ANHYDROUS ETHER SOLUTION

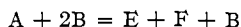
Alcohol, moles per 1000 g. of ether	1.0	0.5
Acid chloride, moles per 1000 g. of ether	0.5	1.0
Moles of chloride reacted in ten hours	0.229	0.163

Development of an Equation for Calculating the Velocity Constants for the Reaction of Alcohols with *p*-Nitrobenzoyl Chloride in Ether Solution at Infinite Dilution.—The experiments just described, showing the great influence on the speed of the reaction conditioned by changing the concentration of the alcohol, both strengthened the earlier conviction that the reaction was of the third order and suggested the notion that two

³ This excellent method for testing the order of a reaction was employed first by van't Hoff over forty-five years ago, "Études de dynamique chimique," Amsterdam, 1884. Its usefulness was emphasized by A. A. Noyes in the course of an investigation of the rate of reaction of ferric chloride with stannous chloride, Noyes, *Z. physik. Chem.*, 16, 554 (1895).

molecules of alcohol might be required for each molecule of chloride used. Such a process would be in harmony with certain general views⁴ concerning the mechanism of organic chemical reactions. The first step could be taken to be the addition of a molecule of alcohol to the acid chloride. The unstable complex could then react with another molecule of alcohol, splitting out the ester and hydrogen chloride and giving back a molecule of alcohol.⁵

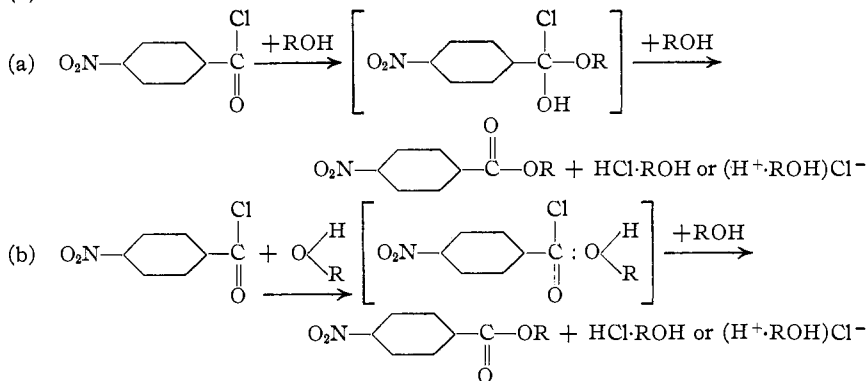
The equation for the reaction may be symbolized as follows⁶



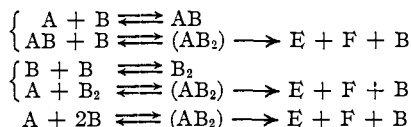
where A = acid chloride and B = alcohol. By using the ideas of the activity theory as applied to reaction rates,⁷ and Brönsted's assumption of the critical complex,⁸ an equation has been developed on the basis of this mechanism for calculating the velocity constants of these esterification reactions at infinite dilution.

⁴ See, for example, Stieglitz, *Am. Chem. J.*, **39**, 60 (1908); *THIS JOURNAL*, **32**, 221 (1910).

⁵ It is conceivable that the reaction might be formulated either on the basis of the ordinary conception of valency (a) or by making use of the electronic theory of valence (b).



Actually by rates of reaction studies, it cannot be determined whether or not the mechanism takes any one of the following courses, all of which lead to the same "complex," AB₂.



⁶ The integration of this equation and its use for chemical reactions of the third order under ideal conditions has been considered in detail by F. E. E. Germann, *J. Phys. Chem.*, **32**, 1748 (1928).

⁷ An excellent survey of the activity theory and a bibliography have been published by Harned and Seltz, *THIS JOURNAL*, **44**, 1475 (1922).

⁸ J. N. Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925).

According to Brönsted

$$\frac{-dC_A}{dt} = \frac{-dC_B}{dt} = KC_B^2 C_A \frac{f_B^2 f_A}{f_x} \quad (1)$$

where C 's are concentrations, f 's are activity coefficients, and f_x refers to the critical complex, AB_2 . The activity theory differs from this formulation only in replacing f_x by unity.

The alcohols give rise to very abnormal solutions, as shown by molecular weight determinations from freezing-point measurements in non-polar solvents.⁹ Unquestionably these solutions differ enough from ideality to warrant consideration. Experiments already mentioned have shown in two cases that the acid and ester formed have practically no effect on the rate of the reaction. Even greatly changing the concentration of the acid chloride does not produce a very marked influence on the rate. It appeared reasonable, therefore, to assume that the substances, other than the alcohols, did not give wide deviations from ideal solutions. Nothing could be known, of course, of the values for the critical complex, but it seemed reasonable to assume (f_A/f_x) constant for all the solutions considered, or, in other words, that these two activity coefficients varied in the same way. This was equivalent to assuming f_A constant, if the activity theory be used. For simplicity it was further assumed that f_B depended on C_B only.

In accordance with the general method for dealing with rates of reactions in a changing environment, developed in the preceding paper,¹⁰ the following equation may be written to express the relation between the activity coefficients of the alcohols and their concentrations

$$f^2 = \frac{1}{1 - 2gC} \quad (2)$$

where g is a constant dependent on the alcohol and the solvent in which it is dissolved and C is concentration expressed in moles per thousand grams of solvent.¹¹

⁹ E. Beckmann, *Z. physik. Chem.*, **2**, 638, 715 (1888); **4**, 532 (1889); J. E. Eykman, *ibid.*, **2**, 964 (1888); **4**, 497 (1889); E. Paternò, *Gazz. chim. ital.*, **19**, 640 (1889); K. Auwers, *Z. physik. Chem.*, **12**, 689 (1893); Wilhelm Biltz, *ibid.*, **29**, 249 (1899); C. R. Bury and F. S. Brown, *J. Phys. Chem.*, **30**, 694 (1926).

¹⁰ Scatchard, *THIS JOURNAL*, **52**, 52 (1930).

¹¹ The following equations may be used to express empirically the relation between activity coefficient and concentrations. The last of the series was chosen because it leads to the fewest complications.

$$\begin{aligned} f &= e^{gC} \\ f &= 1 + gC \\ f &= \frac{1}{1 - gC} \end{aligned} \quad \left\{ \begin{aligned} f &= \sqrt{\frac{1}{1 - 2gC}} \\ f^2 &= \frac{1}{1 - 2gC} \end{aligned} \right.$$

Substituting this value for f^2 in the Brönsted Equation 1 above

$$\frac{-dC_B}{dt} = K_3^0 \frac{C_B^2 C_A}{(1 - 2gC)} \quad (3)$$

where K_3^0 is the third-order constant at infinite dilution.

If x is the fraction of B transformed

$$C_B = C_0(1 - x) \\ C_{A_0} = C_0D, C_A = C_0(D - x)$$

Substituting these values in Equation 3

$$\frac{-d(C_0)(1 - x)}{dt} = K_3^0 \frac{C_0^3(1 - x)^2(D - x)}{1 - 2gC_0(1 - x)} \quad \text{or} \quad (4)$$

$$C_0 \frac{dx}{dt} = K_3^0 \frac{C_0^3(1 - x)^2(D - x)}{1 - 2gC_0(1 - x)} \quad (5)$$

$$K_3^0 dt = \frac{dx}{C_0^2(1 - x)^2(D - x)} - 2g \frac{dx}{C_0(1 - x)(D - x)} \quad (6)$$

For the case where $D = 1$

$$K_3^0 dt = \left(\frac{1}{C_0^2} \frac{dx}{(1 - x)^2} \right) - \left(\frac{2g}{C_0} \frac{dx}{(1 - x)^2} \right) \quad (7)$$

Integrating, evaluating the integration constant by the condition $x = 0$, when $t = 0$, and combining terms

$$K_3^0 t = \frac{x(2 - x)}{2C_0^2(1 - x)^2} - \frac{2g}{C_0} \frac{x}{(1 - x)} \quad (8)$$

For the case where $D \neq 1$

$$K_3^0 dt = \frac{dx}{C_0^2(1 - x)^2(D - x)} - \frac{2g}{C_0} \frac{dx}{(1 - x)(D - x)} \quad (9)$$

Integrating, evaluating the integration constant by the condition $x = 0$ when $t = 0$, and combining terms

$$K_3^0 t = \frac{x}{C_0^2(D - 1)(1 - x)} - \frac{1}{C_0^2(D - 1)^2} \ln \frac{D - x}{D(1 - x)} - \frac{2g}{C_0(D - 1)} \ln \frac{D - x}{D(1 - x)} \quad (10)$$

For the special case where $C_0 = 1$ and $D = 1/2$

$$K_3^0 t = -\frac{2x}{1 - x} - 4 \ln \frac{(1 - 2x)}{(1 - x)} + 4g \ln \frac{(1 - 2x)}{(1 - x)} \quad (11)$$

Or, in terms of y , the fraction of A transformed

$$y = 2x \text{ or } x = y/2 \\ K_3^0 t = -\frac{2y}{2 - y} - 4 \ln \frac{2(1 - y)}{2 - y} + 4g \ln \frac{2(1 - y)}{2 - y} \quad (12)$$

For the special case where $C_0 = 1/2$ and $D = 2$

$$K_3^0 t = 4 \frac{x}{1 - x} - 4 \ln \frac{2 - x}{2(1 - x)} - 4g \ln \frac{2 - x}{2(1 - x)} \quad (13)$$

Or, in terms of y , the fraction of A transformed, $x = 2y$

$$K_3^0 t = \frac{8y}{1 - 2y} - 4 \ln \frac{(1 - y)}{(1 - 2y)} - 4g \ln \frac{(1 - y)}{(1 - 2y)} \quad (14)$$

These new equations, (7), (12) and (14), exhibit the peculiarity that the first part of each corresponds to the usual integrated form of equations for reactions of the third order. The second part is the integrated form of the equation for a second-order reaction, multiplied by the constant, g . In using the new equation for obtaining values of K_3^0 , the constant, g , was evaluated from the data of the last observations in experiments at molal and half molal concentrations. In one case, that of *n*-amyl alcohol, where data on but a single run at half-molal concentration were available, using the last observation of this half-molal run led to an absurd value for g . By taking the point next to the last, the value for g was much more reasonable. As a check, in this case, both g and K_3^0 were recalculated

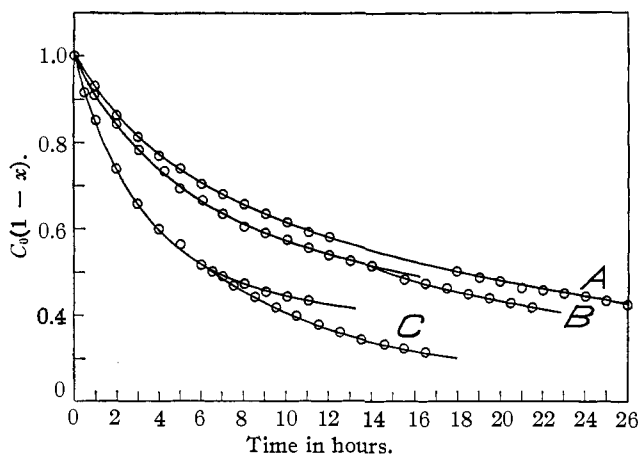


Fig. 2.—Plot of $C_0(1-x)$ against t in hours for three alcohols. A, *n*-butyl alcohol, molal and half molal; B, ethyl alcohol, molal and half molal; C, methyl alcohol, molal and half molal.

lated by the method of least squares, using all thirty available observations. The value of g thus obtained was -0.12 , against -0.13 obtained by the first method. The value for K_3^0 , found in this way, was 0.106 instead of 0.108 . For inactive amyl alcohol the value of g was very small, -0.01 . In other words, the deviation from ideality of solutions of this alcohol in anhydrous ether apparently is very small. In all cases except *iso*-amyl alcohol the sign of the constant, g , is negative. The reason for the positive sign in this single instance is not quite clear. Considerably more study ought to be given to this alcohol.

With methyl and ethyl alcohols, the method adopted for calculating values of g gave very absurd results (-9.58 and -1.23 , respectively). This circumstance led to the surmise that in these cases the hydrogen chloride evolved was producing a marked effect. Such a conclusion was borne out by the experiment showing that ethyl *p*-nitrobenzoate had no

appreciable effect on the rate with which ethyl alcohol reacted with *p*-nitrobenzoyl chloride. This view was substantiated further by plotting the values of $C_0(1-x)$ against t in the case of three alcohols, for molal and half-molal concentrations. For methyl alcohol the curves were markedly divergent; for ethyl alcohol the agreement was much better. With butyl alcohol, where experiment had shown the effect of added hydrogen chloride to be negligible, the curves were continuous (see Fig. 2).

If the assumption be made, in the cases of methyl and ethyl alcohols, that the effect of hydrogen chloride is equal to that attributable to the abnormality of the alcohol solutions, a reasonable value for g may be calculated by the following method.

For the third-order reaction, equal molal concentrations, the rate may be expressed by the equation

$$dx/dt = K_3^0 C_0^2 (1-x)^3 f_B^2 \quad (15)$$

In accordance with the assumption that the effect of hydrogen chloride on the rate be equal to that of the alcohol

$$f_B^2 = \frac{1}{1 - 2g(C_B + C_{HCl})} = \frac{1}{1 - 2gC_0} \quad (16)$$

Equation 15 may now be written

$$\frac{dx}{C_0^2(1-x)^3} = \frac{K_3^0 dt}{(1-2gC_0)} \quad (17)$$

but

$$\frac{dx}{C_0^2(1-x)^3} = K_3 dt$$

Therefore, Equation 17 may be written as follows

$$K_3 = \frac{K_3^0}{(1-2gC_0)} \text{ or } K_3^0 = K_3(1-2gC_0) \quad (18)$$

In accordance with Equation 18 the relation between the third-order constants at molal and half-molal concentrations may be expressed in terms of g , as follows

$$K_3^1(1-2g) = K_3^{0.5}(1-g) \quad (19)$$

Using the third-order constants at molal and half-molal concentrations, K_3^1 and K_3^0 , the calculated values of g were -0.65 for methyl alcohol and -0.21 for ethyl alcohol. These values, in turn, gave the constants, K_3^0 , 0.497 and 0.144 , respectively, for the two alcohols.

In the cases of five other alcohols, where data were available on experiments made with at least two different concentrations, the new equation gave results accurate within the limits of experimental error.

The deviations of the data from the equations for second- and third-order reactions and from the third-order equations for non-ideal solutions were determined by the following method. For each of the equations t was calculated, using the values of K and x or K , x and g in the case of

the third-order equation for non-ideal solutions. The calculated values of t were plotted against observed values of x , on a large scale. Values of x were read off the plot at the times of observation. The differences between observed and calculated values of x were plotted against t , in hours. For n -butyl alcohol, to take an example, it was found that the

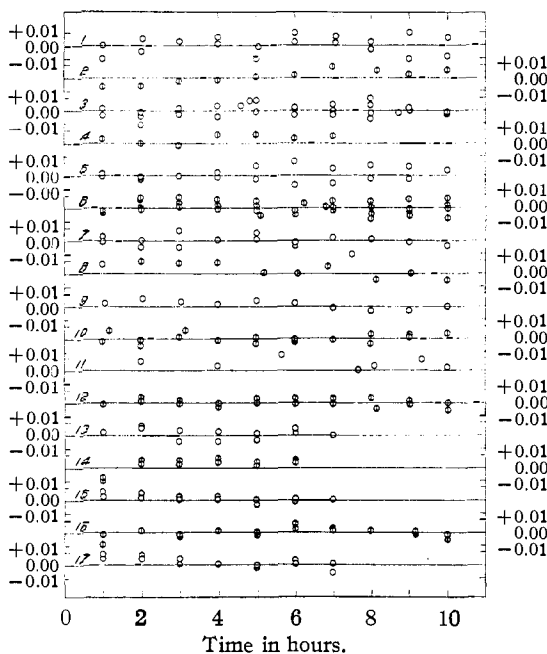


Fig. 3.—Deviations of observed values of the fraction of alcohol transformed in time, t , from the values calculated by the equation for third-order reactions. Methyl alcohol, molal (1), half molal (2); ethyl alcohol, molal (3), half molal (4); n -propyl alcohol, molal (5); n -butyl alcohol, molal (6), half molal (7), molal in alcohol, half molal in acid chloride (8), half molal in alcohol, molal in acid chloride (9); n -amyl alcohol, molal (10), half molal (11); inactive amyl alcohol, molal (12), half molal (13); *iso*-amyl alcohol, molal (14), half molal (15); n -hexyl alcohol, molal (16), half molal (17).

deviations reached as high as 7% for the second-order equation. On the other hand, they were only 2% for the third-order equation, formulated either for ideal or non-ideal solutions. Similar results were found for the other alcohols. In Fig. 3 the deviations of the observed from the calculated values of x are presented graphically. The constants obtained for the eight alcohols considered in this paper are summarized in Table III.

TABLE III

SUMMARY OF THE VELOCITY CONSTANTS FOR THE REACTION BETWEEN ALCOHOLS AND *p*-NITROBENZOYL CHLORIDE IN ANHYDROUS ETHER SOLUTION

Alcohol	$K_{\frac{1}{2}}^{\dagger}$	$K_{\frac{1}{2}}^{0, \ddagger}$	$K_{\frac{1}{2}}^{\ddagger}$	$K_{\frac{1}{2}}^{0, \ddagger}$	$K_{\frac{1}{2}}^{\ddagger}$	g
Methyl	0.184	0.141	0.215	0.300	0.497	-0.65
Ethyl	.0853	.057	.103	.121	.144	-.21
<i>n</i> -Propyl	.06580731
<i>n</i> -Butyl	.0739	.046	.0826	.0944	.118	-.25
	.0824 ^a	.053 ^b	.0827 ^a	.1066 ^b		
<i>n</i> -Amyl	.077	.048	.0895	.0919	.108	-.13
Inactive amyl	.035	.0195	.0373	.0386	.0387	-.01
<i>Iso</i> -amyl	.0695	.0325	.0751	.0668	.0571	+.16
<i>n</i> -Hexyl	.0815	.053	.0940	.111	.1375	-.28

^a Concentrations were molal in alcohol and half molal in acid chloride.^b Concentrations were molal in acid chloride and half molal in alcohol.

The values of these constants are averages, weighted for time. They were obtained from the ratio $\Sigma Kt/\Sigma t$. In connection with the two earlier papers, to which reference has been made,² it should be noted that the relative order in which the constants stand is the same, with one exception, whichever equation be used in calculating these constants. The order of *n*-butyl and *n*-amyl alcohols is reversed, if the third-order constants at half-molal concentration or at infinite dilution be used in making the comparison. It should be said, in all fairness, that, however, the constants for these two alcohols are calculated, they are very close together.

The writer is profoundly grateful to Professor George Scatchard of this Institute for unstinted help in developing the theoretical aspects of the problem, to Professor James F. Norris for his long-sustained interest in the work, and to many other associates at the Massachusetts Institute of Technology for significant suggestions. The data used were obtained partly by Dr. F. Cortese ("Thesis," Ph.D., Massachusetts Institute of Technology, 1926) and partly by the writer.

Summary

The reaction of alcohols with *p*-nitrobenzoyl chloride in anhydrous ether solution is of the third order, instead of the expected second order.

The mechanism of the reaction requires two molecules of the alcohol to one of the acid chloride. In other words, the reaction is second order with respect to the alcohol and first order with respect to the acid chloride.

Taking into account the well-known abnormality of alcohol solutions, an equation has been developed for calculating the third-order constants at infinite dilution.