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THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. III. FIRST CONTRIBUTION ON THE CARBON-CHLORINE BOND: THE RATE OF THE REACTION BETWEEN DIPHENYLCHLOROMETHANE AND ETHYL ALCOHOL

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The influence of molecular structure on the reactivity of a chlorine atom in organic compounds is marked. This fact has been noted in a qualitative way since such compounds were studied. It is only recently, however, that attempts have been made to get a more definite conception of chemical reactivity by measuring quantitatively the relative rates at which the members of a series of analogous compounds react with a fixed reagent. Of the investigations in this field those that have the closest bearing on the work to be described have been published by Olivier,[2] who determined the rates at which benzyl chloride and certain of its derivatives react with ethyl alcohol, and by Conant and Kirner,[3] who have studied the rates at which the chlorine atom in certain compounds reacts with potassium iodide.

The investigation to be described in this and subsequent papers[4] was undertaken with the intention of studying the effect on the carbon–chlorine bond of a change in type of the halogen compound. For example, the replacement of two hydrogen atoms by one oxygen atom in an alkyl chloride leads to the formation of an acyl chloride (CH_3CH_2Cl and CH_3COCl). Such a change has a profound influence on the lability of the carbon–chlorine bond, and is worthy of detailed investigation. In the past the compounds studied comparatively have belonged to the same type, such as those formed by replacing by substituents one hydrogen in the benzene ring in benzyl chloride.

Since acetyl chloride is such a reactive compound it is difficult to measure the rate at which it reacts with another substance. The rate at which benzoyl chloride reacts with alcohol, however, can be measured. Its use as a type compound is advantageous, because the effect on the carbon–chlorine bond of replacing hydrogen in the benzene ring can be determined and can be compared with the effect of similar replacements on a com-

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[1] From the thesis of Avery A. Morton presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1924.

[2] Olivier, *Rec. trav. chim.*, **42**, 773 (1923).

[3] Conant and Kirner, THIS JOURNAL, **46**, 235 (1924).

[4] See Norris and Banta, THIS JOURNAL, **50**, 1804 (1928); Norris and Blake, *ibid.*, **50**, 1808 (1928); Norris and Gregory, *ibid.*, **50**, 1813 (1928).

pound not containing oxygen. The simplest comparison would be between benzoyl chloride and benzyl chloride (C_6H_5COCl and $C_6H_5CH_2Cl$), but since there is such a wide difference between the reactivities of the two substances they cannot be studied under the same conditions. The replacement of one hydrogen atom linked to the methane carbon atom in benzyl chloride leads to a marked increase in the reactivity of the chlorine atom. The rate at which diphenylchloromethane reacts with ethyl alcohol can be measured under the same conditions as those used in the case of benzoyl chloride. As a consequence, the relative effects on the lability of the carbon–chlorine bond of one oxygen atom and of one hydrogen atom and one phenyl radical can be determined, and also the effect on this bond of similar replacements in the two type compounds. These effects are marked. The results lead to conclusions that have not been adequately recognized in the past in regard to the activation of atoms as the result of the replacement of hydrogen by other atoms or groups. The results obtained are described in the papers to which reference has been made.

This communication deals with a detailed study of the methods used in determining the velocity constant of the reaction between diphenylchloromethane and ethyl alcohol.

In the earlier part of the investigation the rate of the reaction was determined in the usual way by removing from time to time a sample of the reaction mixture and determining by titration the amount of hydrochloric acid formed. Although in the case of diphenylchloromethane the results were fairly accurate, the method was abandoned because the chloride was hydrolyzed to some extent when the analyses were made.

A method was developed that could be used for both the substituted alkyl chlorides and the acyl chlorides studied, because there was no opportunity for hydrolysis to take place. The reacting substances were placed in a conductivity cell and the resistance was measured as the reaction proceeded. The method has many advantages over one involving periodic analyses by the usual procedures. The reaction is carried out in a closed vessel and, consequently, there is no opportunity for contamination or extraneous changes which might be brought about during the process of analysis. The advantage which is most important when such reactive substances as acyl chlorides are studied comes from the fact that measurements can be made rapidly and at very short intervals. It was found possible to determine the velocity constant of a reaction that was complete in five minutes.

The results of the study of the applicability and accuracy of the method are described below. The work involved a redetermination of the conductivity of hydrochloric acid in ethyl alcohol, the effect of the influence of non-electrolytes on the conductivity, the influence of traces of water on the value of the velocity constant, the determination of the mechanism of the reaction, which was found to be a reversible one, and the development by Professor F. L. Hitchcock of the Department of Mathematics of the Massachusetts Institute of Technology of a new method of calculating the constant from the experimental results.

The velocity constants of the reaction at 25 and 0° were measured in order to calculate the temperature coefficient, which was useful in the comparison of the alkyl and acyl chloride studied. The rate of the reaction is markedly affected by a change in temperature; the rate nearly quadrupled for a rise of ten degrees.

Experimental Details

The measurements were made in conductivity cells similar to Washburn's type B,[5] but with the electrodes lightly platinized and one arm of each cell bent over and down into a mixing vessel from which the reactants could be transferred to the cell. Over a two year interval the cell constants did not vary more than 0.01% from the first determinations. A Leeds and Northrup bridge with extension coils and two resistance boxes containing Curtis coils of 100,000 and 1000 ohms, respectively, made by the same firm were used. The source of current was an improved form of induction coil known as the audio oscillator. This was tuned to a thousand cycles. A two stage amplifier connected in the manner described by Hall and Adams[6] enabled one to obtain a minimum of one part in five thousand very easily. Grounded shields were used to prevent any stray electrical effects. The thermostat and leads were also grounded. Every ordinary precaution, such as calibration, etc., was taken.

The alcohol was purified by first distilling it from dilute sulfuric acid to remove any amines. It was then refluxed over a mixture of calcium oxide and sodium hydroxide, after which two more refluxings over freshly ignited calcium oxide were carried out. Wherever corks were used they were covered with tin foil and suitable precautions were taken to insure the presence of dry air. The density at 25°, 0.78506, reported by the Bureau of Standards, Circular 19, was used as the criterion of pure alcohol. The alcohol used had this density within ±0.00002.

In the first six runs in absolute alcohol, the five runs in dilute alcohol and the two runs at zero degrees, the diphenylchloromethane was prepared by refluxing diphenylcarbinol with concentrated hydrochloric acid for at least two hours. The oil was then extracted with alcohol free ether, dried over anhydrous calcium chloride, and finally fractionally distilled in a vacuum. In runs seven to ten inclusive the compound was prepared by a method developed by Blake[4] in which hydrochloric acid was bubbled into a solution of the carbinol in specially purified petroleum ether in the presence of calcium chloride to remove water. After the old calcium chloride had been replaced twice with fresh material, the solution was filtered and the petroleum ether then removed by evacuating at room temperature. The purity was determined by refluxing duplicate samples of the chloride for two hours with an alcoholic solution of silver nitrate and comparing the amount of silver chloride formed with the amount theoretically possible.

The best determinations made of the conductance of hydrochloric acid in absolute alcohol at 25° are those of Goldschmidt.[7] His values were re-

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[5] Washburn, This Journal, **38**, 2431 (1916).

[6] Hall and Adams, *ibid.*, **41**, 1515 (1919).

[7] Goldschmidt, *Z. physik. Chem.*, **89**, 129 (1914).

calculated into terms of moles per 1000 g. of ethyl alcohol, since it is easier to make up the reaction mixture on the basis of weight formality. No great error is made in our case if the weight formality is calculated by simply multiplying his volume concentration by the ratio of the weights of the alcohol in the two solutions. Thus a 0.1 formal solution by volume becomes (1000 × 0.1)/785.06 or 0.12738 formal solution by weight. The specific conductance is calculated by the usual formula. Table I gives the original data with the recalculated values.

TABLE I

SPECIFIC CONDUCTANCE OF ETHYL ALCOHOL

Moles HCl per 1000 g. of C_2H_5OH. Temp., 25°

Vol., liters	Weight formality	Molecular conductance	$\bar{L} \times 10^3$
10	0.12738	35.0	3.50
20	.06369	40.4	2.02
40	.03185	46.3	1.158
80	.01593	52.7	0.659
160	.00796	59.0	.369
320	.00398	65.3	.204
640	.00199	70.4	.110
1280	.00099	74.2	.058
2560	.00050	76.9	.003

These values were checked with good agreement by solutions of hydrochloric acid in ethyl alcohol which were made up on the basis of weight formality. The specific conductance was plotted against weight formality so that the concentration of hydrochloric acid could be determined at any time from the conductivity measurement.

In order to obtain accurate results it is necessary to take into account the presence of a non-electrolyte in the solution. At the beginning of the reaction diphenylchloromethane and at the end the diphenylmethylethyl ether is present. Both of these lower the conductivity of hydrochloric acid in ethyl alcohol and it is therefore necessary to obtain some idea of the magnitude of this correction. A number of determinations were made with benzene, chlorobenzene, bromobenzene, naphthalene, dibromobenzene, diphenyl, diphenylmethane and naphthylphenylmethane as non-electrolytes. For the purposes of this work, that is, up to 0.12 formal, the percentage lowering of the specific conductivity for a fixed concentration of a given non-electrolyte with varying concentrations of hydrochloric acid is constant. On the other hand with a fixed concentration of hydrochloric acid the percentage lowering is directly proportional to the concentration of a given non-electrolyte. The effect of one non-electrolyte was not, however, the same as that of another. The differences between the various non-electrolytes could not be accurately related either to viscosities or molecular volumes. Table II shows the data for molecular volume and percentage lowering of the specific conductivity at 0.1 weight formal concentration. Where densities are not recorded in the literature they were determined. Measurement of the density of a solid at 25° was made by the molecular solution volume method of Traube.[8]

TABLE II

PERCENTAGE LOWERING OF SPECIFIC CONDUCTIVITY OF HYDROCHLORIC ACID IN ETHYL ALCOHOL PRODUCED BY NON-ELECTROLYTES

Concentration of HCl up to 0.12 moles and of non-electrolyte up to 0.1 mole per 1000 g. of ethyl alcohol. Temperature, 25.0°.

Non-electrolyte	Density	Molecular weight	Molecular volume	Lowering, %
Benzene	0.876	78.08	89.13	1.42
Chlorobenzene	1.104	112.5	102.0	1.64
Bromobenzene	1.561	157.0	105.0	2.05
Naphthalene	1.077	128.1	118.9	2.51
Dibromobenzene	2.022	235.9	116.6	2.64
Diphenyl	1.043	154.1	147.8	2.91
Diphenylmethane	1.006	168.2	167.3	3.15
Naphthylphenylmethane	1.129	218.2	193.3	3.91

As a rough approximation molecular volumes were used and a lowering of 3.2% in a 0.1 formal solution of diphenylchloromethane was chosen as an empirical value for the correction. It is probably not far from being the correct value. It was applied by means of the equation $\overline{L}_c = \overline{L}_0 \, 100/(100-32f)$ where $\overline{L}_c$ is the corrected and $\overline{L}_0$ the observed specific conductance and f is the weight formality.

When the equation for a monomolecular irreversible reaction was applied it was found that the velocity constant was constant for about the first quarter of the run and then gradually became lower. Such an effect also occurs when the velocity is measured by titrating the hydrochloric acid. The most likely cause is that the reaction is reversible. A simple equation was developed by Hitchcock and Robinson[9] for the special case. The differential form of this equation is $dy/dt = k_1(X_0-y) - k_2y_2$, where y is the concentration of hydrochloric acid or diphenylmethylethyl ether formed; t is the time, X_0 equals the initial concentration of diphenylchloromethane and k_1 and k_2 are the velocity constants in the forward and reverse directions, respectively. Upon integration this equation becomes

$$k_2 = \frac{1}{t}\frac{2.303}{b + y_\infty}\left(\log\frac{b+y}{y-y} - \log\frac{b}{y_\infty}\right)$$

where $b = (X_0Y_\infty)/(X_0-y_\infty)$ and y_∞ = concentration of hydrochloric acid at infinite time; k_1 is then obtained by the equation $k_1 = k_2(y\alpha^2)/(x_0-y_\infty)$.

The data given in Table III are for the eighth run. The first column

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[8] Traube, *Ahren's Vortrage*, **4,** 255 (1899).

[9] Hitchcock and Robinson, "Differential Equations in Applied Chemistry," p. 52, John Wiley and Sons, Inc., **1923.**

gives the corrected time. This correction was necessary because of the time required to mix the samples and bring the mixture to constant temperature. The maximum correction in any run was 1.3 minutes for this. In most of the runs it was much less. The second column is the specific conductance corrected for the concentration of non-electrolyte; the third column is $k_2 \times 10^5$; the fifth column is $k_1 \times 10^5$ as calculated by the reversible equation. The last column contains the calculation of k_1 on the basis of a monomolecular reaction only.

Table III

Velocity Constants for the Reversible Reaction between Diphenylchloromethane and Ethyl Alcohol

Temperature = 25 ± 0.01°. Cell constant = 1.0080. Time in minutes. Formality of diphenylchloromethane 89.80% pure = 0.07060. Zero time correction = +0.05 min.

Corr. time, min.	$\bar{L} \times 10^6$	Concd. HCl $\times 10^5$	$k_2 \times 10^5$	$k_1 \times 10^5$	$k_1 \times 10^5$
3.6	49	81	274	318	323
6.1	76	129	254	296	302
10.1	119	213	258	300	300
16.1	178	337	256	298	302
20.1	212	414	256	298	299
32.1	312	654	260	302	300
38.1	359	771	260	302	302
56.1	483	1095	256	298	299
84.1	654	1580	258	300	300
383.0	1599	4772	258	300	...
447.0	1707	5175	263	306	...
508.0	1785	5468	265	308	...
1205.0	2073	6576	268	312	...
1693.0	2096	6656	265	308	...
2703.0	2100	6678	...	...	...

x_0 = 0.0760. y_∞ = 0.06678. b = 1.234. Reversible equation k_1 = 0.00301. k_2 = 0.00259. Monomolecular equation k_1 = 0.00302.

Ten runs were made in absolute alcohol with diphenylchloromethane of varied purity and concentration. The results for these runs are given in Table IV.

The constants given for each run calculated from the equation for a reversible reaction are the average for about twelve observations during the course of the reaction. These observations generally agreed within less than 1% of the average and were never more than 3% from the average. The constants calculated from the equation for a first order reaction are based on observations up to approximately 25% conversion.

The very first observation made, usually within a minute after mixing, and the final observations, when the solution had been standing for twenty hours or more in the cell, were not of course within such accuracy but were generally within 10% of the average.

TABLE IV

VELOCITY CONSTANTS FROM THE REVERSIBLE REACTION BETWEEN DIPHENYLCHLOROMETHANE AND ETHYL ALCOHOL

Temperature, 25 ± 0.01°

Run No.	Diphenylchloromethane Concn.	Diphenylchloromethane Purity	Final conversion, %	Reversible equation $k_1 \times 10^5$	Reversible equation $k_2 \times 10^4$	Monomolecular equation $k_1 \times 10^5$
1	0.09790	97.75	94.1	310	21	302
2	.10008	97.75	92.6	307	27	306
3	.08808	97.80	87.1	268	52	266
4	.02618	97.80	84.3	261	230	259
5	.09680	96.56	93.4	304	23	304
6	.13925	96.56	93.8	304	15	304
7	.06470	89.86	94.0	300	31	299
8	.07060	89.86	94.6	301	26	302
9	.10667	99.98	86.4	277	48	276
10	.11330	99.98	89.6	281	37	280
			Average	291	51	290

The runs were made in pairs with different concentrations of diphenylchloromethane in each. The constants are nearly identical for each pair of runs. We cannot therefore see any effect due to a difference in concentration. Varying degrees of purity of the diphenylchloromethane cannot be said to have any effect since runs 7 and 8 where the material was only 89.56% pure are very close to runs 5 and 6 where the purity was 96.56%. A variation therefore may be due to impurities in the alcohol.

The most likely impurity in the ethyl alcohol is water. Accordingly five runs were made with different concentrations of water. The conductivity of hydrochloric acid in mixtures of water and alcohol was taken from Goldschmidt's[7] data. It was recalculated on a basis of weight formality as was done with the absolute alcohol. The correction for the presence of a non-electrolyte was assumed to be the same. Table V gives the results of these five runs.

TABLE V

THE EFFECT OF WATER ON THE VELOCITY CONSTANT OF THE REACTION BETWEEN DIPHENYLCHLOROMETHANE AND ETHYL ALCOHOL

Temperature, 25 ± 0.01°

No.	Water by weight, %	Formality of water	Formality of $(C_6H_5)_2C(H)Cl$	$k_1 \times 10^5$	$k_2 \times 10^4$
	0	0	....	291	51
11	0.15	0.0834	0.0990	316	26
12	.58	.3206	.1191	358	12
13	1.07	.5896	.1065	407	9
14	2.39	1.3258	.1242	532	15
15	7.19	3.989	.0815	1150	68

Good constants were obtained in all of these runs except in the case of number 15. The constants for that run increased continuously from the start. Near the end of the reaction it was nearly five times as large as at the beginning. The slope of the curve would lead one to suspect that the reaction between water and diphenylchloromethane proceeds simultaneously with that between ethyl alcohol and diphenylchloromethane. The value recorded here is an average for the first 40% of the run. These results show clearly that the presence of water has a marked effect. It is not, however, sufficient to account for all of the error. From 0% of water to 0.15% by weight, assuming that it is a straight line function, a change of 0.017 of water changes the k by 1.8. This would correspond to a change in the density of 0.00003, an amount which is detectable. If it is not a straight line function then the curve would tend to become more and more nearly parallel to the axis on which the value for the constant is plotted. The nearer the alcohol approached the absolute purity, the greater would be the change. In such a case the lowest value for the constant would be the more nearly correct. At this portion of a curve where concentration of water is plotted against the value for k, there seems to be a departure from the straight line. It is not possible, however, with the present data to say that the variation in the value of k for the first ten runs is positively due to traces of water.

The constant in the reverse direction is not nearly so accurate as the one in the forward direction. A consideration of the equation shows why this must be true, for the amount of hydrochloric acid present is very small in the early part of the run and this amount in the equation is squared.

Attempts to verify experimentally the calculated value were unsuccessful because of the high velocity. The reversibility of the reaction was shown however, by passing hydrochloric acid into a solution of the diphenylmethylethyl ether dissolved in a mixture of dry benzene and petroleum ether. Calcium chloride was then added to remove the ethyl alcohol formed. Distillation of the compound in a vacuum gave a product which analyzed 98.6% diphenylchloromethane.

For simplicity, a measurement of reaction velocity by a physical method is much to be preferred over a chemical one. The results in this case were very satisfactory but it was thought well to check the method by titrating the acid formed with sodium hydroxide and phenolphthalein as an indicator. A sample was removed from the reaction vessel, run into ice cold water, treated with a definite volume of cold carbon disulfide to remove the cloudiness from the precipitated organic compound and titrated with alkali. All ordinary precautions were made to stop the reaction and hasten the titration. The value for the first quarter of the run after making suitable corrections from blank experiments was 319×10^{-5} for k_1. This is 11% higher than the average obtained from the conductivity runs. The difference is believed to be due to the necessary presence of water in the reaction, which is largely avoided in the conductivity measurements.

Two runs were made at zero degrees with absolute alcohol. The thermostat for this was a glass bottle filled with cracked ice and water and surrounded with asbestos magnesia packing. Partington's[10] data for the conductance of hydrochloric acid in absolute alcohol at zero degrees were used. The values were converted to weight formality and the corrections for non-electrolyte were assumed to be the same as at 25°. The density of the alcohol was 0.8064 obtained by extrapolating the values given by the Bureau of Standards. The order of magnitude of k can be considered as the only significant value. Table VI below summarizes these two experiments.

TABLE VI

VELOCITY CONSTANT OF THE REACTION BETWEEN DIPHENYLCHLOROMETHANE AND ETHYL ALCOHOL AT 0°

No. of run	Concn.	Purity	$k_1 \times 10^6$
16	0.07745	99.98	10.4
17	.05502	99.98	11.3

By means of the equation $\log k_2/k_1 = A(T_2-T_1)/(T \times T_2)$ we obtain a value for A of 4630 as the temperature coefficient.

Summary

1. A method was developed for the determination of the velocity constants of the reaction between diphenylchloromethane and ethyl alcohol based on the measurement of the electrical conductivity of the solution as the reaction proceeded.

2. The reaction between diphenylchloromethane and ethyl alcohol was found to be reversible.

3. A new method has been developed for calculating the velocity constants of reversible reactions.

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[10] Partington, *J. Chem. Soc.*, **99**, 1937 (1911).