

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY,  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 25]

**THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC  
COMPOUNDS. VI. FOURTH CONTRIBUTION ON THE  
CARBON-CHLORINE BOND: THE RATES OF THE REACTIONS  
OF BENZOYL CHLORIDE AND CERTAIN OF ITS DERIVATIVES  
WITH ISOPROPYL ALCOHOL**

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RECEIVED APRIL 9, 1928

PUBLISHED JUNE 5, 1928

In the first investigation of the relative reactivities of the carbon-chlorine bond in acyl chlorides, the rates at which these chlorides react with *isopropyl* alcohol were determined. This alcohol was selected because the reactivity of its hydrogen atom is low and as a consequence the reaction velocities are much smaller and easier to measure than the velocities of the corresponding reactions with ethyl alcohol. Certain difficulties were encountered in making very accurate measurements and the later work with the acyl chlorides was carried out with ethyl alcohol at 0°. The results obtained with this alcohol, to be published later, show that the relative rates with which the several acyl chlorides react as measured by either *isopropyl* alcohol or ethyl alcohol are approximately the same.

The velocities were measured of the reactions between the acyl chlorides and *isopropyl* alcohol by determining from time to time the amount of hydrochloric acid formed. The latter was measured by observing the conductivity of the solution. It was necessary to determine the conductance of solutions of hydrochloric acid in *isopropyl* alcohol at different concentrations. It was found impossible to get results of the highest degree of accuracy because there was a slow reaction between the acid and the alcohol at 25°. The error introduced in this way was shown to affect the value of the velocity constant to not more than 2%. Other sources of error were unavoidable but it is safe to say that the results are accurate to within less than 10%. The results are valuable as they can be used in making comparisons when such a possible error is of no great significance. The constants determined are shown in Table I.

The results show that the halogens increase and the methyl group decreases the reactivity of the carbon-chlorine bond. The effect of these substituents in benzoyl chloride is the reverse of their effect in diphenylchloromethane.<sup>2</sup> This is a significant fact. The results obtained from the study of the reaction of a large number of acyl and substituted alkyl chlorides with ethyl alcohol lead to the conclusion that the activation of an atom in a given compound produced as the result of the substitution of

<sup>1</sup> From the thesis of Dwight V. Gregory presented in partial fulfillment of the requirements for the degree of Master of Science, 1922.

<sup>2</sup> Norris and Banta, *THIS JOURNAL*, **50**, 1804 (1928).

TABLE I  
FIRST ORDER VELOCITY CONSTANTS OF THE REACTIONS OF CERTAIN ACYL CHLORIDES  
WITH *ISOPROPYL* ALCOHOL

Temp., 25.0°. Concentration approximately 0.1 Formal per 1000 g.

Acyl chloride	<i>K</i>	<i>K</i>	Average	Ratio of constant to that of benzoyl chloride
Benzoyl.....	0.00371	0.00360	0.00365	1
<i>p</i> -Chloro benzoyl.....	.00550	.00569	.00559	1.53
<i>p</i> -Bromo benzoyl.....	.00645	.00655	.00650	1.78
<i>p</i> -Iodo benzoyl.....	.00546	.00511	.00528	1.26
<i>o</i> -Nitro.....	.00682	.00706	.00694	1.90
<i>p</i> -Nitro benzoyl.....	.033	.040	.036	10.0
<i>p</i> -Methyl benzoyl.....	.00240	.00229	.00235	0.64

hydrogen by another atom or group is determined by the nature not only of the substituent but the molecule modified. When the negative chlorine atom replaces hydrogen in benzoyl chloride, the effect of the negative oxygen atom in the chloride takes part in the changed reactivity of the acyl chloride. The lability of the acyl carbon-chlorine bond is increased. On the other hand, when the same negative atom is introduced into diphenylchloromethane in which the oxygen atom of the acyl chloride is replaced by the more positive hydrogen atom and the phenyl radical, the combined effect leads to decreased reactivity of the analogous carbon-chlorine bond. In the case of the introduction of the positive methyl radical into the two molecules the effects are reversed. It appears, therefore, that the lability of the carbon-chlorine bond studied is increased when either a negative atom or group (Cl or NO<sub>2</sub>) is introduced into a molecule containing negative atoms or when a positive group (CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, etc.) is introduced into a molecule containing positive atoms or groups. The lability of the carbon-chlorine bond is decreased when a negative substituent is introduced into the molecule containing positive atoms or a positive group is introduced into a molecule containing negative atoms and groups. These conclusions hold in regard to a large number of derivatives of diphenylchloromethane and of benzoyl chloride.

In both series of compounds bromine is more effective than chlorine. The former depresses reactivity more than the latter in the substituted alkyl chloride and increases reactivity more than chlorine in the acyl chloride.

#### Experimental Details

The difficulty encountered in an attempt to determine accurately the conductivity of hydrochloric acid of different concentrations in *isopropyl* alcohol was traced to the fact that the resistance of the solutions changed slowly. Staud in this Laboratory showed that a solution of 0.0756 *N* hydrochloric acid changes in resistance equivalent to a change in concentration at the rate of 0.4% per hour and that one of 0.006 *N* changed at the

rate of 2% per hour. In order to keep the error due to this fact as low as possible, the values of all velocity constants were calculated from observations made at times of less than one hour. In this way this error was less than 2%.

A number of check determinations of the conductivity of the acid in *isopropyl* alcohol were made at different concentrations and the results plotted. The curves differed by 3% at 0.1 *N* and 4% at 0.001 *N*. The values of the constants are affected by this uncertainty. New data are being determined and the results will be published later.

All observed conductivities were corrected for the effect of the non-electrolyte present. It was shown that 0.1 *N* propyl benzoate lowers the conductivity of hydrochloric acid 6.1%. The lowering was independent of the strength of the acid within the limits of concentration used and was proportional to the strength of the ester. These results were used in the experiments with benzoyl chloride. In the case of the other compounds a further correction was made based on change in the non-electrolyte.

The values of the constants were calculated in the usual way from observations made up to 30% conversion. Up to this point the value of the term  $\log (X_0)/(X_0-X)$  in the equation for a first order reaction divided by the time remained a constant. A time correction was avoided by taking as concentration at zero time the concentration observed after the reaction had proceeded for several minutes.

By limiting the observations to those obtained within one hour, the error caused by the reaction between hydrochloric acid and *isopropyl* alcohol was reduced to less than 0.4%.

The methods of preparation of the compounds used and the purity of the latter are indicated in Table II.

TABLE II  
PREPARATION AND PROPERTIES OF COMPOUNDS STUDIED

The melting points are uncorrected

Benzoyl chloride. . . .	Fractionated, b. p. 197.2–197.3°. Analysis, 99.9–100.25%.
<i>p</i> -Chloro chloride. . . .	From acid, m. p. 239°. Chloride fract. 3 times, dim. pressure. Analysis, 100.4–100.1%.
<i>p</i> -Bromo chloride. . . .	From acid, m. p. 250–252°. Chloride fract., dim. pressure. Analysis, 101.4 and 100%.
<i>p</i> -Iodo chloride. . . . .	From acid, m. p. 265–266°. Chloride fract., dim. pressure. Analysis, 101 and 102.7%.
<i>o</i> -Nitro chloride. . . . .	Chloride fract., dim. pressure. Analysis, 100.6 and 99.5%.
<i>p</i> -Nitro chloride. . . . .	From acid, m. p. 240°. Chloride fract., dim. pressure. Analysis, 100.2 and 100.3%.
<i>p</i> -Methyl chloride. . . .	From acid, m. p. 179°. Chloride fract. 3 times. Analysis 99.9 and 99.3%.

The *isopropyl* alcohol was distilled several times from lime. Its density was 0.7843<sub>4</sub><sup>25°</sup>. The only accurate density available when this work was

done was that obtained by Lebo<sup>3</sup>:  $0.78556 \frac{20^\circ}{4^\circ}$ . Later determinations by Brunel<sup>4</sup> gave the value  $0.7808 \frac{25^\circ}{4^\circ}$ .

### Summary

1. First order velocity constants have been determined for the reactions between *isopropyl* alcohol and benzoyl chloride and the following derivatives of benzoyl chloride: *p*-chloro, *p*-bromo, *p*-iodo, *o*-nitro, *p*-nitro and *p*-methyl.

2. A comparison of the activating influence of substituents on the reactivity of the carbon-chlorine bond in derivatives of benzoyl chloride and of diphenylchloromethane shows that negative atoms (Cl, Br, NO<sub>2</sub>) increase the lability of the bond in acyl chlorides and decrease the lability of the bond in derivatives of diphenylchloromethane. The positive methyl group increases reactivity in the acyl and decreases reactivity in the alkyl compounds.

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## NITROGEN TRICHLORIDE AND UNSATURATED KETONES. II

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RECEIVED APRIL 16, 1928

PUBLISHED JUNE 5, 1928

The reaction of nitrogen trichloride with benzalacetophenone<sup>2</sup> forms among other products 2-chloro-1-dichloro-amino-1,3-diphenylpropanone-3. The addition is probably to the  $\text{—C=C—}$  bond as in the corresponding reaction with the unsaturated hydrocarbons<sup>3</sup> and does not involve the carbonyl group.

The reaction has now been studied with benzalacetone. The products obtained with this compound are 2-chloro-1-dichloro-amino-1-phenylbutanone-3 (I), the dichloride of benzalacetone, ammonium chloride and a large amount of nitrogen gas. Product I was reduced by concentrated hydrochloric acid<sup>4</sup> to the corresponding amino chloro ketone II. If the reaction mixture containing I is allowed to stand for several days at room temperature, II will crystallize out as the hydrochloride. Its formation is no doubt due to the hydrochloric acid produced by the decomposition of

<sup>3</sup> Lebo, *THIS JOURNAL*, **43**, 1005 (1921).

<sup>4</sup> Brunel, *ibid.*, **45**, 1336 (1923).

<sup>1</sup> This paper is an abstract of a part of the thesis submitted by David Craig in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the State University of Iowa.

<sup>2</sup> Coleman and Craig, *THIS JOURNAL*, **49**, 2593 (1927).

<sup>3</sup> Coleman and Howells, *ibid.*, **45**, 3084 (1923).

<sup>4</sup> The reducing action of hydrochloric acid on chloro-amines was reported by Berg. His best reference is *Ann. chim. phys.*, [7] **3**, 338 (1894).