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THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. IV. SECOND CONTRIBUTION ON THE CARBON-CHLORINE BOND: THE RATES OF THE REACTIONS OF CERTAIN DERIVATIVES OF DIPHENYLCHLOROMETHANE WITH ETHYL ALCOHOL AND WITH ISOPROPYL ALCOHOL[1]

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In this paper and the one by Norris and Blake[2] which follows are recorded the results of the determinations of the rates of the reactions between ethyl and *iso*propyl alcohols and certain derivatives of diphenylchloromethane. The investigation was undertaken to determine the effect of atoms and groups, and their positions relative to the carbon–chlorine bond, on the readiness with which the chlorine atom reacts with a fixed reagent under fixed conditions.

The results show that the lability of the chlorine atom as measured by the velocity constants of the reactions is markedly affected. The value of the constants varied between 0.01 and 1200 times that of the constant of the reaction between alcohol and the original molecule into which the substituents were introduced.

The velocity constants were determined in the way described in detail in the paper by Norris and Morton.[3]

In Table I are given the relative values of the constants observed by Banta and by Blake.

TABLE I

RELATIVE VELOCITY CONSTANTS OF THE REACTIONS BETWEEN ETHYL ALCOHOL AND CERTAIN DERIVATIVES OF DIPHENYLCHLOROMETHANE

Temperature 25.0°. Concentration of chloride approximately 0.1 formal by weight. Time in minutes.

Substituent	Relative values of constants	Substituent	Relative values of constants	Substituent	Relative values of constants
No substituent	1	*p*-Methyl	16.2	*o*-Methoxy	93
o-Chloro	0.01	*p,p'*-Dichloro	0.15	*p*-Methoxy	1200 (?)
m-Chloro	.045	*p,p'*-Dimethyl	413	*p*-Phenoxy	31.6
p-Chloro	.42	*p*-Ethyl	20.9	α-Naphthyl	7.2
o-Methyl	2.9	*p*-Bromo	0.33	Benzylphenylchloromethane	0.0004
m-Methyl	2.1	*p*-Phenyl	12.8		

The following conclusions can be drawn from the values given in the table.

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[1] From the thesis of Clifford Banta presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1922.

[2] Norris and Blake, THIS JOURNAL, **50**, 1808 (1928).

[3] Norris and Morton, *ibid.*, **50**, 1795 (1928).

(1) The influence on the activation of the carbon–chlorine bond is not in accord with the orienting effect of the substituent; chlorine decreases and methyl increases reactivity.

(2) Of the substituents studied only chlorine and bromine decreased reactivity.

(3) The groups that increased reactivity had their greatest effect when in the para position. For example, the relative velocity constants of the *o*-methyl and *p*-methyl derivatives were 2.9 and 16.2.

(4) Chlorine, which reduced reactivity, was most effective in the ortho position, the relative values of the ortho and para derivatives being 0.01 and 0.42.

(5) It appears from (3) and (4) above that reactivity is affected by the nature of the group and its position. The effect of the presence of a group in the ortho position is to reduce reactivity. If the atom or group also reduces reactivity the two effects work in the same direction; if the atom or group increases reactivity the effects are opposed.

(6) The groups that increase reactivity fall into the following series when para compounds are considered, the most effective being placed first: CH_3O, C_6H_5O, C_2H_5, CH_3, C_6H_5 and $C_{10}H_7$.

(7) Bromine like chlorine decreased reactivity and was more effective.

(8) A comparison of the relative velocity constant of benzylphenylchloromethane, 0.0004, with that of *p*-tolylphenylchloromethane, 16.2, leads to an important conclusion. In one compound $C_6H_5CH_2$- replaces $CH_3C_6H_4$- in the other. The relative positivity of these radicals as measured by their effect on the ionization constants of the corresponding acids, $C_6H_5CH_2COOH$ (5.4×10^{-5}) and $CH_3C_6H_4COOH$ (4.5×10^{-5}), are approximately the same. It follows, therefore, that the influence of a radical on the electrolytic ionization of an acid containing the radical is not a measure of the influence of the radical on the activation of the atoms within a molecule in which it is present. This conclusion is significant in that the degree of ionization is related to the equilibrium attained in a reaction, whereas reactivity is measured by the rates at which the reaction proceeds.

(9) A comparison of the results with those obtained by Olivier[4] in the study of the rates of the reactions at 83° between an aqueous solution of ethyl alcohol and certain derivatives of benzyl chloride shows that the effects of the introduction of the substituents into benzyl chloride and into diphenylchloromethane are similar. In the case of the methyl derivatives of benzyl chloride the relative velocity constants of the ortho, meta and para compounds are, respectively, 4.84, 1.39 and 10.6; in the case of the analogous derivatives of diphenylchloromethane the relative constants are 2.9, 2.1 and 16.2. For the corresponding chloro derivatives the values are,

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

respectively, 0.355, 0.237, 0.62 and 0.01, 0.045, 0.42. In both cases methyl increases and chlorine decreases reactivity but the effect of the halogen is greater in the case of the diphenylchloromethane derivative. In both cases bromine has a greater effect than chlorine.

(10) A comparison of the relative velocity constants of *p*-chlorodiphenylchloromethane (0.42) and *p*,*p*′-dichlorodiphenylchloromethane (0.15) and of the corresponding methyl derivatives (16.2 and 413) show that the constant of the disubstituted derivative is of the order of the square of the constant of the mono derivative; in the case of chlorine, which depresses reactivity, the value is slightly less than the square and in the case of methyl, which increases reactivity, the value is greater.

(11) The velocity constant of the reaction between *iso*propyl alcohol and diphenylchloromethane was determined. The value obtained was 11% of that of the reaction with ethyl alcohol. In the case of *p*,*p*′-dichlorodiphenylchloromethane the velocity with *iso*propyl alcohol was 15% of that with ethyl alcohol. These values serve to compare the relative lability of the hydrogen of the hydroxyl group in ethyl alcohol and in *iso*propyl alcohol. A previous determination of this value based on the study of the reaction between these alcohols and *p*-nitrobenzoyl chloride in ethereal solution gave 11.7%.[5]

Additional conclusions in regard to the effect of substituents on the reactivity of the carbon–chlorine bond in derivatives of diphenylchloromethane are given in the paper by Norris and Gregory,[6] where the effect of the same substituents on the reactivity of the carbon–chlorine bond in derivatives of benzoyl chloride is considered.

Table II

Velocity Constants of the Reversible Reaction between Ethyl Alcohol and Certain Derivatives of Diphenylchloromethane

Concentration of chloride approximately 0.1 weight formal. Temperature 25.0°. Time in minutes.

Substituent	Constant	Average
No substituent	(0.00246), 0.00264, 0.00267	0.00266
o-Chloro	.0000253, 0.0000254	.0000254
p-Chloro	.00108, 0.00106	.00107
p-Methyl	.0417, 0.0430, 0.0453	.0433
p-Phenyl	.0379, 0.0375, 0.0333	.0362
p,*p*′-Dichloro	.000383, 0.000416	.00040
Benzylphenylchloromethane	.00000110, 0.00000114	.000000112

The following values were obtained when *iso*propyl alcohol was substituted for ethyl alcohol.

Diphenylchloromethane	0.000288, 0.000280	0.000284
p,*p*′-Dichloro	.0000580, 0.0000616	.0000598

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[5] Norris and Ashdown, This Journal, **47**, 837 (1925).

[6] Norris and Gregory, *ibid.*, **50**, 1813 (1928).

Experimental Results

The work described in this paper was the first to be completed on the determination of the velocity constants of the reactions between diphenylchloromethane and its derivatives. The calculations of the constants based on a reaction of the first order showed that in certain cases the values decreased as the reaction proceeded. In the case of very rapid reactions satisfactory observations could be made only after a large percentage of the chloride had been converted. As the constants calculated in this way gave unreliable results the reaction was studied in detail by Morton,[3] who showed that it was reversible and applied a method of calculation that gave agreeing values of the constant. The results given in Table II are those obtained from the recalculation by Professor A. A. Morton of the experimental data of Dr. Banta.

Preparation and Properties of the Substances Used.—In all cases the derivatives of diphenylchloromethane were prepared by the action of hydrogen chloride on the corresponding carbinol dissolved in ether or benzene. This method was originally described by Montague,[7] who prepared a number of dreivatives of diphenylchloromethane.

When the reaction was complete the solutions were freed from acid, dried with calcium chloride and evaporated. If the chloride proved to be a solid it was recrystallized, usually from petroleum ether; if a liquid, it was distilled under diminished pressure. In the case of liquid chlorides that could not be distilled, the solutions in benzene or ether were thoroughly dried, evaporated in a current of dry air at room temperature to constant weight and analyzed. If the product so obtained proved to be deficient in chlorine the percentage purity was calculated from the analysis and taken into account in making up the solutions for the determination of the velocity constants. The largest variation from the theoretical amount of chlorine occurred in the case of *p*-bromodiphenylchloromethane, which contained 11.79 instead of 12.59% of the halogen. The product was accordingly 93.6% pure. It was shown by Morton[3] that the impurities introduced into diphenylchloromethane made by a procedure similar to that described here had little effect on the velocity constant, provided the actual weight of the chloride used was known.

TABLE III

PROPERTIES OF THE SUBSTANCES USED. COMPOUNDS MARKED WITH AN ASTERISK HAVE NOT BEEN DESCRIBED BEFORE

Compound or derivative	M. p. of corresponding carbinol, °C.	B. p., °C.	M. p., °C.	Side chain chlorine, % Theoretical	Found
Diphenylchloromethane	67–68	167 (16 mm.)	17–18	17.51	17.47, 17.50
p,p'-Dichloro	92–94	......	63	13.06	13.01, 12.98
p-Phenyl	93–96	......	*71–72.5	12.72	12.62, 12.60
p-Chloro	57–59	*172–173 (6 mm.)	....	14.96	14.86, 14.88
p-Methyl	51.5–53	*147–148 (2 mm.)	....	16.37	16.25, 16.22
o-Chloro	65	*Decomposed at 90	....	14.96	14.59, 14.54
Benzylphenyl	67	Decomposed	....	16.37	15.02, 15.01
p,p-Dimethyl	67–69	......	*41–43.5	15.37	14.04
p-Bromo	59–61	*188–191 (10 mm.)	....	12.59	11.77, 11.80

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[7] Montague, *Rec. trav. chim.*, **25,** 403 (1906); **24,** 115 (1905); **26,** 266 (1907); **27,** 327, 355 (1908); **31,** 311 (1912).

The method of Schulze[8] for the determination of side chain chlorine was used. In certain cases the time of refluxing the halide with the alcoholic solution of silver nitrate was increased to two hours. Experiments with *p*- and *o*-chlorodiphenylcarbinol showed that the halogen in the ring was not removed by the solution of silver nitrate.

The ethyl alcohol used in the determination of velocity constants was purified in the usual way and dried over lime. The density of the samples used varied from d_4^{25}, 0.78501 to 0.78511. The *iso*propyl alcohol (from petroleum) was purified by the method of Lebo.[9] It boiled at 82.3–82.4°. The samples used varied in density from d_4^{25}, 0.7824 to 0.7821.

Summary

1. The velocity constants of the reaction between ethyl alcohol and the following derivatives of diphenylchloromethane have been determined: *o*-chloro, *p*-chloro, *p,p'*-dichloro, *p*-bromo, *p*-methyl, *p*-phenyl. Similar constants for the reactions between ethyl alcohol and benzyl phenylchloromethane, *iso*propyl alcohol and diphenylchloromethane, and *iso*propyl alcohol and *p,p'*-dichlorodiphenylchloromethane have been determined.

2. The effect of substituents in diphenylchloromethane on the reactivity of the side chain halogen is marked. Halogen atoms depress reactivity, the greatest effect resulting from substitution in the ortho position. The methyl and phenyl radicals increase reactivity, the greatest effect resulting from substitution in the para position.

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THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. V. THIRD CONTRIBUTION ON THE CARBON–CHLORINE BOND: THE RATES OF THE REACTIONS OF CERTAIN DERIVATIVES OF DIPHENYLCHLOROMETHANE WITH ETHYL ALCOHOL

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In this paper are reported the results of the determination of the rates at which nine derivatives of diphenylchloromethane react with ethyl alcohol. The compounds which had not been previously prepared were selected in such a way that the results could be used along with those obtained by Banta[2] in determining the effect of the position of a substituent on the reactivity of the carbon–chlorine bond.

In some of the compounds the chlorine atom was exceedingly labile.

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[8] Schulze, *Ber.*, **17**, 1675 (1884).

[9] Lebo, THIS JOURNAL, **43**, 1005 (1921).

[1] From the thesis of John Twiss Blake presented in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, 1924.

[2] Norris and Banta, THIS JOURNAL, **50**, 1804 (1928).