This has been explained on the assumption that resorcinol is an inhibitor whose oxidation is induced by that of catechol to form poly-hydroxylbenzenes whose effects are similar to those of pyrogallol or hydroquinone.

BERKELEY, CALIFORNIA RECEIVED SEPTEMBER 24, 1935

[CONTRIBUTION FROM SIR JOHN CASS TECHNICAL INSTITUTE]

The Reaction between Diphenylchloromethane and Ethyl Alcohol

BY F. G. KNY-JONES AND A. M. WARD

The results of a study of the rate of displacement of chlorine from diphenylchloromethane in ethyl alcoholic solution, obtained by Norris and Morton[1] differ in a number of respects from those obtained by one of us.[2]

Norris and Morton determined the velocity of the displacement from measurements of changes in the conductance of ethyl alcoholic solutions of the chloro compound, and concluded that the reaction is reversible, $CHPh_2Cl + EtOH$ (excess) $\rightleftharpoons CHPh_2OEt + HCl$, the direct reaction proceeding, under their experimental conditions, from 84.3 to 94.6% toward completion (Norris and Morton, Table IV, p. 1801); the factors which influenced this variation were not discussed, and the values of k for the postulated reverse reaction varied from 0.0015 to 0.0230. Ward[2] did not detect the reverse reaction in his kinetic study, which was based upon titration with alcoholic alkali of the hydrogen chloride formed. We did not obtain evidence of the reverse reaction by titrating alcoholic hydrogen chloride solutions of the final products.

Norris and Morton[1] (p. 1802) were unable to verify experimentally the calculated value for the reverse reaction and recorded but one experiment to show that the reaction was reversible; in this they passed hydrogen chloride into a solution of diphenylmethyl ethyl ether, dissolved in a mixture of dry benzene and petroleum ether, to which calcium chloride was added to remove the ethyl alcohol formed. The fact that they obtained diphenylchloromethane under these conditions does not afford any proof, however, of reversibility under the conditions of the kinetic experiments.

The velocity coefficients obtained by Ward (*e. g.*, $k = 0.00341$, 0.00349) are considerably higher than those of Norris and Morton ($k = 0.00281$ to 0.00310), which are higher also than those of Norris and Banta ($k = 0.00266$).[3] The values of k for the forward reaction were found to increase rapidly with increase in the water content of the alcohol, and the differences in the three sets of results may well be due to varying small amounts of water in the alcohol. According to Norris and Morton[1] (Table V, p. 1801) the extent of the reverse reaction diminished with increasing concentrations of water present. The equilibrium constant (K) for the reactions

$$CHPh_2Cl + EtOH \text{ (excess)} \rightleftharpoons CHPh_2OEt + HCl$$

is given by

$$K = \frac{k_1}{k_2} = \frac{[CHPh_2OEt][HCl]}{[CHPh_2Cl]}$$

where k_1 is the velocity coefficient of the forward reaction, k_2 that of the reverse reaction, and equilibrium concentrations are shown in square brackets. If the initial and equilibrium concentrations in g./mole/liter of diphenylchloromethane are C and $(1 - \alpha)C$, under the conditions of Norris and Morton's experiments $k_1/k_2 = \alpha^2C/(1-\alpha)$. The percentage conversions, calculated from their data (Table V), are shown.

Water, % by weight	0.15	0.58	1.07
Formality of $CHPh_2Cl$	.0990	.1191	0.1065
$k_1 \times 10^5$	316	358	407
$k_2 \times 10^4$	26	12	9
Conversion, %	93.0	96.3	97.8

Even if some 0.5% of water were present, about 4% of chloro compound should therefore be unchanged.

The failure to detect the reverse reaction in Ward's experiment might be due (1) to continued hydrolysis during the titrations, which were carried out by addition of alcoholic sodium hydroxide to a sample of the reaction mixture. Norris and Morton[1] (p. 1802), in checking results obtained by their conductivity method, added the reaction mixture to ice-cold water, removed cloudiness by means of carbon bisulfide, and then

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[1] Norris and Morton, THIS JOURNAL, **50**, 1795 (1928).

[2] Ward, *J. Chem. Soc.*, 2285 (1927).

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

titrated; (2) to water present in the alcohol, which was dried over lime, but the densities of the solvents used were not measured.

Further experiments, therefore, were carried out in which the alcohol used was purified by heating with quicklime and calcium, and fractionated (d^{20}_4 0.78940; Osborne, McKelvy and Bearce[4] give d^{20}_4 0.78934; the latter corresponds with Norris and Morton's value, d^{25}_4 0.78506). Diphenylchloromethane was prepared as previously,[5] and chlorine was determined by dissolving a sample in alcohol and titrating with sodium hydroxide, with warming, until displacement was complete.

Experiments were carried out by dissolving a known weight of chloro compound in the purified alcohol at 25.0°, adjusting the total volume to 250 ml., and leaving in the thermostat for two days; 50-ml. samples were then (1) titrated directly with standard alcoholic sodium hydroxide (approx. $N/20$); (2) added to about 200 ml. of ice-cooled water, free from carbon dioxide, and titrated with standard aqueous sodium hydroxide (approx. $N/20$); (3) added to 200 ml. of ice-cooled water, containing some 50 ml. of carbon bisulfide; the acidity of the mixture was previously removed by means of dilute sodium hydroxide. The mixture was well shaken, and then titrated as in (2). Phenolphthalein was used throughout as indicator.

RESULTS OF EXPERIMENTS

Chloro compound, g.		5.0014	4.7940	5.3020	8.1916
Chlorine, %		17.44	17.44	17.50	17.50
Titers, ml. $N/20$	(1)	98.3	93.7	104.3	161.3
	(2)	98.3	93.4	104.3	161.6
	(3)	98.1	93.2	104.5	161.3
Calcd. titer, x% displ.	$x = 100$	98.2	94.2	104.6	161.5
	$x = 94.6$	92.9	89.1	98.9	152.8
	$x = 84.3$	82.8	79.4	88.1	136.1

The end-points in procedures (1) and (2) were generally discharged by boiling; the further additions of $N/20$ alkali, necessary to produce permanent end-points after boiling, in the four series of experiments were

(1)	0.21	0.13	0.34	nil.	ml.
(2)	0.32	0.50	0.04	0.33	ml.

These results confirm that displacement was complete in the two processes.

The foregoing experiments, standing alone, do not disprove the findings of Norris and Morton concerning reversibility for the equilibrium position may be so rapidly displaced under the conditions of titration that any remaining chloro compound is completely hydrolyzed. It must be borne in mind, however, that hydroxyl ions are not effective in this hydrolysis, which depends upon a slow ionization of the diphenylchloromethane. To obtain evidence on this, three experiments were carried out.

(1) Diphenylchloromethane (about 0.5 g.) was dissolved in dry ethyl alcohol (about 50 ml.) at 17° and at once titrated with alcoholic sodium hydroxide ($N/20$) in presence of phenolphthalein. Good end-points were obtained.

Time after mixing, min.	1/2	2	3	6	13
Titer (total), ml.	0.10	0.26	0.34	0.78	1.49

The temperatures at which the solutions were titrated can be considered to approximate to room temperature, and as the time of titration did not exceed three to five minutes, any displacement error would not have exceeded about 0.5 ml. This is very much smaller than the differences required from Norris and Morton's equilibrium values.

(2) Diphenylchloromethane (about 0.5 g.) was dissolved in ethyl alcohol (50 ml.), at once added to about 200 ml. of ice-cold water, and titrated at the times shown, against $N/20$ aqueous sodium hydroxide.

Time, min.	1	2	5	12
Titer, ml.	4.40	5.57	6.27	7.63

The rapidity of reaction of the aqueous alcoholic emulsion was much too great to allow any deduction to be drawn concerning the possible equilibrium, the difference between the titers for complete and 94.6% displacement being of the same order as the above titration values, after two minutes.

(3) The experiment was as in (2), but the alcoholic solution was added to ice-cold water containing carbon bisulfide, previously neutralized.

Time, min.	1/2	2	9	15
Titer, ml.	1.45	1.55	1.95	2.20

These results, showing an initial rapid reaction, followed by a slow change, indicate that rapid displacement of halogen takes place before the compound is extracted by the carbon bisulfide, but that afterward the reaction is slow.

The foregoing results show that titration with alcoholic alkali is the most satisfactory titration

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(4) Osborne, McKelvy and Bearce, *Bull. Bur. Stand.*, **9**, 245 (1913).

(5) Ward, *J. Chem. Soc.*, 2288 (1927).

technique for arriving at the displacement figure and no evidence is obtained by titration methods for reversibility.

Summary

1. Norris and Morton, from conductance measurements, considered the reaction between diphenylchloromethane and ethyl alcohol to be reversible. Ward, by a titration method, found the reaction to be irreversible.

2. The titration method has now been examined in greater detail. No evidence is obtained for reversibility.

SIR JOHN CASS TECHNICAL INSTITUTE
LONDON, ENGLAND

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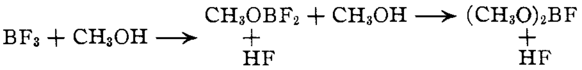
[CONTRIBUTION NO. 47 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

A New Method for the Preparation of Alkoxyboron Halides and their Reaction with Metals

BY CORLISS R. KINNEY, H. THERON THOMPSON AND LEE C. CHENEY

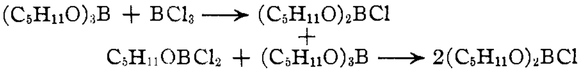
Alkoxyboron halides were first prepared by Gasselin[1] in 1894 by the action of methyl alcohol on boron trifluoride.



$$BF_3 + CH_3OH \longrightarrow \underset{\substack{+\\ HF}}{CH_3OBF_2} + CH_3OH \longrightarrow \underset{\substack{+\\ HF}}{(CH_3O)_2BF}$$

In 1932 Bowlus and Nieuwland[2] observed that alcohols higher than methyl or ethyl did not produce fluoro esters, but a complex hydrocarbon mixture. The chloro esters were first investigated by Ramser and Wiberg[3] and later by Wiberg and Sütterlin[4] who prepared the methyl and ethyl derivatives from the corresponding alcohols or ethers and boron trichloride.

Preliminary experiments on the action of metals on diethoxyboron chloride indicated that larger groups would be desirable; consequently diisoamyloxyboron chloride was prepared and studied. The substance was prepared first using Wiberg and Sütterlin's method, but the yield was not satisfactory. Several attempts were made to prepare the substance from triisoamyl borate and dry hydrogen chloride, thionyl chloride, and phosphorus pentachloride[5] but the desired product was not obtained. With boron trichloride, however, the chloro ester was obtained and in much increased yields.



$$(C_5H_{11}O)_3B + BCl_3 \longrightarrow \underset{\substack{+\\ C_5H_{11}OBCl_2}}{(C_5H_{11}O)_2BCl}$$
$$C_5H_{11}OBCl_2 + (C_5H_{11}O)_3B \longrightarrow 2(C_5H_{11}O)_2BCl$$

Diisoamyloxyboron chloride did not react with "molecular silver" at room temperature, but did react readily with sodium or zinc when warmed. The reaction was exothermic and became violent unless cooled. Unexpected gaseous products were observed even at 70° in a benzene solution. The gas contained hydrogen chloride and probably isoamylene and hydrogen. The liquid product did not react with water to form hydrogen, indicating that $(C_5H_{11}O)_2BNa$ or possibly $(C_5H_{11}O)_2BB(OC_5H_{11})_2$ was absent. On distillation only triisoamyl borate and boric anhydride were obtained.

The reaction was obviously complex and involved secondary reactions. Without doubt the sodium removed the chlorine atom and the resulting radical, instead of combining with another of its kind, decomposed into an isoamyl radical and isoamyl metaborate.

$$(C_5H_{11}O)_2BCl + Na \longrightarrow (C_5H_{11}O)_2B\text{—} + NaCl$$
$$(C_5H_{11}O)_2B\text{—} \longrightarrow C_5H_{11}OBO + C_5H_{11}\text{—}$$

The unsaturated hydrocarbon gas and the hydrogen are accounted for by the decomposition of the isoamyl radical into isoamylene and nascent hydrogen, and the hydrogen chloride by the action of the hydrogen on another molecule of the chloro ester.

$$C_5H_{11}\text{—} \longrightarrow C_5H_{10} + H$$
$$(C_5H_{11}O)_2BCl + H \longrightarrow (C_5H_{11}O)_2B\text{—} + HCl$$

Finally, the isolation of triisoamyl borate and boric anhydride are to be expected because the attempt to isolate a metaborate by fractional distillation always results in the orthoborate and boric anhydride.

Experimental Part

The Reaction of Diethoxyboron Chloride with Metals.—Diethoxyboron chloride reacted readily with sodium or dry zinc dust when warmed slightly. Gases were evolved and a liquid product distilling between 110 and 150° was

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[1] Gasselin, *Ann. chim. phys.*, [7] **3**, 83 (1894).

[2] Bowlus and Nieuwland, THIS JOURNAL, **54**, 2017 (1932).

[3] Ramser and Wiberg, *Ber.*, **63**, 1136 (1930).

[4] Wiberg and Sütterlin, *Z. anorg. allgem. Chem.*, **202**, 1 (1931).

[5] Schiff, *Ann. Suppl.*, **5**, 154 (1867).