another 3.5 hours. Thirty ml. of dilute (1:5) acetic acid was added, followed by 5 ml. of 10% hydrochloric acid. The organic layer was washed with water and sodium chloride, dried over sodium sulfate, and evaporated to dryness. The white solid was extracted with several portions of warm benzene, the benzene evaporated, the product dehydrogenated by treatment with 0.50 g. of palladium-on-charcoal catalyst[27] at 300–350° for 30 minutes, and then chromatographed on alumina. The least strongly adsorbed blue-fluorescent band gave 0.11 g. of tan solid which was sublimed at 180° (1 mm.) and then treated with 0.08 g. *s*-trinitrobenzene in benzene–ethanol. There was obtained 15 mg. of orange-brown plates, m.p. 158–179°. The more strongly adsorbed, purple-fluorescent band of the chromatogram gave 0.07 g. dark solid which was sublimed at 180° (1 mm.) and then treated with 0.08 g. of *s*-trinitrobenzene in benzene–alcohol. There was obtained 67 mg. of black needles, m.p. 233.0–235.0°. The ultraviolet absorption spectra showed that neither of the two products was benz[j]-fluoranthene; they were not further investigated.

(c) A solution of 0.41 g. of XIV in 15 ml. of absolute ethanol was hydrogenated in the presence of 50 mg. of Adams catalyst. During 3.5 hours, 35.9 ml. (S.T.P.) of hydrogen was absorbed (105% of theoretical for the conversion of XIV to the carbinol). The product was heated with 0.30 g. of palladium-on-charcoal catalyst[27] at 300–310° for 50 minutes; a small amount of tarry material which sublimed during this period was discarded. The product was then sublimed at 300° (2–3 mm.) and the dark-purple plates dissolved in benzene–ethanol and treated with 0.10 g. of 2,4,7-trinitrofluorenone.[20] The black crystals obtained had m.p. 250.5–255.5° (reported[3] for the orange-red 2,4,7-trinitrofluorenone complex of III, m.p. 255–256°; no material was available for a mixed melting point). The complex was chromatographed on alumina and eluted with benzene, and the deep red eluate shaken with 25 ml. of concentrated sulfuric acid for about 5 minutes. The resulting colorless solution was washed with water, 10% sodium bicarbonate solution, and saturated sodium chloride, dried over calcium chloride, and evaporated to dryness. There was obtained 0.0060 g. of a pale violet oil. The ultraviolet absorption spectrum showed that the product was not III; it was not further investigated.

BRUCETON, PA. RECEIVED JUNE 10, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Demonstration of Exchange and Friedel–Crafts Reactions of Gaseous Organic Chlorides on Solid Aluminum Chloride

BY MONTE BLAU AND JOHN E. WILLARD

Recent work in our laboratory[1] has shown that rapid exchange of chlorine occurs between solid aluminum chloride and liquid carbon tetrachloride. The observed characteristics of the reaction have suggested strongly that it, and possibly also certain related Friedel–Crafts type reactions, must occur on the solid surface rather than through the medium of dissolved aluminum chloride molecules or CCl_3^+ and $AlCl_4^-$ ions in solution. The purpose of the present communication is to report: (1) experiments on the exchange of chlorine between six different gaseous organic halides and solid aluminum chloride which demonstrate with certainty that this type of reaction can occur on an aluminum chloride surface without the necessity for a solvent; (2) an experiment which shows that a Friedel–Crafts reaction between carbon tetrachloride and benzene can take place between gaseous reactants in contact with solid aluminum chloride.

Experimental

All of the experiments reported here were carried out on a vacuum line using techniques similar to the most rigorous described in the previous work.[1] In each test a sample of the vapor of the organic halide to be tested was admitted from a reservoir of the carefully degassed liquid through a phosphorus pentoxide drying train to a 500-ml. flask coated on the inside with ten to twenty mg. of radioactive aluminum chloride. The pressure of the vapor used was in each case below its vapor pressure at the reaction temperature. Pressures were measured with a closed-end mercury manometer. The aluminum chloride was prepared *in situ* by heating aluminum with silver chloride containing radiochlorine (Cl^{36}) and subliming the product into the flask where it was condensed on the walls with the aid of liquid air.

When the organic vapor had stood in contact with the aluminum chloride for the desired length of time it was frozen out in a side tube and sealed off. The tube so removed was opened, and while the contents were still frozen a mixture of water and carbon tetrachloride was added to dissolve both inorganic and organic products. The radioactivity in the aqueous and in the organic fraction was then determined with a solution counter, the count in the organic fraction being corrected for the lower counting efficiency due to the higher density of the solution.

After the desired number of runs had been made with a given preparation of aluminum chloride, the flask was opened and the residual activity was determined by dissolving and counting the aluminum chloride. In those cases where a non-volatile organic product was left with the aluminum chloride, qualitative tests were made of its solubility in different solvents.

Blank determinations showed that no detectable amount of aluminum chloride was sublimed from the reaction flask to the side tubes when they were cooled with liquid air for the purpose of condensing and sealing off the reaction products. Check determinations also showed that hydrolysis during the washing procedure could not have contributed significantly to the amount of inorganic chloride found.

Except for *n*-propyl and *n*-amyl chlorides the organic chlorides were used as they came from the manufacturers' bottles, without further purification other than vacuum distillation through phosphorus pentoxide. The types used were: Mallinckrodt "Low Sulfur" carbon tetrachloride; Baker "Analyzed" chloroform; Eastman ethyl chloride, and benzyl chloride. The amyl and propyl chlorides were purified by washing with concentrated sulfuric acid, sodium carbonate solution, and water, followed by drying over calcium chloride and distillation from phosphorus pentoxide through a Vigreux column. The second 5 ml. of distillate from 15 ml. of compound was used in the experiments. In the case of the amyl chloride the refractive index was checked and found to be 1.4119^{20}_{D}, in agreement with literature values. Runs with unpurified material gave essentially the same results as those with purified reagents.

Results

Exchange Reactions and Hydrogen Chloride Formation.—The data of Table I show that under the conditions of these experiments exchange of chlorine occurred readily between solid aluminum chloride and gaseous carbon tetrachloride, chloroform, ethyl chloride, *n*-propyl chloride, *n*-amyl chloride and benzyl chloride with a contact time of a few minutes at room temperature. Exchange was observed at −10° in run 5 with carbon

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(1) Wallace and Willard, THIS JOURNAL, 72, 5275 (1950).

TABLE I

REACTIONS OF GASEOUS ORGANIC CHLORIDES WITH SOLID RADIOACTIVE ALUMINUM CHLORIDE

Run	Reactant	Pressure, cm.	Vap. pres. at react. *T*, cm.	Temp., °C.	Time, min.	% Exchange[a]			Appearance of surface after reaction
						Total	Organic	Inorg.	
1	CCl_4	9	11.5	25	25		9.8	0	Unchanged
2	CCl_4	9	11.5	25	25		2.9	0	Unchanged
3	CCl_4	9	11.5	25	25		3.4	0	Unchanged
4	CCl_4	9	11.5	25	25	2.5	..	..	Unchanged
5[b]	CCl_4	1	1.8	−10	120	16.1	..	..	Unchanged
6	CCl_4	9	11.5	25	2	4.0	..	..	Unchanged
7	CCl_4	9	11.5	25	2	4.1	..	..	Unchanged
8	CCl_4	9	11.5	25	2	2.9	..	..	Unchanged
9	CCl_4	9	11.5	25	2	2.9	..	..	Unchanged
10	CCl_4	9	11.5	25	2	1.7	..	..	Unchanged
11[c]	C_2H_5Cl	10	120	25	5		3.8	0	Unchanged
12[c]	*n*-C_3H_7Cl	10	33.9	25	5		7.6	0.2	Unchanged
13	*n*-C_3H_7Cl	10	33.9	25	10		5.2	0.1	Unchanged
14	*n*-C_3H_7Cl	10	33.9	25	900		69.4	11.4	Brown
15[c]	$CHCl_3$	10	19.9	25	5		2.9	0	Unchanged
16[c]	*n*-$C_5H_{11}Cl$	2.5	3.2	25	5		4.9	39.0	Deep-brown
17[c]	*n*-$C_5H_{11}Cl$	2.5	3.2	25	5		0.6	18.9	Deep-brown
18[c]	$C_6H_5CH_2Cl$	0.09[d]	0.12	25	3		0.3	8.7	Light yellow
19	$C_6H_5CH_2Cl$	0.30	0.56	50	5		0.3	12.4	Brown
20[e]	CCl_4^* C_6H_6	3 3	11.5 9.3	25	10		7.9[e]	20.5	Deep-brown

[a] % exchange = (activity in gaseous reaction products)/(activity in $AlCl_3^*$ surface at start of run) × 100. [b] $AlCl_3^*$ from runs 1–4 resublimed prior to using it for run 5. [c] Fresh $AlCl_3^*$ preparation. [d] Reaction flask filled four times and products pooled. [e] Consists of unreacted CCl_4^* plus any sufficiently volatile labeled organic reaction products.

tetrachloride. Propyl chloride, *n*-amyl chloride, and benzyl chloride all produced a yellow or brownish color on the aluminum chloride, and in each of these cases inorganic chloride (hydrogen chloride) was found in the products of the reaction which were condensed with liquid air and sealed off from the system.

It should be emphasized that comparisons between runs are of only broad qualitative significance because it is not possible to reproduce the surface area of the aluminum chloride from one preparation to another and because in a series of successive runs on a single deposit the activity of the readily accessible surface layers is progressively depleted by the surface reaction. As would be expected, the percentage of the aluminum chloride radioactivity removed by successive exposures to carbon tetrachloride decreased (Table I, runs 1 to 4) but then increased when a fresh surface had been exposed by resubliming the aluminum chloride (run 5).

The hydrogen chloride found in the products of the reactions of propyl, amyl, and benzyl chlorides with the aluminum chloride surface could have been formed by either a condensation reaction between two organic chloride molecules with a splitting out of hydrogen chloride, or by a dehydrohalogenation to give an olefin. The formation of a brownish deposit when these chlorides came in contact with the aluminum chloride was presumably due to the formation of non-volatile complexes between the aluminum chloride and reaction products. In the case of the propyl chloride (run 14) it was possible by careful heating to sublime aluminum chloride away from the colored deposit. The sublimed aluminum chloride was white and a brown transparent film which was readily soluble in acetone remained on the glass. No gas pressure was developed in the system as a result of the sublimation. In another run with propyl chloride the volatile reaction products removed from the system were washed with cold silver nitrate solution. The silver chloride produced was equivalent to 7% of the propyl chloride estimated from the pressure and volume of the gas condensed, thus giving an independent check on the formation of inorganic chloride.

When amyl chloride was admitted to aluminum chloride the white surface seemed to disappear for a few seconds, following which a deep brown color formed on the surface. This reaction was much faster than the formation of the brown film with propyl chloride, and a correspondingly larger quantity of hydrogen chloride was produced. The brown residue in the reaction flask following these experiments was insoluble in ether, carbon tetrachloride, and acetone but disappeared when water was added. Likewise, the brown film formed in the benzyl chloride experiment did not dissolve readily in acetone but disappeared when water was added.

Friedel–Crafts Reaction.—When it was observed that chlorine would exchange between organic chlorides and aluminum chloride in the absence of any liquid it was of interest to determine whether a Friedel–Crafts type of reaction would occur under similar circumstances. The simplest procedure available for testing this possibility was to mix gaseous carbon tetrachloride tagged with radiochlorine with gaseous benzene in the presence of aluminum chloride, and to test for the production of radioactive hydrogen chloride which would be produced in a reaction of the type $x\mathrm{C_6H_6} + \mathrm{CCl_4^*} \xrightarrow{\mathrm{AlCl_3}} (\mathrm{C_6H_5})_x\mathrm{CCl^*}_{(4-x)} + x\mathrm{HCl^*}$. Benzene vapor was first allowed to stand with radioactive aluminum chloride for 10 min. and then condensed with liquid air and shown to contain no hydrogen chloride. No color change occurred during this operation. Carbon tetrachloride at a pressure of 3 cm. was then allowed to exchange with the aluminum chloride for 10 min., following which benzene was admitted over a period of about 15 sec. until the total pressure was 6 cm. During the first 2 min. after admission of the benzene the surface turned deep brown and the pressure dropped from a total of 6 cm. to 5.2 cm. The reaction was allowed to proceed for 10 min. during which time the pressure did not change further. The gaseous products were then removed and counted. The fact that activity was found in the inorganic fraction (Table I) can only be explained if a Friedel–Crafts type reaction occurred. The reduction in pressure as the reaction proceeded is probably due to formation of essentially nonvolatile phenylchloromethanes which would cause the removal of more than one molecule of reactants from the gas phase for each molecule of gaseous hydrogen chloride formed. The brown film left in the reaction flask dissolved in ether turning green as it dissolved but forming a colorless solution.

Summary

A variety of gaseous organic chlorides have been found to exchange chlorine with solid aluminum chloride. Some of these undergo reactions on the surface with evolution of hydrogen chloride.

Gaseous carbon tetrachloride and benzene have been found to undergo a Friedel–Crafts type reaction on an aluminum chloride surface.

These observations are consistent with earlier work[1] which suggested that an aluminum chloride surface is necessary for exchange between liquid carbon tetrachloride and aluminum chloride.

MADISON, WISCONSIN RECEIVED MAY 12, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Reactions of Naphthoquinones with Malonic Ester and its Analogs. I. Reactions with Malonic Ester[1]

BY ERNEST F. PRATT AND WERNER E. BOEHME

It has been found that 1,4-naphthoquinone and malonic ester in pyridine solution react to give a blue, crystalline solid (I). An improved synthesis (40% yield) of I from potassium 1,4-naphthoquinone-2-sulfonate and sodiomalonic ester has been developed. Compound I has been characterized by conversion in good yields to twelve different products to which structures have been assigned. A number of interrelations among these products have been established.

Products from the reaction of 1,4-benzoquinone with active methylene compounds have been well characterized in several instances.[2] Under the alkaline conditions usually employed the reactions were ordinarily of the Michael type proceeding *via* 1,4-addition. Evidence has accumulated that related reactions occur with 1,4-naphthoquinone but none of the products have been adequately characterized.[3]

Professor Louis F. Fieser and Dr. Yolanda Pratt observed that 1,4-naphthoquinone reacted with malonic ester in pyridine at room temperature to give a precipitate from which a low yield of dark blue needles could be obtained by extraction with and recrystallization from benzene.[4] The characterization of this product and a more practical synthesis are described in this paper.

The results of elementary analyses agreed satisfactorily with the values calculated for Ia. By using acetone in place of benzene for the isolation, the solvent-free compound (I) was obtained. Acetylation of I gave the orange diacetate (II) which was readily reduced by sodium hydrosulfite to the colorless bis-hydroquinone diacetate (III).

Oxidation of Ia with silver oxide in benzene gave green needles of the diquinone (VIIa). The oxidation equivalent calculated from the amount of metallic silver obtained agreed satisfactorily with the theoretical value. Oxidation with silver oxide in acetone or with chromic anhydride in acetic acid gave the solvent-free product (VII).

Reduction of either Ia or VII with sodium hydrosulfite gave the colorless bis-hydroquinone (IV) which rapidly turned blue upon exposure to the air. When a solution of the bis-hydroquinone (IV) was mixed with a solution of the diquinone (VII) at room temperature a dark blue precipitate appeared in only a few minutes. The results of elementary analyses and melting point and mixture melting point determinations indicated that disproportionation had occurred to give Ia.[5] The yield was nearly quantitative.

Acetylation of II or IV or reductive acetylation of Ia under rigorous conditions gave the tetraacetate (V). A diacetate different from II (see Experimental), but which could also be acetylated to V, was obtained by reductive acetylation of Ia under

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(1) From the Ph.D. thesis of W. E. Boehme, May, 1948.

(2) For a brief review see J. H. Wood, C. S. Colburn, Jr., L. Cox and H. C. Garland, THIS JOURNAL, **66**, 1540 (1944). Also see M. V. Ionescu, *Bull. soc. chim.*, **41**, 1094 (1927).

(3) R. Craven, *J. Chem. Soc.*, 1605 (1931); W. Kesting, *Z. angew. Chem.*, **41**, 358 (1928); *J. prakt. Chem.*, **138**, 215 (1933); C. Liebermann, *Ber.*, **33**, 566 (1900), and earlier papers. Liebermann, in his first paper (*ibid.*, **31**, 2093 (1898)) states without experimental confirmation that 1,4-naphthoquinone reacts with sodiomalonic ester in the same fashion as 2,3-dibromo-1,4-naphthoquinone which reacted in the orthodox manner cleaving out sodium bromide. His products, therefore, were quite different from the one obtained under our conditions.

(4) Personal communication. An oxidation product was also prepared but no structures were determined or further characterization done. We wish to thank these investigators for deferring to our interest in the problem.

(5) We do not feel that the possibility that compound I (or Ia) is a quinhydrone formed from one molecule each of IV and VII has been definitely eliminated. We prefer, however, the interpretation given in the body of the paper chiefly because it more simply explains the reactions Ia → II → III → V.