and of *o*-cresol with *m*-cresol were not separated under the conditions of these experiments.

Experimental

Preparation of Azo Dyes.—The method of Cheronis[8] was followed using 0.01 molar quantities of reactants. In many cases it was found that the dyes could be recovered in almost pure state by acidifying the final reaction mixture and filtering the product. The dyes so recovered were recrystallized from alcohol–benzene or alcohol alone as required. In other cases the dyes could not be isolated in crystalline form either as the free acid or by salting out of the sodium salts. The reaction mixtures containing these dyes were treated in the same manner as the mixtures described below.

The preparation of dyes from phenol mixtures was accomplished by the same method except that no attempt was made to isolate the crystalline products. The resulting reaction mixture was acidified with an excess of hydrochloric acid and extracted with benzene or chloroform to remove unreacted phenol. A small portion (1–3 drops) of the aqueous solution was then diluted with 2 ml. of ethanol and spotted, by means of a small platinum wire loop, at the appropriate position on the paper strip.

Development of the chromatograms was accomplished by the usual methods with an apparatus similar to that of Steward,[9] consisting of a stainless steel trough (2.25 × 1.5 × 6.5 in.) suspended by brackets from the lugs in the top of a conventional museum specimen jar (20 × 60 cm.). The irrigating solvents (*vidi supra*) were prepared by thoroughly shaking the mixture in a separatory funnel and allowing to stand until completely separated. The organic phase was used for irrigation. The paper strips (14 × 56 cm. Whatman No. 1 filter paper) were first sprayed to the point of fiber saturation with aqueous 4% sodium carbonate, dried, spotted with the dye and suspended from the trough in the jar. They were allowed to remain undisturbed for one hour before adding the irrigating solvent in order to allow them to attain equilibrium with the aqueous phase of the solvent mixture which had previously been placed in the bottom of the jar.

Acknowledgment.—The author wishes to express appreciation of a Grant-in-Aid of Research by the Graduate School of the University of Minnesota. Thanks are also due Mr. Wayne L. Meek for preparation of the dyes.

[8] N. D. Cheronis, "Semimicro and Macro Organic Chemistry," Thomas Y. Crowell Co., New York, N. Y., 1942, p. 285.

[9] F. C. Steward, W. Stepka and J. F. Thompson, *Science*, **107**, 451 (1948).

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The Exchange Reaction between Hydrogen Chloride and Chlorine in the Gaseous State

BY W. H. JOHNSTON[1] AND W. F. LIBBY

The occurrence of a rapid exchange reaction between HCl and Cl_2 in the gaseous state was noted briefly by Dodgen and Libby[2] in 1949. The present paper describes the discoveries that the homogeneous exchange is slow, is catalyzed by ordinary glass surfaces, and that a rapid photochemical exchange reaction occurs.

Anhydrous tank gases from the Matheson Company and radiochlorine-36 ($t_{1/2}$ = 2 × 10^6 yr.) from the Isotopes Division of the Atomic Energy Commission were used. The gases were measured with a Bourdon gage in a known volume of Pyrex vacuum line. The reactions were carried out generally in 500-cc. Pyrex flasks some of which were coated with a mixture of saturated long-chain fluorocarbons (du Pont perfluorolube oil, FCD 335). Following the reaction the mixed gases were expanded into a trap at liquid nitrogen temperature and separated by distillation under vacuum with a bath of ethanol and water at −130°. The HCl^{36} and $ClCl^{36}$ were counted in a cylindrical annular volume surrounding a Geiger counter. The specific activities of the initial gases were measured in units of counts per minute per millimole of "Cl." Pure chlorine free of HCl was obtained by the distillation following the reaction and its specific activity was measured in the same manner. The over-all pressure balance and activity balance were measured and were found to be between 90 and 100%. The extrapolation of the data to zero exchange at zero time was a further check on the separation.

In the photochemical studies nearly monochromatic light of 3650 Å. wave length was obtained with a medium pressure mercury arc (G. E. lamp, AH-4) and appropriate filters. Relative intensities were obtained with a Bowen type Photometer[3] and 931-A photomultiplier tube. Absolute intensities were measured with the uranyl oxalate actinometer[4] and, independently, with a thermopile and moving coil galvanometer.[5] All readings were referred to a reference light source which was known to be stable. All photochemical studies were done in a fluorocarbon coated vessel where the rate of the dark reaction was negligible by comparison.

Most of the experimental data on the dark exchange reaction are shown in Table I. The sparsely covered surface was a Pyrex glass bulb which was uniformly spotted with very small droplets of the fluorocarbon. The largely covered surface had a maximum of four per cent. of the Pyrex uncovered.

TABLE I

DARK EXCHANGE IN VARIOUS SURFACES AT 25°

Run	Surface	HCl m./l. × 10^3	Cl_2 m./l. × 10^3	Exchange, %	Time, min.	Half-time, min.
6	Pyrex	0.52	1.48	64	4.0	3
7	Pyrex	.46	1.54	90	7.5	3
8	Packed pyrex	.43	2.26	100	9.0	2
9	Packed pyrex	.45	2.29	103	5.0	2
10	Sparse fluoro.	.83	0.78	9	2.5	19
11	Sparse fluoro.	.85	0.74	16	5.0	20
12	Sparse fluoro.	.81	0.73	28	9.0	21
5	Large fluoro.	.88	1.66	49	11.0 hr.	11 hr.
1	Complete fluoro.	.85	1.52	42.5	12.5 hr.	16 hr.
2	Complete fluoro.	.87	1.64	26.5	7.0 hr.	16 hr.
3	Packed fluoro.	.88	1.35	78.5	11.1 hr.	5 hr.
4	Packed fluoro.	.87	1.36	43	4.0 hr.	5 hr.

It is clear from the data of Table I that the reaction is heterogeneous at room temperature.

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[1] Atomic Energy Commission Predoctoral Fellow. This paper is taken in part from the thesis presented by W. H. Johnston to the Faculty of the University of Chicago in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Present address: Department of Chemistry, Purdue University, Lafayette, Indiana.

[2] H. Dodgen and W. F. Libby, *J. Chem. Phys.*, **17**, 951 (1949).

[3] E. J. Bowen, *Proc. Roy. Soc.* (*London*), **A154**, 349 (1936).

[4] (a) W. G. Leighton and G. S. Forbes, THIS JOURNAL, **52**, 3139 (1930); (b) G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934); (c) L. J. Heidt and F. Daniels, *ibid.*, **54**, 2384 (1932).

[5] (a) A. Farkas and H. W. Melville, "Experimental Methods in Gas Reactions," Macmillan, Ltd., London, 1939, pp. 250–254. (b) J. D. Strong, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York, N. Y., 1938, pp. 305–341.

The measurements of the absolute light intensities for the photo-chemical study by both the uranyl oxalate actinometer and a thermopile gave concordant values at 4.4 × 10^{16} quanta per minute for the beam passing through the reaction vessel.

The data on the quantum yield for the photo-exchange are shown in Table II. The quanta absorbed per minute were calculated from the known incident beam and the measured fractional absorption by the reaction mixture. The initial exchange rate is given in the last column as the exchange at one minute. The quantum yield is given by the product of the total number of molecules of HCl times the initial exchange rate divided by the quanta absorbed per minute. As shown in Table II the quantum yield is 110.

TABLE II

PHOTO-EXCHANGE AND QUANTUM YIELD

Run	HCl,[a] millimole	Cl_2, millimoles	Quanta[b] absorbed per min. × 10^{16}	Exchange, %	Time, min.	Half-time, min.	Initial exchange rate, %/min.
1	0.27	1.49	2.6	9	5	37	1.9
2	.27	1.59	2.6	49	41	42	1.6
3	.22	1.11	2.3	30.5	20	38	1.8
4	.19	1.99	2.2	79.5	90	39	1.8
Mean	0.24	1.25	2.4	..	..	39	1.8

Molec. HCl exchanged at 1 min. = 2.6 × 10^{16}

Quanta absorbed per min. = 2.4 × 10^{16}

Quantum yield = 110[b]

[a] Vol. = 0.510 liter. [b] Light of 3650 Å. wave length.

It appears likely that the photo-exchange occurs through Cl atoms exchanging rapidly with both HCl and Cl_2 molecules. Further work of a more quantitative character should reveal important data on the kinetics of this simple system.

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Addition Reactions in Phospho-organic Syntheses. II. The Addition of Phosphorus Pentachloride to Normal Olefins

BY GENNADY M. KOSOLAPOFF AND JOHN F. MCCULLOUGH

The investigations of the addition of phosphorus pentachloride to a variety of olefins that have been made by Thiele,[1] by Bergmann and Bondi[2] have shown that the reaction proceeds in accord with the Markovnikov rule and yields adducts of type $RCHCl—CH_2PCl_4$, which, on treatment with water, readily yield unsaturated phosphonic acids $RCH=CHPO(OH)_2$. Bergmann and Bondi[2] and one of us[3] noted that aliphatic olefins tend to retain the elements of hydrogen chloride in the hydrolytic step and treatment with alkali may be necessary to form the unsaturated acids.

Recent patents[4] indicate that aliphatic terminal olefins of the general type $RCH=CH_2$ may undergo the addition reaction in the reverse sense, *i.e.*, contrary to Markovnikov rule. To clarify this point, a typical olefin of this category, 1-butene, was subjected to the reaction of addition. The product was converted to the phosphonyl dichloride, which was esterified with ethanol. The resulting diethyl chlorobutanephosphonate was dehydrohalogenated with alcoholic potassium hydroxide and the unsaturated ester, thus formed, was ozonized. Formaldehyde could not be detected in the product, although it would have been the expected ozonolysis product from the anti-Markovnikov adduct. Hydrogenation of the unsaturated ester and hydrolysis of the ester linkage of the product yielded *n*-butanephosphonic acid, identical with an authentic sample.[5]

These results showed that the orientation of the addition reaction is in accord with the Markovnikov rule, and that the substances described in the aforementioned patents[4] are products of normal addition.

Experimental.—The nomenclature used in this section follows from the results obtained in the investigation. The locations of phosphorus and chlorine are reversed in respect to their assignment in the patent literature.[4]

2-Chlorobutylphosphorus Tetrachloride.—A stream of *n*-butene (C.P. grade, supplied by the Mathieson Chemical Corporation) was passed into a suspension of 154 g. of phosphorus pentachloride in 500 ml. of benzene, with good stirring and ice-cooling. The addition was continued until 70 g. of the olefin was absorbed by the mixture in the course of 2 hours. After continued stirring for 8 hours, the mixture was allowed to stand overnight in an ice-bath. The resulting adduct formed the usual "creamy" suspension in benzene, which was then used for subsequent reactions.

2-Chlorobutanephosphonyl Dichloride.—Preliminary experiments indicated that a direct hydrolysis or alcoholysis of the adduct yields intractable products: an acid which is extremely resistant to crystallization and a diethyl ester which tends to decompose on distillation. Hence, the reaction product described above was treated *in situ* with 38.5 g. of phosphorus pentoxide and the mixture was stirred for 2 hours at room temperature, for 2 hours at 35° and for 2 hours at 50°. This temperature regime has been specified[4] and was followed as closely as possible. Repetition of several such runs failed to show any necessity for the low temperature operation, as no apparent action took place until the temperature had been raised to 50°. The unreacted phosphorus pentachloride was removed by rapid decantation and filtration through glass wool. Distillation of the filtrate yielded the phosphonyl dichloride in the form of colorless oily liquid which distilled sharply at 127° at 24 mm. and which was obtained in 40–41% yield (average of several runs). The yield reported in the literature[4] was 48%.

Diethyl 2-Chlorobutanephosphonate.—The esterification was again carried out in a manner indicated by the literature.[4] The dichloride (51 g.) was added dropwise to 100 ml. of absolute ethanol with ice cooling and stirring under reduced pressure maintained by a water-pump. After evacuation for 12 hours, the mixture was distilled, yielding 48 g. of the ester (88%). The latter boiled at 120–124° at 4 mm. or 78–80° at 0.3 mm. Its physical constants were found to be $n^{30}{}_D$ 1.4389–1.4394, and $d^{30}{}_4$ 1.0939. This gave *MR* calcd. for $ClC_4H_8PO(OEt)_2$ 54.64, and *MR* found 54.98. It may be noted that the phosphonyl dichlorides and phosphonates cited as patent examples[4] have considerably wider boiling point ranges than the above.

Diethyl 1-Butenephosphonate.—The above ester (21.5 g.) was added dropwise to an ice-cooled and vigorously stirred solution of 5.5 g. of potassium hydroxide in 65 ml. of absolute ethanol. After 15 minutes the mixture was filtered and distilled. There was obtained a total of 16 g. of crude product (the reaction was not forced to completion

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(1) J. Thiele, *Chem. Ztg.*, **36**, 657 (1912).

(2) E. Bergmann and A. Bondi, *Ber.*, **63**, 1158 (1930); **64**, 1455 (1931); **66**, 278 (1933).

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(4) W. H. Woodstock, U. S. Patent 2,495,799 to Victor Chemical Works; January 31, 1950; *C. A.*, **44**, 3517 (1950); 2,471,472 to Victor Chemical Works; May 31, 1949; *C. A.*, **43**, 7499 (1949).

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