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^{18}
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).

[3] G. M. Kosolapoff and W. F. Huber, THIS JOURNAL, **68**, 2540 (1946); (the material referred to was contained in the original manuscript of that paper).

[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).

[5] G. M. Kosolapoff, THIS JOURNAL, **67**, 1180 (1945).

in order to avoid partial saponification). As a result of combined distillation of products of two such runs there was obtained a 46.3% yield of the unsaturated ester, which boiled at 99–100° at 1 mm.; $n^{29.6}{}_D$ 1.4376, $d^{29.6}{}_4$ 1.0112; *MR* found: 50.3; *MR* calcd., 49.53. The discrepancy of 0.8 unit is undoubtedly the conjugation exaltation effect.

***n*-Butanephosphonic Acid.**—The above ester (0.5 g.) in 25 ml. of ethanol was added to 0.3 g. of 5% palladium-on-charcoal catalyst and the mixture was subjected to the flow of hydrogen through a gas disperser placed at the bottom of the vessel. The reaction was complete within 30 minutes at room temperature. After filtration, the solution was treated with 100 ml. of concentrated hydrochloric acid and the whole was refluxed overnight. The alcohol was then largely distilled from the mixture and the residual liquid was refluxed for an additional 6 hours with a further addition of hydrochloric acid (50 ml.). Evaporation of the solution by means of an infrared lamp to near dryness, final drying by a similar evaporation with two small portions of benzene, and crystallization from benzene with a little charcoal, readily yielded substantially the theoretical yield of *n*-butanephosphonic acid, which melted at 105.5–106.0° whether alone or when mixed with an authentic specimen.

2-Chlorobutanephosphonic Acid.—The phosphonyl dichloride (17.8 g.) was added to 50 ml. of water and was permitted to hydrolyze with stirring and gentle warming. Removal of volatiles under reduced pressure yielded 14.7 g. of crude solid acid. Recrystallization from benzene gave the pure compound in the form of colorless plates which melted at 88–90° with slight decomposition. Titration of the substance with a *p*H meter was impossible as each addition of the standard alkali gave unstable voltage, indicating a rapid cleavage of hydrogen halide. A rapid addition of 0.1 *N* sodium hydroxide to methyl orange end-point, followed by acidification with nitric acid and addition of silver nitrate gave 18.6% chlorine content, against the theoretical value of 20.5%. The compound was not investigated further, but it was evident that its link to the chlorine atom was decidedly weak.

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The Dielectric Constant of Formamide[1]

BY GORDON R. LEADER

Formamide has long been known to have a high dielectric constant, but until recently, there have been no accurate values available for this property, the only reported determination being that of Walden[2] who gave its dielectric constant as >84. In 1947, Burdun and Kantor[3] reported measurements made by the Drude–Coolidge method with wave lengths in the range 1–5 meters. They found $\epsilon = 109 \pm 1.5$ at $20 \pm 1°$ and conclude from the absence of dispersion in this region that this is equivalent to the static value. An earlier reference to values for the dielectric constant of formamide determined by Burdun was made by Vasenko[4] who reported that $\epsilon = 126.07 - 0.7206\, t$ between 18 and 25°. Recently measurements of greater precision have been made in this Laboratory in the temperature range 15 to 35° which confirm in a general way the results of Burdun and Kantor, but indicate a smaller variation of dielectric constant with temperature than has previously been reported.

Capacitance measurements were made using a General Radio Type 821-A Twin-T Impedance Measuring Circuit.[5] Radio frequency current was supplied to the Bridge from a General Radio Type 1001-A Standard Signal Generator. A Hallicrafters Model S-40A multi-band receiver was used as null detector. Because of the relatively high conductivity of even carefully purified formamide, capacitance measurements were made at a frequency of 10 mc. The cell used was very similar in design to that described by Connor, Clarke and Smyth,[6] and was plugged directly into the unknown terminals of the bridge in order to minimize the effect of lead inductance. The cell construction was modified from the design of Connor, Clarke and Smyth chiefly in that the insulating plug was made of Teflon, and the lower portion of the central electrode which passed through the plastic was made of smaller diameter than the body of the electrode in order to reduce the invariant capacity of the cell and to permit a more rigid fit of this tapered stem in the similarly tapered hole in the plastic. The plug was held securely in place with the aid of small washers placed under the General Radio plugs and overlapping slightly on the plastic. The cell was made of brass, and all parts coming into contact with the liquids measured were first silver plated and then gold plated.

Temperature control was secured by circulating water through the cell jacket from a thermostat whose temperature was regulated to ±0.05°. Temperatures were measured using a 0.1° thermometer calibrated by the National Bureau of Standards. It was established by measurements on water and methanol whose dielectric constants are accurately known at these temperatures that within the temperature range 15 to 35° the cell contents were held at the indicated bath temperatures.

The procedure in making measurements was essentially that described by Connor, Clarke and Smyth.[6] The constants in the equation: $C = C_0 + C_v\epsilon$ were determined by measurements of the capacity of the cell when filled with purified benzene and chlorobenzene as reference substances.[7] To secure greater accuracy in measurement of the small capacities involved with these liquids, a heterodyne beat apparatus of the type described by Chien[8] was used, together with a calibrated General Radio Type 722N Precision Condenser. It was found that $C_0 = 1.80 \pm 0.01$ $\mu\mu$f and $C_v = 3.800 \pm 0.005$ at all temperatures from 15 to 35°. Determination of C_v was also carried out at each of the temperatures studied by measurements at 1 mc. with the Twin-T Bridge of the capacity of the cell when filled with purified methanol and water. The values of Albright and Gosting[9] for the dielectric constants of these substances were used. In this manner also a value of $C_v = 3.800 \pm 0.005$ was obtained, independent of temperature in the 15 to 35° range.

At 10 mc. the inductance of the cell and residual

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(1) Based on research performed for the U. S. Army Signal Corps, Fort Monmouth, N. J. under contracts W36-039-sc-32265 and W36-039-sc-38184.

(2) Walden, *Z. physik. Chem.*, **46**, 175 (1903).

(3) Burdun and Kantor, *Doklady Akad. Nauk. S. S. S. R.*, **67**, 985 (1949).

(4) Vasenko, *J. Phys. Chem.* (*U. S. S. R.*), **21**, 361 (1947).

(5) Sinclair, *Proc. Inst. Radio Eng.*, **28**, 310 (1940).

(6) Conner, Clarke and Smyth, THIS JOURNAL, **64**, 1379 (1942).

(7) Davies, *Phil. Mag.*, **21**, 1, 1008 (1936).

(8) Chien, *J. Chem. Ed.*, **24**, 494 (1947).

(9) Albright and Gosting, THIS JOURNAL, **68**, 1062 (1946).