

relative changes in chlorite concentration through glucose oxidation imposes a severe strain upon the assumption that the mean chlorite concentration is equal to the geometric mean.

In equation 5,  $k_D h^{1.5} t C_0$  is by far the most important factor, for at the mid-point of the experiments the exponential factor contributed less than 2%, and  $B$ , usually 10%, of the total. Thus, for higher values of  $G_0/C_0$ ,  $k_D h^{1.5} t C_0$  appears somewhat low, which implies that the geometric mean,  $(C_0 C)^{1/2}$ , gives slightly low values. This in turn would ex-

plain the slightly high values for glucose previously reported.<sup>1</sup>

The agreement, however, of calculated with experimental chlorite values appears adequate to substantiate the assumption involved in the derivation, particularly in view of the wide ranges of time and of concentrations of reactants.

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## COMMUNICATIONS TO THE EDITOR

### THE EXCHANGE OF HYDROGEN BETWEEN AMMONIUM SALTS AND ALCOHOLS

Sir:

The exchange reactions of hydrogen bonded to nitrogen, like those of hydrogen bonded to oxygen, have generally been considered to be immeasurably fast. Brodskii and Sulima<sup>1</sup> attributed the rapid exchange to the presence of free electron pairs, and predicted that hydrogen exchange of ammonium ions, in analogy to tetrahedral carbon, would be slow. To test this hypothesis, they measured the rate of exchange of a number of ammonium salts in aqueous solutions of the corresponding acids. The reactions were studied, using deuterium as a tracer, by analyzing the salt precipitated at intervals by the addition of acetone. The slowest exchange observed, that between ammonium nitrate and 54% aqueous nitric acid, had a half-time between one and ten minutes at 0°. Because of the importance of this result to the theory of acid-base reactions, we have repeated this experiment using tritium as a tracer and have observed a half-time of about three minutes.

In order to find a reaction with a half-time which would permit more accurate kinetic measurements, we have investigated the exchange of hydrogen between alcohols and substituted ammonium salts. Butyl alcohol labeled with tritium was added to a solution of the salt in chloroform. At intervals the salt was precipitated from aliquots of the solution by addition of hexane, and the extent of exchange was determined by comparing the tritium content of the precipitate with the value found after equilibrium had been attained. With both salt and alcohol at concentrations of 0.1 *M*, the half-time of exchange at 0° was found to be about ten hours for diethylammonium chloride and two minutes for trimethylammonium chloride. That the large difference in the rates of exchange is not simply related to the acidity constants of the salts was shown by the observation that the half-time for the exchange reaction of a 0.2 *M* solution of guanidinium nitrate in ethyl alcohol was less than

(1) A. I. Brodskii and L. V. Sulima, *Doklady Akad. Nauk S.S.S.R.*, **74**, 513 (1950).

one minute at 0°. These and similar exchange reactions are being further investigated in order to establish the factors influencing the rates of exchange.

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### THE APPARENT CONDUCTIVITY OF HEXAPHENYLETHANE IN SULFUR DIOXIDE SOLUTION

Sir:

The conductivity which has been observed with solutions of hexaphenylethane in liquid sulfur dioxide<sup>1</sup> has, in conjunction with observations of color<sup>2</sup> and spectroscopic data,<sup>3</sup> been subject to several chemical interpretations<sup>3b,4</sup> which differ in detail but which all assume an ionization mechanism involving only hexaphenylethane and sulfur dioxide. This conductivity is now found to be an artifact of at least two processes, namely, reaction with dissolved oxygen and a photochemical transformation.

Experiments employing crystalline samples of ethane of purity established by quantitative oxygenation<sup>5</sup> and a refinement of the conductivity technique of Lichtin and Glazer<sup>6</sup> which avoids all contact of the solute with oxygen prior to dissolution reveal a lack of reproducibility like that apparent in older work.<sup>1</sup> Although irradiation with a Burton ultraviolet lamp produces slow but large increases in conductivity, variable exposure to light cannot be the sole source of the discrepancies since consistent data do not result from experi-

(1) (a) P. Walden, *Z. physik. Chem.*, **43**, 443 (1903); (b) M. Gomberg and L. H. Cone, *Ber.*, **37**, 2033 (1904).

(2) M. Gomberg and F. W. Sullivan, *THIS JOURNAL*, **44**, 1829 (1922).

(3) (a) K. H. Meyer and H. Wieland, *Ber.*, **44**, 2557 (1911); (b) L. C. Anderson, *THIS JOURNAL*, **57**, 1673 (1935).

(4) (a) M. Gomberg, *Chem. Rev.*, **1**, 102 (1924); (b) P. Walden "Chemie der Freien Radikale," S. Hirzel, Leipzig, 1924, p. 154; (c) W. A. Waters, "Chemistry of Free Radicals," Oxford Press, London, 1948, p. 35; (d) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 712.

(5) N. N. Lichtin and G. R. Thomas, *THIS JOURNAL*, **76**, 2594 (1954).

(6) N. N. Lichtin and H. Glazer, *ibid.*, **73**, 5537 (1951).

ments performed in the dark. The fact that increasingly efficient degassing of the solvent prior to dissolution of ethane leads to progressive diminution of the conductivity of solutions prepared and measured in the dark suggests production of an electrolyte by reaction with a gaseous impurity. This reagent has been identified by exposing a solution in degassed sulfur dioxide to a large excess of oxygen in the dark and observing a hundredfold increase in conductivity to a level somewhat greater than the highest comparable values obtained without degassing of the solvent. The conductivity of the resulting solution does not change upon irradiation whereas that of solutions in degassed sulfur dioxide increases.

Table I summarizes some of the relevant data.

TABLE I<sup>a</sup>

Dilution l./mole of C <sub>2</sub> Ph <sub>6</sub>	Conductivity, <sup>b</sup> mho cm. <sup>-1</sup> × 10 <sup>6</sup>	Purity of solute <sup>c</sup>	Treatment of solvent
208.1	70.4	95.5	No degassing
216.0	58.2	97	No degassing
276.9	141.1	97	No degassing
219.2	9.86	94	Pumped 1 hr.
236.3	2.67	94	Pumped 4 hr.
226.2	0.95	97	Pumped 3 hr., redistilled from hexaphenylethane
111.7	3.77	97	Pumped 2 hr.
111.7	362.1	97	Above solution after treatment with oxygen
250	206	97	Above solution, diluted

<sup>a</sup> Data with light excluded. <sup>b</sup> Corrected for solvent conductivity which varied from  $0.15 \times 10^{-6}$  to  $0.3 \times 10^{-6}$  mho cm.<sup>-1</sup>. <sup>c</sup> By quantitative oxygenation.<sup>5</sup>

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#### PHOTOCHEMICAL REACTIONS OF METHYL DIAZOACETATE WITH POLYHALOMETHANES

Sir:

Preliminary studies indicate that the photochemical reactions of methyl diazoacetate with polyhalomethanes are typical free radical chain reactions and that methyl polyhalopropionates are formed which suffer dehydrohalogenation during the reaction and isolation to give methyl polyhaloacrylates. The unexpected identities of the acrylates obtained suggest a 1,2-shift of a halogen atom in an intermediate free radical as postulated in previous work (see equation 4 below).<sup>1</sup>

A solution of methyl diazoacetate (12 g., 0.12 mole) in chloroform (248 g., 2.08 moles) was irradiated by a quartz mercury discharge tube immersed in it. Nitrogen (2.64 l. at S.C., 97%) was evolved

(1) W. H. Urry and J. R. Eiszner, *THIS JOURNAL*, **74**, 5822 (1952).

over a period of eight hours. Products identified after distillation were methyl chloroacetate (5.55 g., 0.051 mole, b.p. 47–52° at 18 mm.,  $n_D^{20}$  1.4660, mol. wt. Rast, 106, gave N-phenylglycine, m.p. 127°<sup>2</sup> when treated by the method of Koelsch<sup>3</sup> in an attempt to form the anilide), and presumed methyl  $\alpha,\beta,\beta$ -trichloropropionate (2.35 g., 0.02 mole, b.p. 85–90° at 18 mm.,  $n_D^{20}$  1.4626, mol. wt. Rast, 198). Treatment of the latter product with ammonium hydroxide gave  $\alpha,\beta$ -dichloroacrylamide<sup>4</sup> (m.p. 134.5–136°).

*Anal.* Calcd. for C<sub>3</sub>H<sub>3</sub>ONCl<sub>2</sub>: Cl, 50.7. Found: Cl, 52.1.

Its saponification gave  $\alpha,\beta$ -dichloroacrylic acid<sup>5</sup> (m.p. 84–85°) which was converted to its silver salt.

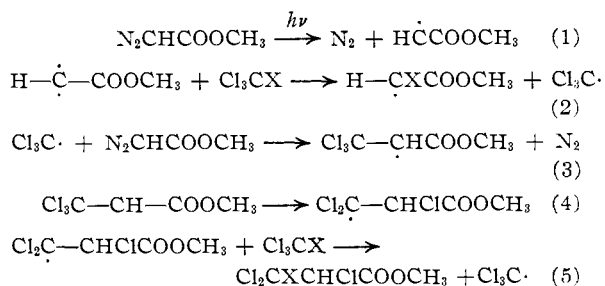
*Anal.* Calcd. for C<sub>3</sub>HO<sub>2</sub>Cl<sub>2</sub>Ag: Ag, 43.52. Found: Ag, 43.43.

In a similar experiment, the irradiation of methyl diazoacetate (15 g., 0.15 mole, b.p. 27–28° at 4 mm.,  $n_D^{20}$  1.4703) in bromotrichloromethane (208 g., 1.05 mole) gave nitrogen (3.20 l. at S.C., 96%) over a period of sixteen hours. Hexachloroethane (0.7 g., m.p. 183–184°, m.p. of mixture with authentic sample 183–184°) was identified as a product, and a series of fractions shown to be mixtures of methyl  $\beta$ -bromo- $\alpha,\beta,\beta$ -trichloropropionate and methyl  $\alpha,\beta,\beta$ -trichloroacrylate (9.1 g., b.p. 90–115° at 5 mm., average mol. wt. Rast, 237) were obtained. Saponification of this mixture gave a quantitative yield of  $\alpha,\beta,\beta$ -trichloroacrylic acid<sup>6</sup> (m.p. 71–73°, m.p. of mixture with authentic sample 72°), and its reaction with ammonium hydroxide gave  $\alpha,\beta,\beta$ -trichloroacrylamide<sup>7</sup> (m.p. 97–98°, m.p. of mixture with authentic sample 97–98°).

*Anal.* Calcd. for C<sub>3</sub>H<sub>2</sub>ONCl<sub>3</sub>: Cl, 61.00. Found: Cl, 60.84.

The same  $\alpha,\beta,\beta$ -trichloroacrylic acid and amide were obtained as derivatives of the product obtained in a similar reaction of methyl diazoacetate with carbon tetrachloride.

The structures of the acrylates identified suggest the following reaction sequence (where X = H in the chloroform reaction, X = Cl in carbon tetrachloride and X = Br in bromotrichloromethane).



(2) P. Walden, *Z. physik. Chem.*, **10**, 639 (1892).

(3) C. F. Koelsch and D. Tenenbaum, *THIS JOURNAL*, **55**, 3049 (1933).

(4) H. J. Prins, *J. prakt. Chem.*, **89**, 420 (1914).

(5) A. L. Koblansky, A. S. Wolkenstein and A. Orłowa, *ibid.*, **145**, 12 (1936).

(6) J. Böeseken and J. F. Garriere, *Rec. trav. chim.*, **34**, 179 (1915).

(7) G. Gilta, *Bull. soc. chim. Belg.*, **39**, 587 (1930).