

for this and the chlorine-hydrogen peroxide reaction seems strong enough to warrant their revision. One such revision has been carried out.

Anomalies in the temperature coefficients of processes in aqueous iodine solutions find no counterpart in the absorption of visible light by

these solutions. Gaseous iodine in air and iodine dissolved in carbon tetrachloride are virtually indistinguishable with a spectrophotometer. Aqueous iodine solutions differ from them in three spectrophotometrically measurable ways.

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Thermal and Photochemical Exchange Reactions of Bromine

BY J. NORTON WILSON AND ROSCOE G. DICKINSON

Several reactions involving exchange of bromine atoms between elementary bromine and bromine compounds in carbon tetrachloride solutions have been investigated in this Laboratory with the use of radioactive bromine. The results obtained from the study of the thermal reactions between bromine and arsenious bromide, stannic bromide, ethylene bromide, and trichlorobromomethane and the photochemical reaction between bromine and trichlorobromomethane are here described.

Experimental Method.—The thermal exchanges were investigated in general as follows. A solution of radioactive bromine in carbon tetrachloride was divided into two portions: the bromine was extracted from one of these portions and converted to silver bromide for electroscopic measurements; the other portion of the solution was mixed with a solution of the bromine compound to be investigated, and the mixture, hereafter referred to as the reaction mixture, was kept at a definite temperature for a convenient time; a precipitate of silver bromide was then prepared from either the bromine or the bromine compound in the mixture. The extent of exchange was then calculated from the known composition of the reaction mixture and the relative electroscopic activities of the two silver bromide precipitates, and is reported here as percentage of complete exchange. The electroscopic measurements were made by a method described elsewhere.¹

The method used to prepare the dilute highly radioactive solutions of bromine used in the photochemical experiments may be of interest: a small amount of highly radioactive sodium bromide was prepared by the method of Erbacher and Philipp² from a large amount of ethylene bromide which had been exposed to slow neutrons from a radon-beryllium source. The sodium bromide, dissolved

in a small amount of water, was shaken with a dilute solution of bromine in carbon tetrachloride. As was expected from the known rapidity of the exchange between bromine and bromide ion in aqueous solution,³ exchange was rapid; the resulting solution of radioactive bromine was dried with phosphorus pentoxide, distilled and diluted to the desired concentration with carbon tetrachloride.

Experiments with Stannic and Arsenious Bromides.—The reaction mixtures were subjected immediately after mixing to vacuum distillation at 25° to remove bromine. The residue of metallic bromide was then hydrolyzed and the resulting bromide ion was precipitated as silver bromide for radioactivity measurements. Exchange was apparently complete with solutions containing 4 mole per cent. of bromine and 2 mole per cent. of either metallic bromide. Since the extent of exchange was calculated on the basis of the initial composition of the solution, exchange was probably completed before an appreciable fraction of the bromine had distilled away, *i. e.*, within about ten minutes. The time elapsing between the initial mixing of the solutions and the conclusion of the distillation was about thirty minutes.

Experiments with Ethylene Bromide.—The reaction mixtures were sealed in glass ampoules and kept in the dark at the desired temperature for a convenient time; the bromine was then extracted with sodium nitrite solution and converted to silver bromide. No exchange beyond the limits of experimental error was detected in a solution of the composition 24 mole per cent. Br₂, 28 mole per cent. C₂H₄Br₂, which was kept at 100° for sixty-five minutes. Experiments using lower concentrations and temperatures similarly indicated no exchange. In no experiment was the apparent extent of exchange greater than 3%; this value is less than the estimated experimental error.

Experiments with Trichlorobromomethane.—The thermal reactions were carried out similarly to those involving ethylene bromide. At concentrations of approximately 0.3 moles of bromine and 1 mole of CCl₃Br per liter, the apparent extents of exchange observed in solutions kept for four minutes at 25°, forty minutes at 95° and fifty minutes at 115° were, respectively, -5, 7 and 9%. These measurements are obviously uncertain by at least 5% of

(1) Wilson and Dickinson, *THIS JOURNAL*, **69**, 1358 (1937).

(2) Erbacher and Philipp, *Z. physik. Chem.*, **A176**, 169 (1936).

(3) Roginskii and Gophtein, *Physik. Z. Sowjetunion*, **7**, 672 (1935).

complete exchange and possibly more; it is doubtful whether any appreciable exchange occurred.

The photochemical experiments were carried out as follows. A solution of radioactive bromine and trichlorobromomethane in carbon tetrachloride was frozen with liquid air; the space above the solution was evacuated in order that oxygen might be largely removed. The solution was melted and separated *in vacuo* into two approximately equal portions which were then sealed off. One portion was thermostated and illuminated for a measured time with filtered radiation from a 500-watt tungsten lamp; the filter transmitted chiefly in the range 5000 to 6100 Å. The other portion was kept in the dark at the same temperature for the same time. After the illumination was completed, both solutions were cooled in the dark; the bromine was extracted from the same volume of each and converted to silver bromide for electroscopic measurements. A small volume of each solution was also analyzed for bromine.

A thermal exchange experiment was performed using the same technique; the solution was separated *in vacuo* into two portions; bromine from one portion was converted immediately to silver bromide; the other portion was kept in the dark at a high temperature for some time before the bromine extraction.

The results obtained with solutions containing about 0.003 mole of bromine and 0.08 mole of trichlorobromomethane per liter were as follows: thermal, solution heated at 76° for seventy-five minutes, ~3% exchange; photo-

chemical, solution illuminated at 76° for seventy minutes, 98% exchange. Two experiments in which solutions containing 0.003 mole of bromine and 0.02 mole of trichlorobromomethane per liter were illuminated at 76° for twenty minutes resulted in 86 and 97% exchange. Other experiments at higher temperatures or with longer illumination times also gave 85 to 100% exchange.

Summary

Investigation of the exchange of bromine between radioactive bromine and various bromine compounds has led to the following results: a rapid exchange occurs with arsenious bromide and with stannic bromide at room temperature in carbon tetrachloride solution (!); in the same solvent no exchange beyond the limits of experimental uncertainty was observed to occur with either ethylene bromide or trichlorobromomethane in the dark at 100°; a rapid exchange with trichlorobromomethane is induced by green light at 76°.

A convenient method has been described for the preparation of dilute and highly radioactive solutions of bromine in carbon tetrachloride.

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The Molecular Structures of Glyoxal and Dimethylglyoxal by the Electron Diffraction Method

BY JAMES E. LUVALLE¹ AND VERNER SCHOMAKER

Introduction.—Extension to open chain heteroatomic aliphatic compounds of the structural investigations² of the constitutional effect of different bonds upon adjacent bonds should provide useful information concerning the electronic structures and the extent of resonance in these molecules. The recent electron diffraction studies of formaldehyde³ and acetaldehyde⁴ have given a reliable value for the carbon-oxygen double bond distance. We have now extended the investigation of compounds containing the carbonyl group to glyoxal and dimethylglyoxal, both of which

contain a pair of conjugated carbon-oxygen double bonds and present the possibility of free rotation around the carbon-carbon bond connecting the adjacent carbonyl groups. Furthermore, both substances are colored, glyoxal being the simplest colored compound whose molecules have a conjugated system. Of the compounds glyoxal, dimethylglyoxal, oxalyl chloride, oxamide, and oxalic acid, it is found that glyoxal and dimethylglyoxal are colored whereas the remaining compounds are colorless. All five of these compounds may be represented by the formula RCORCO and the difference in color between the first two compounds and the remaining three compounds suggests that there may be a structural difference between the two groups of compounds. Oxalyl chloride is now under investigation in these Laboratories by the electron diffraction method, and the X-ray study of crystals of oxamide is also under way.

(1) Julius Rosenwald Fellow.

(2) (a) L. Pauling, L. O. Brockway and J. Y. Beach, *THIS JOURNAL*, **57**, 2705 (1935); (b) L. Pauling and L. O. Brockway, *ibid.*, **59**, 1223 (1937); (c) L. Pauling, H. D. Springall and K. J. Palmer *ibid.*, **61**, 927 (1939); (d) V. Schomaker and L. Pauling *ibid.*, **61**, 1769 (1939).

(3) D. P. Stevenson, J. E. LuValle and V. Schomaker, *ibid.*, **61**, 2508 (1939).

(4) D. P. Stevenson, H. D. Burnham and V. Schomaker, *ibid.*, **61**, 2922 (1939).