Acknowledgment.—The author is indebted to The Research Corporation for support of this research.

Experimental

A mixture of 45.9 g. (0.26 mole) of NBS, 27.1 g. (0.33 mole) of cyclohexene (found by iodometric titration to contain 0.05 mole of cyclohexene hydroperoxide per liter), and 185 ml. of C. P. anhydrous benzene was stirred and brought to reflux in twenty-six minutes; six minutes later the NBS was shown by testing with potassium iodide to be completely consumed. After cooling and filtering off succinimide, the filtrate was fractionally distilled; in addition to solvent and unchanged cyclohexene, 21.0 g. (50.3%) of 3-bromocyclohexene, b. p. 45–47° at 10 mm. and 6.7 g. of a colorless oil, b. p. 51–57° at 1 mm.,[5] were obtained. Careful fractional recrystallization of solids which separated from the residues left after removal of each of the above liquid fractions gave a total of 0.44 g. (1%, based on NBS) of N-phenylsuccinimide, m. p. 155.2–155.7° (cor.) unchanged by admixture with an authentic sample.

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(5) On long standing at 0°, this oil deposited 1.31 g. of massive colorless crystalline material, tentatively identified as 3,6-dibromocyclohexene[1] (m. p. 107.5–108.3° (cor.). *Anal.* Calcd. for $C_6H_8Br_2$: C, 30.03; H, 3.36. Found: C, 30.43; H, 3.61); the residual oil was shown to consist of at least 60% 1,2-dibromocyclohexane (b. p., m. p., mixed m. p. with an authentic sample; separated from reactive unsaturated dibromides by virtue of its inertness toward trimethylamine at room temperature).

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The Bromine-Sensitized Photochemical Formation of Hexabromoethane from Carbon Tetrabromide

BY L. B. SEELY, JR., AND J. E. WILLARD

When very dilute solutions (10^{-3} M) of bromine in purified and degassed liquid carbon tetrabromide were illuminated at 95° with light of wave length between 4100 and 4500 Å., more bromine was produced. We have assumed that this was due to the formation of hexabromoethane from two molecules of carbon tetrabromide with the consequent liberation of one molecule of bromine.

Our interest in this reaction was occasioned by the simplicity and symmetry of the reacting molecules, the unusual nature of the process as characterized by the formation of a carbon-to-carbon bond, the relation of this reaction to other reactions involving an attack by a light-activated halogen on a halogen–carbon bond and, lastly, the possibility of tracer studies as a means of investigating the mechanism.

Precise studies of this reaction have been carried out on carbon tetrachloride solutions. The carbon tetrachloride was purified according to procedures previously described.[1] The carbon tetrabromide was purified by repeated recrystallizations from carbon tetrachloride. The bromine was distilled in vacuum from anhydrous calcium bromide and sealed in small bulbs for later introduction into the reaction mixture. The mixture of tetrahalides was purified and degassed by flushing with pure nitrogen, evacuating while frozen and distilling several times in vacuum.

At 0.5 M carbon tetrabromide, 2×10^{-3} M bromine and 50° the reaction proceeded with a quantum yield of about 1.0×10^{-3} mole of bromine per einstein of light absorbed. Under other conditions quantum yields between 10^{-4} and 10^{-2} were recorded. An increase in the bromine concentration caused a decrease in the quantum yield. The quantum yield increased with increase in the carbon tetrabromide concentration but the quantitative dependence on this concentration varied with the bromine concentration. The temperature coefficients were likewise dependent on the bromine concentration.

The explanation of this behavior appears to be the existence of two reaction mechanisms, prevailing in different bromine concentration ranges, with a transitional range between. At bromine concentrations above 3×10^{-3} M (0.5 M carbon tetrabromide, 50°) the reaction followed the rate law

$$\frac{d[C_2Br_6]}{dt} = \frac{kI_{abs}f([CBr_4])}{[Br_2]^2}$$

The experimental evidence to date indicates that $f([CBr_4])$ should be the first power. This has been hard to rationalize in terms of the usual mechanisms, since two carbon tetrabromide molecules are required to produce one hexabromoethane molecule, and since the light dependency is first power.

At bromine concentrations below 1×10^{-3} M, there is evidence that the rate law becomes independent of both carbon tetrabromide and bromine, following the law

$$d[C_2Br_6]/dt = k'I_{abs}$$

This is the law to be expected if the process determining the concentration of tribromomethyl free radicals is the combination of these radicals. Further studies in this region may provide experimental evidence concerning such processes.

At bromine concentrations above 1×10^{-3} M the quantum yield for the photo-activated exchange of free bromine with the bromine in carbon tetrabromide (determined by means of radiobromine) was very much higher than the quantum yield for the formation of hexabromoethane and was very sensitive to trace amounts of impurities.

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(1) Dickinson and Leermakers, THIS JOURNAL, **54**, 3853 (1932).

The Glycogen Content of *Phymatotrichum Sclerotia*[1]

BY DAVID R. ERGLE

In a recent chemical study[2] of the mycelial and sclerotial stages of *Phymatotrichum omnivorum*

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(1) Published with the approval of the Director of the Texas Agricultural Experiment Station as Technical Paper No. 996.

(2) Ergle and Blank, *Phytopathology*, **37**, 153–161 (1947).