ence of acetyl peroxide (1–5 mole per cent.). Carbon tetrabromide and ethylene (in the light) gave 1,1,1,3-tetrabromopropane ($n^{20}D$ 1.6090), b. p. 65–68° (0.3 mm.).

Anal. Calcd. for $C_3H_4Br_4$: Br, 90.0. Found: Br, 89.8.

It is significant that in every case studied only the mono addition product of carbon tetrabromide to the olefin was formed; there was practically none of the product which would be formed by the addition of two or more molecules of the olefin to one molecule of carbon tetrabromide (*cf.* ref. 1). The mono addition product was formed even when the olefin contained an aromatic radical. Thus, when a mixture of styrene and carbon tetrabromide (dissolved in carbon tetrachloride) was illuminated, a nearly quantitative yield of 1,1,1,3-tetrabromo-3-phenylpropane was obtained (b. p. 123°(0.1 mm.); m. p. 57–59°).[3]

Anal. Calcd. for $C_9H_8Br_4$: Br, 73.4; mol. wt., 436. Found: Br, 73.3; mol. wt., 451.

Bromoform reacts extremely slowly with olefins when illuminated in the manner indicated. The yield of addition product was only 1% at the end of twelve hours. However, a nearly quantitative yield of the mono addition product was obtained when a mixture of octene-1 and bromoform was heated at 80° in the presence of a small amount of acetyl peroxide (1–5 mole per cent.). The product was a tribromo-*n*-nonane (b. p. 99–102° (0.3 mm.), $n^{20}D$ 1.5178), the structure of which has not been definitely established.

Anal. Calcd. for $C_9H_{17}Br_3$: Br, 65.8; mol. wt., 365. Found: Br, 65.1; mol. wt., 361.

The unusual behavior of the tetrahalogenated methanes containing at least one bromine atom, in yielding exclusively one-to-one addition products with olefins, is readily explained by the mechanism suggested in our previous papers.[1]

(3) Hydrolysis of this compound with hydrochloric acid and a small amount of cuprous chloride gave cinnamic acid. The acid thus obtained did not depress the melting point of an authentic sample of cinnamic acid.

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ELECTRONIC PROCESSES IN LIQUID DIELECTRIC MEDIA. THE PROPERTIES OF METAL-AMMONIA SOLUTIONS

Sir:

New experimental results appear significant in the elucidation of the properties of dilute liquid ammonia solutions of alkali and alkaline earth metals. Extremely dilute sodium solutions (some 10^{-5} molar) observed in the temperature range -35 to $-75°$ displayed a marked increase in electrical conductivity upon irradiation with visible light. It is particularly important that the quantum efficiency of this photoconductivity is an inverse function of the concentration of the solution. This fact renders the effect experimentally observable with reasonable light intensities only at the low concentrations employed.

Dilatometric measurements (at constant temperature), in which sodium was extracted from dilute solutions by metallic mercury, indicated a volume change amounting to some 700 cc. per mole of solute (temperature $-35°$, concentration of solutions some 3×10^{-3} molar). That is, the dissolving of metallic sodium under these conditions results in an expansion nearly thirty times as great as the volume of the solid metal sample.

The close parallelism of the above photoconductivity experiments to those of Hilsch and Pohl[1] dealing with solid solutions of alkali metals in alkali halide crystals suggests a mechanistic explanation similar to that commonly accepted[1] for the latter case. Whereas in ionic crystals the electrons are trapped at vacant negative ion sites, giving "F centers," in the solutions in question they are trapped in cavities which they have "dug" in the solvent. That these cavities are relatively enormous (of the order of 7×10^{-8} cm. in radius) is indicated by the very great expansion attendant upon dissolving the metal to form highly dilute solutions. The bodily mobility of such huge ions would be negligible, but thermal or photoexcitation may raise the trapped electrons to the conduction band. The mobility of a conduction electron would appear to be limited by "redigging" its cavity and by capture in a cavity containing a trapped electron, forming a pair analogous to the "F' centers" of Hilsch and Pohl. The importance of this latter process is indicated by the above inverse dependence of the photoeffect upon concentration.

Considerations of quantum mechanics lend theoretical support to the above model. These considerations, which visualize the electron trapped in a spherical cavity, lead to the following results: (1) the ground state of the system is an "S" state of total energy -0.21 volt (-4800 cal./mole) in a cavity of radius 7.6×10^{-8} cm. (1100 cc./mole); (2) all other states are unstable; (3) photoconductivity follows a transition from the ground state to the lowest "P" state; (4) *two* electrons trapped in the same cavity are appreciably stable with respect to either two electrons in separate cavities or one trapped and one conducting electron. The absorption spectrum and magnetic susceptibility of metal ammonia solutions are in at least qualitative agreement with these calculations which will be described in detail later.

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(1) For literature references, see N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," Oxford Press, New York, N. Y., 1940.