

enlargement. However, enlarged color prints can so far not be made by the individual, and reproduction of color pictures for periodicals or books is expensive.

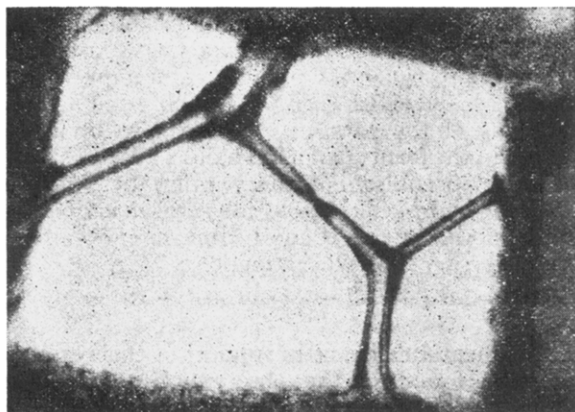


Fig. 1.—GR-S Rubber milled ten minutes, dissolved in benzene. Enlarged print from Kodachrome A film. Magnification is approx. 5000.

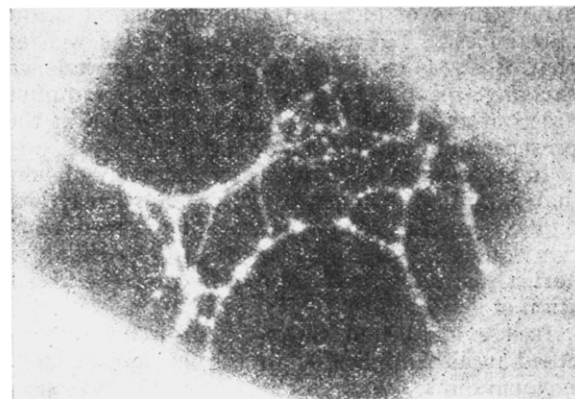


Fig. 2.—Pale crepe milled thirty minutes, dissolved in benzene. Ultra-illumination by incident light. Magnification is approx. 5000.

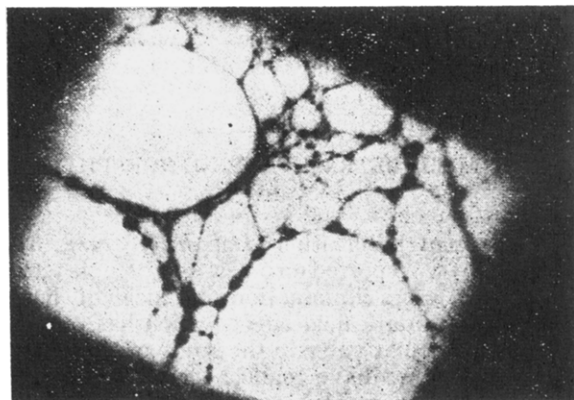


Fig. 3.—Pale crepe milled thirty minutes, dissolved in benzene. Print from positive film. Magnification is approx. 5000.

Since color photographs are definitely superior to regular black and white film for recording fine microstructures, we made enlargements on regular printing paper using the Kodachrome picture as negative. We have termed the so produced positive "light-field ultramicrophotograph," because the result is really a reversed ultramicroscopic effect. Wherever a specific color of the preparation is not the predominant factor in its study, this technique enables one to obtain very satisfactory prints from the color slide. Besides this, the light background generally offers a better contrast.

If no Kodachrome is available or desired and one still wants to benefit by this technique, one can expose the dark-field negative to a film and produce a positive which, if then used for making prints, will again give a light-field background.

The microphotographs are offered as illustrations.

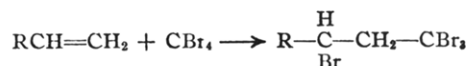
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RECEIVED DECEMBER 12, 1945

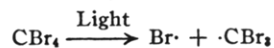
#### ADDITION OF CARBON TETRABROMIDE AND BROMOFORM TO OLEFINS

Sir:

When a mixture of an olefin and carbon tetrabromide is heated at 70–90° in the presence of 1–5 mole per cent. of a diacyl peroxide, the carbon tetrabromide adds to the olefin.



The mechanism of this type of addition has been discussed in previous papers.<sup>1</sup> However, carbon tetrabromide differs from the halides there mentioned in that its addition is initiated not only by diacyl peroxides but by visible light.



For example, a mixture of octene-1 (56 g.) and carbon tetrabromide (600 g.) was heated to 75° for seven hours in an apparatus illuminated internally by a mercury-filled coil coated with a fluorescent material so that it gave a white light.<sup>2</sup> Distillation of the reaction mixture yielded a product (196 g. = 88% on the basis of the octene-1 used) which boiled at 127° (0.02 mm.). The substance was 1,1,1,3-tetrabromo-*n*-nonane ( $n_D^{20}$  1.5488).

*Anal.* Calcd. for  $\text{C}_9\text{H}_{16}\text{Br}_4$ : Br, 72.1; mol. wt., 444. Found: Br, 72.8; mol. wt., 441.

Excellent yields of the same substance were also obtained when a similar mixture of octene-1 and carbon tetrabromide was heated to 80° in the pres-

(1) Kharasch, Jensen and Urry, *Science*, **102**, 128 (1945); Kharasch, Urry and Jensen, *THIS JOURNAL*, **67**, 1626 (1945); Kharasch, Jensen and Urry, *ibid.*, **67**, 1864 (1945).

(2) Carbon tetrachloride, phosphorus trichloride and a number of other substances add to olefins when mixtures of olefins with these halides are exposed to ultraviolet light.

ence of acetyl peroxide (1-5 mole per cent.). Carbon tetrabromide and ethylene (in the light) gave 1,1,1,3-tetrabromopropane ( $n_D^{20}$  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°).<sup>3</sup>

*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.),  $n_D^{20}$  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.<sup>1</sup>

(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 in-

verse 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  $3 \times 10^{-3}$  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<sup>1</sup> dealing with solid solutions of alkali metals in alkali halide crystals suggests a mechanistic explanation similar to that commonly accepted<sup>1</sup> 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  $7 \times 10^{-8}$  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  $7.6 \times 10^{-8}$  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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RECEIVED DECEMBER 19, 1945

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