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Photochemical Studies with Rigid Hydrocarbon Solvents at Low Temperatures

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Experiments aimed at the production of free radicals by the photolysis of suitable solutes in rigid hydrocarbon glasses at 77°K. have been performed. Acetophenone and diphenylmercury are not decomposed by irradiation in a rigid solvent at 77°K., whereas they do decompose by non-chain processes at room temperature in fluid solvents. Tetramethyltetrazene, $(CH_3)_2N—N=N—N(CH_3)_2$, is completely decomposed at 77°K., and partially reforms when the solvent melts. $(CH_3)_2N_3$ radicals may be present, but no definitive spectrum of this species was obtained. S_2Cl_2 is completely dissociated by irradiation at 77°K., and a new absorption band at 237 mμ appears. This may be due to SCl. The spectrum previously attributed to SCl_2 is probably due to S_2Cl_2. Complex effects following the irradiation of bromine, bromal and bromopicrin are described. Iodine solutions in the hydrocarbon glass used here become yellow upon cooling, but are not decolorized by irradiation.

A number of experiments aimed at the production of trapped free radicals at low temperatures have been described recently.[2,3] Of particular interest to us is the work of Norman and Porter involving visible or ultraviolet irradiation of suitable substrates in hydrocarbon or EPA glasses at the temperature of liquid nitrogen (77°K.). Using spectroscopic methods for detecting the effects of irradiation, these authors have obtained evidence for the dissociation of molecular iodine and of ethyl iodide, and for the production of CS from CS_2, ClO from ClO_2, and benzyl from a number of compounds.

To the extent that this technique is generally applicable, it will be of great value to the study of the properties of free radicals and other unstable species. The experiments reported below have been performed in order to further investigate the method. Our work has not resulted in the production and unequivocal identification of a free radical or other primary photochemical product. In two cases, it has been clearly demonstrated that the quantum yield for photo-dissociation in a rigid solvent is extremely low. In other cases, spectroscopic changes have been produced by irradiation, but definitive identification of the products was not possible. It is possible that apparently minor variations in technique will have important effects in experiments like those reported here. We believe that the accumulation of empirical experience will be helpful in the further development of this method for the study of unstable species. For this reason, our experiments are described below in considerable detail.

Materials.—Philips "Pure Grade" isopentane and 3-methylpentane were allowed to stand over sodium wire. They were then passed through activated silica gel several times, as recommended by McConnell and Tunnicliff.[4] The very slight absorption of the solvents in 1-cm. cells at 210 mμ indicated that the concentration of benzene or toluene was less than 10^{-5} *M*.

Acetophenone, diphenylmercury, bromal and bromopicrin were Eastman Kodak products. Tetramethyltetrazene was kindly supplied by Dr. H. W. Kruse of the Naval Ordnance Test Station, China Lake, California; it had been prepared as described by Renouf.[5] The sulfur monochloride was reagent grade.

Apparatus and Technique.—Spectra were recorded using a Cary model 11 M recording spectrophotometer. Figure 1 depicts the low temperature apparatus. The outer aluminum container C can be mounted snugly and reproducibly in the spectrophotometer, with quartz windows W in the light path. The steel lid L has metal ground joints for evacuation and for attachment of the Pyrex glass liquid nitrogen reservoir R. The Pyrex cell P is made with a large bore neck for ready degassing, and to avoid formation of a concave meniscus in the light path when the solution is frozen, due to thermal contraction. The path length was usually 1.5 cm. Quartz windows were cemented to Pyrex tubes with an epoxy cement.[6] These seals withstood repeated cooling to 77°K and deteriorated only very slowly in contact with hydrocarbon solvents at room temperature.

Most of the experiments were performed with a 5:1 isopentane-3-methylpentane mixture as the glass-forming solvent. Generally speaking, solute concentrations of less than 10^{-3} *M* were used, and clear glasses were obtained on cooling. Greater concentrations often resulted in formation of a semi-opaque mass on cooling, suggesting that crystallization of the solute had occurred. Glasses were formed as rapidly as possible by immersing most of the solution in liquid nitrogen, but leaving an upper portion clear to allow for the *ca.* 25% thermal contraction. Measurements with a copper-constantan thermocouple showed that, using this technique, solutions became rigid in about a minute and attained liquid nitrogen temperature in about three minutes. At about 88°K., the thermocouple wires could be moved sluggishly within the glass; at about 95°K., the mixture was quite fluid.

Irradiations were carried out with an Osram HBO 200 watt high pressure mercury arc at a fixed distance from the cell (7.5 cm.) with no lenses. Tests with a thermocouple frozen in just above the light path showed that irradiation of a pure hydrocarbon glass resulted in no warmup provided the reservoir was full of liquid nitrogen. If the nitrogen was just above the light path, there was a steady state warmup of 6°. This could be decreased by using water as an infrared filter. While recording spectra, liquid nitrogen could be removed from the light path. Thermocouple measurements showed that, provided some liquid nitrogen remained in contact with the bottom of the cell, there was no warmup. An approximate estimation of the light output of the arc was obtained. A sample of HBr gas at a pressure

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[2] F. O. Rice and M. Freamo, THIS JOURNAL, **73**, 5529 (1951); F. O. Rice and F. Scherber, *ibid.*, **77**, 291 (1955); I. L. Mador and M. C. Williams, *J. Chem. Phys.*, **22**, 1627 (1954); E. Whittle, D. A. Dows and G. C. Pimental, *ibid.*, **22**, 1943 (1954); P. A. Giguere, *ibid.*, **22**, 2085 (1954); H. P. Broida and J. R. Pellam, *Phys. Rev.*, **95**, 845 (1954); Livingston, Zeldes and Taylor, *ibid.*, **94**, 725 (1954).

[3] (a) I. Norman and G. Porter, *Nature*, **174**, 508 (1954); (b) *Proc. Roy. Soc. (London)*, **A230**, 399 (1955).

[4] H. McConnell and D. Tunnicliff, *J. Chem. Phys.*, **23**, 927 (1955).

[5] E. Renouf, *Ber.*, **13**, 2173 (1880).

[6] Epibond AN-101, The Furane Plastics Co., Los Angeles, California.

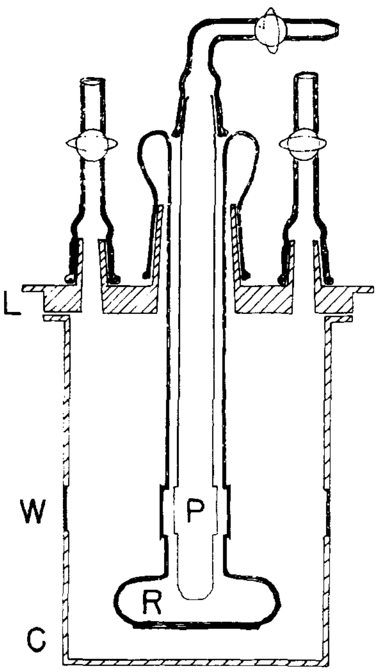


Fig. 1.—Low temperature apparatus.

of 20 cm. in a quartz cell of length 10 cm. was exposed at the standard distance of the arc (7.5 cm.), and Br_2 molecules were produced at the rate of 3 × 10^{15}/sec. The HBr absorbed essentially all of the light from 207 to 247 mμ, and relatively little of longer wave length light, so that 3 × 10^{15} quanta/sec. may be taken as a measure of the light impinging on the cell in this spectral range.

Figure 2 illustrates the importance of degassing the solvent before freezing, as emphasized by Potts.[7] Figure 2 also illustrates the results of several experiments that were performed on the production of CS_2 in 5:1 isopentane–3-methylpentane, this being close to the ratio recommended by Potts for general low-temperature work. Essentially the same results were obtained using as a solvent 1:1 isopentane–3-methylpentane, which is close to the ratio recommended by Norman and Porter. Either mixture will serve as a matrix for production of the relatively stable species, CS.

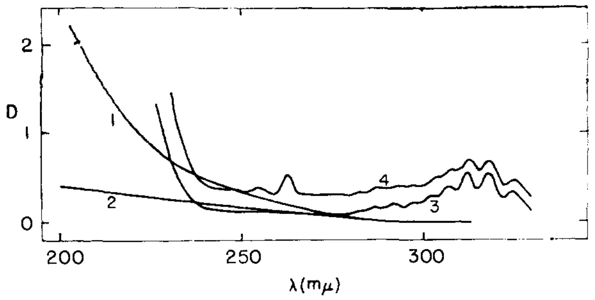


Fig. 2.—Preliminary experiments on frozen glasses: 1, absorption of pure hydrocarbon glass without degassing; 2, same after degassing; 3, *ca.* 10^{-2} *M* CS_2 in hydrocarbon glass before irradiation; 4, after 10 min. irradiation (displaced upward by 0.2 *D*).

Results

Acetophenone.—There is evidence that the phenyl radical is formed in the photolysis of acetophenone vapor.[8] Acetophenone has a weak absorption band at 280 mμ (ϵ ~10^3) showing fine structure, and a strong structureless band ($\epsilon_{max.}$ 1.25 × 10^4) at 240 mμ. Photolysis of a 10^{-3} *M* solution at room temperature resulted in the formation of one molecule of benzene per molecule of acetophenone decomposed. In the irradiation of a 4.7 × 10^{-5} *M* solution (1.5 cm. cell), the rate of decomposition (measured by the absorption at 240 mμ) was 5 × 10^{14} molecules/sec., indicating a quantum yield of the order of 0.1–1.0.

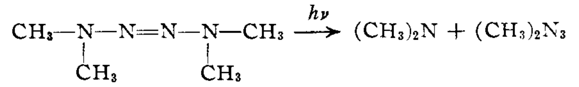
Irradiation of a 4.7 × 10^{-5} *M* solution in 5:1 isopentane–3-methylpentane at 77°K. effected no detectable decomposition after ten times the exposure necessary for complete decomposition at room temperature. Since photodecomposition in solution is not a chain process, photodecomposition in the rigid medium must have a negligibly small quantum yield.

Diphenylmercury exhibits a weak banded region of absorption around 260 mμ and a strong structureless band at 230 mμ. Irradiation of a 5 × 10^{-5} *M* solution at room temperature effected complete photolysis with formation of benzene and mercury. The latter, which is slightly soluble in hydrocarbons, was identified by its 254 mμ line. Semiquantitative estimation of benzene from its absorption at 210 mμ indicated $^1/_2$–2 molecules of benzene produced per molecule of $Hg(C_6H_5)_2$ decomposed. The rate of disappearance of the latter substance (from the absorption at 230 mμ) was 3 × 10^{14} molecules/sec., again indicating a quantum yield of the order 0.1–1.0.

Irradiation in the glass at 77°K. with ten times the exposure necessary for complete elimination of the 230 mμ band at room temperature produced no detectable decomposition. We conclude that there is no appreciable decomposition in the rigid medium.

A preparation was allowed to warm slowly from 77°K. while being irradiated. Temperature measurements were not made, but it is estimated that photolysis occurred while the sample was in the temperature range 80–120°K. Benzene, but no biphenyl, resulted. Thus even at these low temperatures, hydrogen abstraction by phenyl occurs preferentially to recombination. Separate experiments showed that biphenyl does not undergo photolysis, even at room temperature.

Tetramethyltetrazene, $(CH_3)_2N{-}N{=}N{-}N(CH_3)_2$, appeared to be a promising source of $(CH_3)_2N$ radicals. As shown in Fig. 3, the absorption spectrum of this substance exhibits a broad maximum at 273 mμ (ϵ ~ 2 × 10^4). Irradiation at 77°K. results in the rapid and essentially complete destruction of this peak. No new strong bands appear. On warming, the 273 mμ peak reforms at about 20% of its original intensity. The solution can then be refrozen and re-irradiated, with the same effects. Gas bubbles, presumably N_2, are observed on warming after irradiation. We tentatively postulate the following processes



$$\underset{\displaystyle CH_3}{CH_3{-}N}{-}N{=}N{-}\underset{\displaystyle CH_3}{N}{-}CH_3 \xrightarrow{h\nu} (CH_3)_2N + (CH_3)_2N_3$$

$$(CH_3)_2N + (CH_3)_2N_3 \longrightarrow (CH_3)_4N_4$$

Warm up

$$(CH_3)_2N_3 \longrightarrow (CH_3)_2N + N_2$$

$$(CH_3)_2N + RH \longrightarrow (CH_3)_2NH + R$$

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(7) W. J. Potts, Jr., *J. Chem. Phys.*, **21**, 191 (1953).

(8) H. H. Glazebrook and T. G. Pearson, *J. Chem. Soc.*, 589 (1939).

The postulated final product, dimethylamine, is not detectable spectrophotometrically at the expected concentrations.

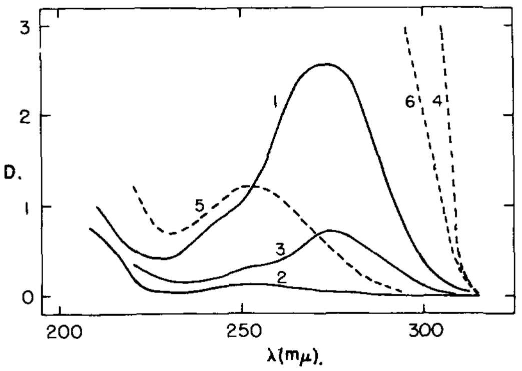

Fig. 3.—Experiments with N_4Me_4: ——, 9.4 × 10^{-5} *M* soln.; ------, 1.53 × 10^{-3} *M* soln.; 1, before irradiation; 2, after 4 min. irradiation; 3, after warm up and refreezing; 4, before irradiation; 5, after 70 min. irradiation; 6, after warm up and refreezing.

It is to be noted that there is a weak band at 250 mμ in the glasses after irradiation. This is in the area covered by the absorption spectrum of $(CH_3)_4N_4$, so it is impossible to say whether it is an impurity in the starting materials that remains present throughout the entire cycle of events (as suggested by the shoulder at this wave length in curves 1 and 3), or whether it is an unstable species that is present in the irradiated glass, and disappears on warming. If the latter is the case, it is plausible to attribute the peak to $(CH_3)_2N_3$.

NH_2 has a well known absorption spectrum in the visible region. No such absorption due to $(CH_3)_2N$ was observed. However, there are no available estimates of the expected intensity of this absorption.

S_2Cl_2 and SCl_2.—Our spectrum for S_2Cl_2 agrees with that recorded by Koch.[9] On irradiation of the compound (Fig. 4) the parent peak at 264 mμ is destroyed and a weak band at 237 mμ is formed. On heating, this disappears, and the 264 mμ band is partially regenerated. Some general background absorption throughout the ultraviolet also appears, perhaps due to the formation of sulfur. The solutions become noticeably turbid.

In order to ascertain whether the 237 mμ maximum was due to SCl, the irradiation of SCl_2 was studied. This was prepared by the method of Lowry and Jessop[10] by chlorination of the monochloride. In agreement with Koch, the spectrum of the product was found to be identical with that of S_2Cl_2, but with extinction coefficients in the ultraviolet about a factor of ten less. Moreover, irradiation in the glass produced the same effects as with S_2Cl_2; the 264 mμ maximum was destroyed at the same rate, and a 237 mμ maximum appeared with the same intensity relative to the 264 mμ peak.

Because of these observations, we suspect that the observed spectrum of "SCl_2" is mainly due to the presence of S_2Cl_2. One would not expect the two molecules to have identical ultraviolet absorption spectra, and Lowry and Jessop report that the dichloride is about 15% dissociated at 0°. Moreover, we found that, if the "SCl_2" were kept in contact with Cl_2 at about two atmospheres for a few days, a dilute solution of the product showed an "extinction coefficient" at 264 mμ, about half those previously observed. The absorption increased on standing, and in half an hour the "extinction coefficient" had increased to the value before chlorination.

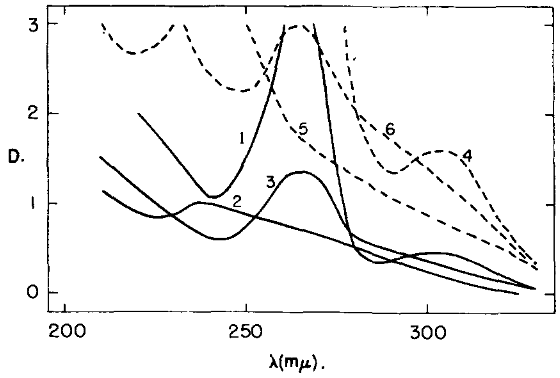

Fig. 4.—Irradiation of S_2Cl_2: ——, 1.61 × 10^{-4} *M* soln.; ------, 6.41 × 10^{-4} *M* soln.; 1, before irradiation; 2, after 10 min. irradiation; 3, after warmup and refreezing; 4, before irradiation; 5, after 40 min. irradiation; 6, after warmup and refreezing.

Further investigations of the kinetics and equilibria in the system S_2Cl_2, SCl_2, Cl_2 are needed but it is reasonable to conclude that S_2Cl_2 is actually present as the light absorbing species in the SCl_2 samples and that the photochemical effects are due to S_2Cl_2. The hypothesis that the peak at 237 mμ obtained by irradiation is due to SCl remains as an interesting but unconfirmed idea. The compilations by Pearse and Gaydon[11] and by Herzberg[12] do not record a spectrum due to SCl. It does not appear to be very easy to check this hypothesis by further experiments in rigid media. Spectroscopic experiments aimed at the identification of SCl in the gas phase may be fruitful.

Bromine and Iodine.—It should first be noted that Gibson, Blake and Kalm[13] have proposed that hexatriene is formed by the irradiation of benzene in frozen glasses. Our interpretation of the bromine experiments will involve the hypothesis that the small amount of benzene present (10^{-5} *M*) is converted to hexatriene during irradiation. Prolonged irradiation of a glass containing 8 × 10^{-4} *M* Br_2 produced no reduction in the visible band of Br_2, nor any other spectroscopic change. As the glass melted, a strong broad band with a maximum at 310 mμ appeared and then disappeared on further warming. This effect was conditional upon prior irradiation, and we propose that it is due to a typical complex formation between olefin and halo-

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[9] H. P. Koch, *J. Chem. Soc.*, 394 (1949).

[10] T. M. Lowry and G. Jessop, *ibid.*, 323 (1931).

[11] R. W. B. Pearse and A. G. Gaydon, "Identification of Molecular Spectra," 2nd edition, J. Wiley and Sons, Inc., New York, N. Y., 1950.

[12] G. Herzberg, "Molecular Spectra and Molecular Spectra. I. Spectra of Diatomic Molecules," 2nd edition, D. Van Nostrand Co., Inc., New York, N. Y., 1950.

[13] G. E. Gibson, N. Blake and M. Kalm, *J. Chem. Phys.*, **21**, 1000 (1953).

gen, in this case bromine and hexatriene. If the hexatriene was 10^{-5} M and completely complexed, the extinction coefficient of the complex would be of the order of 10.[4] This hypothesis was strengthened by the following experiment. A dilute benzene solution in a glass was irradiated and allowed to warm; bromine was added in the dark and the solution quickly refrozen. Warmup then resulted in the appearance of the 310 mμ band.

It may be recalled that Freed and Sancier[14] have observed low temperature complex formation between iodine and olefins prior to addition.

We found that iodine solutions of molality 10^{-3} gave a brown opaque mass on cooling. A 10^{-4} M solution resulted in a clear, pale yellow glass, which was not decolorized by prolonged irradiation. These results are contrary to those reported by Norman and Porter[3a] who state that they were able to reversibly decolorize a 10^{-3} M solution in hydrocarbon glasses by irradiation. In the ultraviolet, as well as a broad band probably resulting from the small concentration (*ca.* 10^{-5} M) of benzene–iodine complex, the glass showed a general absorption throughout the ultraviolet; this effect might be attributed to crystallization, in spite of the fact that glass appears clear (*cf.* Ham[15]).

Bromal, CBr_3CHO.—It was hoped that this compound would be a good source of CBr_3 and CHO radicals. It exhibits no characteristic absorption bands, but continuous absorption in the far ultraviolet. A 3.8×10^{-3} M solution had optical densities of 1.0 at 250 mμ and 2.0 at 237 mμ. Irradiation at 77°K. produced no detectable change in the spectrum. On warming in the dark to 90°K., where the glass is losing rigidity, a broad band with maximum at 270 mμ appeared, persisted as the glass became liquid, and disappeared on further warming. Irradiation of a glass at 90°K. caused the band to appear with much greater intensity, and the intensity continued to increase after irradiation had ceased.

It is clear that this band is due to an intermediate semi-stable product, and that the photochemical decomposition of bromal is a complex process.

Bromopicrin, CBr_3NO_2.—It may first be noted that Br_2 and NO_2 have similar spectra. However, as stable products, they are readily distinguished, because NO_2 rapidly dimerizes to N_2O_4, with a quite different spectrum as soon as the glass is melted.

Bromopicrin has a spectrum similar to that of bromal. Irradiation of a 4×10^{-3} M glass resulted in the formation of molecular bromine, even with the employment of an infrared filter. Irradiation of a 4×10^{-4} M solution resulted in no bromine, but in the appearance of a strong band with maximum at 270 mμ, analogous to that observed with bromal. This effect was, however, not very reproducible.

Discussion.—The technique of producing and stabilizing free radicals in a frozen matrix presents a number of problems. The identification of a radical principally on the basis of spectroscopic changes produced by irradiation of a suitable substrate in a frozen medium often will not be possible. In most of the successful instances of the application of this technique by Norman and Porter, the spectrum of the radical produced was already known from flash photolysis or some other spectroscopic experiment. The experiments described above on S_2Cl_2 and $(CH_3)_4N_4$ are examples where unstable species have evidently been trapped in the glass, but such species cannot be identified by spectrophotometric observations alone. Electron magnetic resonance would be a useful additional tool. Chemical analyses for products is difficult when it is necessary to work with very dilute solutions.

One problem which we believe is not yet solved is the question of whether or not the solute has precipitated in a microcrystalline form during the cooling of the solution to form a glass. The visual clarity of the glass is no certain guarantee that microcrystallization has not occurred.

In the present work we have concentrated on the use of a 4:1 isopentane–3-methylpentane mixture for our glass forming solvent. Conceivably a glass of different composition, for example the 2:3 isopentane–3-methylpentane mixture recommended by Norman and Porter, might yield different results. However, the results with $(CH_3)_2N_4$ and S_2Cl_2 indicate that unstable species can in fact be trapped in the medium used. The negative results for diphenylmercury and acetophenone must then be attributed to the Franck–Rabinowitch cage effect.[16]

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[14] S. Freed and K. M. Sancier, THIS JOURNAL, **74**, 1273 (1952).

[15] J. Ham, *ibid.*, **76**, 3875 (1954).

[16] J. Franck and F. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).