

fluoroethylene and dicyclopentadienylnickel in diglyme yield II, as red crystals of m.p. 68–73°. *Anal.* Calcd. for  $C_{12}H_{10}F_3ClNi$ : C, 47.2; H, 3.3; Cl, 11.6. Found: C, 47.3; H, 3.26; Cl, 11.5. The  $^1H$  and  $^{19}F$  n.m.r. spectra of II establish a structure similar to I. Proton spectra of the two complexes are nearly identical (Table I). The  $^{19}F$  n.m.r. spectrum of II is particularly interesting, consisting of two equally intense AB quartets and two equally intense resonances. Intensity ratio of the AB quartets to the single fluorine resonances is 2:1. Thus each AB quartet corresponds to a  $CF_2$  group, and each single fluorine resonance to a fluorine atom of a CFCI group. For each of two possible arrangements of the bicyclic system in II, with the  $H\gamma$  protons pointed toward and the fluorinated cyclobutane ring bent away from the nickel atom or *vice versa*, there are two alternative orientations of the CFCI group. The fluorine atom of the CFCI group may be closer to the nickel atom than the chlorine atom or the reverse may occur. Hence II could exist in four different configurations. Nevertheless, the  $^{19}F$  n.m.r. spectrum shows that only two forms are present. Since the two isomers are produced in equal amounts, they probably differ only in orientation of their CFCI groups.

possessing a norbornadienyl group (M. Dubeck, *J. Am. Chem. Soc.*, **82**, 6193 (1960)). We have also prepared this compound confirming the previously reported proton n.m.r. results. Neglecting those absorptions attributable to the  $\pi$ -cyclopentadienyl and the ester groups, there are three groups of bands with intensity ratio 2:2:1 increasing to high field. In the fluoroolefin-dicyclopentadienyl-nickel adducts there is also a group of three absorptions with two groups of peaks of equal intensity and one of half the intensity (Table I). However, the arrangement of these absorptions is different, being one in which there is a 1:2:2 intensity pattern increasing toward high field. Hence, in I and II the unique proton resonance appears at lowest field with chemical shift ( $\tau \sim 4.5$ ) very different from that of the single proton ( $\tau 7.82$ ) in the dimethyl acetylenedicarboxylate adduct, but with chemical shift similar to that found for the corresponding central protons in other  $\pi$ -allylmetal complexes.<sup>3,6</sup> From the acetylene  $CF_3C\equiv CCF_3$  and dicyclopentadienylnickel we have prepared a new compound having a proton n.m.r. spectrum very similar to the complex obtained by Dubeck. Again, with increasing field, the sequence of relative intensities for comparable absorptions is 2:2:1 rather than 1:2:2.

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#### SPECIFIC, SENSITIVE ELECTRONIC DETECTION OF IODINE VIA CARRIER INJECTION INTO AN ANTHRACENE CRYSTAL

Sir:

It is well established in studies of the bulk conductivity of anthracene that charge carriers can be produced by a pulse of light at the crystal surface<sup>1,2</sup> and by electrode injection.<sup>3</sup> The recent work of Kearns, Tollin and Calvin<sup>4</sup> suggested that injection of carriers into an electron donor such as

(1) See G. C. B. Garrett in "Semiconductors," edited by N. B. Hannay, Reinhold Publishing Corp., New York, N. Y., 1959, for a review of information on photoconductivity in anthracene.

(2) R. G. Kepler, *Phys. Rev.*, **119**, 1226 (1960).

(3) H. Kallmann and M. Pope, *J. Chem. Phys.*, **32**, 300 (1960).

(4) D. Kearns, G. Tollin and M. Calvin, *ibid.*, **32**, 1020 (1960); D. Kearns and M. Calvin, *J. Am. Chem. Soc.*, **83**, 2110 (1961).

phthalocyanine or violanthrene could occur as well when an electron acceptor such as *o*-chloranil was deposited on its surface. The injection of carriers at such a surface should depend on the nature and extent of the charge-transfer interaction, and it therefore occurred to us that one might expect rather specific, sensitive changes in the bulk conductivity of an organic crystal exposed to various materials in the gas phase.

We examined the effect of exposure to iodine, water, sulfur dioxide, oxygen, hydrogen chloride and nitrogen dioxide on the bulk dark conductivity of anthracene. Single-crystal slices with large faces parallel or perpendicular to the cleavage plane were cut from large single crystals obtained from Harshaw Chemical Co., and conducting gold paint electrodes applied. The geometry was chosen to attempt to exclude rigorously surface conductance: a high impedance current electrode painted on one face of a crystal slice and a low impedance electrode surrounded by a guard ring on the other face. The crystal was mounted in a Teflon holder which in turn was placed in a glass cell, and guard rings painted around the walls of these mounts to assure no surface conducting path around the periphery of the cell. Measurements were performed using a Cary Vibrating Reed Electrometer Model 31-31V and a Keithley DC Power Supply Model 240. That surface conductance was not being measured was further established by (a) the fact that materials such as sulfur dioxide, hydrogen chloride, and oxygen known to increase the surface conductivity, probably *via* a change in surface mobility of carriers rather than through formation of additional carriers,<sup>5</sup> produced no effect in the present experiments; (b) the fact that when a Teflon plug (of the same size as the anthracene crystals) or a stilbene crystal were placed in an iodine ambient, no change in conductivity was observed.

Experiments were conducted both by introducing iodine into the evacuated cell or by flowing a carrier gas stream containing iodine over the crystal in the same type of cell provided with an outlet. Measurable changes in the conductivity of anthracene were observed at vapor pressures as low as  $10^{-5}$  mm. in the static system and at concentrations as low as 0.2 part per million in the flow system. In the flow system response began within 10 seconds of exposure and reached 50% of its maximum value in 30 seconds with a further slow increase for 20–30 minutes. In the static system the maximum response occurred in less than 3 minutes.

The data presented are typical of the response observed. Perpendicular to the AB plane, the conductivity increased 1.5, 6 and 30 times at vapor pressures of iodine of  $10^{-4}$ ,  $10^{-2}$ , and  $10^{-1}$  mm., respectively. Parallel to the AB plane, no response was observed at vapor pressures lower than  $10^{-3}$  mm., but above this pressure the change in conductivity was greater than that observed perpendicular to the AB plane, *e.g.*, 15 fold at  $10^{-2}$  mm., and 175 fold at  $10^{-1}$  mm.

(5) A. G. Chynoweth and W. G. Schneider, *J. Chem. Phys.*, **22**, 1021 (1954); A. G. Chynoweth, *ibid.*, **22**, 1029 (1954); W. G. Schneider and T. C. Waddington, *ibid.*, **25**, 358 (1956).

The change in conductivity was less than a factor of 1.2 for exposure of anthracene to moist air (~60% humidity), sulfur dioxide, oxygen or hydrogen chloride at concentrations ~10,000 times greater than those at which the crystal responds to iodine with a twofold increase in conductivity. Nitrogen dioxide, however, does affect the bulk dark conductivity in a manner comparable to iodine. One might expect charge-transfer and/or nuclear substitution to occur with nitrogen dioxide under these conditions.

When a mixture of hydrogen chloride, sulfur dioxide, and water saturated air was flowed over the surface of a crystal at a rate of 1 liter/min., no effect was observed. When small concentrations of iodine were added to this mixed gas stream, a response about 3 times larger than that normally found was observed. In another preliminary experiment, a *lowering* of the photoconductivity was observed when iodine was placed in the cell and the crystal was illuminated with ultraviolet light. No change in the activation energy of conduction of anthracene ( $E_a \sim 0.8$  ev.) occurred in ambients containing up to 0.07 mm. of iodine, but only a small temperature range (10–12°) was accessible for study. Further work on these aspects of the problem is in progress.

The possibility of diffusion of iodine into the lattice as an explanation of the observed effects can be eliminated since solid state diffusion is a relatively slow process. The diffusion constant of anthracene C-14 into anthracene, for example, is estimated as  $10^{-10}$  cm.<sup>2</sup>sec.<sup>-1</sup> at 450°K.<sup>6</sup> Diffusion *via* cracks or voids might be expected to be more rapid, but hardly to yield the reproducibility from crystal to crystal observed in this work.

We believe that this demonstration of a fairly specific and highly sensitive electronic phenomenon from the interaction of a gas-phase acceptor with a hydrocarbon crystal suggests the possibility of utilizing this effect in the electronic detection of other chemical compounds. Support of the U. S. Army Chemical Center under Subcontract SCE-17250-60 with Melpar, Inc., and helpful discussions with Drs. D. Rosenblatt, D. Fox and J. Roth are gratefully acknowledged.

(6) J. N. Sherwood and S. J. Thompson, *Trans. Faraday Soc.*, **56**, 1443 (1960).

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#### IONIC SPECIES IN GAMMA IRRADIATED ORGANIC GLASSES AT -196°

Sir:

The role of ionic processes in the radiation chemistry of liquid organic systems can be plausibly inferred from indirect evidence.<sup>1</sup> Excluding polymerization, there is a limitation arising from the difficulty of distinguishing between ionic and non-ionic mechanisms. Thus, reduction by H-atoms may not be distinguishable from reduction by electrons.

(1) L. J. Forrestal and W. H. Hamill, *J. Am. Chem. Soc.*, **83**, 1535 (1961).

Spectrophotometry of gamma irradiated samples which form known cationic and anionic species in rigid media provides a relatively simple and powerful tool for studying primary ionic processes in radiation chemistry. Naphthalene is an appropriate substance for such an experiment. Of necessity, concurrent identification of absorbing free radical species is involved, and these methods have been described by others.<sup>2</sup>

Solvents, single or mixed, included tetrahydro-2-methylfuran, 3-methylpentane, isopentane, methylcyclohexane, diethyl ether and ethanol. Samples were prepared air-free in Pyrex cells, unless shown to be unaffected by air. Glassed solutions were maintained at -196° during Co<sup>60</sup> gamma-irradiation and subsequent spectrophotometry. The dose rate was  $8.7 \times 10^{19}$  ev./lit. min. and the dose range  $1-5 \times 10^{21}$  ev./lit.

Among the significant results we have observed are these: (a) chemically prepared sodium naphthalenide in tetrahydro-2-methylfuran and gamma-irradiated naphthalene in this solvent or in a hydrocarbon, all at -196°, exhibit the same well known spectrum of C<sub>10</sub>H<sub>8</sub><sup>-</sup>. For Na<sup>+</sup>C<sub>10</sub>H<sub>8</sub><sup>-</sup> at -196° in tetrahydro-2-methylfuran, we observed  $\lambda_{max}$  at 3250, 3700, 4350, 4550, 4650, 7600, 8400 Å., in essential agreement with reported values.<sup>3</sup> For radiation-produced C<sub>10</sub>H<sub>8</sub><sup>-</sup> we observed  $\lambda_{max}$  at 3250, 3700, 4350, 4550, 4650, 7800, 8650 Å.  $G(\text{C}_{10}\text{H}_8^-)$  is 1.4 at 0.01% naphthalene and 4.0, its maximum, at 1%, using the reported extinction coefficients<sup>3</sup> of Na<sup>+</sup>C<sub>10</sub>H<sub>8</sub><sup>-</sup>. In all cases the color is removed by illumination. Entirely similar results were obtained throughout using biphenyl.

(b) Gamma irradiation of pure tetrahydro-2-methylfuran produced a broad absorption band originating at ca. 4000 Å. and increasing monotonically to the limit of observation at 13,000 Å. This band, which is quickly removed by illumination, does not appear when ~0.5% of naphthalene or biphenyl is present. Both solvent and solute anion bands appear when ca. 0.5% or less of solute is present, and the solute bands are markedly enhanced by illumination in the solvent band. Sodium-potassium alloy plus 10% dimethoxyethane in tetrahydro-2-methylfuran at -196° produced an absorption band at 6000 Å. Bleaching this band gives absorption extending from 4000 to 13,000 Å. as noted above.<sup>4</sup>

(c) Gamma irradiation of carbon tetrachloride in 3-methylpentane or isopentane-methylcyclohexane produces a broad absorption band with  $\lambda_{max}$  4880 Å. The yield of color centers saturates at ca. 10 mole % carbon tetrachloride and the color is removed rapidly by illumination in the 4880 Å. band. No 4880 Å. absorption appears in polar matrixes, such as tetrahydro-2-methylfuran, diethyl ether-isopentane-ethanol, ethanol, etc.

Values of  $G(\text{HCl})$  for thawed samples containing carbon tetrachloride in various matrixes were 1.3 for hydrocarbons; 2.5 for 95% methylcyclohexane-isopentane, 5% diethyl ether; 7 for tetrahydro-2-methylfuran. Correspondingly,  $\text{OD}_{4880} = 1.49$  in

(2) H. T. J. Chilton and G. Porter, *J. Phys. Chem.*, **63**, 904 (1959).

(3) G. J. Hoijsink and P. J. Zandstra, *Mol. Phys.*, **3**, 371 (1960).

(4) H. Linschitz, M. G. Berry and D. Schweitzer, *J. Am. Chem. Soc.*, **76**, 5833 (1954).