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.^{2}sec.$^{-1}$ at 450°K.[6] 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).

CHEMISTRY DIVISION MORTIMER M. LABES
THE FRANKLIN INSTITUTE OREST N. RUDYJ
LABORATORIES FOR RESEARCH AND DEVELOPMENT
PHILADELPHIA 3, PA. PAUL L. KRONICK

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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.[1] Excluding polymerization, there is a limitation rising from the difficulty of distinguishing between ionic and nonionic mechanisms. Thus, reduction by H-atoms may not be distinguishable from reduction by electrons.

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.[2]

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^{60} gamma-irradiation and subsequent spectrophotometry. The dose rate was 8.7×10^{19} ev./lit. min. and the dose range $1\text{–}5 \times 10^{21}$ 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 $C_{10}H_8^-$. For $Na^+C_{10}H_8^-$ at −196° in tetrahydro-2-methylfuran, we observed λ_{max} at 3250, 3700, 4350, 4550, 4650, 7600, 8400 Å., in essential agreement with reported values.[3] For radiation-produced $C_{10}H_8^-$ we observed λ_{max} at 3250, 3700, 4350, 4550, 4650, 7800, 8650 Å. G-($C_{10}H_8^-$) is 1.4 at 0.01% naphthalene and 4.0, its maximum, at 1%, using the reported extinction coefficients[3] of $Na^+C_{10}H_8^-$. 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.[4]

(c) Gamma irradiation of carbon tetrachloride in 3-methylpentane or isopentane-methylcyclohexane produces a broad absorption band with λ_{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(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, OD_{4800} = 1.49 in

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

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

(3) G. J. Hoijtink 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).

100% methylcyclohexane-isopentane and OD_{4800} = 1.16 in 95% methylcyclohexane–isopentane, 5% diethyl ether.

(d) In a matrix of tetrahydro-2-methylfuran containing biphenyl or naphthalene, addition of carbon tetrachloride suppresses formation of the corresponding aromatic hydrocarbon anions. Thus in systems containing 1 mole % naphthalene, $G(C_{10}H_8^-)$ was 3.96, 1.50, 0.0 with 0, 0.16 and 1.57 mole % carbon tetrachloride, respectively.

(e) Irradiation of pure ethanol produces a broad absorption band at λ_{max} 5400 Å.[5] Illumination of the ethanol band with a 4760 Å. narrow band pass filter bleaches the entire band.

9 mole % carbon tetrachloride completely removes this band and 0.1 mole % biphenyl reduces the OD_{5400} from 0.71 for pure ethanol to a value OD_{5400} = 0.40, with the appearance of biphenyl anion bands.

(f) Yields of $C_{10}H_8^-$ per 100 ev. for 0.28 mole % naphthalene in 3-methylpentane for various additives were: none, 0.15; 1% isobutylene, 0.31; 5% isobutylene, 0.44; 5% methylcyclohexane, 0.42; 1% triethylamine, 0.36.

We interpret the preceding facts in this way: (a) in classical terms, "free" electrons are produced in condensed media with about the same $G(e^-) = 3$ as in gases. The average electron encounters some 10^3 molecules, given by (mole fraction $C_{10}H_8)^{-1}$ at 50% attachment in tetrahydro-2-methylfuran.

(b) Electrons are trapped and solvated in tetrahydro-2-methylfuran, and presumably other polar media, since solvent color centers photolyze to produce $C_{10}H_8^-$ in presence of naphthalene.

(c) The color center is probably CCl_4^- since this should bleach readily by photoionization whereas a neutral entity could not be photolyzed readily in a rigid medium because of an exaggerated "cage effect" in the contracted solvent. In polar media one expects CCl_4^- to solvolyze because of the enhanced solvation energy for Cl^-, which is eventually converted to HCl. The result in tetrahydro-2-methylfuran indicates that CCl_3 does not absorb in the interval examined. If the color were due to a free radical, it should not be affected by adding ether to the matrix.

(d) The ability of carbon tetrachloride to suppress aromatic anion formation supports the view that it is an efficient reagent for "free" electrons.

(e) The phenomena of electron solvation, bleaching and solute effects are not specific to tetrahydro-2-methylfuran but extend to ethanol and, presumably, to various other polar media.

(f) Enhancement of $G(C_{10}H_8^-)$ in non-polar media by chemically unreactive solutes of relatively low ionization potential indicates positive hole migration and trapping. The large $G(C_{10}H_8^-)$ in tetrahydro-2-methylfuran can be attributed in part to ion–moledule reaction forming $C_5H_{10}OH^+$, thus trapping the positive hole.

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[5] R. S. Alger, T. H. Anderson, and L. A. Webb, *J. Chem. Phys.*, **30**, 695 (1959).

P. S. RAO
J. R. NASH
J. P. GUARINO
M. R. RONAYNE
W. H. HAMILL

DEPARTMENT OF CHEMISTRY AND
RADIATION LABORATORY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA

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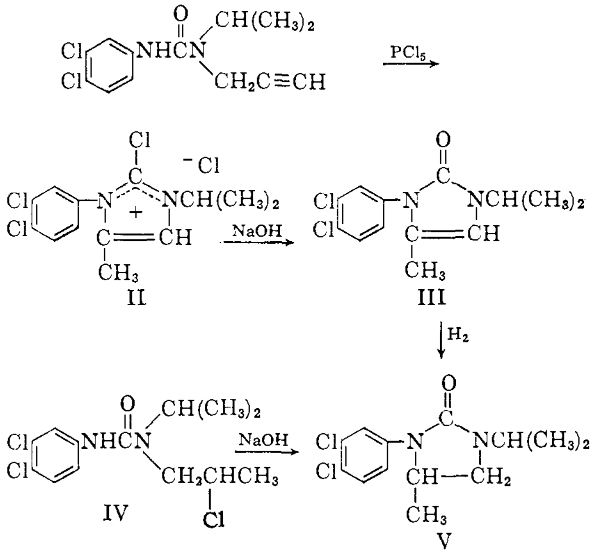
THE PREPARATION OF 2-IMIDAZOLONES: A NOVEL RING CLOSURE OF PROPYNYL UREAS WITH PHOSPHORUS PENTACHLORIDE

Sir:

We wish to report a novel ring closure effected by treating a propynyl urea with phosphorus pentachloride.[1] A stable imidazolium chloride is obtained which on treatment with base is converted quantitatively to an imidazolone.



The propynyl urea I with PCl_5 in refluxing benzene gives the cyclized imidazolium chloride II as a white hygroscopic crystalline solid, m.p. 275° dec. *Anal.* Calcd. for $C_{13}H_{14}Cl_4N_2$: C, 46.60; H, 4.13; Cl, 41.80; N, 8.25. Found: C, 46.40; H, 4.20; Cl, 41.95; N, 8.30. The infrared spectrum of II now shows a C=C absorption at 6.15 μ and no longer shows the C≡C band in the 4.5 μ region.

An aqueous solution of II, made slightly alkaline with NaOH, deposits the imidazolone III quantitatively: small white granules, m.p. 111.6–112.2°. *Anal.* Calcd. for $C_{13}H_{14}Cl_2N_2O$: C, 54.60; H, 3.70; Cl, 25.02; N, 9.62. Found: C, 54.75; H, 3.88; Cl, 24.95; N, 9.72.

The structural assignment for III and hence II is unambiguous as determined by proton nuclear magnetic resonance. The τ values for all protons are consistent for III[5]: a doublet at 8.72 τ (methyl

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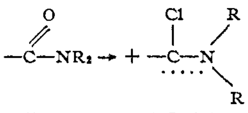
[1] The conversion of amides and ureas to imide chlorides by treatment with phosphorus pentachloride is well known. Recent reports[2,3,4] show the formation of stable amide chlorides of the type



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[3] H. Eilingsfeld, M. Seefelder and H. Weidinger, *ibid.*, **72**, 836 (1960).

[4] F. Klages and W. Grill, *Ann.*, **594**, 21 (1955).

[5] The n.m.r. data rule out two alternate ring closures which can be postulated *a priori*.