Radical Formation by the Photolysis of Hydrogen Iodide at 77°K. in Alkane, Alkane—Alkene, and Alkene Matrices[1]

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Abstract: Reactions of hot hydrogen atoms, thermal hydrogen atoms, and iodine atoms in 3-methylpentane (3-MP) glasses at 77°K. have been investigated by using e.s.r. to observe the trapped radicals formed by photolysis of HI in the glasses. 3-Methylpentyl radicals produced by abstraction of hydrogen from the solvent by hot hydrogen atoms are the predominant species found immediately following photolysis of the HI, both in pure 3-MP and in 3 mole % alkene solutions. In ethene and isobutene solutions in 3-MP, evidence is also found for C_2H_5 and t-C_4H_9 radicals, formed by addition of thermal H atoms to the alkene. In butene-2 and pentene-1 solutions in 3-MP, spectra attributable to allylic radicals gradually replace the 3-methylpentyl spectrum on standing at 77°K. The spectra formed by photolysis of HI in 3-MP containing vinyl halides were also investigated in a search for evidence for C_2H_4X radicals. No e.s.r. spectra were found for H atoms, I atoms, or iodine-containing radicals in any of the systems studied. Decay curves for the 3-methylpentyl radicals suggest that a first-order process predominates, probably combination of the radicals with I atoms born in close proximity. Radical spectra were also observed for the photolysis of HI in pure 3-methylpentene-1.

Photochemical production of atoms in the solid state is limited because the dense medium favors primary recombination of the potential fragments of a molecule which has absorbed a photon. Photolysis of HI in solid solvents probably offers the most favorable case for a sufficiently high quantum yield of cage escape to provide enough thermal atoms for study of their reactions. The small size of the H atom favors its escape, as does the fact that conservation of momentum leads to nearly all of the kinetic energy of the separating partners being carried by the H. When activation is by 2537-Å. radiation, this energy is 20 kcal./mole if the iodine atom is produced in the $I(^2P_{1/2})$ excited state and 41 kcal./mole if it is produced in the $I(^2P_{3/2})$ ground state.[2]

Nash, Williams, and Hamill[3] have demonstrated that photolysis of 0.01 mole % HI in deuterated 3-methylpentane with 2537-Å. radiation causes hot hydrogen atom attack on the solvent to form HD by abstraction. The quantum yield is 0.2 both in the liquid at 298°K. and in the solid glass at 123°K. The quantum yield for thermal H atom formation, which is about 0.8 at 298°K., decreases with temperature and may be estimated to be about 0.1 at 77°K.

On the basis of these[3] results, one would predict that the photolysis of HI in 3-MP at 77°K. would produce 3-methylpentyl radicals with an initial quantum yield of 0.2 and I atoms with a yield of about 0.4 (0.3 from photodissociation of HI and 0.1 from the $H + HI \rightarrow H_2 + I$ reaction of the thermal H atoms). In the presence of added alkenes some thermal H atoms might be expected to add to the double bond producing new radicals. Other possible reactions include combination of radicals, combination of I atoms with radicals and with alkenes, and abstraction of hydrogen from the solvent by $I(^2P_{1/2})$ atoms.[4]

We have examined the e.s.r. spectra of solutions of HI and alkenes in 3-MP glass at 77°K. during and following photolysis to seek evidence for the radical species formed and the reactions which they undergo. Our interest in these studies has stemmed from a need for more specific information on radical species formed by I and H in organic solids to assist in the interpretation of reactions produced in the radiolysis of alkyl halides[5] and solutions of alkyl halides in hydrocarbons.

Experimental Section

3-Methylpentane (Phillips pure grade) was further purified by prolonged stirring with concentrated sulfuric acid, followed by washing, drying, and fractional distillation, or by passing through a column of freshly activated alumina. These procedures decreased the upper wave length onset of absorption by a 1-cm. thickness from 2700 to 2200 Å. Gas chromatographic analysis indicated no impurities in excess of 10 p.p.m. The purified samples were stored under vacuum in a vessel coated with metallic sodium.

Hydrogen iodide was prepared from Merck reagent grade aqueous HI by first removing iodine by shaking with mercury or red phosphorus and then allowing the frozen solution to warm in the presence of excess P_2O_5 on the vacuum line. The dry HI was distilled three times from a bath at 200°K. to a bath at 77°K.

Phillips research grade ethene, propene, and 2-methylpentene-1, and Phillips pure grade isobutylene, *cis*-butene-2, and isomeric butene-2 were used. After passing through P_2O_5, they were stored on the vacuum line over sodium mirrors to remove peroxides.

Matheson vinyl chloride and K & K Laboratories vinyl bromide and iodide were used as received.

Samples, prepared on the vacuum line, were sealed in 4-mm. o.d. Suprasil tubes. These were illuminated and examined for e.s.r. signals while immersed in liquid nitrogen in a Varian liquid nitrogen dewar. E.s.r. measurements were made with a Varian V-4500 spectrometer using 100-Kc./sec. modulation. Line separations in gauss were estimated from the known line separation (507 gauss) of the hydrogen doublet induced in quartz sample tubes by γ irradiation.

Illumination was provided by an unfiltered end-window Hanovia low-pressure mercury lamp giving an intensity of about 6×10^{14} photons cm.$^{-2}$ sec.$^{-1}$ at 2537 Å. or a grating monochromator using a band width of 300 Å. with an intensity of 2.6×10^{15} photons cm.$^{-2}$ sec.$^{-1}$ at 2500 Å. and 1.1×10^{16} photons cm.$^{-2}$ sec. at 3000 Å.

The molar absorbancy index of HI at a concentration of 2.8×10^{-3} M in 3-MP glass at 77°K., as determined in this work, is 140

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(2) For references and a review of spectroscopic information on HI, see R. M. Martin and J. E. Willard, *J. Chem. Phys.*, **40**, 2999 (1964).

(3) J. R. Nash, R. R. Williams, Jr., and W. H. Hamill, *J. Am. Chem. Soc.*, **82**, 5974 (1960).

(4) S. V. Filseth and J. E. Willard, *ibid.*, **84**, 3806 (1962).

(5) (a) H. W. Fenrick, S. V. Filseth, A. L. Hanson, and J. E. Willard, *ibid.*, **85**, 3731 (1963); (b) H. W. Fenrick and J. E. Willard, *ibid.*, in press.

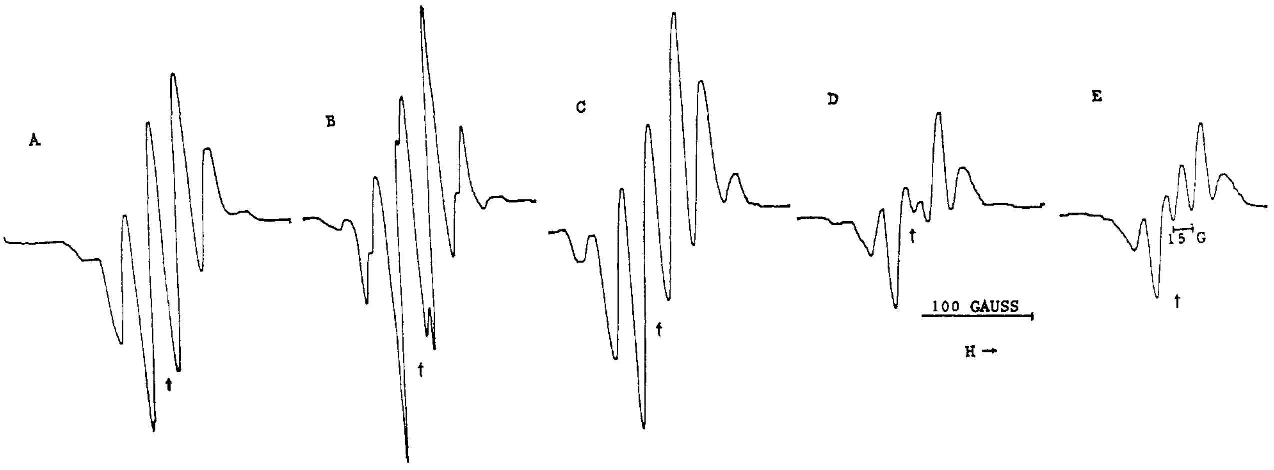

Figure 1. E.s.r. spectra of 3-MP glass containing 0.1 mole % HI photolyzed at 77 °K. with 2500-Å. radiation: (A) no additive, modulation (mod.) 800, sensitivity (sens.) 40; (B) 3 mole % ethene present, mod. 800, sens. 40; (C) 3 mole % *cis*-butene-2 present, immediately after 20-min. photolysis, mod. 800, sens. 160; (D) same as C, but 8 hr. after photolysis, mod. 800, sens. 200; (E) same as C, but 18 hr. after photolysis, mod. 1250, sens. 200.

l. mole^{-1} cm.$^{-1}$ at 2500 Å. Using this value, and an averaged effective light path length for the sample in the e.s.r. tube, it can be estimated that *ca.* 10^{14} photons sec.$^{-1}$ were absorbed from the monochromator beam at the start of illumination. When photolysis was carried out with the sample in the e.s.r. cavity, about 50% of this radiation was cut out by the cavity window.

Results and Discussion

Radicals Produced in 3-MP–HI Glass. Figure 1A shows the e.s.r. spectrum produced by a 90-min. photolysis of 0.1 mole % HI in 3-MP at 77 °K. with the low-pressure mercury arc. Prolonged photolysis of 3-MP without HI present produced no detectable radicals. An identical spectrum was obtained by photolysis with a band at 3000 Å. with the monochromator, or by exposing pure 3-MP to γ radiation. Other workers have observed similar six-line spectra with 24-gauss line spacing and a 1:5:10:10:5:1 intensity ratio from the γ irradiation of 3-MP[6a,b] and from the 2537 Å. photolysis of benzene in 3-MP.[6c] The number of lines and their intensity ratios are the same as observed[5] for ethyl radicals from the radiolysis of glassy ethyl iodide, for which the line splitting is about 27 gauss. These results imply that the unpaired electron is coupled equally to each of five protons. This might result from abstraction of H from the 2 position to form C–Ċ–C(C)C–C with equal coupling to the five β protons, or from abstraction of the tertiary H to form C–C–Ċ(C)C–C with equal coupling to five β protons and very little to the other two β protons. The similarity of the radical spectrum generated by the photochemically produced H atoms to that obtained by the radiolysis of 3-MP implies that the radiolytically produced radicals must also be formed by loss of an H, rather than by loss of the methyl group from the 3-position as previously suggested.[6b] Abstraction of a methyl group by photochemically produced hydrogen atoms of this energy is without precedent. The earlier work[3] on hydrogen yields has established the fact that H atom abstraction does occur.

Accurate evaluation of the quantum yield of radical formation in the 3-MP glass is precluded by the fact that the absorbancy at 2500 Å. increased during irradiation, indicating the formation of a new species absorbing in this region. A rough estimate, based on the intensity of the e.s.r. signal as compared with a standard sample and the estimated absorption of light by HI, gives a value of 0.1, which is in the same range as the value of 0.2 predicted from determinations[3] of H_2 yield.

The growth in absorbancy at 2500 Å. continued after cessation of irradiation. In a typical case the value, which was 0.39 prior to irradiation, increased to 0.54 and 1.09 after 30 and 240 min. exposure to the ultraviolet source and grew further to 1.18 during 90 min. following the exposure. The only species in the system which might have a higher molar absorbancy index than HI at this wave length and grow following irradiation is $C_6H_{13}I$. (At 2500 Å. the absorbancy index of CH_3I is *ca.* five times that of HI in the vapor state.[7]) It is plausible that the growth in absorbancy results from the production of $C_6H_{13}I$ by the combination of C_6H_{13} radicals with I atoms which have been formed in close proximity.

Radicals Produced in 3-MP–HI–Alkene Glasses. Glasses containing ethene, propene, isobutene, *cis*-butene-2, mixed butene-2 isomers, and 2-methylpentene-1, at about 3 mole % in 3-MP, with HI concentrations of 10^{-1} mole % were irradiated at 2500 Å. Each of these systems, except that containing the propene, gave e.s.r. signals indicative of radical species in addition to 3-methylpentyl radical. Without HI present no e.s.r. spectrum was found from identical alkene-containing glasses.

In some cases the spectrum of the second radical was observable in the presence of the 3-methylpentyl radical, and sometimes only after the latter had decayed. It is often difficult to resolve the spectra of two alkyl radicals because of the similarity of line splittings, whereas allyl radicals can be distinguished from alkyl by the splitting of *ca.* 15 gauss, as compared to *ca.* 24 gauss.

The splitting of about 27 gauss for ethyl radicals, as contrasted to 24 gauss for 3-methylpentyl, makes it

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(6) (a) J. A. Staples, "Electron-Spin Magnetic Resonance of Radical Intermediates in Gamma-Irradiated Hydrocarbons," USAF, Doc. No. NARF-63-4T, MR-N-299, available from Clearinghouse, U. S. Department of Commerce, as Report No. AD417705; (b) K. Fueki and Z. Kuri, *J. Am. Chem. Soc.*, **87**, 923 (1965); (c) B. N. Shelimov, N. V. Folk, and V. V. Voevodsky, *Rept. Acad. Sci. USSR*, **144**, No. 3 (1962).

(7) G. M. Harris and J. E. Willard, *J. Am. Chem. Soc.*, **76**, 4678 (1954).

Figure 2. A, B, and C are e.s.r. spectra of 3-MP glass containing 0.1 mole % HI photolyzed at 77°K. with 2500-Å. radiation: (A) 3 mole % vinyl chloride present, immediately after 2-hr. photolysis, mod. 800, sens. 10; (B) same as A, but 6 hr. after photolysis, mod. 800, sens. 20; (C) same as A. but 24 hr. after photolysis, mod. 800, sens. 25; (D) pure 2-methylpentene-1 containing 0.1 mole % HI photolyzed at 77°K. with 2500-Å. radiation, mod. 1250, sens. 80.

possible to see the presence of the former in the ethene system (Figure 1B). A ten-line spectrum 206 gauss wide, extending beyond the six-line 3-methylpentyl spectrum, was attributable[8] to *t*-butyl radicals and showed the presence of the latter in the system with added isobutene. This persisted at about one-fourth its initial intensity after 30 hr. at 77°K. following irradiation. Reduction of the isobutylene concentration from 3 to 0.5 mole % gave samples which showed only the 3-methylpentyl spectrum. This suggests that HI competes effectively for the thermal H atoms when present in one-fifth the concentration of the alkene.

Among the radicals observed here, the smaller radicals decay faster than the larger. Thus, the C_2H_5 lines of Figure 1B disappeared faster than those of the somewhat larger 3-methylpentyl radical, and the spectrum of *t*-butyl radical from the isobutene experiment was more persistent than that of C_2H_5 from the C_2H_4 experiment.

The samples containing *cis*-butene-2 and mixed butene-2 isomers gave six-line spectra (Figure 1C), with 24-gauss splitting. These were similar to each other and similar, with slightly different relative line intensities, to the 3-methylpentyl spectrum. On standing at 77°K. for 18 hr. these spectra underwent gradual alteration through seven-line spectra (Figure 1D) to spectra of five prominent lines with the splitting of about 15 gauss typical of allylic radicals[9] (Figure 1E). These changes suggest a preferential disappearance of 3-methylpentyl radicals relative to allylic radicals,

Photolysis of HI in 3-MP containing 3-methylpentene-1 gave an initial 3-methylpentyl radical spectrum similar to that of Figure 1A. On standing for 24 hr., this showed a change similar to that illustrated in Figure 1D for butene-2. Further standing yielded six lines of *ca.* 15-gauss splitting which, after 48-hr. additional time, converted to some eight poorly resolved lines of 15-gauss splitting.

Radicals Produced in 3-MP–HI–Vinyl Halide Glasses. It has been speculated that a 30-line, 1000-gauss-wide e.s.r. spectrum observed in the radiolysis of polycrystalline ethyl iodide[5] might possibly be due to the C_2H_4I radical. In the present work solutions of 10^{-1} mole % HI in 3-MP containing 3 mole % C_2H_3I, C_2H_3Br, and C_2H_3Cl were photolyzed with light absorbed by the HI with the thought that C_2H_4X radicals might be formed by addition of H atoms to the vinyl halides. For both the C_2H_3I and C_2H_3Cl glassy solutions, the spectrum immediately after an hour photolysis was of the type of Figure 2A, attributable to the 3-methylpentyl radical. The C_2H_3Br sample gave a 3-methylpentyl-type spectrum with added lines on the low-field side very similar to those resulting[5,10,11] from the radiolysis of C_2H_5Br at 77°K. It has been suggested[10] that these are due to the C_2H_4Br radical. Photolysis of a C_2H_3Br–3-MP solution which did not contain HI produced no e.s.r. spectrum.

On standing for 6 hr. following photolysis, the spectrum of the C_2H_3Cl samples underwent a gradual change in which the 3-methylpentyl lines decayed, while the line at the position just to the left of the highest line of Figure 2A remained essentially unchanged, yielding the spectrum of Figure 2B. The spectrum after standing for 24 hr. is shown in Figure 2C. An almost identical residual spectrum was observed for the C_2H_3Br sample, and a similar, though less prominent, asymmetric component was observed in the case of C_2H_3I. The identity of the responsible radical is not known.

Radicals Produced in HI–Alkene Glasses. Irradiation of HI in 2-methylpentene-1 glass gave the spectrum shown in Figure 2D with seven or more weak lines of 15-gauss splitting superimposed on a major line. It is similar to that reported for the radiolysis of 2-methylpentene-1 and attributed to the $C{-}C{-}\underset{\cdot}{C}{-}C(C){=}C$ radical.[9] Pure 2-methylpentene-1 illuminated under the same conditions shows no radical spectrum. These results imply abstraction of hydrogen from the alkene by hot hydrogen atoms.

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(8) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(9) P. B. Ayscough and R. E. Evans, *Trans. Faraday Soc.*, **60**, 801 (1964).

(10) F. W. Mitchell, B. C. Green, and J. W. T. Spinks, *J. Chem. Phys.*, **36**, 1095 (1962).

(11) P. B. Ayscough and C. Thomson, *Trans. Faraday Soc.*, **58**, 1477 (1962).

Abell and Piette[12] have attributed the e.s.r. spectra obtained from the photolysis of HBr in alkene matrices to addition of bromine to the double bond. The spectra do not, however, have the asymmetry around the free electron *g* value attributed to bromine-containing organic radicals in radiolyzed organic bromides[10,11,13] and in the photolyzed HI–C_2H_3Br–3-MP glass reported above. Symons[14] has favored the alternative assignment to allylic radicals formed by H abstraction. This is plausible if hot H atoms were available. Interpretation of the results is complicated by the fact that light at wave lengths below 2800 Å. was removed by a filter.[12] Neither gaseous HBr nor C_2H_4 absorbs light in the wave length range used. Therefore, it appears that absorption by an HBr–C_2H_4 complex must have been involved. The energy of a photon of 2800 Å. is 17 kcal./mole greater than the bond energy of gaseous HBr.

Fate of Hydrogen Atoms. The hydrogen atoms produced by the photolysis of HI in the glass matrices studied do not give an e.s.r. signal.[15] This is consistent with the fact that the hydrogen doublet is not observed in γ-irradiated organic solids at 77°K.[18] It implies that the atoms are rapidly consumed by abstraction, addition, or combination reactions.

The work of Nash, Williams, and Hamill[3] suggests that about one-third of the H atoms which escape primary recombination become thermalized and that two-thirds react as hot atoms. In the 3-MP–alkene–HI glasses, the thermal atoms have the alternatives of reacting with HI, which is present at 10^{-3} mole fraction, with alkene, which is present at 0.03 mole fraction, or with other H atoms or radicals or impurities. The signal attributed to ethyl radical in Figure 1B and that attributed to the *t*-butyl radical in the 3-MP–isobutene glass indicate that a large fraction of the thermal H atoms must have added to the double bond in these systems. If similar fractions formed radicals in the other 3-MP–alkene glasses, the spectra were hidden by the 3-methylpentyl spectrum.

Previous workers have generated HCO radicals in CO matrices[19] and C_2H_3[20] radicals in Ar matrices at 4°K. by the reaction of CO and C_2H_2 with H atoms produced by the photolysis of HI. At this temperature these addition reactions must have required hot hydrogen atoms. Considerable evidence is available about hot hydrogen atoms produced by the photolysis of hydrogen halides in gaseous systems.[21]

Fate of I Atoms. It is known that H atoms are formed by photolysis of HI in 3-MP glass.[3] Therefore, I atoms must also be formed. Their rate of diffusion and combination with other iodine atoms or radicals should be at least as slow as that of CH_3 and C_2H_5 radicals, both of which can be seen by e.s.r. in these matrices. Although some of the atoms may be produced in the excited $I(^2P_{1/2})$ state[2] and may be able to abstract secondary H atoms from the solvent,[4] it is improbable that this process is efficient enough to consume a large fraction of the atoms. It may be estimated that the concentration of I atoms in the matrices studied was of the order of 10^{-4} *M*. No e.s.r. signal attributable to I atoms or to iodine-containing radicals was found over the range of 3000–6000 gauss, using a variety of power levels and modulation frequencies. It appears that line-broadening effects in the solid state obscure the 18-line I atom spectrum, which has been observed in vapor phase photostationary state studies.[22]

Decay Kinetics of 3-Methylpentyl Radicals. The intensity of the e.s.r. spectrum due to 3-methylpentyl radicals produced by 60 to 90 min. photolysis of 10^{-3} mole fraction HI in 3-MP at 77°K. always showed an initial relatively rapid decay of about 20% of the radicals, followed by a much slower decay. Second-order plots (1/peak intensity *vs.* time) did not give straight lines. Resolution of the original decay curve suggests that the shorter-lived process may be first order. If this interpretation is correct,[23] it requires combination of each radical with a partner formed concurrently with the radical and in close proximity. This may be the iodine atom originally present in the HI molecule from which the hot hydrogen atom which formed the radical was produced. Such reaction would produce $C_6H_{13}I$, consistent with the observed increase in optical absorption at 2500 Å.

Reaction of radicals with the relatively high concentration of HI in the system does not seem to account for either of the observed radical decay rates, since the latter were not altered by varying the HI concentration from 10^{-3} to 10^{-2} *M*.

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(12) P. I. Abell and L. H. Piette, *J. Am. Chem. Soc.*, **84**, 916 (1962).

(13) R. M. A. Hahne and J. E. Willard, *J. Phys. Chem.*, **68**, 2582 (1964).

(14) M. R. C. Symons, *ibid.*, **67**, 1567 (1963).

(15) The hydrogen doublet is easily observed at 77°K. in empty Pyrex, quartz, or Suprasil tubes which have been exposed to γ-radiation or to prolonged intense irradiation with low-pressure Hg arcs. It has also been observed[16] in Ar matrices at 4°K. and in aqueous acids at 77°K.[17]

(16) C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, *Phys. Rev.*, **112**, 1169 (1958).

(17) See, for example, R. Livingston and J. Weinberger, *J. Chem. Phys.*, **33**, 499 (1960).

(18) See, for example, V. V. Voevodsky, Fifth International Symposium on Free Radicals, Uppsala, Sweden, Almquist and Wiksell, Stockholm, 1961; Paper A-1.

(19) (a) T. E. Ewing, W. E. Thompson, and T. C. Pimentel, *J. Chem. Phys.*, **32**, 927 (1960); (b) F. J. Adrian, E. L. Cochran, and V. A. Bowers, *ibid.*, **36**, 1661 (1962).

(20) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *ibid.*, **40**, 213 (1964).

(21) For examples and references, see R. M. Martin and J. E. Willard, *ibid.*, **40**, 3007 (1964).

(22) S. Aditya and J. E. Willard, *J. Chem. Phys.*, in press.

(23) Methyl radicals formed from methyl chloride or methyl bromide in 3-MP glass at 77°K. by dissociative electron attachment, using electrons from the photoionization of TMPD, have been found[24] to decay by a clear-cut first-order process. This is interpreted as the result of retention of the dissociation partners in the same solvent envelope under conditions requiring a low activation energy or steric barrier for recombination.

(24) R. F. C. Claridge and J. E. Willard, *J. Am. Chem. Soc.*, **87**, 4992 (1965).