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Ionic Intermediates in γ -Irradiated Organic Glasses at -196° ¹

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γ -Irradiation at -196° of 3-methylpentane glasses containing alkene or aromatic solutes produces three types of color centers. One of these is attributable to solvated electrons or to solute anions. Another can be identified as positive ions of the solutes which appear to be formed through charge transfer from solvent. The third type correspond to free radicals (ref. 4). Absorption bands arising from carbon tetrachloride and other alkyl halide solutes are also attributed to cations in irradiated glasses. The efficiency of positive charge transfer is less than that for electron capture by solutes. Yields of cations are enhanced by solutes which attach electrons.

Introduction

A general method has been developed for spectrophotometric observation of intermediates produced and trapped in γ -irradiated organic glasses at -196° which has provided information about electron solvation, simple and dissociative attachment, and photodetachment²⁻⁴ as well as solvent and solute cations.⁵ This and the following report⁶ present evidence for the production of positive ions of alkenes, aromatic hydrocarbons, and aromatic amines.

Experimental

Methods of solvent purification, cell preparation, γ -irradiation, and spectrophotometry were described previously.² Special precautions were required to purify 3-methylpentane (3MP). Several passes through silica gel decreased aromatic and unsaturated impurities to less than $5 \times 10^{-3} M$, as determined by v.p.c. A Cary Model 14-R spectrophotometer allowed routine measurement from 200 to 2000 $m\mu$. Cells of radiation-resistant ultrapure fused silica were used for the ultraviolet region, as required. Otherwise Pyrex cells were satisfactory. Corning filters used were No. 2600, transmitting in the 750–1050 $m\mu$ interval, and No. 3385 which cuts off at 530 $m\mu$. Absorbed γ -doses for all experiments were 6.5×10^{18} e.v./g. unless otherwise noted.

The measurements of λ_{max} for well defined bands are reliable within 1 $m\mu$. Values of optical density are subject to uncertainty of about 0.02 unit owing to optical irregularities of dewar and cell windows, turbidity of liquid nitrogen, and, when necessary, correction for radiation coloration of Pyrex. There was no evident decay of optical density of irradiated samples excluded from moderate illumination. The monochromatized light beam had no effect. Measurements of rather small optical density reported in this work have mainly qualitative significance.

Results

γ -Irradiation of 3MP glasses containing various alkene solutes generally produced two absorption bands, one at ca. 1800 $m\mu$, the other at various positions in the visible region. Optical bleaching of the band at 1800 $m\mu$ also removed the visible band.

Since 2-methylpentene-1 (2MP-1) alone forms a satisfactory glass, various tests were used to identify the two bands. Irradiation of pure 2MP-1 produced a broad structureless absorption band (600–2500 $m\mu$) with an optical density (O.D.) of 0.90 at λ_{max} 1800 $m\mu$ and a small shoulder at 680 $m\mu$ with an O.D. of ca. 0.05. Adding 2.6 mole % carbon tetrachloride to 2MP-1 completely prevented the appearance of the 1800 $m\mu$ band and increased O.D.₆₈₀ to 0.20. Adding 0.13 mole % naphthalene also removed the 1800 $m\mu$ band, increased

the band at 680 $m\mu$, and produced naphthalene anions. The effect of biphenyl on the 1800 $m\mu$ band of 2MP-1 with a concomitant appearance of biphenyl anion absorption at 410 $m\mu$ is summarized in Table I.

TABLE I
BIPHENYL IN 2-METHYLPENTENE-1

Mole % $C_{12}H_{10}$	O.D. ₄₁₀ ^a	O.D. ₁₈₀₀ ^b
0	0.00	0.90
0.003	.05	.87
.05	.32	.58
.13	.63	.00

^a Dose = 1.1×10^{18} e.v./g. ^b Dose = 6.5×10^{18} e.v./g.

The effects of naphthalene, biphenyl, or carbon tetrachloride upon the 2MP-1 band at 1800 $m\mu$ suggest that the color centers are electrons trapped by alkene. Optical bleaching of this band in the presence of small amounts of naphthalene or biphenyl does not result in observable electron transfer to solute because the aromatic anions themselves also bleach very easily in hydrocarbon glasses. For this reason triphenylmethyl (trityl) chloride was used instead to attach electrons since this gives recognizable trityl radicals which do not bleach.⁴ Irradiation of 0.007 mole % trityl chloride in 2MP-1 gave an O.D. of 0.76 at 1800 $m\mu$, 0.13 at 680 $m\mu$, and 0.09 at 340 $m\mu$ (a trityl radical band). Optical bleaching of the 1800 $m\mu$ band removed the 680 $m\mu$ band and increased O.D.₃₄₀ to 0.27, indicating that the 1800 $m\mu$ band is due to the "solvated" electron.

These facts also suggest that the 680 $m\mu$ band is due to the 2MP-1 cation. Removal by bleaching trapped electrons and enhancement by adding electron scavengers were observed to be properties of authentic cations from aromatic amines.⁶

In other experiments various solutes were tested for their ability to attach electrons or to produce observable cations.

Negative Ion Spectra.—Irradiation of repeatedly purified 3MP gave O.D.₁₈₀₀ = 0.34. This may be due to electrons attached either by a small amount of alkene impurity or by unsaturates produced during irradiation. It appears that pure alkane traps electrons very inefficiently or not at all. Large bands at 1800 $m\mu$ were observed for 1–2% cyclohexene, 2MP-1, isobutylene, hexene-1, or cyclopentene in 3MP. In each case, 0.12 mole % carbon tetrachloride reduced O.D.₁₈₀₀ to zero. No absorption at 1800 $m\mu$ was observed for 2% ethylene or propylene. A large band at ca. 1800 $m\mu$ was also observed for triethylamine in 3MP, but none for 1% ammonia in 3MP. Maxima at 1200 $m\mu$ were observed for 50% diethyl ether in 3MP, for MTHF alone, and for 4% MTHF in 3MP.

If one assumes that the yields of solvated electrons in pure MTHF and 2MP-1 are equivalent to the limiting yields of naphthalene anions in these glasses, then the extinction coefficients (ϵ) and oscillator strengths (f) can

(1) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission.

(2) M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 4230 (1962).

(3) J. P. Guarino, M. R. Ronayne, and W. H. Hamill, *Radiation Research*, **17**, 379 (1962).

(4) W. H. Hamill, J. P. Guarino, M. R. Ronayne, and J. A. Ward, *Discussions Faraday Soc.*, in press.

(5) Cationic color centers were not observed under the experimental conditions used previously (ref. 2, 3). Their identification rests largely upon the work of E. P. Bertin using 2-methylpentene-1 and 3-methylpentane glasses with alkyl halides and carbon dioxide. The work is to be published.

(6) M. Kondo, M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *J. Am. Chem. Soc.*, in press.

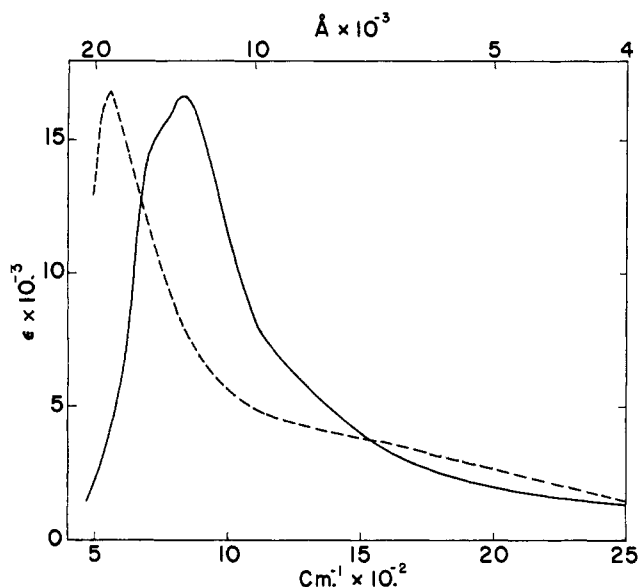


Fig. 1.—Extinction coefficient vs. wave number for MTHF (—) and 2 MP-1 (---).

be evaluated. Graphs of extinction coefficients vs. wave number ($\bar{\nu}$) appear in Fig. 1. Since $f = 4.3 \times 10^9 \int \epsilon(\bar{\nu}) d\bar{\nu}$ we obtain $f \approx 0.8$ in MTHF and $f \approx 0.2$ in 2MP-1. When it was subsequently found that O.D.₁₈₀₀ was greater at a given dose for 20 mole % 2MP-1 in 3MP than in pure 2MP-1, the effect of concentration was investigated further. These results appear in Fig. 2 which shows that the largest yield observed at 4.8 mole % 2MP-1 is four times that in pure 2MP-1. The corresponding maximum oscillator strength in these binary mixtures is at least 0.8. Several compositions of MTHF in 3MP were irradiated at 1.1×10^{18} e.v./g. giving O.D.₁₂₀₀ values of 0, 0.43, 0.87, and 0.65 at 0, 4, 20, and 100% MTHF. Again, yields are higher in some mixtures than in MTHF alone, the maximum value of the oscillator strength approximating unity.

The dependence of trapped electron yields upon glass composition suggested that corresponding anion yields should also be measured. At 0.15 mole % biphenyl and 1.1×10^{18} e.v./g., $G(\text{C}_{12}\text{H}_{10}^-)$ was 1.57, 1.05, and 0.71 for three glasses consisting of 100% 3MP, 5% 2MP-1 in 3MP, and 100% 2MP-1, respectively.

Positive Ion Spectra.—A simple test for distinguishing between cationic and anionic color centers is the effect of adding a little carbon tetrachloride which depresses or removes negative ion absorption and enhances bands due to cations. Table II summarizes results of this test for some compounds.

TABLE II
EFFECT OF CARBON TETRACHLORIDE ON CATION ABSORPTION BANDS IN 3MP

Solute	$\lambda_{\text{max}}, \text{m}\mu$	O.D. 0% CCl ₄	O.D. 0.12% CCl ₄
1% cyclohexene	710	0.12	0.38
20% 2MP-1	680	0.05	.25
1% cyclopentene	700	.15	.50
8% toluene	1075, 425	0.10, 0.07	0.60, 0.30
2% benzene	930, 450	0.12, 0.04	0.52, 0.19
2% isobutylene	400	0.15	0.19

The effect of carbon tetrachloride on two species of color center in alkane-alkene mixtures appears in Table III.

The addition of 1.4 mole % 2-propyl chloride also removed the 1800 m μ band and increased O.D.₆₈₀ to 0.58. Several compounds considered likely to undergo

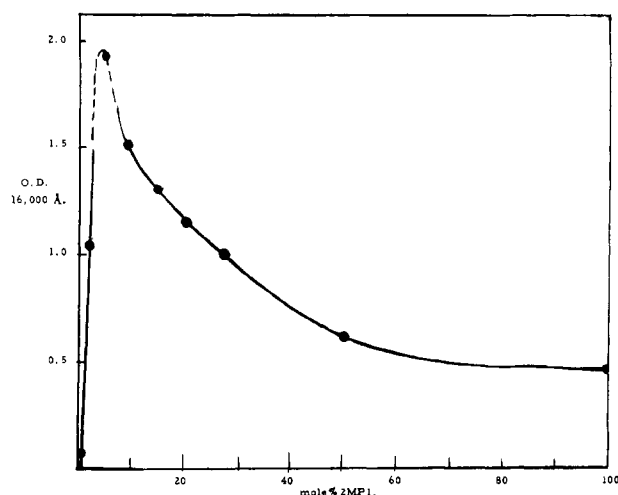


Fig. 2.—Optical density vs. composition for 2 MP-1 in 3MP.

proton transfer reactions with positive ions were tested. The addition of 4% MTHF, 1% triethylamine, or 4% 1-propanol all removed the 680 m μ band in the 20% 2MP-1-80% 3MP glass.

TABLE III
EFFECT OF CARBON TETRACHLORIDE ON ABSORPTION BANDS IN 20% 2MP-1-80% 3MP^a

Mole % CCl ₄	O.D. _{1800 mμ}	O.D. _{680 mμ}
0.00	2.24	0.05
.01	0.90	.10
.12	.00	.25
2.6	.00	.33

^a Dose = 6.5×10^{18} e.v./g.

Competition for positive charge occurs between toluene and 2MP-1. With 0.12 mole % carbon tetrachloride and 2 mole % toluene in 3MP, O.D.₁₀₇₅ of toluene cation was 0.35. Adding 0.12 mole % carbon tetrachloride plus 2 mole % toluene to 20% 2MP-1 in 3MP prevented formation of toluene cations and promoted O.D.₆₈₀ for 2MP-1 cations to 0.29.

The Carbon Tetrachloride Cation.—The irradiation of carbon tetrachloride in alkane glasses yields a species absorbing at 480 m μ ; some results are summarized in Table IV. This band bleaches easily upon illumination at ca. 500 m μ . The yield for this absorption band does not correlate with the efficiency of carbon tetrachloride for electron attachment. Almost 1 mole % carbon tetrachloride is needed to give one-half the limiting O.D. for the 480 m μ band. Only 0.1 mole % carbon tetrachloride eliminated the electron band from MTHF, 2MP-1, cyclohexene, etc., and only 0.3 mole % carbon tetrachloride is required to prevent anion formation from naphthalene or biphenyl.³ At ca. 2 mole % the two latter solutes attain saturation yields of anions.² The dependence of O.D.₄₈₀ upon concentration of carbon tetrachloride is much weaker.

TABLE IV
480 M μ BAND FROM CARBON TETRACHLORIDE IN 3MP^a

Mole % CCl ₄	O.D. _{480 mμ}
0.00	0.00
0.12	.29
2.58	.67
5.16	.90
11.7	.98

^a Dose = 6.5×10^{18} e.v./g.

This band was previously attributed to CCl_4^- , in part because of its susceptibility to optical bleaching, and in part because it was not observed in polar glasses

and assumed to solvolyze.² This interpretation is not compatible with the observation in this work that the 480 $m\mu$ band is not observed when carbon tetrachloride is irradiated in a 2MP-1 glass. In Table V, the effect of 2MP-1 on this band, and the alkene cation band, is presented.

TABLE V
EFFECT OF 2MP-1 ON THE 480 $m\mu$ BAND FROM CARBON
TETRACHLORIDE IN 3MP^a

Mole % 2MP-1	O.D. ₄₈₀	O.D. ₆₈₀
0 ^b	0.67	0.00
4 ^b	.46	.04
20 ^b	.17	.43
100 ^b	.00	.60
0 ^c	.29	.00
2 ^c	.19	.08
20 ^c	.00	.25

^a Dose = 6.5×10^{18} e.v./g. ^b 2.6 mole % CCl_4 . ^c 0.12 mole % CCl_4 .

Although identifiable anions of naphthalene and other solutes are produced efficiently in alkane-alkene glasses, the O.D.₄₈₀ from carbon tetrachloride is depressed by 2MP-1. While carbon tetrachloride enhances alkene cation bands, it can also be shown that carbon tetrachloride competes with 2MP-1 for positive charge. When 1.4 mole % 2-propyl chloride was added to 20% 2MP-1, O.D.₆₈₀ was 0.58 and there was no other absorption. In contrast, O.D.₆₈₀ with 2.6 mole % carbon tetrachloride was 0.33. Since the latter is a much better electron acceptor, the results are consistent with the hypothesis that carbon tetrachloride forms a positive ion absorbing at 480 $m\mu$. Similarly, the addition of 1% carbon dioxide, which is expected to react only with electrons, to 25% 2MP-1 in 3MP enhanced O.D.₆₈₀ to 0.57.⁵ Several other additives with carbon tetrachloride in 3MP depress O.D.₄₈₀. Some of these have already been shown to suppress yields of other color centers tentatively identified as cations. Olefins and aromatic compounds presumably compete through charge transfer and the other through ion-molecule reactions. Results are summarized in Table VI.

TABLE VI
EFFECT OF VARIOUS ADDITIVES ON THE 480 $m\mu$ BAND OF CARBON
TETRACHLORIDE^a IN 3MP^b

%	Additive	O.D. ₄₈₀	%	Additive	O.D. ₄₈₀
	None	0.29	1	Triethylamine	0.05
1	Cyclohexene	.27	1	MTHF	.07
2	Isobutylene	.16	4	MTHF	.00
8	Toluene	.00	4	1-Propanol	.08
2	Benzene	.00			

^a 0.12 mole % CCl_4 . ^b Dose = 6.5×10^{18} e.v./g.

In addition, although O.D.₄₈₀ for 11.7 mole % carbon tetrachloride in 3MP is 0.98, the addition of 0.18 mole % naphthalene decreased O.D.₄₈₀ to 0.69. Since no naphthalene anions appear, the effect does not involve competitive electron attachment. The expected O.D.₃₂₀ of naphthalene anions without carbon tetrachloride would be 2.4 at this dose.

The assignment of the 480 $m\mu$ band to a cation from carbon tetrachloride raises the problem of accounting for the efficient optical bleaching of this species. Either photodecomposition or positive charge exchange appear to be required. γ -Irradiation of 0.12 mole % carbon tetrachloride and 1.0 mole % cyclohexene in 3MP gave both the 710- $m\mu$ band of cyclohexene cation and the 480- $m\mu$ band of carbon tetrachloride. Illumination with Corning filter No. 2600 bleached the 710- $m\mu$ band and slightly increased the 480- $m\mu$ band. Then illuminating in the 480- $m\mu$ band with tungsten light using

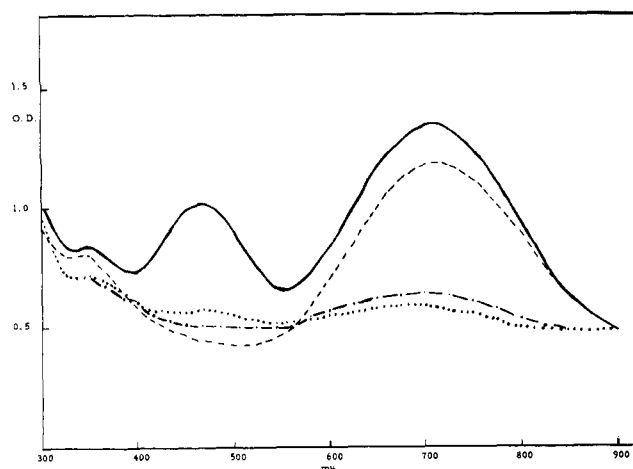


Fig. 3.—Optical densities for the CCl_4^- cation band at 480 $m\mu$ and the $\text{C}_6\text{H}_{10}^-$ cation band: immediately following γ -irradiation (—); 5-min. bleach with No. 3961 filter (---); 10-min. bleach with No. 2600 filter (....); 5-min. bleach with No. 3961 filter (-.-.-). All bleaching measurements were made consecutively.

Corning filter No. 3961 removed these color centers while the 710- $m\mu$ band reappeared at about one-half its initial optical density. Finally, bleaching again with the 2600 filter removed the 710- $m\mu$ band and produced a small band at 480- $m\mu$. This experiment was repeated at twice the dose and the order of bleaching was reversed. These results appear in Fig. 3. Transfer of positive charge was also observed in experiments with 2.6 mole % carbon tetrachloride and 20 mole % 2MP-1 in 3MP and with 2.6 mole % carbon tetrachloride and 4 mole % 2MP-1. In the former, bleaching the 680 $m\mu$ alkene cation band, using the 2600 filter, decreased the O.D.₆₈₀ from 0.43 to 0.31 and increased the 480- $m\mu$ band from 0.17 to 0.19. Subsequent bleaching of the 480- $m\mu$ band using the 3961 filter increased O.D.₆₈₀ to 0.34. In the latter, bleaching with the 3961 filter decreased the O.D.₄₈₀ from 0.46 to 0.00, while increasing the O.D.₆₈₀ from 0.04 to 0.15. These charge transfers provide additional evidence that the 480- $m\mu$ band of carbon tetrachloride is due to a cation. γ -Irradiation of 3MP glasses containing monochloro compounds (ethyl chloride, methyl chloride, 2-propyl chloride, and cyclohexyl chloride) all gave a band at 270 $m\mu$ with an O.D. of ca. 1.0 which indicates that this band may be due to 3MP^+ , rather than to the positive ion of the chloride, but the evidence is inconclusive. Several other halides produced absorption bands in the visible region. These results appear in Table VII.

TABLE VII
ABSORPTION MAXIMA FOR VARIOUS HALOGEN-CONTAINING
COMPOUNDS IN 3MP^a

%	Solute	λ_{max} , $m\mu$	O.D.
2	CCl_4	480	0.67
1	CCl_3F	430	.68
1	CCl_3Br	485	.89
1	CHCl_3	440	.29
1	CBr_4	510	.50

^a Dose = 6.5×10^{18} e.v./g.

Irradiation of styrene in 3MP produced bands previously identified with styrene anion at 400 and 590 $m\mu$ ² in addition to a new band, not observed in MTHF, at 460 $m\mu$. Benzene and toluene gave cation bands in this region (see Table II). To identify this 460 $m\mu$ band, 1 mole % methyl chloride was added to 1 mole % styrene in 3MP. Results appear in Table VIII.

TABLE VIII
YIELDS OF STYRENE ANION AND CATION IN 3MP^a

	O.D. _{400 mμ}	O.D. _{460 mμ}
1% C ₆ H ₆	1.05	0.10
1% C ₆ H ₆ + 1% CH ₂ Cl	0.44	.41
0.1% C ₆ H ₆	0.61	~ .00

^a Dose = 6.5×10^{18} e.v./g.

Enhancement of the 460-mμ band and depression of the 400 mμ band by methyl chloride suffice to identify the responsible species as cation and anion, respectively. The relatively inefficient formation of cation in the 0.1% styrene solution is characteristic of cation yields in general.

In runs with benzene and toluene in 3MP the cation bands noted in Table II appear together with absorption extending from *ca.* 700 to >2000 mμ which bleaches easily to remove the cation bands. On the other hand, in MTHF the cation bands of benzene and toluene are not observed but small new bands appear at 390 and 290 mμ for benzene and at 450 and 295 mμ for toluene. The yield of solvated electrons in MTHF is diminished by these solutes. Optical bleaching of solvated electrons in this matrix enhances the bands of benzene and toluene which are therefore assigned to the solute anions. The infrared absorption bands of these solutes observed in 3MP is not observed in MTHF.

Discussion

The spectra of several anions, which serve as standards in this work, can be established by chemical preparation (*e.g.*, sodium naphthalenide). The conjugate molecules, in turn, can be used to demonstrate corresponding anion formation by γ-irradiation in appropriate rigid media. The ability of any reagent to attach electrons can be demonstrated, independently of observing any new absorption band, by using it competitively with an authentic anion former to depress the measurable absorption of the latter. This method appears to have quantitative reliability. A variation of this method is possible when the solvent or solute gives rise to an accessible absorption band following irradiation. When such a band can be depressed by a reagent known to attach electrons, then the responsible solvent or solute is an anion former. The band may arise either from the anion or from a free radical, as occurs with benzyl chloride. An alternative qualitative method to demonstrate electron attachment by a solute is to measure the depression of the solvated electron band.

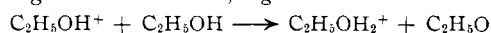
Solvated electrons, once identified, serve as convenient sources of low energy electrons through photodetachment. When a species of color center is increased in number by releasing these electrons, it can be identified as an anion or a free radical arising from dissociative attachment. In this case a series of reagents RX, RY, RZ should give rise to the common spectrum of R. Dissociative electron attachment provides a predictable, systematic procedure for producing stabilized free radicals in good yields, as demonstrated here for allylic and benzylic radicals as well as triphenylmethyl.⁴ This method should prove useful for e.s.r. studies. When a colored species is diminished in number by generating photoelectrons it is presumably a cation.

Positive holes have some mobility but apparently less than electrons. The ability to produce appreciable yields of solute cation at small solute concentration clearly demonstrates an indirect effect and the evidence points to positive charge exchange. Positive hole mobility in a molecular matrix is expected to be limited since positive charge exchange between the ground state of the ion and the ground state of the molecule is forbidden by Franck-Condon restrictions. The pri-

mary positive ion will usually have electronic as well as vibrational excitation. After a few jumps the ion relaxes and the hole is trapped. The ground state solvent ion can still transfer charge to an acceptor of lower ionization potential. The magnitude of the required inequality is controlling and unpredictable, but some measurements indicate that it may easily amount to 1 e.v.⁷ Qualitatively, the likelihood of finding the hole on a solute molecule is greater the lower its ionization potential. Vibrational excitation of either the donor or acceptor may promote transfer not otherwise possible by supplying the energy defect associated with the Franck-Condon losses. This phenomenon appears to be involved in the results reported in Fig. 3.

Persistence of immobilized positive holes is clearly impossible without complementary electron attachment, and the probability *P* of forming a stabilized center of either sign plausibly should depend upon the cross product, P^+P^- , of trapped holes and trapped electrons. If the solvent itself does not trap electrons, or traps them inefficiently, addition of an anion-forming solute should promote yields of stabilized positive holes, although not necessarily of solute cations. Conversely, if one finds large yields of solvated electrons in a one-component system (*e.g.*, MTHF for which *f* (e⁻) ~ 0.8), positive hole migration must be rather limited.

Yields of solute cations in hydrocarbon media are strongly promoted by alkyl halides.^{5,6} On the other hand, these same solutes do not produce significant yields of cations in MTHF, alcohol, etc., even with added electron acceptors. It must be concluded that there is little or no positive charge exchange in polar media, although ionization potentials of these polar molecules are usually greater than those of alkanes. The effect appears to be associated with an ion-molecule reaction of H or H⁺ transfer which occurs with large cross section for alcohols, ethers, amines, etc.⁸ Following such a reaction, *e.g.*



the potential energy stored in the positive ion has been diminished by at least the C-H or O-H dissociation energy, and positive charge exchange cannot now take place.

If all of the available electrons are attached in pure MTHF or in 2MP-1 and in their solutions, then for various concentrations of reference solute acting as electron acceptor, the sum of the yields of acceptor anions and solvated electrons is constant. It follows that O.D. (e⁻) would be linear in O.D. (solute anion). From the data in Table I, and for similar data in MTHF, plots of O.D. *vs.* O.D. were not linear and depart in the sense that not all electrons are solvated. Oscillator strengths less than unity support this evidence. Even more striking is the ability of 0.1% carbon tetrachloride to prevent electron trapping by 20% 2MP-1 in 3MP (Table III). The mechanism of trapping electrons, either in MTHF or in 2MP-1, is not clear.

The fact that even small concentrations of either MTHF or 2MP-1 in 3MP give rather good yields of trapped electrons, with no evident change in spectra relative to pure additive, suggests that single molecules rather than the medium may be involved. The striking maximum in Fig. 2, corresponding to *f* ~ 1, at only *ca.* 5% 2MP-1 suggests that either positive holes or electrons are being conducted by a network of more or less contiguous carbon-carbon double bonds. Conduction of the hole to the trapped electron by a growing polymer ion can be ruled out since no detectable yield of polymer is present in the thawed samples.⁹

(7) E. Lindholm, *Arkiv Fysik*, **8**, 433 (1954).

(8) T. F. Moran and W. H. Hamill, *J. Chem. Phys.*, **39**, 1413 (1963).

(9) According to observations by J. Gallivan.

The failure of ethylene, propylene, and ammonia to trap electrons, although several other olefins and triethylamine do so, cannot be explained. We can only observe that these molecules all have fairly high ionization potentials relative to their analogs which were found to be effective. This suggests that trapping the positive hole by solute in 3MP is prerequisite to anion stability, but this assumption appears to be inconsistent with $G(\text{C}_{12}\text{H}_{10}^-) = 1.57$ for 0.15% biphenyl in 3MP.

It is usually assumed that charge transfer from solvent to solute will occur only when the ground state ionization potential of the solvent is greater than that of the solute. The frequent observation and identification of solute cations in good yields from various alkene, aromatic, and amine compounds having lower ionization potentials than 3MP supports this view. However, small concentrations of various alkyl halides pro-

duce cations although their ionization and appearance potentials exceed those of 3MP. The best studied example is carbon tetrachloride.¹⁰ The ion CCl_4^+ cannot be detected in a mass spectrometer at pressures several times greater than normal and the appearance potential of CCl_3^+ is 11.65 e.v.¹¹ It may be that some solvent cations are produced in excited states, which could then account for these results. There is extensive evidence from mass spectrometry for ionic excitation¹² and no evident reason to exclude this possibility in condensed phases.

(10) S. Leach and R. Lopez-Delgado have recently reported (*Compt. rend.*, **256**, 1299 (1963)) observing a color center produced by ultraviolet excitation of benzene in 7% carbon tetrachloride in alkane glass. They follow our original suggestion that CCl_4^- is responsible.

(11) J. B. Farmer, I. H. S. Henderson, F. P. Lossing, and D. G. H. Marsden, *J. Chem. Phys.*, **24**, 348 (1956).

(12) C. E. Melton and W. H. Hamill, unpublished results.

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Consecutive Ion-Molecule Reactions in Ethylene¹

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Reactions of positive ions with ethylene molecules have been studied at pressures up to a few tenths of a millimeter in the source chamber of a mass spectrometer. Confirming earlier studies with different procedures, the data show that increasingly heavy polymeric ions appear to be formed in chains of consecutive reactions between ions and C_2H_4 molecules. Some specific chains of such reactions are suggested. The sequence involving the ions C_2H_4^+ , C_3H_5^+ , C_3H_9^+ , and $\text{C}_7\text{H}_{13}^+$ is the dominant mechanism for the initial propagation of ionic polymerization of ethylene at low pressure in the gas phase. Cross sections for the reactions of primary and secondary ions with C_2H_4 have been estimated from the concentration dependences of the intensities of the ionic species. The mass spectrometric results found by us and others are correlated with the observations on the radiolysis of ethylene.

Several investigators have used conventional techniques to study the radiolysis of gaseous ethylene at pressures ranging from 10 to 1000 mm.^{2a,b} The main radiolytic products are acetylene and hydrogen, but they account for only about 10% of the C_2H_4 destroyed. The remainder is converted to products higher in molecular weight, mainly polymer.³ To understand some of the mechanisms of gas-phase radiolysis of C_2H_4 , we have used techniques of "high pressure" mass spectrometry⁴ to investigate ionic reactions in this gas. Field,⁵ who ionized the gas with an electron beam, as well as Melton and Rudolph,⁶ who employed a Po^{208} α -source as the ionizing agent, have already identified ionic reactions in ethylene at relatively high pressures in the source chambers of their mass spectrometers; but their approaches, both experimental and theoretical, differ considerably from ours. Comparison of the results, particularly of reaction mechanisms and cross sections, is therefore worthwhile. In additional contrast to the efforts of these workers, who were mainly interested in ionic reaction mechanisms *per se*, we have attempted to correlate the mass spectrometric results with those obtained from radiolysis studies. Thus the "high pressure" experiments may be regarded as an effort to bridge at least partially the gap between kinetic experiments at ordinary pressures and low-pressure studies on the primary events of excitation and ionization by radiation.

A. Experimental

The mass spectrometer used in this work has been described previously.^{4,7} Two different designs of the source were used in the measurements on C_2H_4 . Source 1, employed in earlier work, admitted the electrons through a hole 0.001 in. in diameter and had a slot measuring 0.001×0.080 in. for exit of the ions. The repeller was hemicylindrical in shape. The pressure in this source chamber was determined by calculation from the measured pressure in the gas reservoir. Experience with this source led to construction of an improved assembly, source 2 (Fig. 1). The side tube and double ring seal provide for direct measurement of the pressure in the chamber. The pressure was measured by a calibrated dual-range McLeod gage. The electron beam, collimated by aligned slits, enters the chamber through a 0.003×0.040 in. slot, while the exit slot for the positive ions is 0.003×0.080 in. The electrons travel parallel to the length of the ion exit slit. The repeller is a flat plate. The ionizing current of electrons (energy = 144 e.v.) in this source is much lower than that used by other workers; when the filament emission is 250 μA , the trap current is only 0.02 μA . Thermocouples welded to opposite corners of the chamber recorded a temperature of $122 \pm 2^\circ$ with current flowing through the electron-emitting filament. The mean distance between the plane of the ionizing electron beam and the plane of the ion slit is estimated to be 3.2 mm.

The Phillips research grade C_2H_4 (99.84%) used in these experiments was further purified by repeated condensation in liquid nitrogen and pumping with a mercury diffusion pump.

The procedure was in general the same as that employed in the studies on methane,⁴ except for the improvement that the rather large amount of data was processed by the IBM-704 computer at this laboratory.

B. Results

1. "High Pressure" Mass Pattern of C_2H_4 .—In sharp contrast to the relatively simple mass spectra of primary ions observed on electron impact of ethylene at low pressures ($\approx 10^{-5}$ – 10^{-6} mm.), a very extensive pattern of singly-charged ions is found at a source pressure of 0.20 mm. The data given in Table I come from source 2; but a fairly similar pattern is

(1) Work performed under the auspices of the Atomic Energy Commission.

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