the limited applicability of the result, no attempt was made to explain the band shift in terms of other simple models.

The similarity of cation and anion spectra fails in the near-infrared region where a broad band at about 1200 mμ appeared for cations of all four butadienes, but not for anions. Since photobleaching decreases the infrared band and the visible bands proportionately, all arise from a common ionic species. A similar band was observed for olefin cations and attributed to a σ–π transition. The same assignment is applicable to cations of butadiene homologs.

Molecular Ions. VII. Positive Ions of Olefins in γ-Irradiated Organic Glasses

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Abstract. Vinylene- and vinylidene-type olefins appear to form their molecular cations in γ-irradiated alkyl chloride or alkane glass. Cations of vinyl-type olefins apparently react completely with solvent molecules. Molecular cations of the first two types of olefin have a broad absorption band at about 600–800 mμ which has been assigned to a transition of a σ electron to the half-occupied π orbital of the ions. λ_{max} of the cation band shifts noticeably depending on the number and position of alkyl groups adjacent to the ethylenic bond. In pure γ-irradiated olefin glasses, positive charge migrates to solute molecules efficiently.

Positive charge migration has been observed in several γ-irradiated organic matrices at −196°, including aliphatic halides and alkanes.[3] The evidence for this effect is the formation of appreciable yields of authentic molecular positive ions of additives at small concentrations (*e.g.*, Wurster's Blue from tetramethyl-*p*-phenylenediamine.[3a]) In an alkane matrix such yields are strongly enhanced by addition of a small amount of alkyl halides or other electron scavengers because ejected electrons are efficiently scavenged by the reaction

$$RX + e \longrightarrow R\cdot + X^-$$

thereby inhibiting charge recombination and increasing the yield of stabilized positive ions. Because of the above reaction and comparatively high ionization potentials, alkyl chlorides are especially suitable *as matrices* for positive charge transfer to additives. A considerable number of molecular positive ions have been prepared in such matrices, particularly aromatic amines,[3a] aromatic hydrocarbons,[3b,c] both aliphatic and aromatic ketones,[3d] and conjugated dienes.[3f]

Olefins, because of their relatively low ionization potentials, would be expected to trap positive charge in γ-irradiated alkyl chloride matrices. All olefins of vinylene- (–CH=CH–) and vinyldene-type (CH_2=C<) which were tested produced a broad absorption band at about 600–800 mμ in such matrices while vinyl-type (CH_2=CH–) olefins did not. To test whether the band is due to a cationic color center or not, several procedures have been developed.[3] Addition of aromatic amines such as dimethylaniline should depress the yield of cationic color centers. Polar substances such as alcohol should also decrease the yield because they are known to scavenge positive charge by proton transfer. The tests indicated that the band at 600–800 mμ for vinylene and vinylidene olefins is associated with a cationic species. The same band appeared also when such olefins were added to the 3-methylpentane matrix and were attributed to some cations of the olefins.[4] Because the bands appear in the red and near-infrared spectral region for many olefins, they will be designated as R-band. It will be shown in this work that the R-band is attributable to the molecular cation of olefin. For vinyl-type olefins, the molecular cation apparently reacts further with a neutral molecule to produce a carbonium ion.

Experimental Section

Olefins were obtained from Aldrich Chemical Co. and K & K Laboratories. They were purified by passing through an alumina column, distilling under vacuum, and in some cases by storing over a sodium mirror under vacuum for several days. The solvents, *n*- and *sec*-butyl chloride (BuCl), CCl_4, CCl_3Br, and 3-methylpentane (3MP) were purified on a silica gel column followed by distillation. The olefin solution was introduced to a 0.16-cm thick Suprasil optical cell in air, unless otherwise stated, and the cell was plunged into liquid nitrogen. Procedures of irradiation and optical measurements have been described.[3a] All results described here refer to samples which were γ-irradiated and examined at −196°. All matrices were glassy solids except CCl_4 and CCl_3Br which were polycrystalline.

Results

γ-Irradiated pure BuCl (*n*- and *sec*-) glasses produce an absorption band at about 400–600 mμ which has been attributed to the solvent-trapped positive hole ($BuCl^+$).[3c] Addition of olefins caused the ($BuCl^+$) band to decrease or disappear, and a new band, designated as R-band, appeared at about 600–800 mμ for

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[1] On leave from the Institute of Physical and Chemical Research, Tokyo, Japan.

[2] The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is A.E.C. Document No. COO-38-504.

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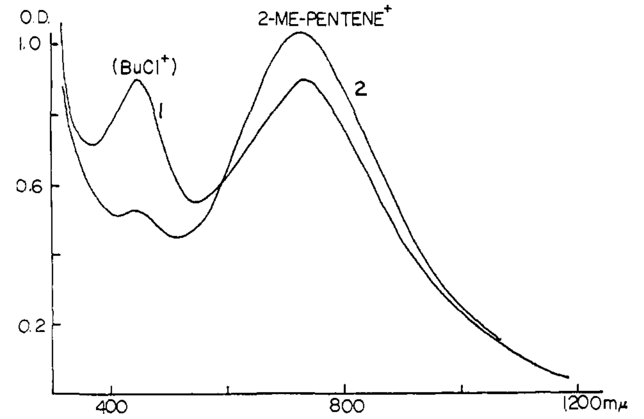

Figure 1. Absorption spectra of γ-irradiated glassy solution of 5 mole % 2-MP-1 in *sec*-BuCl: (1) after irradiation, dose = 5.6 × 10^{19} ev ml^{-1}; (2) after photobleaching (1) with filtered tungsten light (300–500 mμ).

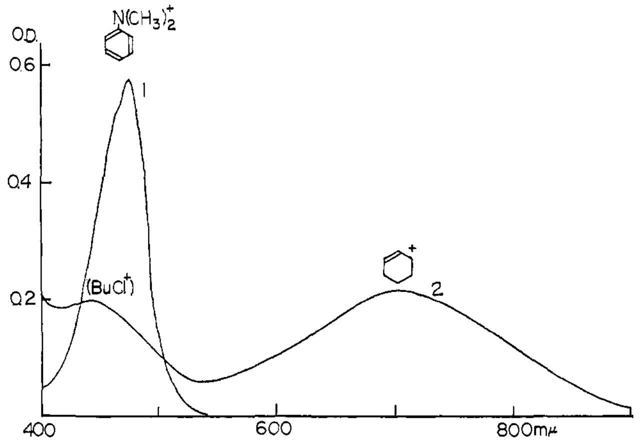

Figure 2. Absorption spectra of γ-irradiated glassy solutions of cyclohexene in *sec*-BuCl with and without dimethylaniline: (1) 5 mole % cyclohexene + 1 mole % dimethylaniline, (2) 5 mole % cyclohexene. Dose = 1.7 × 10^{19} ev ml^{-1} for both.

vinylene- and vinylidene-type olefins. The optical absorption spectrum for 5 mole % 2-methylpentene-1 (2MP-1) in *sec*-BuCl at −196° after γ irradiation is shown in Figure 1. The band at about 450 mμ is due to residual absorption of the solvent-trapped positive hole, and the R-band at about 725 mμ is characteristic for the solute, 2MP-1. Photobleaching the ($BuCl^+$) band, using filtered tungsten light at λ <500 mμ, decreased the 450-mμ band and increased the 725-mμ band as shown by spectrum 2 of Figure 1.

Cyclohexene has been used repeatedly as an additive in radiation chemistry. In γ-irradiated 3MP at −196° it gives rise to an R-band at about 710 mμ. Addition of 5 mole % cyclohexene to BuCl glass produced a similar band at 708 mμ and depressed the ($BuCl^+$) band. When dimethylaniline was added to the cyclohexene solution in BuCl, both the ($BuCl^+$) and the 708-mμ bands disappeared and a new band attributable to dimethylaniline cation[3a] appeared (Figure 2). This indicates that the amine has scavenged all positive charge which otherwise would be distributed between cyclohexene and BuCl itself. Furthermore, addition of a small amount of ether or alcohol to the olefin + BuCl system suppressed the formation of both ($BuCl^+$) and the R-band.

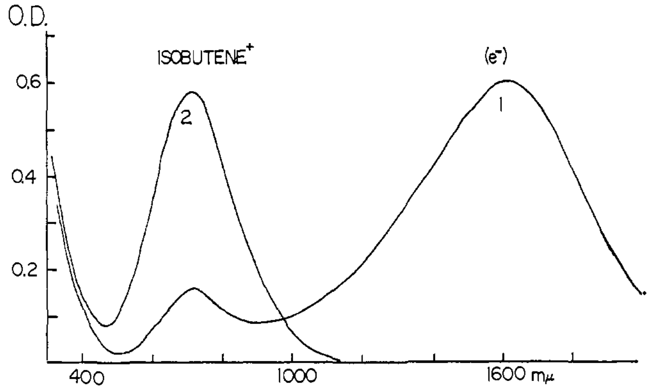

Figure 3. Absorption spectra of γ-irradiated glassy solutions of isobutene in 3MP with and without isopropyl chloride: (1) ~5 mole % isobutene, (2) ~5 mole % isobutene + 0.5 mole % isopropyl chloride. Dose = 6.7 × 10^{19} ev ml^{-1} for both in a 1 cm × 1 cm cell.

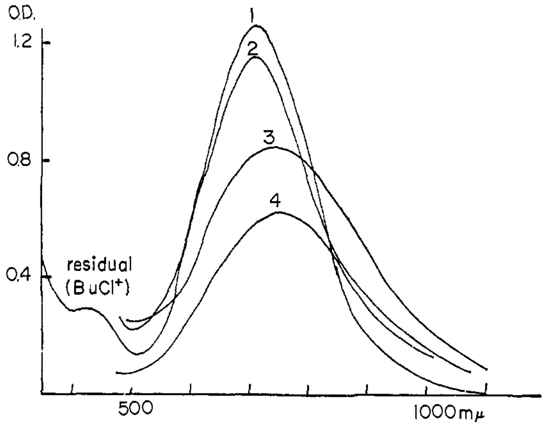

Figure 4. Absorption spectra of γ-irradiated solutions of cyclohexene in various matrices: (1) 10 mole % cyclohexene in *sec*-BuCl, dose = 4.2 × 10^{19} ev ml^{-1}; (2) 4 mole % cyclohexene + 2 mole % isopropyl chloride in 3MP, dose = 7.9 × 10^{19} ev ml^{-1}; (3) 4 mole % cyclohexene in CCl_3Br, dose = 5.0 × 10^{18} ev ml^{-1}; (4) 3 mole % cyclohexene in CCl_4, dose = 5.0 × 10^{18} ev ml^{-1}.

The R-band at about 700 mμ also appeared when ~5 mole % isobutene in 3MP was γ-irradiated at −196°, as shown by curve 1 of Figure 3 which includes the solvent-trapped electron band at about 1600 mμ. Photobleaching at >1000 mμ removed completely both the electron and the R-bands.[4] Addition of 0.5 mole % isopropyl chloride as an electron scavenger greatly enhanced the intensity of the R-band and eliminated the electron band as shown by curve 2 of Figure 3.

In polycrystalline matrices of CCl_4 or CCl_3Br, cyclopentene and cyclohexene also produced R-bands at about 750 mμ with a little shift from the λ_{max} in 3MP or halide glasses for the same olefins. By way of example, Figure 4 shows the absorption spectra of irradiated cyclohexene in several matrices. Figure 5 demonstrates the optical density (OD) of the cyclohexene R-band in 3MP as a function of the olefin concentration. The R-band maxima for various olefins in BuCl are summarized in Table I where it is seen that the number and positions of alkyl groups adjacent to the ethylenic bond have a noticeable effect upon the R-band maxima. As the number of methyl groups in α position to the double bond increases, the R-band

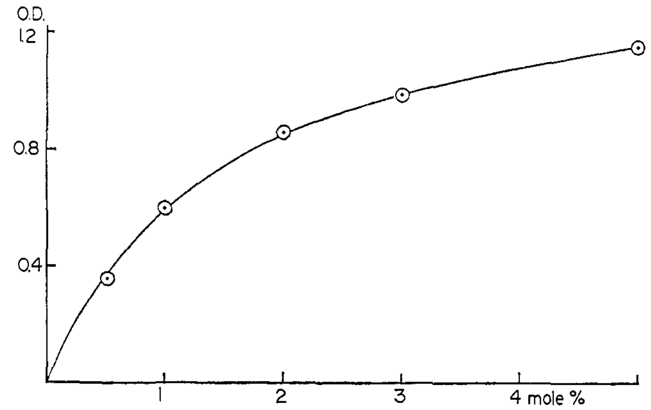

Figure 5. Optical density (OD) of cyclohexene R-band (λ 708 mμ) plotted against the concentration of cyclohexene in 3MP containing 1 mole % isopropyl chloride. Dose = 8.3 × 10^{18} ev ml^{-1}, in a 1 cm × 1 cm cell.

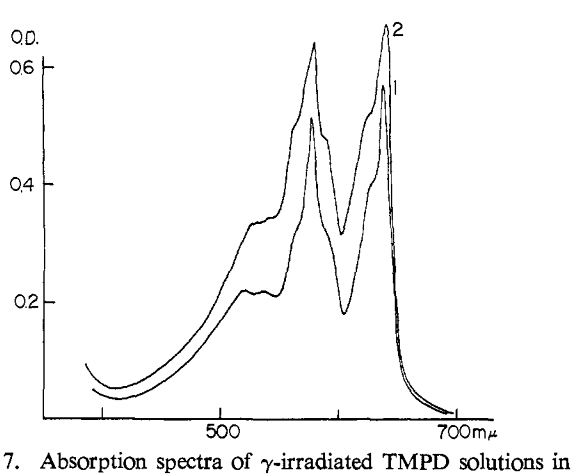

Figure 7. Absorption spectra of γ-irradiated TMPD solutions in hexenes: (1) 0.15 mole % TMPD in hexene-1, (2) 0.15 mole % TMPD in hexene-2. Dose = 2.5 × 10^{19} ev ml^{-1}.

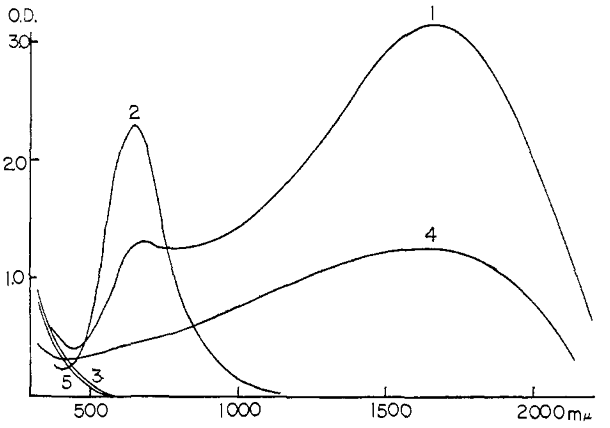

Figure 6. Absorption spectra of γ-irradiated hexene-1 and hexene-2 with and without isopropyl chloride: (1) deaerated pure hexene-2, (2) 2 mole % isopropyl chloride in deaerated hexene-2, (3) after photobleaching (1) at >1000 mμ, (4) deaerated pure hexene-1, (5) 2 mole % isopropyl chloride in deaerated hexene-1. Dose = 1.7 × 10^{19} ev ml^{-1}, in a 1 cm × 1 cm cell.

maximum shifts toward red as entries 7, 19, and 25 show. In the extreme case of entry 25, λ_{max} attains 860 mμ and a second band at 365 is also observed. Even *cis* and *trans* isomers have considerably different λ_{max} as seen for entries 7–8, 12–13, 14–15, 16–17, and 21–22. The ring shape of cyclic olefins affects λ_{max}, indicating an effect of ring strain (see entries 27, 28, 32; also compare 26 and 1). In methylcyclohexenes the effect of the methyl group decreases as the substituent moves away from the double bond, and even in 4-methylcyclohexene the effect of methyl still seems to be significant (31 *vs.* 28). In the series of 1,1-dialkylethylenes (1–6), the bathochromic effect of substituents increases with the degree of branching. The same effect is observed in the series of entries 7, 14, 16 and 8, 15, 17, with the exception of 2,4,4-trimethylpentene-2.

Table I does not include data for olefins of vinyl type, which decreased the (BuCl+) band without producing an R-band characteristic of the solute in the interval 400–2000 mμ. It should be pointed out that ionization potentials of vinyl-type olefins are higher by about 0.5 ev than those of vinylene or vinylidene types.

Pure hexene-1 and hexene-2 formed translucent glasses at −196°. The absorption spectrum of γ-irradiated pure deaerated glassy hexene-2 is shown by curve 1 of Figure 6. Addition of a small amount of isopropyl chloride (2 mole %) gave the spectrum described by curve 2. The λ_{max} of 630 mμ agrees fairly well with λ_{max} 650 mμ in *sec*-BuCl. Spectrum 3 of Figure 6 for pure hexene-2 shows that bleaching all solvent-trapped electrons eliminates the R-band completely. Deaerated pure hexene-1 produced an absorption band shown by spectrum 4. Addition of isopropyl chloride did not reveal any R-band as spectrum 5 shows. When 0.15 mole % tetramethyl-*p*-phenylenediamine (TMPD) was added to pure hexene-1 or hexene-2, the spectra of Figure 6 were replaced with those of Figure 7 which shows the formation of TMPD+.[3a]

Table I. The Band Maxima of Olefin Cations in BuCl

No.	Olefin	λ_{max}	No.	Olefin	λ_{max}
	Simple olefins				
1	2-Methylpropene	715	21	*cis*-3-Methylpentene-2	660
2	2-Methylbutene-1	706			
3	2-Methylpentene-1	720	22	*trans*-3-Methylpentene-2	650
4	2,3-Dimethylbutene-1	735	23	2,4-Dimethylpentene-2	766
5	2,3-Dimethylpentene-1	750	24	2,4,4-Trimethylpentene-2	400
6	2,3,3-Trimethylbutene-1	785	25	Tetramethylethylene	866 and 365
7	*cis*-Butene-2	580			
8	*trans*-Butene-2	630			
9	*cis*-Pentene-2	595	26	Methylenecyclohexane	720
10	*cis*- and *trans*-Hexene-2	650	27	Cyclopentene	665
11	*cis*-Heptene-2	640	28	Cyclohexene	708
12	*cis*-Octene-2	625	29	1-Methylcyclohexene	820
13	*trans*-Octene-2	670			
14	*cis*-4-Methylpentene-2	630	30	3-Methylcyclohexene	745
15	*trans*-4-Methylpentene-2	670	31	4-Methylcyclohexene	715
			32	Cyclooctene	630
16	*cis*-4,4-Dimethylpentene-2	685		Nonconjugated dienes	
			33	1,5-Hexadiene	...
17	*trans*-4,4-Dimethylpentene-2	756	34	3-Methyl-1,5-hexadiene	...
18	*cis*-2,2-Dimethylhexene-3	720	35	2-Methyl-1,5-hexadiene	707
19	2-Methylbutene-2	650	36	4-Vinylcyclohexene	713
20	2-Methylpentene-2	720	37	1,5-Cyclooctadiene	652

Several nonconjugated dienes were also irradiated in *sec*-BuCl glass. 1,5-Hexadiene and 3-methyl-1,5-hexadiene, which contain only vinyl groups and have relatively high ionization potentials, suppressed the ($BuCl^+$) band but gave no R-band. 2-Methyl-1,5-hexadiene, 4-vinylcyclohexene, and 1,5-cyclooctadiene, which contain vinylene or vinylidene groups and have relatively low ionization potentials, gave a single R-band similar to the bands for vinylene- or vinylidene-type olefins.

Discussion

Olefins. γ-Irradiation of an alkyl halide glass induces the following sequence of reactions.

$$RX \xrightarrow{\gamma} RX^+ + e \qquad (1)$$

$$RX + e \longrightarrow R\cdot + X^- \qquad (2)$$

$$RX^+ + RX \longrightarrow RX + RX^+ \qquad (3)$$

$$RX^+ + S \longrightarrow RX + S^+ \qquad (4)$$

That is, the positive charge generated by ionization migrates and is trapped by solute, S, to produce solute cation, or is trapped by the matrix itself.[3c] As an example, in pure BuCl glass the migrating positive charge is trapped and gives rise to the band at about 450 mμ.[3c] Since addition of any olefin caused the decrease of this band and the appearance of a new band (R-band for vinylene- and vinylidene-type olefins), and since the intensity of the R-band decreased with the addition of positive charge traps (dimethylaniline, ether, alcohol), it follows that the R-band arises from some positive species of the olefin. One possible product is the protonated species produced by either of the reactions

$$\left.\begin{array}{l} C_4H_9Cl + \text{olefin}^+ \\ C_4H_9Cl^+ + \text{olefin} \end{array}\right\} \longrightarrow \cdot C_4H_8Cl + (\text{olefin})H^+ \qquad \begin{array}{r}(5)\\(6)\end{array}$$

The carbonium ions produced from alcohols in FSO_3H–SbF_5 at $-60°$, however, are found not to absorb at wavelengths >210 mμ.[5] Also, the R-bands in CCl_4 or CCl_3Br (Figure 4) cannot plausibly be attributed to carbonium ions.

Another possibility to be considered is that the R-band is due to a charge-transfer complex involving olefin cation and solvent molecule. But since the R-band maximum is unchanged in different matrices (Figure 4) with ionization potentials ranging from 10.2 for 3MP to 11.5 ev for CCl_4,[6,7] complex formation seems improbable. Therefore, we tentatively assign the R-bands to molecular positive ions of olefins, which is also intrinsically plausible for reasons to be given below. Molecular cations of olefins are well known from mass spectrometry.[8]

Since ethylene itself does not absorb at wavelengths longer than 200 mμ,[9] a transition from the π orbital to any unoccupied level is ruled out for ground-state $C_2H_4^+$, and similarly for other olefins. Therefore the R-bands, which are the only ones observed between 400 and 2000 mμ, are attributed to a transition from the C=C σ orbital to the singly occupied π orbital. The π level can be measured approximately from the ionization potential, I_π, and it ranges from 8.7 to 9.5 ev for the olefins studied. However, no measure of the sp^2 σ level for C=C is available although a semi-theoretical calculation was carried out for the carbon atom of various valence states.[10] As a rough guide, we equate the level with the σ level for C–C which can be identified with the ionization potential, $I_\sigma \cong 10.2$ ev for higher alkanes.[11] The difference, $I_\sigma - I_\pi$, which is roughly 1 ev for vinylene- and vinylidene-type olefins, should correspond to the red end of the ~700 mμ bands because ionization potential is defined for the 0–0 transition. Figures 1, 2, 3, 4, and 6 show that the R-band has the red end at about 1200 mμ which is roughly 1 ev.

Since vinyl-type olefins suppress the ($BuCl^+$) band but do not give a band at ~700 mμ, we presume that these olefins transfer a proton or H atom (reactions 5 or 6), instead of an electron (reaction 4). For equations 5 or 6 the thermochemistry can be expressed by the following steps for the typical case of hexene-1.

$$C_4H_9Cl^+ + C_6H_{12} \longrightarrow C_4H_9Cl + C_6H_{12}^+$$

$$C_6H_{12}^+ + e \longrightarrow C_6H_{12} \qquad -I_1$$

$$C_4H_9Cl \longrightarrow \cdot C_4H_8Cl + H \qquad D_1$$

$$C_6H_{12} + H \longrightarrow \cdot C_6H_{13} \qquad -D_2$$

$$\cdot C_6H_{13} \longrightarrow C_6H_{13}^+ + e \qquad I_2$$

If we assume that D_2 and I_2 remain about the same for any type olefin tested, then the enthalpy change of reactions 5 or 6 depends mainly upon the ionization potential of olefin. It appears to be slightly exothermic for vinyl olefins ($I \cong 9.5$ ev) and slightly endothermic for the other olefins ($I \cong 9$ ev).

The spectrum for γ-irradiated pure hexene-2 in Figure 6, curve 1, shows both the solvent-trapped electron band (e^-) at ~1600 mμ and the R-band at 630 mμ. Since photobleaching the e^- band completely removed the R-band also (curve 3, Figure 6), the yield of solvent-trapped electron cannot be smaller than the yield of the cationic species responsible for the R-band. Addition of isopropyl chloride suppresses the e^- band by trapping electrons as Cl^- and thereby protecting trapped positive charge. In pure hexene-1, no distinctive band appeared in the visible region. The broad band covering the whole spectral region is regarded as due to the solvent-trapped electron. Even in the presence of isopropyl chloride in hexene-1, no new band appeared between 400 and 2000 mμ (curve 5, Figure 6). Since the hexene-1 molecular cation should be produced and it can be assumed to have R-band character, the absence of any band indicates that the cation has reacted further. A possible reaction is dimerization to the molecular cation of dimeric olefin, $C_{12}H_{24}^+$, but this ion would be expected to give an R-band. Secondly, proton or H-atom transfer of the type

$$C_6H_{12}^+ + C_6H_{12} \longrightarrow C_6H_{13}^+ + C_6H_{11} \qquad (7)$$

is ruled out. On the basis of thermochemistry, reaction

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7 can be expressed by

$$C_6H_{12}^+ + e \longrightarrow C_6H_{12} \qquad -I_1$$

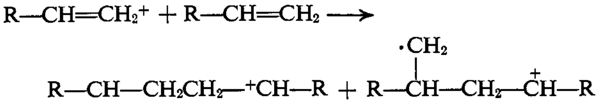
$$C_6H_{12} \longrightarrow C_3H_7\dot{C}HCH{=}CH_2 + H \qquad D_1$$

$$C_4H_9CH{=}CH_2 \longrightarrow C_4H_9\dot{C}H{-}\dot{C}H_2 \qquad D_2$$

$$C_4H_9\dot{C}H{-}\dot{C}H_2 + H \longrightarrow C_4H_9\dot{C}H{-}CH_3 \qquad -D_3$$

$$C_4H_9\dot{C}H{-}CH_3 \longrightarrow C_6H_{13}^+ + 1 \qquad I_2$$

where $D_1 \cong 3.94$,[12,13] $D_2 \cong 2.60$,[12,13] $D_3 \cong 4.25$,[12,13] $I_2 \cong 7.50$[14] (in ev). The over-all reaction is endothermic even for vinyl-type olefins whose $I \cong 9.5$. This result explains why the hexene-2 cation is kept stably in irradiated pure hexene-2. On the other hand, the lack of hexene-1 cation in irradiated hexene-1 (curves 4 and 5 of Figure 6) is explained as follows. Wagner, *et al.*,[15] studied radiolysis of terminal olefins and proposed the following reaction to account for *n*-dodecene and 5-methylundecene as major products from hexene-1.



$$R{-}CH{=}CH_2^+ + R{-}CH{=}CH_2 \longrightarrow R{-}CH{-}CH_2CH_2{-}{}^+CH{-}R + R{-}\underset{}{\overset{\cdot CH_2}{\overset{|}{C}}}H{-}CH_2{-}\overset{+}{C}H{-}R \qquad (8)$$

The enthalpy change for reaction 8 is found to be exothermic by ~0.3 ev for vinyl olefins ($I \cong 9.5$ ev) and endothermic by ~0.2 ev for vinylene and vinylidene olefins ($I \cong 9$ ev). We are therefore inclined to adopt the mechanism of Wagner, *et al.*, to account for the lack of molecular cations in irradiated hexene-1. Other olefins of the same type, pentene-1 and heptene-1, also formed glassy solids at −196° and gave no band in the visible and near-infrared regions, similar to hexene-1.

Ayscough and Evans[16] and Smith and Pieroni[17,18] studied epr spectra of γ-irradiated olefins at −196° and found that vinyl olefins gave alkyl radicals.[19] They also adopted the mechanism of Wagner, *et al.*, and ascribed the spectrum to the radical formed by reaction 8. Both groups found that in vinylene or vinylidene olefins allylic radicals were produced predominantly and assumed reactions of the type of (7). Since reaction 7 is endothermic, however, it would be necessary to assume that excited cations undergo reaction 7 to yield allylic radicals. It will be shown below that in pure hexene-2 not all positive ions initially produced are stabilized as molecular cations.

Since only 0.15 mole % TMPD eliminated the hexene-2 cation band and produced TMPD$^+$ in both hexene-1 and hexene-2, it is concluded that in these olefins positive charge migrates efficiently to the solute. Also, any chemical reaction in hexene-1 which stabilizes positive charge (such as reaction 8) must be rather inefficient. Since the molar absorptivity, ϵ, of TMPD$^+$ is known as 19,300,[3a] G (yield per 100 ev of absorbed energy) of positive charge trapped by TMPD is 0.52 for the hexene-2 solution of Figure 7. Therefore, the G for stabilized hexene-2$^+$ of Figure 6 (curve 2) would be <0.5 because not all positive charge trapped by TMPD would necessarily have been trapped as hexene-2$^+$.

Dienes. Conjugated dienes behave quite differently from simple olefins in respect to producing molecular ions,[3f] while nonconjugated dienes are analogous to simple olefins. 1,5-Hexadiene and 3-methyl-1,5-hexadiene which contain only vinyl groups and have relatively high ionization potentials, ~9.5 ev,[20] behave like vinyl olefins in BuCl. This indicates that these dienes undergo proton or H-atom transfer (reaction 5 or 6). The rest of the dienes in Table I give a typical R-band at about 600–700 mμ indicating that charge transfer (reaction 4) takes place and that the positive charge is localized at one of the ethylenic bonds.

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