# Role of Defects in Radiation Chemistry of Crystalline Organic Materials. 3. Geometrical and Electronic Structures of Alkene Radical Anion and Cation in Alkene/n-Alkane Mixed Crystals As Studied by ESR Spectroscopy

## Kaoru Matsuura, Hachizo Muto,\* and Keichi Nunome

Government Industrial Research Institute, Nagoya, Hirate-cho, Kita-ku, Nagoya, 462, Japan (Received: May 1, 1991; In Final Form: July 10, 1991)

An ESR study has been made in order to elucidate the electronic structures of alkene radical anion and cation, the former radical being first detected in the hexene/n-hexane mixed crystals irradiated at 4.2 K along with the cation. The present work extended to the hexene and butene isomers has resulted in evidence that both anions with vinylene and vinylidene groups have pyramidal structures with  $\sigma$ -character, which differ from the planar or twisted structures of corresponding cations. The proton hyperfine couplings of their anions were only about one-third as large as those for the cations:  $[A](two \alpha - H) = [0.45,$ 0.1, -0.25 mT;  $a(\text{two pairs of } \beta$ -H) = 1.38 and 0.56 mT for the 3-hexene anion, and  $a(\text{two } \alpha$ -H) = 1.3 mT and  $a(\text{two pairs } \beta$ of  $\beta$ -H) = 4.6 and 2.9 mT for the cation. The differences in the geometrical structures and in the sizes of the proton couplings of the anion and cation radicals were discussed on the basis of a simple molecular orbital calculation. It has been found that the anion is stabilized by admixing [2s;C) atomic orbitals (AO) with a lower core integral than [2p;C) AO to the unpaired electron orbital and that the small  $\beta$ -proton couplings mainly originate from low extent of hyperconjugation due to a wide energy separation of C=C  $\pi$ -antibonding and C-H pseudo- $\pi$ -bonding orbitals.

#### Introduction

The mixed crystals of organic compounds serve as a good system for the investigation of the role of impurities and defects in radiation chemistry and are expected to provide for a better understanding of the radiation chemistry of the organic compounds themselves.<sup>1</sup> From point of view, we have studied the low-temperature radiolysis of mixed crystals such as binary alkanes with different chain lengths,<sup>1</sup> alkene/alkane,<sup>2</sup> and alkyne/alkane<sup>3</sup> using electron spin resonance (ESR) spectroscopy. Previously we found that 3-hexene radical anion was stably trapped along with the corresponding cation in 3-hexene/n-hexane mixed crystals irradiated at 4.2 K.<sup>2</sup> Alkene anions had not been detected by other spectroscopies as well as ESR until our preliminary work,<sup>2</sup> since they have large negative electron affinities (EA =  $-2.3 \text{ eV}^4$ ) and are very unstable.

In the present work, we have extended the ESR study to hexene and butene isomers including 1-, trans-2-, and trans-3-hexene and 1- and trans-2-butene. It was found from the obtained ESR parameters that both alkene anions with vinylidene (CH2=CH-) and vinylene (-CH=CH-) groups have pyramidal structures in the anti configuration. The  $\alpha$ - and  $\beta$ -proton hyperfine couplings of the anions were very small and were only about one-third as large as those of the corresponding cations, which are known to have planar or twisted structures.<sup>5-11</sup> It was found that the size of  $\beta$ -proton couplings of the anions had a conformational dependence of  $2\pi$  period, which differs from  $\pi$ -period for planar

cations. The difference in the radical structures and the tremendous difference in the sizes of the couplings of the cations and the anions were discussed on the basis of a semiempirical molecular orbital calculation. The assignment to the anion was confirmed by a competitive electron-capture reaction in 3-hexene/1chlorohexane/n-hexane mixed crystals.

## **Experimental Section**

*n*-Hexane- $h_{14}$  of gas chromatographic standard grade (>99.5%), 1-, trans-2-, and trans-3-hexene, 1- and trans-2-butene, and 1chlorohexane (>99%) were obtained from Tokyo Kasei Kogyo Co. Ltd., and *n*-hexane- $d_{14}$  (>99 atom % D) was from Aldrich Co. Ltd. They were used without further purification. The sample preparations of the polycrystalline mixed crystals are described in our previous paper.<sup>1a</sup> The samples were irradiated by X-rays at 4.2 K with 45 kV and 40 mA for 15 min. Perdeuteriated *n*-hexane  $(n-C_6D_{14})$  was also used as a matrix since it gives a well-resolved ESR spectrum compared with the protiated matrix because of the smaller superhyperfine interactions of dueterons than those of protons in the neighboring molecules.

# Results

4 K Irradiation of trans-3-Hexene/n-Hexane. Figure 1a shows the first-derivative absorption ESR spectrum obtained for the trans-3-hexene (4.0 mol %)/n-C<sub>6</sub>D<sub>14</sub> mixed crystals irradiated at 4.2 K. Figure 1b is the spectrum measured after the sample was illuminated with infrared light (for 5 s by a 60-W tungsten lamp using a VR69 filter (Toshiba Co. Ltd.) from a distance of 10 cm). It was the same spectrum as that obtained for the pure  $n-C_6D_{14}$ irradiated at 4.2 K. The pure deuteriated alkanes irradiated at 4.2 K give structureless broad ESR spectra because of pairwise trappings of radicals, which differ from the well-resolved spectra obtained by irradiation at 77 K.<sup>12</sup> No new radical species was formed from the solute ion radicals by photoillumination. The difference spectrum obtained by subtracting the spectrum in Figure 1b from that in Figure 1a is shown in Figure 1c. It is the superposition of the spectra of 3-hexene cation and anion in addition to a small amount of trapped electrons, as is reported previously.<sup>2</sup> This may be the second case that a radical cation was stably trapped in alkane matrices. ESR detection of alkene cation in alkane matrix has been reported only for tetramethylethylene/

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Figure 1. First-derivative absorption ESR spectra observed for *trans*-3-hexene (4.0 mol %)/*n*-hexane- $d_{14}$  mixed crystals (a) irradiated at 4.2 K and (b) after illumination of infrared light. (c) Difference spectrum ((a) – (b)). (c') Difference spectrum in an expanded magnetic field scale, which was obtained for the mixed crystals containing 8.0 mol % of *trans*-3-hexene. (d) and (e) Simulated spectra of 3-hexene cation and anion, respectively, using the ESR parameters listed in Table I (a pair of  $\alpha$ -proton couplings and two pairs of  $\beta$ -proton couplings (1.38, 0.56 mT) × 2H and (g) a set pairs of  $\alpha$ - and  $\beta$ -proton couplings: [0.95, 0.5, 0.1] mT × 2 $\alpha$ H and a pair of couplings (1.38 mT) × 2 $\beta$ H (see text).

3-methylpentane glassy mixtures.<sup>5</sup> The formation of trapped electrons was suppressed at a higher solute concentration, as is shown in Figure 1c' for the 3-hexene (8.0 mol %)/n-C<sub>6</sub>D<sub>14</sub> mixed crystals. The simulated spectra of the cation and the anion are shown in Figure 1d,e. The spectrum assigned to the anion could be reproduced only by a pair of equivalent  $\alpha$ -proton couplings (|0.45, 0.1, -0.25| mT) and two pairs of equivalent  $\beta$ -proton couplings ( $a(H_{\beta} \times 2) = 1.38, a(H_{\beta} \times 2) = 0.56$  mT; Figure 1e). It could not be reproduced by any other set of couplings: such as two pairs of  $\beta$ -proton couplings ( $a(H_{\beta} \times 2) = 1.38$  mT,  $a(H_{\beta} \times 2) = 0.56$  mT; Figure 1f) or a set of each pair of  $\alpha$ - and  $\beta$ -proton couplings,  $|\mathcal{A}|(H_{\alpha} \times 2) = |0.95, 0.5, 0.1|$  mT) and  $a(H_{\beta} \times 2) = 1.38$  mT, respectively (Figure 1g). The ESR parameters finally obtained for the anion and the cation are listed in Table I.

Irradiation of the *trans*-3-hexene (4.0 mol %)/*n*-hexane- $h_{14}$ mixed crystals also yielded the alkene anion and cation radicals. The difference spectrum obtained by subtracting the remaining spectrum after photoillumination from the original spectrum is shown in Figure 2a. The spectrum of the anion is essentially the same as that obtained in the  $C_6D_{14}$  matrix except for the broader ESR line widths. The shoulder of the outermost line on the high magnetic field side, which originates from the two  $\alpha$ -proton couplings, is not clearly observed because of the g anisotropy and of an inhomogeneous line broadening due to the dipolar couplings of protons in the neighboring protiated matrix molecules. The  $\beta$ -proton couplings obtained for the *trans*-3-hexene anion in the protiated matrix slightly differ from those in the deuteriated matrix, but their differences are small:  $(1.36, 0.60) \pm 0.1$  mT  $\times 2\beta$ -H in protiated matrix and (1.38, 0.56)  $\pm 0.1 \text{ mT} \times 2\beta$ -H in deuteriated matrix.

**Competitive Electron-Capture Reaction.** The assignment of the 3-hexene anion was confirmed by a competitive reaction of electron capture between 3-hexene (2.0 mol %) and 1-chloro-*n*-hexane- $h_{13}$  (2.0 mol %) molecules in C<sub>6</sub>D<sub>14</sub> matrix. The results are shown



Figure 2. (a) ESR spectra of the 3-hexene anion and cation radicals obtained by subtracting the remaining spectrum after photoillumination from the original spectrum measured after irradiation at 4.2 K. (b) Simulated spectra of the 3-hexene cation. (c) Observed and (d) simulated spectra of the 3-hexene anion in an expanded scale of the static magnetic field strength.



Figure 3. First-derivative absorption ESR spectra observed for *trans*-3hexene (2.0 mol %)/1-chloro-*n*-hexane (2.0 mol %)/*n*-hexane- $d_{14}$  mixed crystals (a) irradiated at 4.2 K and (b) after illumination of infrared light. (c) Difference spectrum ((a) – (b)). (d) ESR spectrum observed for pure *n*-hexane- $d_{14}$  irradiated at 4.2 K. (e) Difference spectrum ((a) – (d)). (f) Simulated spectrum of 3-hexene cation using the parameters listed in Table I and (g) that of chain-end alkyl radical (CH<sub>2</sub>CH<sub>2</sub>-C<sub>4</sub>H<sub>9</sub>) which is selectively formed by dissociative electron attachment to the 1chloro-*n*-hexane molecules (see the text).

in Figure 3. The spectrum obtained by irradiation at 4.2 K (Figure 3a) did not change by illumination of infrared light (Figure 3b) except for the decay of color centers in the quartz sample tube (Figure 3c). Figure 3e shows the difference spectrum obtained by subtracting the spectrum of pure  $n-C_6D_{14}$  irradiated at 4.2 K (Figure 3d) from the original spectrum of the mixed crystals (Figure 3a). The 3-hexene anion and a small amount of trapped electrons were not formed in this mixed crystal. Instead of them, the chain-end alkyl radical (CH2CH2C4H9) was selectively formed by dissociative electron attachment to 1-chloro-n-hexane molecules along with the trans-3-hexene cation. Parts f and g of Figure 3 show the simulated spectra of the 3-hexene cation and the chain-end alkyl radical, respectively. The ESR parameters used for the simulation of the cation are listed in Table I and those for the alkyl radical are [3.15, 2.00, 1.62] mT for two  $\alpha$ -protons and 4.5 and 2.2 mT for two  $\beta$ -protons. It may be noteworthy that the trans-3-hexene cation did not decay by photoillumination as well as alkyl radical (Figure 3a,b). This behavior differs from that in the trans-3-hexene/ $n-C_6D_{14}$  mixed crystals and indicating that the recombination of the alkene ions is initiated by electron detrapping from the anions.

		coupling, mT		
molecule		anion	cation	
3-hexene				
in $C_6D_{14}$	$\alpha H \times 2$	0.45, 0.10, -0.25	1.3	
	βH × 2	1.38	4.6	
	$\beta H \times 2$	0.56	2.9	
in C <sub>6</sub> H <sub>14</sub>	$\alpha H \times 2$	0.45, 0.10, -0.25	1.3	
	βH × 2	1.36	4.6	
	$\beta$ H $\times 2$	0.60	2.9	
2-hexene	$\alpha H \times 2$	0.55, 0.20, -0.15	1.3	
	$\beta$ H $\times 2$	1.45	3.9	
	$\beta$ H $\times 2$	0.86	3.9	
1-hexene	$\alpha H \times 2$	10.95, 0.60, 0.251		
	$\alpha H \times 1$	11.30, 0.70, 0.10		
	$\beta H \times 1$	1.64		
	$\beta$ H × 1	0.88		
2-butene	$\alpha H \times 2$	10.65, 0.30, -0.05		
	$\beta$ H $\times 2$	1.74		
	$\beta$ H $\times 2$	0.82		
1-butene	$\alpha H \times 2$	10.95, 0.60, 0.251		
	$\alpha H \times 1$	11.30, 0.70, 0.10		
	8H × 1	1.64		
	$\beta H \times 1$	0.88		

<sup>a</sup> The errors associated in determination of  $\alpha$ - and  $\beta$ -proton couplings are ±0.1 and ±0.05 mT, respectively, except for ±0.05 mT for  $\alpha$ -protons of 3-hexene anion in C<sub>6</sub>D<sub>14</sub> matrix.



Figure 4. (a) ESR spectrum of 2-hexene anion and cation radicals in *n*-hexane- $h_{14}$  matrix, which was obtained by subtracting the remaining spectrum after photoillumination from the original spectrum measured after irradiation at 4.2 K and (c) the expanded spectrum of (a). (b) and (d) Simulated spectra of 2-hexene cation and anion, respectively. (e) The first derivative absorption ESR spectrum observed for 1-hexene radical anion. (f) Simulated spectrum of 1-hexene anion. The ESR parameters used for these simulations are listed in Table I.

trans-2- and 1-Hexene/n-Hexane. Irradiation of the trans-2-hexene/n-hexane- $h_{14}$  and 1-hexene/n-hexane- $h_{14}$  mixed crystals yielded the corresponding alkene anion and cation radicals at 4.2 K except for the 1-hexene cation, as are shown in Figure 4a,c,e. No formation of the 1-hexene cation may be due to the higher ionization potential (IP) of the vinylidene group (CH<sub>2</sub>=CH--; 9.64 eV for 1-butene<sup>4</sup>) than that of the vinylene group (--CH=CH--; 9.07 eV for trans-2-butene<sup>4</sup>). Figure 4b,d,f shows the ESR spectral simulations for their ions using ESR parameters listed in Table I.

**Butene Isomers**/*n*-**Butane.** The results for the mixed crystals of 1-butene/*n*-butane- $h_{14}$  and *trans*-2-butene (4.0 mol %)/*n*-butane- $h_{14}$  are shown in Figure 5a,c, respectively, where the dif-



**Figure 5.** First-derivative absorption ESR spectra of (a) 1-butene and (c) *trans*-2-butene radical anions in *n*-butane- $h_{10}$  matrix. They are the difference spectra between before and after photoillumination. (b) and (d) are their simulated spectra, respectively, using the ESR parameters listed in Table I.

ference spectra between before and after photoillumination are given. The 4.2 K irradiation of these crystals yielded only the corresponding alkene anion, as their spectral simulations are shown in Figure 5b,d. Since the difference of IP of 2-butene (IP = 9.07 eV) and *n*-butane molecules (10.63 eV) is larger ( $\Delta$ IP = 1.50 eV) than that ( $\Delta$ IP = 1.18 eV) between 3-hexene (~9.0 eV) and *n*-hexane (10.18 eV),<sup>4</sup> butene cations are expected to be more easily formed in an *n*-butane matrix than hexene cations in an *n*-hexane matrix. The reason for no formation of butene cations in an *n*-butane matrix is not clear. There may be other factors controlling hole transfer, such as molecular packings in mixed crystals.

The ESR spectrum of the 1-butene anion (Figure 5c) is almost identical with that of the 1-hexane anion (Figure 4e), reflecting the similarity of their molecular structures with a vinylidene group ( $H_2C=CH-$ ). From the spectral simulations, it was found that the rotation of the CH<sub>3</sub> group in the 2-butene anion was frozen at 4.2 K as well as those in the 2-hexene anion and cation radicals, resulting in only two resolved hyperfine couplings of the three CH<sub>3</sub> proton couplings (Table I).

#### Discussions

**Proton Couplings of Anions.** Three pairs of equivalent proton couplings were obtained for 3-hexene and 2-butene anions with a vinylene group ( $-CH_2CH=CHCH_2-: 2H_{\alpha}, 2H_{\beta 1}$ , and  $2H_{\beta 2}$ , Table I). This result indicates that both anions have  $C_2$  symmetry of their parent molecules. The 2-hexene anion also has three pairs of equivalent couplings, suggesting near  $C_2$  symmetry with respect to the C=C bond ((H)CH<sub>2</sub>CH=CHCH<sub>2</sub>C<sub>2</sub>H<sub>5</sub>). For the 2-hexene and 2-butene anions, only two CH<sub>β</sub> proton couplings of the each CH<sub>3</sub> group was resolvably observed, and other CH<sub>β</sub> coupling was estimated to be less than 0.1 mT from their spectral simulations. The 1-hexene and 1-butene anions with a vinylidene group have two CH<sub>β</sub> proton couplings (1.64 and 0.88 mT) which sizes resemble those of other alkene anions (1.36–1.74 and 0.56–0.88 mT) and suggesting radical structures and spin density distributions similar to those of the vinylene compounds.

The dipolar tensors of the two  $\alpha$ -protons in every anion were estimated to be (0.4, 0, -0.4)  $\pm$  0.1 mT (Table I), suggesting that near each half of the unpaired electron spin density resides in the equivalent C=C  $\alpha$ -carbon  $\pi$ -orbitals. However, the most reliable anisotropic term of the  $\alpha$ -protons may be B = (0.35, 0, -0.35) $\pm 0.05$  mT obtained for the 3-hexene anion in *n*-hexane-d<sub>14</sub> matrix, where the line shape due to the  $\alpha$ -proton couplings was most clearly observed. The value is slightly smaller than that reported for the corresponding cation |0.5, -0.25, -0.25| mT.<sup>6</sup> The cause may



Figure 6. Hyperfine coupling constants for  $\alpha$ - and  $\beta$ -protons and total energies obtained by INDO MO calculation for (a) trans-2-butene radical anion with a pyramidal structure. Open and closed circles indicate the observed  $\beta$ - and  $\alpha$ -proton hyperfine couplings for the alkene radical anions, respectively, and (b) for 1-butene radical anion with a twisted structure around C=C bond.

TABLE II: B20 Values and Conformation of C-H6 Bonds with Respect to the Unpaired Electron Orbital for Alkene Radical Ions

	anion						
					cation		
molecule	back <sup>a</sup>	front <sup>b</sup>	$\theta_1$ , deg	$\theta_2$ , deg	$B_2\rho$ , mT	$\theta_1$ , deg	$\theta_2$ , deg
3-hexene	1.67	0.84	25	35	5.2	30	30
2-hexene	2.2-1.8	1.3-1.1	25-35	35-25	5.1	19	41
1-hexene	2.27	1.13	32	28			
2-butene	2.3-2.0	1.4-1.1	20-30	40-30			
1-butene	2.27	1.13	32	28			

 $^{ab}B_{2P}$  values for the  $\beta$ -protons located on the (a) back and (b) front lobe sides of the unpaired electron orbitals of  $\alpha$ -carbon atom.

originate from the difference in the effective nuclear charges  $Z_{eff}$ , as was shown by the following calculations for the anisotropic terms using McConnell and Barfield's formula.<sup>13</sup> For the  $\alpha$ -proton attached to  $\alpha$ -carbon atom with an unpaired electron density  $\rho$ = 0.4, the calculated term was (0.57, -0.04, -0.53) and (0.71, -0.53)-0.13, -0.58) mT for the anion and cation with  $Z_{eff} = 3.08$  and 3.43,14 respectively, where planar structures were assumed for both ions for simplicity. The larger nuclear charge of the cation attracts the electron toward the  $\alpha$ -carbon atom (shrinking the electron cloud) and gives rise to a larger dipolar hyperfine interaction.

The isotropic terms of the  $\alpha$ -protons for alkene anions are also small  $(a(H_a) = \pm (0.1-0.7) \text{ mT})$  as compared with those for alkene cations ( $\sim$ 1.5 mT). This result strongly suggests that the anions have pyramidal radical structures with  $\sigma$ -character.  $\sigma$ -type radicals have small  $\alpha$ -proton couplings by cancelling the contributions of spin polarization and spin delocalization.<sup>1</sup>

 $\cos^2 \theta$  Rule for  $\beta$ -Proton Couplings. The alkene cations are known to have planar structures except for vinylidene compounds.<sup>6-8</sup> The conformations of the two C-H<sub> $\beta$ </sub> bonds (angles  $\theta_1$ ,  $\theta_2$ ) and the  $B_2\rho$  value in McConnell's cos<sup>2</sup>  $\theta$  rule for  $\beta$ -proton couplings were estimated for the vinylene type of alkene cations presently observed:  $B_{2\rho} = 5.2 \text{ mT}$ ,  $\theta_1 = \theta_2 = 30^\circ$ , and  $B_{2\rho} = 5.1 \text{ mT}$ ,  $\theta_1 = 19^\circ$ ,  $\theta_2 = 41^\circ$  for 3-hexene and 2-hexene cations, respectively. The large  $B_{2\rho}$  values agree with those reported for alkene cations in Freon matrices (5.7-5.1 mT)<sup>6</sup> and confirm the present assignment.

The  $\beta$ -proton couplings of alkene anions have the following characters:

(a) The sizes of the couplings are very small (0.56, 1.38 mT for 3-hexene) and about 1/5-1/3 as large as those of the corresponding cations (2.9, 4.6 mT).

(b) The couplings are pairwisely composed; one is about half or less (0.6-0.9 mT) of the others (1.4-1.7 mT).

The  $B_{2\rho}$  value in the cos<sup>2</sup>  $\theta$  rule is estimated to be 1.4-1.8 mT for hexene and butene anions on the assumption of planar radical structures (it is about 1/4-1/3 as large as that for cations (5.1 mT)). The small  $\beta$ -proton couplings and small  $B_{20}$  value are characteristic of anions, as is discussed later in comparison with the cations. Precisely speaking, the size of the  $\beta$ -proton couplings of pyramidal radicals would show a conformational dependence of  $2\pi$  period with different  $B_{2\rho}$  values for the C-H<sub>d</sub> bonds located on the front and back lobe sides of the unpaired electron orbital<sup>16</sup> (see the insertion in Figure 6). The  $B_2\rho$  values were estimated to be  $B_{2\rho}(\text{back}) = 2.1 \pm 0.3 \text{ mT}$  and  $B_{2\rho}(\text{front}) = 1.2 \pm 0.2 \text{ mT}$  (their

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ratio is  $\sim 2.0$ ) from the CH<sub>3</sub>  $\beta$ -proton couplings of 2-hexane and 2-butene anions, on an assumption that the third proton coupling of each CH<sub>3</sub> group is less than 0.1 mT. The conformational angles were estimated to be  $(\theta_1, \theta_2, \theta_3) = (25^\circ, 145^\circ, 265^\circ) \pm 10^\circ$  for the C-H<sub>R</sub> bonds in both anions. Assumption of the above  $B_{2\rho}$ ratio  $(B_2\rho(\text{back})/B_2\rho(\text{front}) \sim 2.0)$  resulted in the  $B_2\rho$  values of  $2.0 \pm 0.3$  mT for the back lobe side protons and in the conformational angles  $(\theta_1, \theta_2) = (30^\circ, 150^\circ) \pm 5^\circ$  for each pair of  $\beta$ -methylene protons of other alkene anions (Table II). The conformation of near (30°, 150°) estimated for all alkene anions may be reasonable for alkene molecules cooperated in the alkane crystals, since the molecules may have orientations and conformations similar to the host alkane molecules. It is known that alkane molecules in crystals have near (30°, 150°) dihedral angles of the  $CH_{\beta}$  bonds with respect to the normal axis to the transzigzag carbon-chain frame.<sup>17</sup> The different  $B_{2\rho}$  values for back and front lobe side protons were supported by intermediate neglect of differential overlap integral (INDO) MO calculation,<sup>14</sup> which will be described later.

The carboxyl radical anions  $RCH_2COOH^-$  with  $\sigma$ -character have also small  $\beta$ -proton couplings and a conformational dependence with a  $2\pi$  period.<sup>4,18</sup> Alkylamino radical  $CH_2$ — $NH_2$  has an isoelectronic structure with alkene anions. It has also a pyramidal structure in an anticonfiguration.<sup>19</sup> Thus, it may be understood that the radicals with three electrons in a bond have similar pyramidal structures.

INDO MO Calculation. As reported previously, the pyramidal structure in the anticonfiguration of alkene anion was supported by INDO MO calculation,<sup>2</sup> which results are shown in Figure 6a together with the present experimental values. The deviation angle from the plane is estimated to be  $\delta = 10-15^{\circ}$  from comparison between the experimental and calculated values for the CH<sub> $\beta$ </sub> proton couplings. B<sub>2</sub> $\rho$  values for  $\beta$ -proton couplings deduced from the results of INDO MO calculation are  $B_2\rho(\text{back}) = 2.9-2.4$ mT and  $B_{2\rho}(\text{front}) = 1.4-0.93 \text{ mT}$  at  $\delta = 10-15^{\circ}$ . These values and their ratio  $B_2\rho(\text{back})/B_2\rho(\text{front}) = 2.1-2.5$  agree with the experimental values:  $B_2\rho = 2.1$  and 1.2 mT for back and front lobe side protons, respectively, and their ratio is  $\sim 2.0$ . The energy minimum was obtained in the anticonfiguration (Figure 6a), although the angle of the nonplanarity is small ( $\sim 3^{\circ}$ ). The energy minimization procedure also predicted that the C=C bond distance was 1.4 Å, which implies that the bond in the anion has intermediate strength between single and double bonds. The MO calculation for the syn conformation resulted in a large  $H_{\alpha}$  coupling  $(a(H_{\alpha}) = 1.5-2.5 \text{ mT})$  at the nonplanarity angle  $\delta = 10-15^{\circ}$ , which differs from the observed small couplings (0.1-0.7 mT), although it gave agreeable values for the  $\beta$ -proton couplings at the angle. There may remain another possibility that the hexene anions have twisted structures, because it has been reported that the alkene radical cations with vinylidene group have twisted structures.9-11 INDO MO calculations were made for 1-butene radical anion assuming the twisted structure around the C==C bond. The results were shown in Figure 6b. The small isotropic coupling values for  $\alpha$ -protons (±0.7 mT) can be obtained at a twist angle of 15-30°. However, the twisted structure resulted in large  $\beta$ -proton couplings of 2.1-2.5 mT, which cannot explain the observed small  $\beta$ -proton couplings (0.56–1.74 mT). Moreover, the total energy of the anion with any twisted structure was higher than those with planar or pyramidal structures. Thus, the vinylidene type of anion is also suggested to favor the pyramidal structure than the twisted structure.

Comparison of Electronic Structures of Alkene Anion and Cation. The interesting results are the difference in the radical structures of the alkene anion (pyramid) and cation (plane) and the large difference in the sizes of the  $\beta$ -proton couplings. The following is a discussion on the origin of these differences based on a simple MO calculation in Hückel type approximation, since



Figure 7. Valence orbitals for (a) planar and (b) pyramidal radicals with  $-CH_2CH=CHCH_2$ — group. Illustration of the admixing of (c) C-H pseudo- $\pi$ -bonding orbital  $\psi_{CH}$  and (e) C-H pseudo- $\pi$ -antibonding orbital  $\psi_{CH}$  to the C=C  $\pi$ -bonding orbital  $\psi_{C=C}$  (SOMO for the cation). Admixing of (d)  $\psi_{CH}$  and (f)  $\psi^*_{CH}$  orbitals to C=C  $\pi$ -antibonding orbital  $\psi^*_{C=C}$  (SOMO for the anion). Hyperconjugation occurs through admixing of  $\psi_{CH}$  and  $\psi^*_{CH}$  to  $\psi_{C=C}$  and  $\psi^*_{C=C}$ . Each admixing leads to electron delocalization to hydrogen 1s orbitals via two paths: resonances between  $\alpha$ -carbon and  $\beta$ -proton orbitals. The latter path also yields unpaired electron densities via CH bonding (c, d) and antibonding combination (e, f) (indirect path, dotted arrows in (c)) (see text).

simple theory is favorable for deducing the essential difference. In the approximation energy matrix elements are given by eqs 1 and 2 (in standard notation).<sup>14</sup> The molecular orbitals  $(\psi_k)$  are

$$\alpha_{\mu} = \frac{1}{2}(IP + EA)_{\mu} \tag{1}$$

$$\beta_{\mu\nu} = \frac{1}{2} S_{\mu\nu} (\beta_{\mu\mu}{}^{(0)} + \beta_{\nu\nu}{}^{(0)})$$
(2)

approximated by a linear combination of valence orbitals (VO,  $\phi_i$ ):

$$\psi_k = \sum_i r_{ki} \phi_i \tag{M1}$$

We chose  $\pi$ - and pseudo- $\pi$ -orbitals for VOs, which are shown in Figure 7a,b, since we are interested in those  $\pi$ -orbitals of the alkene ions. The valence orbitals of the  $\alpha$ -carbon atoms in the pyramidal radical are expressed by the following hybrid orbital  $|sp_m(j)\rangle$ :

$$|\mathrm{sp}_{m}(j)\rangle = (1 - m^{2})^{1/2}|\mathrm{s}(j)\rangle + m[\cos \delta |\mathrm{p}_{z}(j)\rangle + \sin \delta |\mathrm{p}_{x}(j)\rangle]$$
(M2)

where j is L or R, which denotes the left or right side segment ( $\alpha$ -carbons) of the molecule, respectively.  $\delta$  is the deviation angle of the >C==C groups from the plane (Figure 7b). For planar radicals,  $|sp_m(j)\rangle$  becomes  $|p_z(j)\rangle$  (m = 1 and  $\delta = 0$  in (M2)). The valence orbitals of the  $\beta$ -carbon atoms and  $\beta$ -hydrogen atoms are given by the following expressions of anti-combinations:

$$\phi_{\beta\pi}(j) = 2^{-1/2}(|\mathrm{sp}_3(j,1)\rangle - |\mathrm{sp}_3(j,2)\rangle) \tag{M3}$$

$$\phi_{\mathrm{H}\pi}(j) = 2^{-1/2}(|\mathrm{ls}(j,\mathrm{H}_1)\rangle - |\mathrm{ls}(j,\mathrm{H}_2)\rangle) \tag{M4}$$

First, let us consider only the ethylene group (>C=C<) for simplicity. Figure 8a,e shows the comparison of the  $\pi$ -electronic energy diagrams for the planar and pyramidal radicals assumed for ethylene group, respectively. The antibonding and bonding orbitals and the electronic energies  $E_{C=C^*}$  and  $E_{C=C}$  of pyramidal radicals can be given by the following expressions and equations:

$$\psi^*_{C=C} = 2^{-1/2} [|sp_m(L)\rangle - |sp_m(R)\rangle]$$
(M5)

$$\psi_{C=C} = 2^{-1/2} [|sp_m(L)\rangle + |sp_m(R)\rangle]$$
 (M6)

$$E_{C=C^*} = \alpha_{sp_m} - \beta_{sp_m - sp_m} \tag{3}$$

$$E_{\rm C==C} = \alpha_{\rm sp_m} + \beta_{\rm sp_m-sp_m} \tag{4}$$

$$\alpha_{\rm sp_m} = (1 - m^2)\alpha_{\rm s} + m^2\alpha_{\rm p} \tag{5}$$

<sup>(17)</sup> Nyburg, S. C.; Luth, H. Acta Crystallogr. 1972, B28, 2992.
(18) Muto, H.; Nunome, K.; Iwasaki, M. J. Chem. Phys. 1974, 61, 5311;
1974, 61, 1075.

<sup>(19)</sup> Wood, D. E.; Llyod, R. V. J. Chem. Phys. 1970, 53, 3932.



Figure 8. *π*-electronic energy diagrams for alkene radical ions and their constituent bonds obtained by Hückel type MO calculation, and their correlations. (a) Planar ethylene group (>C=C<) for alkene cations (e) Pyramidal >C=C< group for anions, and (c) C-H<sub>β</sub> pseudo- $\pi$ -bonds. (b) and (d) are the energy diagrams for the cation and anion of substituted ethylene (-CH<sub>2</sub>CH=CHCH<sub>2</sub>-), respectively.  $\Delta E_i$  denotes the energy separation between the unpaired electron orbital for the >C=C< group ( $\psi_{C-C}$  or  $\psi^*_{sp_m \rightarrow sp_m}$ ) and the local CH<sub>β</sub> pseudo- $\pi$ -orbital ( $\psi_{CH}$  or  $\psi^*_{CH}$ ) (see text).

and for planar radicals  $|sp_m(j)\rangle$  is  $|p_z(j)\rangle$  in (M2), (M5), and (M6)  $(m = 1, \delta = 0)$ :

$$E_{C=C^*} = \alpha_p - \beta_{p-p} \tag{6}$$

$$E_{\rm C==C} = \alpha_{\rm p} + \beta_{\rm p-p} \tag{7}$$

The core integral of  $|2s;C\rangle$  AO is larger ( $\alpha_s = -14.05 \text{ eV}$ ) than that of  $|2p;C\rangle$  AO ( $\alpha_p = -5.57 \text{ eV}$ ).<sup>14</sup> Therefore the admixing of the  $|2s\rangle$  AO to the VO lowers the energies of the bonding and antibonding MOs. It also gives rise to a smaller overlap integral  $S(sp_m(L)|sp_m(R))$  for the pyramid (0.202 at  $\delta = 12^\circ$ ) than S- $(p_z(L)|p_z(R))$  for the plane (0.245) and hence gives a smaller resonance integral. As a result, we expect a smaller energy separation between  $\psi^*_{C=C}$  and  $\psi_{C=C}$  for the pyramidal structures than for the planar one (Figure 8a,e). Thus, the admixing of s nature much lowers  $\psi^*_{CmC}$  (SOMO of the anion), and the anion favors the pyramidal structure.<sup>20</sup>

Second, the eigenvalues and eigenvectors of substituted ethylene ions can be obtained by diagonalizing the full energy matrix for the ---CH<sub>2</sub>CH=CHCH<sub>2</sub>-- group. Figure 8b,d shows the energy diagrams obtained for the substituted ethylene cations (planar) and anions (pyramidal), respectively. Their unpaired electron orbitals are given by the following expressions:

$$\psi_{Au} = a[|p_{z}(L)\rangle + |p_{z}(R)\rangle] + b[\phi_{H\pi}(L) + \phi_{H\pi}(R)] + c[\phi_{\beta\pi}(L) + \phi_{\beta\pi}(R)] \quad \text{(for cation) (M7)}$$
  
$$\psi_{Ag} = d[|sp_{m}(L)\rangle - |sp_{m}(R)\rangle] + e[\phi_{H\pi}(L) - \phi_{H\pi}(R)] + f[\phi_{\beta\pi}(L) - \phi_{\beta\pi}(R)] \quad \text{(for anion) (M8)}$$

The square of the coefficient of the H<sub>2</sub> group orbital  $\phi_{H\pi}(j)$  for the cation was larger  $(b^2 = 0.071)$  than that for the anion  $(e^2 =$ 0.052), and predicting larger  $\beta$ -proton couplings for the cation (3.6 mT for the  $CH_{\beta}$  conformational angle of 30°) than that for anion (2.6 mT) in agreement with the present experimental results. The smaller  $\beta$ -proton couplings of anions than cations have been reported for aromatic hydrocarbon ions (pyracene, acenaphthene and alkyl-substituted benzenes) and discussed by many workers by direct diagonalization of the energy Hamiltonian adopted above.<sup>21-23</sup> However, the method does not explicitly give information on the hyperconjugation paths for  $\beta$ -methylene proton spin densities. Purins and Karplus applied a perturbation treatment, which is useful to known the hyperconjugation paths.<sup>23</sup> However, they considered only indirect paths, which will be described later. Since alkene ions are instructive and a good system for understanding the hyperconjugation paths and their differences between the anions and cations, here we applied the perturbation treatment by including all of the interactions as follows.

The energy diagram for the local CH bonding ( $\psi_{CH}$ ) and antibonding orbitals ( $\psi^*_{CH}$ ) is shown in Figure 8c:

$$\psi_{\rm CH} = l\phi_{\beta\pi} + n\phi_{\rm H\pi} \tag{M9}$$

$$\psi^*_{\rm CH} = n\phi_{\beta\pi} - l\phi_{\rm H\pi} \tag{M10}$$

$$l = 0.757, n = 0.653$$
 for  $r_{\rm CH} = 1.09$  Å

$$E_{\rm CH} = 2^{-1}(\alpha_{\rm sp_3} + \alpha_{\rm H\pi}) + \beta_{\rm sp_3-H\pi}$$
(8)

$$E_{\rm CH}^{*} = 2^{-1}(\alpha_{\rm sp_{3}} + \alpha_{\rm H\pi}) - \beta_{\rm sp_{3}-H\pi}$$
(9)

Their energy levels are widely split by a large resonance integral  $\beta_{sp_3-H\pi} = -10.29 \text{ eV}$  and lead to near location of  $\psi^*_{CH}$  to  $\psi^*_{C=C}$ for anion and that of  $\psi_{CH}$  to  $\psi_{C=C}$  for the cation, as shown in Figure 8. Perturbation treatment for substitution of  $\beta$ -methylene groups to ethylene results in the following unpaired electron or-

<sup>(20)</sup> In the case of the cation, the  $\psi_{C-C}$  bonding orbital (SOMO) for the planar structure was as low as that for the pyramidal one, as shown in Figure 8a,e. The favorable structure for the cation can not be deduced based on such a small difference in this simple approximation. The planar or twisted structures for the cations were suggested by more sophisticated MO calculations.<sup>10,11</sup>

<sup>(21)</sup> Bolton, J. R.; Carrington, A.; McLachlan, A. D. Mol. Phys. 1962, 5, 31

<sup>(22)</sup> Colpa, J. P.; de Boer, E. Mol. Phys. 1963, 7, 333.
(23) Purins, D.; Karplus, M. J. J. Am. Chem. Soc. 1968, 90, 6275 and references therein.

 $\psi_{Au} = \psi_{C-C} + \beta(\psi_{C-C},\psi_{CH}) / (E_{C-C} - E_{CH}) [\psi_{CH}(L) + \psi_{CH}(R)] + \beta(\psi_{C-C},\psi^*_{CH}) / (E_{C-C} - E_{CH}) [\psi^*_{CH}(L) + \psi^*_{CH}(R)]$ (M11)

$$= \psi_{C=C} + \delta[\psi_{H\pi}(L) + \psi_{H\pi}(R)] + c[\psi_{\beta\pi}(L) + \psi_{\beta\pi}(R)]$$
(M12)<sup>2</sup>

$$b = 2^{-1/2} [n^2 \beta_{p\alpha-H\pi} + ln \beta_{p\alpha-sp_3}] / (E_{C=C} - E_{CH}) + [l^2 \beta_{p\alpha-H\pi} - ln \beta_{p\alpha-sp_3}] / (E_{C=C} - E_{CH^*})] = 2^{-1/2} [-0.637 - 1.994] / (-14.94) = -0.31 - 0.05 = -0.36 \quad \text{(for planar cation) (10)}$$

$$\psi_{Ag} = \psi^{*}_{sp_{m} \rightarrow sp_{m}} + \beta(\psi^{*}_{sp_{m} \rightarrow sp_{m}}, \psi_{CH}) / (E_{C=C^{*}} - E_{CH})[\psi_{CH}(L) - \psi_{CH}(R)] + \beta(\psi^{*}_{sp_{m} \rightarrow sp_{m}}, \psi^{*}_{CH}) / (E_{C=C^{*}} - E_{CH^{*}})[\psi^{*}_{CH}(L) - \psi^{*}_{CH}(R)]$$
(M13)

$$= \psi^*_{sp_m \to p_m} + e[\phi_{H\pi}(L) - \phi_{H\pi}(R)] + f[\phi_{\beta\pi}(L) - \phi_{\beta\pi}(R)]$$
(M14)<sup>24</sup>

$$e = 2^{-1/2} \{ [n^2 \beta_{sp_m-H\pi} + ln\beta_{sp_m-sp_3}] / (E_{C=C^*} - E_{CH}) + [l^2 \beta_{sp_m-H\pi} - ln\beta_{sp_m-sp_3}] / (E_{C=C^*} - E_{CH^*}) \} = 2^{-1/2} \{ [-0.415 - 1.836] / (14.3 + [-0.787 + 1.836] / (-6.45) \} = -0.11 - 0.11 = -0.22 \text{ (for pyramidal anion) (11)} \end{cases}$$

where each second and third terms in the right sides of (M11) and (M13) come from the admixing process of  $\psi_{CH}$  and  $\psi^*_{CH}$ orbitals to  $\alpha$ -carbon orbitals, respectively, as shown in Figure 7c-f. (M12) and (M14) are the rewritten expressions of (M11) and (M13) by decomposition of  $\psi_{CH}$  and  $\psi^*_{CH}$  to  $\phi_{H\pi}$  and  $\phi_{\beta\pi}$ . They imply that the admixing of H<sub>2</sub> group orbitals  $\phi_{H\pi}$  to  $\alpha$ -carbon orbitals occurs via two paths for both the above mixing processes. One is a direct resonance between the  $\alpha$ -carbon orbital (p<sub>z</sub> or sp<sub>m</sub>) and  $\phi_{H\pi}$ , which is given by the first term in parentheses in eqs 10 and 11. The other (the second term) is a resonance between  $\alpha$ -carbon orbitals and the  $\beta$ -carbon sp<sub>3</sub> hybrid orbital, which gives rise to a mixing of  $\phi_{H_{\pi}}$  to an  $\alpha$ -carbon orbital via  $\psi_{CH}$  or  $\psi^*_{CH}$ (indirect path). In the case of the cation, the admixing of C-H bonding orbitals ( $\psi_{CH}$ ) leads to a very large value -0.31 for the first term in eq 10, giving a large extent of hyperconjugation. This is because of a near location of  $\psi_{CH}$  to  $\psi_{C=C}$  and because the direct and indirect paths additively work, giving the same signs for two terms in the first parentheses in eq 10, since  $\psi_{CH}$  is a bonding combination of  $\phi_{H\pi}$  and  $\beta$ -carbon orbitals  $\phi_{\beta\pi}$ . The mixing via  $\psi^*_{CH}$  antibonding orbitals also contributes to hyperconjugation, although the contribution is small. Namely, the second terms in eq 10 is small (-0.05), because the direct and indirect mixing paths via  $\psi^*_{CH}$  do not additively work, in addition to because of a wide energy separation between  $\psi^*_{CH}$  and  $\psi_{C-C}$  ( $E_{CH^*} - E_{C-C} \gg E_{C-C} - E_{CH}$ ).

Whereas for the anion, the hyperconjugation via the admixing of  $\psi_{CH}$  bonding orbitals is very small (second term in (M13)), and resulting in a small value, -0.11, for the first term in eq 11: the term is about 1/3 the corresponding contribution for the cation, since the energy separation  $E_{CH} - E_{C=C^{\circ}}$  is much larger than  $E_{CH} - E_{C=C}$  for cation.  $\psi^*_{CH}$  orbitals closely locate to the  $\psi^*_{C=C}$  antibonding orbital (third term in (M13)). However, the direct and indirect paths via the admixing of  $\psi^*_{CH}$  oppositely work, and also resulting in a small contribution (-0.11) similar to that via the admixing of  $\psi_{CH}$ . Thus is was clarified that the very large  $\beta$ -proton couplings for the cations mainly originate from a near location of  $\psi_{CH}$  and  $\psi_{C=C}$  orbitals and from cooperation of the direct and indirect hyperconjugation paths which additively work for  $\psi_{\rm CH}$ . For the anion, the small  $\beta$  couplings can be understood as being due to a smaller admixing of  $\psi_{CH}$  because of wider energy separation between  $\psi_{CH}$  and  $\psi^*_{C=C}$  and due to opposite cooperation of direct and indirect hyperconjugation paths for the mixing of  $\psi^*_{CH}$ , which closely locate to  $\psi^*_{C=C}$ .

CNDO MO calculations also gave essentially the similar results. Thus the differences in the radical structures and in the size of the  $\beta$ -proton couplings were reasonably understood in a simple molecular description.

## **Concluding Remarks**

Extremely unstable radical anions of alkenes having large negative electron affinities (EA = -1.7 to -2.3 eV<sup>4</sup>) were detected in *n*-alkane matrices, which are supposed to have larger negative EAs if measurable. They were found to have pyramidal structures and have much smaller  $\alpha$ - and  $\beta$ -proton couplings than those of the corresponding cations. Their differences were understood on the basis of a simple MO calculations.

Alkyne anions have much larger negative EAs  $(-2.6 \text{ eV}^4)$  than alkene anions. We have recently detected the alkyne anions in *n*-alkane matrices for the first time.<sup>3</sup> *n*-Alkanes have been found to be good matrices to trap such unstable radicals.

**Registry No.** (E)-EtCH=CHEt, 13269-52-8; (E)-EtCH=CHEt radical anion, 132294-10-1; (E)-EtCH=CHEt radical cation, 107172-32-7; (E)-MeCH=CHPr, 4050-45-7; (E)-MeCH=CHPr radical anion, 132294-11-2; (E)-MeCH=CHPr radical cation, 65621-64-9; H<sub>2</sub>C=CHBu, 592-41-6; H<sub>2</sub>C=CHBu radical anion, 132294-12-3; H<sub>2</sub>C=CHEt, 106-98-9; H<sub>2</sub>C=CHEt radical anion, 135969-97-0; (E)-MeCH=CHMe, 624-64-6; (E)-MeCH=CHMe radical anion, 58311-62-9; Cl(CH<sub>2</sub>)<sub>5</sub>Me, 544-10-5.

<sup>(24)</sup> Coefficients c and f have expressions similar to those for b and e (eqs 10 and 11), but the coefficients  $n^2$ , ln,  $l^2$ , and -ln involved in the expressions are replaced by ln,  $l^2$ , -ln, and  $n^2$ , respectively.