# EPR Studies of the Formation of Alkene Cations due to Ion–Molecule Reactions in the 77 K Radiolysis of Pentane and Hexane containing Additives

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Radiolysis of the two systems, pentane containing 3 mol% octane, and hexane containing 3 mol% nonane, has been investigated at 77 K in the presence of 1 mol% alkenes. EPR studies of alk-2- and -3-ene additives show the formation of the corresponding alk-2- and -3-ene radical cations, whereas alk-1-enes with linear C—C chains are observed to give (*E*)-pent-2-ene radical cations in the pentane systems and (*E*)-hex-3-ene radical cations in the hexane systems. The effects of the alk-1-ene additives are attributed to the ion-molecule reaction, *i.e.* transfer of H<sub>2</sub> from the parent *n*-alkane radical cations to the alk-1-ene additives to form the alkene radical cations of the parent molecules.

Ausloos and co-workers<sup>1,2</sup> have demonstrated the occurrence of specific ion-molecule reactions in the liquid-phase radiolysis (195 K) of alkanes containing alkenes. The proposed reactions are  $H_2$  transfers from solvent alkane radical cations to solute alkenes, *e.g.* 

$$C_n H_{2n+2}^{+} + C_m H_{2m} \rightarrow C_n H_{2n}^{+} + C_m H_{2m+2}$$
 (1a)

Here,  $C_n H_{2n+2}$ <sup>++</sup> are solvent radical cations of 2-methylbutane, cyclopentane, *etc.*, and  $C_m H_{2m}$  are ethene, propene, *etc.* They confirmed these reactions by analysis of the isotopic compositions of alkanes produced from deuteriated solute alkenes ( $C_m D_{2m}$ ).

$$C_nH_{2n+2}^{*+} + C_mD_{2m} \rightarrow C_nH_{2n}^{*+} + C_mD_{2m}H_2 \qquad (1b)$$

They also found that addition of electron scavengers such as  $CCl_4$  increases the yield of  $C_mH_{2m+2}$ ; this result supports the ion-molecule reaction because electron scavengers interrupt recombination of  $C_nH_{2n+2}$ <sup>+</sup> with electrons. Saitake *et al.*<sup>3</sup> reported that the radiolysis of 2,3-dimethylbutane containing alkenes and electron scavengers at 77 K produces radical cations of tetramethylethene and attributed the result to the ion-molecule reaction. In the present investigation, we wish to report that these types of ion-molecule reactions occur in the radiolysis of solid-phase hexane and pentane systems at 77 K and that the reactions.

$$C_n H_{2n+2}^+ + C_m H_{2m} \rightarrow C_n H_{2n+2} + C_m H_{2m}^+$$
 (2)

$$C_n H_{2n+2}^+ \to C_n H_{2n}^+ + H_2$$
 (3)

# Experimental

Propene, butenes (But), pentenes (Pen) and hexenes (Hex) were used as received. Perdeuteriated pentane and hexane from MSD and perprotiated octane and nonane were purified by use of the molecular sieve 13X.

EPR samples were prepared on a vacuum line and measured amounts of reagents were distilled into quartz EPR tubes. The samples consisted of 1 mol% solute alkenes, 3 mol% solute *n*-alkanes and solvent matrix alkanes. The added solute *n*-alkanes induce the production of voids which are able to trap electrons.<sup>4,5</sup> The trapped electron  $(e_t^{-})$  yields, which depend on chain lengths of the solute *n*-alkanes, were observed to be a maximum at  $n-C_8$  and  $n-C_9$  for matrices  $n-C_5$  and  $n-C_6$ , respectively. The systems will be, hereafter, represented by solute alkene-solute *n*-alkane-matrix *n*-alkane, such as 1% 1-Hex-3%  $n-C_9-n-C_6$ .

The EPR samples were  $\gamma$ -irradiated with a <sup>60</sup>Co source at 77 K with a dose of *ca.* 10 kGy and the spectra were measured at 77 K by using a JEOL EPR spectrometer with 100 kHz field modulation at a microwave power of 0.2 mW. The EPR signals were digitized by a 12-bit A/D converter and fed to a microcomputer. Photobleaching of  $e_t^-$  formed in the alkane systems causes recombination with counter-cations. As a result, the EPR spectra of the recombined radical cations can be observed as difference spectra before and after illumination. The photobleaching was carried out by light with  $\lambda > 1150$  nm and all the EPR spectra observed are represented by difference spectra, of which the central signal is off scale owing to strong  $e_t^-$  singlets.<sup>5</sup> EPR spectral simulations were performed by use of the Lefebvre and Maruani program.<sup>6</sup>

## Results

#### **Cation Formation in Pentane Systems**

As was shown in the previous EPR study,<sup>5</sup> radiolysis of pentane containing 3 mol% octane  $(3\% n-C_8-n-C_5)$  at 77 K produced solute radical cations  $(n-C_8^{++})$  and trapped electrons ( $e_t$ ) together with free radicals ( $R^*$ ) of  $n-C_5$ ; neat  $n-C_5$ was found to give only R<sup>\*</sup>. The added n-C<sub>8</sub> molecules which produce voids for e<sub>t</sub><sup>-</sup> also act as positive charge scavengers. Additives with lower ionization energies than the matrices and other additives are known to have the ability to stabilize radiation-produced positive charges;5,7,8 the values of the ionization energy  $(E_i)$  for related compounds are compiled<sup>9</sup> in Table 1. On addition of (E)- and (Z)-pent-2-enes (2-Pen) to the system, formation of the corresponding radical cations of the alkene additives [(E)- and (Z)-Pen<sup>+</sup>] were observed, as shown in Fig. 1(a) and (b). For (Z)-2-Pen, perdeuteriated pentane was used as the matrix because of the improvement in spectral resolution; the radical cations of (Z)-alkenes generally do not give well resolved spectra; however, the resolutions were considerably improved by the use of perdeuteriated matrices. The dashed-line spectra are simulations and the hyperfine coupling constants used are given in Table

Table 1 Ionization energies of related alkanes and alkenes in the gas phase<sup> $\alpha$ </sup>

|                  | $E_i/eV$ | $E_{\rm i}/{\rm eV}$ |      |
|------------------|----------|----------------------|------|
| n-C.             | 10.55    | 1-Hex                | 9.59 |
| n-C <sub>4</sub> | 10.48    | (E)-2-But            | 9.25 |
| n-C.             | 10.24    | (Z)-2-But            | 9.29 |
| n-C              | 10.21    | (E)-2-Pen            | 9.06 |
| propene          | 9.84     | (Z)-2-Pen            | 9.11 |
| 1-But            | 9.72     | (E)-2-Hex            | 9.16 |
| 1-Pen            | 9.66     | (Z)-3-Hex            | 9.12 |

" Ref. 9.

2. The 3% *n*-C<sub>8</sub>-*n*-C<sub>5</sub> systems containing (*E*)- and (*Z*)-but-2enes (2-But) were also observed to give (*E*)- and (*Z*)-2-But<sup>++</sup>, respectively (Table 2). The values obtained may be compared with those reported by Lund and co-workers<sup>10</sup> who studied EPR spectra of alkene radical cations formed in halogenocarbon matrices. The details of our assignment will be reported elsewhere.<sup>11</sup>

Fig. 2(a) and (b) show the spectra obtained when propene and but-1-ene (1-But), instead of 2-Pen, were added, respec-



**Fig. 1** EPR spectra of (a) (E)-2-Pen<sup>+</sup> in 1% (E)-2-Pen-3%  $n-C_8-n-C_5$  and (b) (Z)-2-Pen<sup>+</sup> in 1% (Z)-2-Pen-3%  $n-C_8-n-C_5^2H_{12}$ . The dashed-line represents the simulated spectra (see Table 2 for the parameters used).



**Fig. 2** EPR spectra of (*E*)-2-Pen<sup>++</sup> in (a) 1% propene-3%  $n-C_8-n-C_5$ , (b) 1% 1-But-3%  $n-C_8-n-C_5$  and (c) 3%  $n-C_8-n-C_5$ . The dashed lines in (c) show changes when  $n-C_8^{-2}H_{18}$  is used instead of  $n-C_8$  and the stick spectrum shows peak positions due to  $n-C_8^{++}$  (a = 22 G).

tively. Propene, 1-But and also 1-Pen (not shown in the figures) gave spectra similar to that for (E)-2-Pen<sup>++</sup>. This suggests the formation of (E)-2-Pen<sup>+</sup>; spectra obtained in halogenocarbon matrices containing these alk-1-enes<sup>12,13</sup> are clearly different from the present spectra. In the case of the 3% n-C<sub>8</sub>-n-C<sub>5</sub> system without alkenes [solid lines in Fig. 2(c)], formation of the octane radical cation,  $n-C_8^{+,5}$  is discernible in the centre of the spectrum, as is shown by the stick spectrum. The  $n-C_8^+$  peaks disappeared when  $n-C_8^2H_{18}$  is used instead of  $n-C_8H_{18}$  [the dashed lines in Fig. 2(c)]; the proton hyperfine coupling constant for  $n-C_8$  $(a = 22 \text{ G})^{14}$  are reduced by a factor of 0.153 on the replacement of deuterium. Weak outer peaks, however, exist, which originate from the matrix  $n-C_5$ . We attribute these outer peaks to (E)-2-Pen<sup>+</sup> because of good agreement of the peak positions with those for (E)-2-Pen<sup>+</sup>. In the previous study,<sup>5</sup> we did not observe the weak outer peaks because of low microwave power measurements at 0.06 mW.

## **Cation Formation in Hexane Systems**

Fig. 3(a) shows the spectrum of  $3\% n-C_9-n-C_6$  without alkene additives  $\gamma$ -irradiated at 77 K. Fig. 3(b), (c) and (d) show the spectral changes when 1% of hexenes [(E)-3-Hex, 1-Hex and (Z)-3-Hex] are added to the  $3\% n-C_9-n-C_6$  system; in the case of (Z)-3-Hex,  $n-C_6^2H_{14}$  is used as the matrix in order to improve spectral resolution. The simulated spectra of (E)-3-

Table 2 Hyperfine coupling constants (G) used for spectral simulation<sup>a</sup>

| Table 2 Hyperine coupling constants (c) used for spectral simulation   |                                |                |                  |                  |  |  |                 |  |  |
|--|--------------------------------|----------------|------------------|------------------|--|--|-----------------|--|--|
|  | $-CH(\alpha)=CH(\alpha')^{-b}$ |                |                  |                  |  | $-CH_3(\beta_{Me})$                    |                 |  |  |
| alkene radical cation  | A <sub>x</sub> <sup>c</sup>    | $A_y^d$        | $A_z^e$          | a <sub>iso</sub> | $a(\beta_1)$                           | $a(\beta_2)$                           | $a(\beta_{Me})$ |  |  |
| (E)-MeCH=CHMe <sup>+</sup><br>(Z)-MeCH=CHMe <sup>+</sup>   | - 2.0<br>- 3.0                 | -18.0<br>-18.0 | - 10.0<br>- 10.0 | - 10.0<br>- 10.3 |  |  | 25.3<br>23.2    |  |  |
| (E)-MeCH=CHCH <sub>2</sub> Me <sup>+</sup><br>(Z)-MeCH=CHCH <sub>2</sub> Me <sup>+</sup>                                   | -2.0<br>-3.0                   | -17.5<br>-16.5 | 11.0<br>10.0     | 10.2<br>9.8      | 53.8<br>58.0                           | 29.0<br>20.0                           | 25.0<br>22.0    |  |  |
| (E)-MeCH=CHCH <sub>2</sub> CH <sub>2</sub> Me <sup>+</sup><br>(Z)-MeCH=CHCH <sub>2</sub> CH <sub>2</sub> Me <sup>+</sup>   | -2.0<br>-3.0                   | 17.5<br>17.5   | 11.0<br>10.0     | - 10.2<br>- 10.2 | 55.6<br>51.2                           | 23.0<br>21.4                           | 25.0<br>23.0    |  |  |
| (E)-MeCH <sub>2</sub> CH=CHCH <sub>2</sub> Me <sup>·+</sup><br>(Z)-MeCH <sub>2</sub> CH=CHCH <sub>2</sub> Me <sup>·+</sup> | -2.0 -2.0                      | -15.5<br>-15.5 | -9.0<br>-9.0     | -8.8 - 8.8       | 44.5 <sup>f</sup><br>38.3 <sup>f</sup> | 33.0 <sup>f</sup><br>33.5 <sup>f</sup> |                 |  |  |

<sup>a</sup> Calculations were made by the use of the Gaussian line-shape function ( $\Delta H = 4.5$  G) under consideration of nuclear Zeeman terms. <sup>b</sup> It is assumed that proton H( $\alpha'$ ) is in the H( $\alpha$ )-C=C plane and that the bond angles between C-H and C=C are 120°. Directions of axes of principal values  $A(\alpha)$  and  $A(\alpha')$  are taken as follows: <sup>c</sup> parallel to C-H, <sup>d</sup> in plane and perpendicular to C-H and <sup>e</sup> perpendicular to the plane. <sup>f</sup>  $a(\beta_1)$  and  $a(\beta_2)$  values at positions 2 and 5 are the same.



Fig. 3 EPR spectra of (E)-3-Hex<sup>++</sup> in (a) 3% n-C<sub>9</sub>-n-C<sub>6</sub>, (b) 1% (E)-3-Hex-3% n-C<sub>9</sub>-n-C<sub>6</sub> and (c) 1% 1-Hex-3% n-C<sub>9</sub>-n-C<sub>6</sub>; (d) EPR spectrum of (Z)-3-Hex<sup>++</sup> in 1% (Z)-3-Hex-3% n-C<sub>9</sub>-n-C<sub>6</sub><sup>2</sup>H<sub>14</sub>. The dashed-line represents simulated spectra (see Table 2 for the parameters used).

Hex<sup>++</sup> and (Z)-3-Hex<sup>++</sup> are represented by dashed lines and the hyperfine coupling constants used are listed in Table 2. The  $n-C_9-n-C_6$  systems containing 1% (E)- and (Z)-2-Hex were also observed to produce the corresponding alkene radical cations of the additives (Table 2). Note that the external features of the spectrum for the system without alkenes [Fig. 3(*a*)] are similar to those for Fig. 3(*b*). This suggests the formation of (E)-3-Hex<sup>++</sup> even if (E)-3-Hex is not added to the  $n-C_9-n-C_6$  system. As is clearly observed in Fig. 3(*c*), the addition of 1-Hex yields (E)-3-Hex<sup>++</sup>. We also observed the formation of (E)-3-Hex<sup>++</sup> in the  $n-C_9-n-C_6$  systems containing 1% 1-But and 1-Pen.

The ratio of the (E)-3-Hex<sup>++</sup> yields in the 3% n-C<sub>9</sub>-n-C<sub>6</sub> systems without additives, with 1% (E)-3-Hex and with 1% 1-Hex was found to be 0.18:0.61:1.0 by comparison of the peak heights of the observed spectra. The G value (the number of radicals formed per 100 eV of absorbed energy) of (E)-3-Hex<sup>++</sup> in the 1% 1-Hex-3% n-C<sub>9</sub>-n-C<sub>6</sub> system was 0.25. This value was obtained by comparison of the areas under the EPR absorption spectra of (E)-3-Hex<sup>++</sup> and the free radical R<sup>+</sup>, which is produced from neat n-C<sub>6</sub> under the same experimental conditions; the G value for R<sup>+</sup> formed in neat n-C<sub>6</sub> irradiated at 77 K has been reported to be *ca.* 4.3.<sup>15</sup> EPR signals of these alkene radical cations, therefore, are very weak and data processing, such as averaging of accumulated signals and smoothing, was performed with a microcomputer to improve the signal-to-noise ratios.

#### Discussion

Our EPR studies showed that the  $3\% n-C_8-n-C_5$  systems containing 1% (*E*)- and (*Z*)-2-Pen produce the corresponding pentene radical cations, (*E*)- and (*Z*)-2-Pen<sup>++</sup>. In the case of the  $3\% n-C_9-n-C_6$  systems also, the *trans* and *cis* forms of the hex-2- and -3-ene additives yielded the radical cations of the corresponding forms of the additives. The results indicate the capture of radiation-produced positive charges by the alkene additives with lower  $E_i$ s than the alkane constituents (Table 1). We therefore expected addition of alk-1-enes to produce the corresponding alk-1-ene radical cations; however, the

present study showed that the 3% n-C<sub>8</sub>-n-C<sub>5</sub> systems containing propene, 1-But and 1-Pen produce (*E*)-2-Pen<sup>++</sup> and that the 3% n-C<sub>9</sub>-n-C<sub>6</sub> systems containing 1-But, 1-Pen and 1-Hex produce (*E*)-3-Hex<sup>++</sup>. This unexpected result may be attributed to the ion-molecule reaction (1*a*) proposed by Ausloos and co-workers.<sup>1,2</sup> The reaction involves H<sub>2</sub> transfer from a matrix alkane radical cation to an H<sub>2</sub> acceptor. In the present study, we consider the alk-1-ene additives to be the H<sub>2</sub> acceptors.

Ausloos and co-workers<sup>1,2</sup> investigated the reactions of the  $H_2$  acceptors; the order of the relative efficiencies of the  $H_2$ -transfer reactions in 2-methylbutane was found to be cyclopropane, ethene, propene, but-1-ene, acetylene and but-2enes. The  $E_i$  of the most efficient cyclopropane is as high as 1 eV (cf. the  $E_i$  of the least efficient but-2-enes).<sup>9</sup> Our EPR study of the 3% n-C<sub>8</sub>-n-C<sub>5</sub> systems containing 1% but-2-enes shows stabilization of the positive charges of the but-2-ene radical cations in the absence of the radical cations derived from the alkane constituents. Hence, but-2-enes are the least efficient  $H_2$  acceptor which may be attributed to preferential transfer of positive charges to but-2-enes in the 2-methylbutane solvents.

In the present study the 3%  $n-C_8-n-C_5$  and the 3%  $n-C_8-n-C_5$  $C_9$ -n- $C_6$  systems, without any other additives, produce alkene radical cations, (E)-2-Pen<sup>++</sup> and (E)-3-Hex<sup>++</sup>, respectively. Werst and Trifunac<sup>16</sup> observed alkene radical cation formations in the pulse radiolysis of liquid alkanes using time-resolved fluorescence-detected magnetic resonance methods, e.g. the tetramethylethylene radical cation (TME<sup>++</sup>) formation in a solution of 2,3-dimethylbutane at 180 K. They attributed the alkene radical cation formation to dehydrogenation [reaction (3)] of the parent alkane radical cations. Saitake et al. also observed EPR spectra of TME'+ in the radiolysis of 2,3-dimethylbutane at 77 K in the presence of the electron scavenger  $SF_6$ .<sup>3</sup> In our study, the yields of (E)-2-Pen'  $^+$  and (E)-3-Hex' were, however, reduced considerably compared with those in the systems containing alk-1-ene additives, e.g. the (E)-3-Hex<sup>+</sup> yield was one fifth of that in the presence of 1% 1-Hex. These results suggest that only some of the matrix cations undergo the dehydrogenation reaction.

Here, we examine the thermodynamics of H<sub>2</sub> transfer (A), charge transfer (B) and dehydrogenation (C). The enthalpy changes,  $\Delta H$ , are calculated from the  $E_i$  (Table 1) and  $\Delta_f H^{\circ 17}$  for gas-phase neutral molecules;  $E_i$  for condensed states and  $\Delta_f H^{\circ}$  for radical cations are generally unavailable at present. Note that only a slight exothermic energy is expected for reaction (C1), n-C<sub>6</sub><sup>++</sup>  $\rightarrow$  (E)-3-Hex<sup>++</sup> + H<sub>2</sub>, *i.e.*  $\Delta H = -0.17$  eV. On the other hand, the value of  $\Delta H$  for reaction (A1), n-C<sub>6</sub><sup>++</sup> + 1-Hex  $\rightarrow$  (E)-3-Hex<sup>++</sup> + n-C<sub>6</sub>, is calculated to be -1.47 eV. Although  $\Delta H$  values are one of the factors determining reactivity, these values support the present result that H<sub>2</sub>-transfer reactions (A1) occur more readily than dehydrogenation (C1). For charge transfer (B1), n-C<sub>6</sub><sup>++</sup> + 1-Hex  $\rightarrow$  n-C<sub>6</sub> + 1-Hex<sup>++</sup>,  $\Delta H$  was calculated to be -0.89 eV. This result also supports the H<sub>2</sub>-transfer reaction (A1).

For reactions in the 3%  $n-C_8-C_5$  system with 1% 1-But, we observed the H<sub>2</sub>-transfer reaction and  $\Delta H$  values comparable to those above were obtained, *i.e.* (A2)  $n-C_5^{++} + 1$ -But  $\rightarrow (E)$ -2-Pen<sup>++</sup>  $+ n-C_4$  (-1.58 eV), (B2)  $n-C_5^{++} + 1$ -But  $\rightarrow n-C_5 + 1$ -But<sup>++</sup> (-0.83 eV) and (C2)  $n-C_5^{++} \rightarrow (E)$ -2-Pen<sup>++</sup>  $+ H_2$  (-0.30 eV). In the 3%  $n-C_8-n-C_5$  system with 1% (E)-2-But, the charge-transfer reaction (B3),  $n-C_5^{++} + (E)$ -2-But  $\rightarrow n-C_5 + (E)$ -2-But<sup>++</sup> (-1.30 eV), was observed. The reaction is more exothermic by 1.0 eV compared with reaction (C2) and less exothermic by 0.19 eV compared with the H<sub>2</sub>-transfer reaction (A3),  $n-C_5^{++} + (E)$ -2-But  $\rightarrow (E)$ -2Pen<sup>++</sup> + n-C<sub>4</sub> (-1.49 eV). These values suggest that the charge-transfer reaction predominates over the H<sub>2</sub>-transfer reaction even if the energetics are unfavourable. In the case of 1-But, however, the charge-transfer reaction was not observed and the  $\Delta H$  value for the reaction was less exothermic by 0.75 eV compared with that of the H<sub>2</sub>-transfer reaction.

We examined the H<sub>2</sub>-transfer reaction concerning ethene additives in the 3%  $n-C_8-n-C_5$  system. The yields of (E)-2-Pen'+ were found to be of the same order of magnitude as in the case without alkene additives, *i.e.* the addition of ethene had no effect on the yields of (E)-2-Pen<sup>+</sup>. Ausloos et al.<sup>1</sup> observed the H<sub>2</sub>-transfer reaction in 2-methylbutane containing ethene. Our result is possibly due to segregation of ethene in the mother crystal of  $n-C_5$ . For the 3%  $n-C_9-n-C_6$  systems containing ethene and propene, the additives again had little effect on the yields of (E)-3-Hex<sup>+</sup>. Relative efficiencies in the production of (E)-3-Hex<sup>+</sup> in the 3%  $n-C_9-n-C_6$  systems containing 1% 1-Hex, (E)-3-Hex, 1-Pen, 1-But and hept-1-ene were found to be 1.0, 0.6, 0.4, 0.4 and 0.3, respectively. 1-Hex is the most efficient and hept-1-ene the least efficient. This may result from the relative abilities of these alkene additives to form suitable mixed crystals with the  $n-C_6$  mother molecules. Ausloos et  $al.^2$  suggest that the H<sub>2</sub>-transfer reaction occurs by way of a loose reaction complex between a solvent radical cation and an H<sub>2</sub> acceptor molecule. It is possible that the preferential occurrence of the H<sub>2</sub>-transfer reaction in the alk-1-ene additives is due to the formation of mixed crystals suitable for the reaction. Hence, we examined the steric effects of branching of alk-1-ene additives on the reaction. The systems examined were  $3\% n-C_8-n-C_5$  containing 1%isobutene (9.23 eV), 2-methylbut-1-ene (9.20 eV), 2-ethylbut-1ene (9.21 eV) and 2-methylpent-1-ene; the  $E_i$  values are given in parentheses.<sup>9</sup> Formation of the corresponding alkene radical cations of the additives in the absence of (E)-2-Pen<sup>++</sup> was observed in the EPR spectra. The results indicate that the charge-transfer reaction occurs preferentially in the branched chain alk-1-enes ( $CH_2 = CRR'$ ). At present, we cannot be certain that charge transfer occurs preferentially because of the branching of alk-1-enes, i.e. the geometrical changes of the reaction intermediates, because the branching of alk-1-enes causes a lowering of  $E_i$  by ca. 0.5 eV and the  $E_i$  values become close to that for (E)-2-But (Table 2). Therefore, the charge-transfer reaction is expected to occur in these systems on the basis of the energetics discussed above. We expect further that the H<sub>2</sub>-transfer reaction would be affected by branching of matrix alkanes because of steric effects of the reaction complexes and experiments are now being undertaken to investigate this.

### References

- A. A. Scala, S. G. Lias and P. Ausloos, J. Am. Chem. Soc., 1966, 88, 5701.
- 2 P. Ausloos, A. A. Scala and S. G. Lias, J. Am. Chem. Soc., 1967, 89, 3677.
- 3 Y. Saitake, T. Miyazaki and Z. Kuri, J. Phys. Chem., 1973, 77, 2418.
- 4 H. Muto, K. Nunome, K. Toriyama and M. Iwasaki, J. Phys. Chem., 1989, 93, 4898.
- 5 T. Ichikawa, M. Shiotani, N. Ohta and S. Katsumata, J. Phys. Chem., 1989, 93, 3826.
- 6 R. Lefebvre and J. Maruani, J. Chem. Phys., 1965, 42, 1480.
- 7 P. W. F. Louwrier and W. H. Hamill, J. Phys. Chem., 1970, 74, 1418.
- 8 J. R. Miller and J. V. Beitz, J. Chem. Phys., 1981, 74, 6746.
- 9 V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev and Ye L. Frankevich, in *Bond Energies, Ionization Potentials and Electron Affinities*, Edward Arnold, London, 1966, p. 151.
- 10 L. Sjoqvist, M. Shiotani and A. Lund, Chem. Phys. Lett., 1990, 141, 417.
- 11 N. Ohta, Z. Dan and T. Ichikawa, unpublished results.
- 12 M. Shiotani, Y. Nagata and J. Sohma, J. Phys. Chem., 1984, 88, 4078.
- 13 J. Fujisawa, S. Sato, K. Shimokoshi and T. Shida, J. Phys. Chem., 1985, 89, 5481.
- 14 K. Toriyama, K. Nunome and M. Iwasaki, J. Phys. Chem., 1981, 85, 2149.
- 15 M. Fukaya, K. Toriyama, M. Iwasaki, T. Ichikawa and N. Ohta, Radiat. Phys. Chem., 1983, 21, 463.
- 16 D. W. Werst and A. D. Trifunac, J. Phys. Chem., 1988, 92, 1093.
- 17 CRC Handbook of Chemistry and Physics, ed. R. C. Weast, CRC Press, Boca Raton, 1988, p. D-96.

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