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Photodissociation Spectroscopy of Hexadiene Radical Ions: Structural Rearrangements in the Gas-Phase Ions

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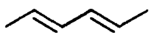
Abstract: Photodissociation spectroscopy was applied to determining the structure of ions formed by electron impact ionization of hexadienes. 1,3-Hexadiene and 2,4-hexadiene gave distinguishable spectra typical of conjugated diene radical cations. 1,4-Hexadiene gave a spectrum identical with those of 2,4-hexadiene ions, indicating complete rearrangement of the double bond into conjugation. However, 1,5-hexadiene gave an entirely distinct spectrum characteristic of unconjugated olefin cations. The laser photodissociation spectra of the three cis–trans isomers of 2,4-hexadiene ions were readily distinguishable, indicating that rotation around the double bond in the radical cation is not facile. The rearrangement of 1,4-hexadiene ions appeared to yield a mixture of cis–cis, cis–trans, and trans–trans structures. MINDO/3 calculations support the observed shift in peak positions among the three cis–trans isomers of 2,4-hexadiene ion. The spectrum of 1,3-hexadiene suggested the retention of cis–trans isomerism.

Ionization of an unsaturated hydrocarbon will normally involve removal of a π electron, and the resulting weakening of the π-bonding system can be expected to increase the lability of the molecule to various rearrangement processes. On such rearrangement which has been of interest is the migration of a double bonds into conjugation, and some recent results using photodissociation spectroscopy to characterize the structures of the radical cations have suggested that migration of a double bond by one position is easy, while migration across two or more positions can involve substantial energy barriers.[1] Another rearrangement, cis–trans isomerization around a double bond, is no less interesting but has been harder to study because of the usually small spectroscopic changes accompanying cis–trans isomerization. The hexadienes have proven to be exceptionally tractable compounds for investigation of both of these questions by photodissociation spectroscopy,[2] and we describe here the picture which has been obtained of these rearrangement processes involving the hexadiene isomers **1**, **4**, **5** and **6**.



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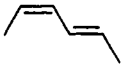
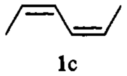
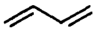


1b



1c



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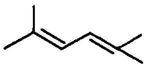

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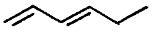

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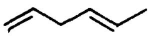

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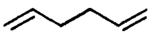

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Experimental Section

Photodissociation spectra[2] were obtained in the UV and visible region of the spectrum for each of the 2,4-hexadiene isomers and for mixed-isomer samples of the 1,3 and 1,4 isomers and 1,5-hexadiene. The UV region was studied by using light from a 2.5-KW Hg–Xe arc lamp with the wavelengths selected by a Schoeffel grating monochromator with two 2-mm slits (nominal band pass (fwhm) of 6.6 nm). The monochromator was also used without slits with a bandwidth (fwhm) estimated to be ~40 nm for the study of 1,5-hexadiene cations. This was necessitated by the lower absolute cross section of the UV peak. The visible region was first analyzed with interference filters to locate the position of the photodissociation peak, and then the region containing the peak was studied with the use of a Chromatix CMX-4 pulsed dye laser. All of the visible peaks fell within the range of coumarin 480 (coumarin 102) dye 4840–5140 Å, so all the isomers could be compared directly with each other. The absolute cross sections were estimated for all isomers by measuring the photodissociation rate at 360 nm immediately after measuring the photon flux at that wavelength. The photon flux was determined by observing the photodissociation rate of 2,5-dimethyl-2,4-hexadiene (**3**), which has a known absolute cross section at 360 nm of 5×10^{-17} cm^2. This technique of determining absolute cross sections has been used extensively and is considered to give absolute cross sections within a factor of 2.

All of the conjugated cations examined here have absolute cross sections of 5×10^{-17} cm^2 for the UV peak, and the 1,5-hexadiene cation peak was estimated to be 5×10^{-18} cm^2. The percent error associated with the relative cross section values is ±20%. The absolute cross sections of the visible peaks were determined by comparing the photodissociation rate at several wavelengths selected by the monochromator in both the UV and visible regions. The relative flux of the arc lamp monochromator source at these wavelengths has been determined by Eppley thermopile measurements. The value of the visible peak absolute cross section is 10^{-17} cm^2 for all of the conjugated ions. The visible region of 1,5-hexadiene cation was examined extensively with both the filters and the laser in the region of the conjugated diene peak, and no photodissociation ($<10^{-19}$ cm^2) was observed.

The sample of 1,3-hexadiene used was a mixture of 3-cis and 3-trans isomers obtained from Chem. Samples Co. as were all of the hexadiene samples. Therefore, the spectrum in Figure 3 is actually a composite spectrum of the two isomers. The sample of 1,4-hexadiene was also a mixture of 4-cis and 4-trans isomers so the spectrum in Figure 4 is also a composite. The three isomers of 2,4-hexadiene were studied separately and their spectra are shown in Figure 2.

Results and Discussion

Spectra of the Conjugated Diene Ions. The ground-state conjugated diene radical cations have a vacancy in the highest occupied π molecular orbital (HOMO). As illustrated in Figure 1, the ion photodissociation spectrum typically has two peaks in the visible–UV region: the higher energy peak has usually been considered to reflect excitation of the single electron from the HOMO into the lowest unoccupied π^* orbital (LUMO), in a transition denoted as type A.[3,4] The lower energy peak is usually considered to be a hole-excitation transition, denoted type I, involving excitation of an inner electron into the vacancy in the half-filled HOMO. This is the assignment of the two photodissociation peaks of conjugated diene radical cations which was first proposed for butadiene[5] and later for various other dienes,[2c] and it has received support from several theoretical studies.[3,4,6]

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[1] Fu, E. W.; Dymerski, P. P.; Dunbar, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 337.

[2] For description of these techniques, see, for instance: (a) Dymerski, P. P.; Fu, E.; Dunbar, R. C. *J. Am. Chem. Soc.* **1974**, *96*, 4109. (b) Dunbar, R. C. *Anal. Chem.* **1976**, *48*, 723. (c) Benz, R. C.; Dunbar, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 6363.

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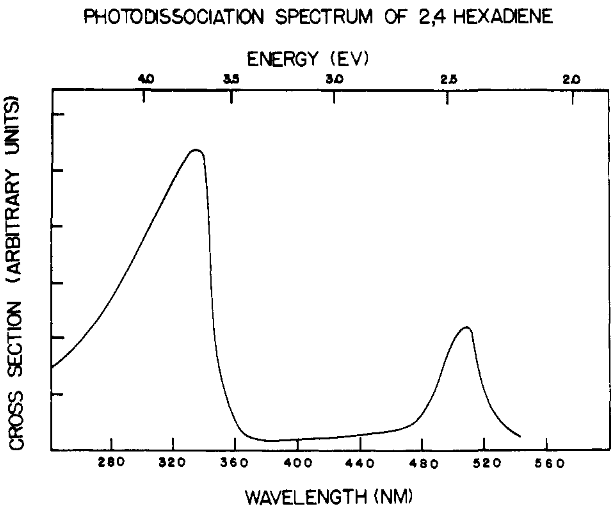

Figure 1. Photodissociation spectrum of 2,4-hexadiene ion (**1**) at ~10-nm resolution.

Substitution of methyl groups on the butadiene skeleton gives a regular pattern of spectral shifts. The low-resolution photodissociation spectrum of butadiene cation (**2**)[5] gives peaks at (2.32 ± 0.04) and (4.0 ± 0.1) eV. In 2,4-hexadiene (1,4-dimethylbutadiene) (**1**) these peaks shift to (2.50 ± 0.04) and (3.7 ± 0.1) eV (mixed-isomer spectrum).[2b] In 2,5-dimethyl-2,4-hexadiene ion (1,1,4,4-tetramethylbutadiene) (**3**) the peaks shift further to (2.65 ± 0.02) and (3.4 ± 0.1) eV.[2b] There is thus an apparently regular methyl shift to the blue of ~0.08 eV/methyl group in the I transition and a shift to the red of 0.15 eV per methyl group in the A transition, upon terminal-methyl substitution of butadiene ion. The visible photodissociation peaks in these three ions are similar in shape, and all have a width (fwhm) of ~0.4 eV, while the UV peaks, also similar in shape and markedly asymmetrical, have a width of ~0.6 eV.

The position of the I transition can be usefully compared with the photoelectron spectroscopic assignment of the energies of the ground and first excited states of the ions, as has been discussed in detail.[5] The most defensible comparison is to compare the optical peak position with the difference between the *adiabatic* first IP and the *vertical* second IP. (In this case, only for **3** do the adiabatic and vertical IPs differ.) The agreement is satisfactory,[7] within the uncertainty, for ions **1**–**3**.

The I transition can also be correlated with molecular orbital calculations of the highest two occupied orbital energies. MINDO/3 calculations[8] (using model geometries and a statistical weighting of 2,4-hexadiene isomers) were made to test the ability of the MINDO parametrization to predict the shift in I peak position between **1** and **2**. The calculation yielded a predicted blue shift of 0.16 eV in going from butadiene to 2,4-hexadiene, in excellent agreement with the observed shift of 0.18 eV. This lends some confidence to the more exacting demands made on the MINDO program in the section on cis–trans isomerization. (It may be noted that the SPINDO parametrization of the INDO method[6] predicts a red shift in this case, and it appears that the MINDO program, while not yielding as good absolute orbital energies as SPINDO, may be preferable in assessing the perturbing effects of substituents on the high-lying occupied orbitals.)

Bond Migrations. The photodissociation spectra of the hexadienes shown in Figures 2–5, give clear evidence for the possibilities of bond shifts following electron impact ionization of the neutrals.

It is clear from Figure 5 that 1,5-hexadiene (**6**) does not rearrange appreciably to any conjugated structure, its spectrum being entirely characteristic of unconjugated olefin radical ions but wholly unlike conjugated diene spectra.[2b] The lack of photodissociation around 500 nm sets a limit on the possible extent of rearrangement of less than 1%. The spectrum is also unlike that of cyclohexene ion.

Comparison of Figure 3 with Figure 2, particularly the UV peaks, suggests that the 1,3 (**4**) and 2,4 (**1**) isomers retain distinct structures. While the differences in the spectra are modest, and a partial rearrangement of the order of 25% cannot be ruled out, it is quite clear that complete rearrangement does not take place. Since the **4** → **1** rearrangement seems an unlikely process in any event, it appears reasonable to conclude that no interconversion of these isomers occurs.

On the other hand, the 1,4 isomer (**5**) evidently rearranges into conjugation, as indicated by the close similarity of Figure 4 to Figure 2. The UV peaks are identical in shape and cross section, and the visible peaks are very similar. Judging from the PES spectra of 1,4 dienes,[9] the I transition in unrearranged **5** would lie far to the red, near 2500 nm, and its spectrum would be entirely unlike that of **1** or **4**, so that the appearance of Figure 4 is conclusive evidence that **5** rearranges into conjugation. The UV peak of **5** is much more similar to that of **1** than **4**, so that the more stable 2,4 isomer **1** is evidently the preponderant rearrangement product. It is tempting to match the maxima in the visible spectrum of Figure 4 to the three cis–trans isomers of **1** and say that the rearrangement yields **1a**–**c** in the approximate ratio 3:2:1. As is seen below, the position and spacing of the three visible-region maxima in Figure 4 are consistent with this suggestion. Judging both from the absence of photodissociation at wavelengths below 280 nm (where strong photodissociation is expected for simple olefins and unconjugated dienes) and from the identity of the cross section in Figures 2 and 4, the rearrangement **5** → **1** is complete upon ionization. The spectrum obtained for **5** remains the same over a wide range of pressures, trapping times, and ionizing voltages, and even under conditions allowing a number of ion–molecule collisions, there is no evidence of any ions retaining the unconjugated structure.

Cis–Trans Isomerization. As is clear in Figure 2, the visible peaks in the spectra obtained for the ions of the three cis–trans isomers of 2,4-hexadiene are definitely distinct. Before concluding that rotation about the double bonds does not occur, however, the possibility must be excluded that the differences arise not from structural differences in the ions but from differing internal energies, with the hot bands associated with larger internal energies shifting the absorption to longer wavelength. There are several lines of argument against the latter possibility. It could be argued that more internal energy would be deposited in the isomer with lower ionization potential; on the basis of the IPs from PES spectra,[9] this would suggest a wavelength order **1c** > **1a** > **1b**, instead of the observed under **1c** > **1b** > **1a**. Second, if the shift to long wavelength for **1c** is due to larger internal energy, it should be possible to shift the peak by collisional relaxation of the ion. However, there was no change in the spectrum of **1c** when the conditions were varied from 10^{-8} torr and 1-s trapping to 10^{-7} torr and 10-s trapping, which corresponds to a calculated number of ion–neutral collisions during the trapping period increasing from about 1 to 100. Figure 6 shows one such comparative pair of spectra which clearly show no tendency for the long-wavelength absorption to diminish with increasing numbers of collisions. Under these high-pressure, long trapping conditions, charge-transfer relaxation, nonreactive collisional relaxation, and IR radiative relaxation would be expected to be effective in reducing any substantial amount of internal energy of the ion.

Further evidence that the photodissociation results in fact reflect structure retention comes from molecular orbital calculations of the π-orbital separation. While, as indicated above, these MINDO/3 calculations should not be asked to give highly precise orbital spacings, it is reasonable to expect a good reflection of the small orbital perturbations corresponding to the different cis–trans configurations. The MINDO/3 result is an ordering of the π–π

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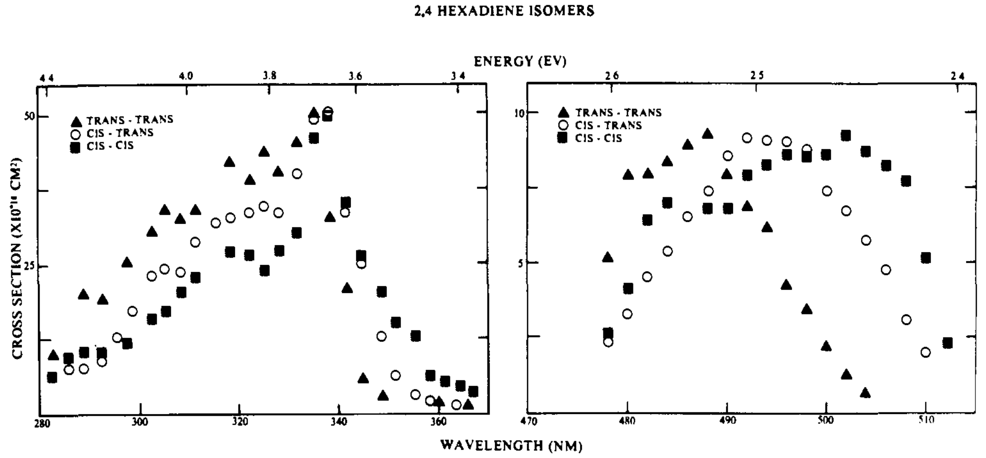

Figure 2. Laser-photodissociation spectrum in the visible region and monochromator spectrum at 6.6-nm resolution in the UV region of the three isomers of 2,4-hexadiene ion (**1a–c**).

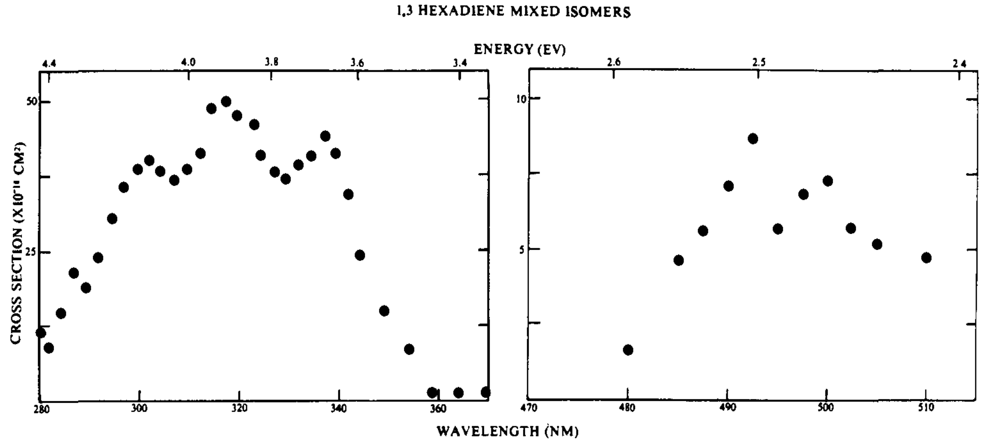

Figure 3. Laser spectrum in the visible and monochromator spectrum in the UV region of 1,3-hexadiene ion (**4**).

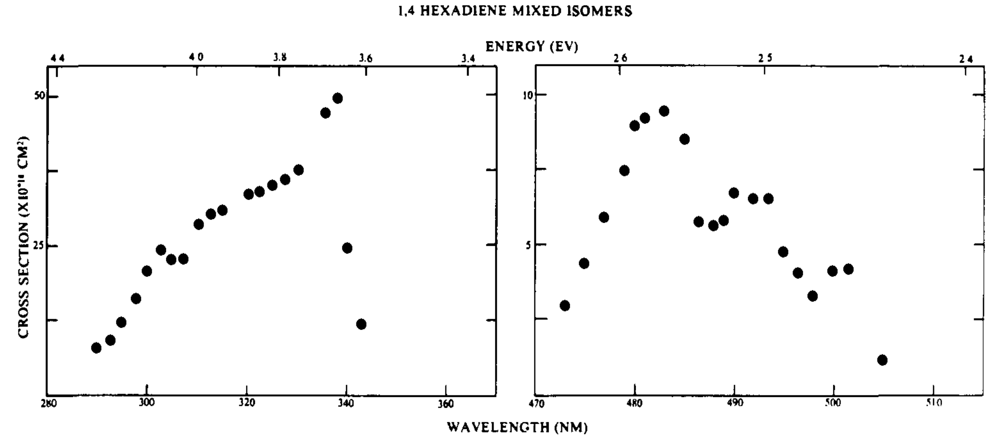

Figure 4. Laser spectrum in the visible and monochromator spectrum in the UV region of ions obtained from ionization of 1,4-hexadiene (**5**).

orbital separation for the three isomers of **1c** < **1b** < **1a**, with an interval of 0.03 eV between each neighboring pair. In Table I the three peak positions for the high-resolution laser spectra are given, along with the intervals from the molecular orbital calculations; both the experimental and theoretical results suggest that the π–π orbital separation increases by about 0.03 eV for each cis double bond in the molecule.

We conclude that the observed spectral differences between the three isomers of **1** do actually reflect distinct structures and that cis–trans interconversion is not complete on a time scale of seconds in this series of isomers. This can be compared with what has been found for other cis–trans isomerizations in unsaturated radical ions: the cis and trans isomers of 1-chloropropene ion were clearly shown from their vibrationally resolved photodissociation spectra to retain distinct structures.[10] The cis and trans isomers of 1,3,5-hexatriene ion give distinct fluorescence emissions,[11] indicating little interconversion on the fluorescence time scale (10^{-8} s), but on the ICR time scale of seconds, only the photodissociation spectrum of the cis isomer is observed,[12] possibly indicating rearrangement on this time scale.

The spectrum of 1,3-hexadiene ion (**4**) in Figure 3 not only shows clearly that rearrangement to the more stable **1** does not occur but also suggests retention of the two cis–trans isomer structures. Only a mixed-isomer spectrum of **4** was obtained, but

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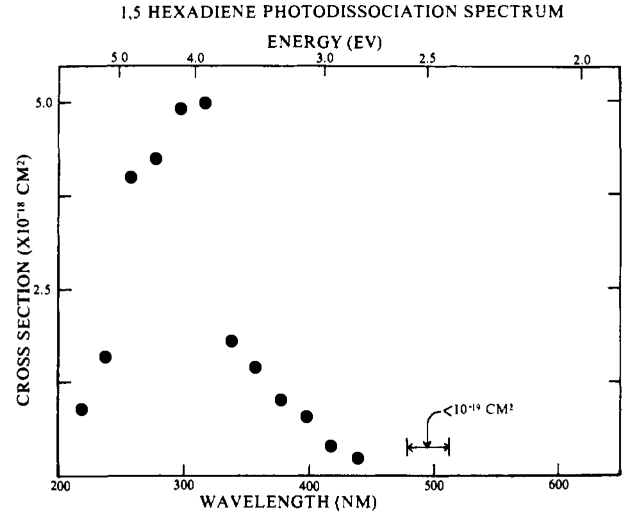

Figure 5. Monochromator spectrum at ~40-nm resolution for 1,5-hexadiene ion (**6**).

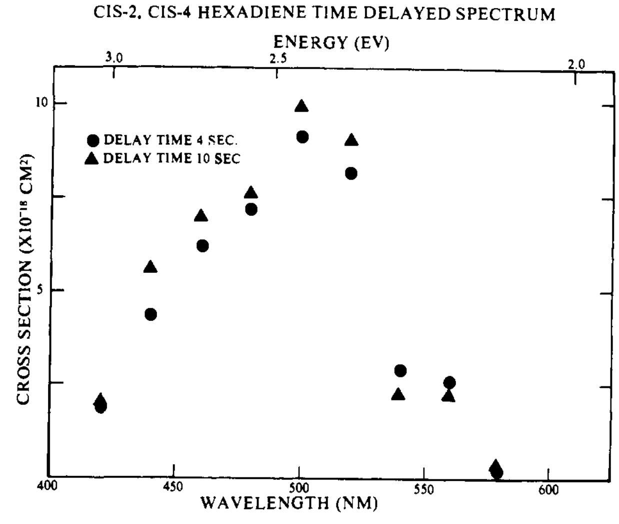

Figure 6. Interference-filter spectra of ion **1c**: (●) shows the spectrum at 4-s trapping time and 3×10^{-8} torr; (▲) shows the spectrum at 10-s trapping time and 10^{-7} torr.

Table I. Orbital Spacing for 2,4-Hexadiene Isomers

	spectral peak position, eV	diff, eV	theor, eV
trans–trans	2.47	0.03	0.03
cis–trans	2.50	0.04	0.03
cis–cis	2.54		

the visible spectrum in Figure 3 suggests two separate peaks. The separation of about 0.04 eV (8 nm) between these maxima is in accord with the shifts found for the 2,4 isomers, and it seems reasonable to take this spectrum as showing the presence of both cis–trans isomers.

Conclusions

The experimental results indicate that there is no rotation around the double bonds in the ionization of 2,4-hexadiene isomers. Each ion structure has a unique photodissociation spectrum, and spectral differences are in accord with the molecular orbital calculations. The spectral differences of the 2,4 isomers are greater in the visible region than those seen for the 1-chloropropene isomers,[10] and there are also differences, though smaller, in the UV region. It would be of interest to reexamine the two isomers of 2-butene[13] at a higher spectral resolution to see if the two spectra are really identical or if there is a shift too small to be seen at low resolution.

Where rearrangement occurred, in the case of 1,4-hexadiene, the 2,4-hexadiene structure was apparently formed. The double bond shift from 1,4 to 2,4 is similar to that seen in the rearrangement of allylbenzene to 1-phenylpropene[14] and most likely the mechanism of rearrangement involves a 1,3-hydrogen shift.[15]

There is no evidence of any conjugated ions formed from 1,5-hexadiene, which is consistent with results for the unconjugated phenylalkenes.[14] A double-bond shift of two positions has not been observed in any spectra except for 1,5-octadiene.[16] In that case, the amount of rearrangement has been estimated to be 30% and must occur as a result of the cyclic nature of the chain.

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Photodetachment of the Azide Anion in the Gas Phase. Electron Affinity of the Azide Radical

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Abstract: We report the formation of the azide anion, N_3^-, in the gas phase using azidotrimethylsilane as the source. The azide anion is formed as a product of a fast ion–molecule reaction between the trimethylsilylnitrene anion, $(CH_3)_3SiN^-$, and azidotrimethylsilane. A photodetachment threshold for N_3^- is obtained which can be equated with the adiabatic electron affinity of the azide radical, N_3, giving EA = 62.1 ± 2.8 kcal/mol.

Introduction

The azide anion, N_3^-, has been the subject of a number of chemical and theoretical studies. It is often employed in the synthesis of organic and inorganic azides, the importance of which is underscored by the volumes completely devoted to describing their chemistry.[1,2] The azide anion is a classical example of a