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Applications of the Equivalent Cores Approximation. The Determination of Proton Affinities and Isocyanide-to-Nitrile Isomerization Energies from Core Binding Energies

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Abstract: Core binding energies were determined for the following gas-phase molecules: CH_2CCH_2, CH_2CO, BH_3CO, HNCO, CH_3CN, CH_3NC, NH_2CN, *t*-BuNC, and C_6H_5NC. By use of the equivalent cores approximation, these data and data from the literature were used to calculate the proton affinities of N_2O, CO_2, HCCF, NCF, NH_2CN, CH_2N_2, HNCO, CH_2CO, HN_3, CH_3NC, and CH_3CN with an estimated accuracy of ±7 kcal mol^{-1}. By a similar method, the isocyanide-to-nitrile isomerization energies for CH_3NC, *t*-BuNC, and C_6H_5NC were calculated to be -30, -27 and -28 kcal mol^{-1}, respectively.

X-ray photoelectron spectroscopy has traditionally been used to deduce information about the electronic structures of molecules.[1,2] The measured core binding energies are usually interpreted in terms of atomic charge, potential, and electronic relaxation energy. In this paper we are concerned with another application of core binding energies, i.e., their use in the determination of thermodynamic data.

The approximation that valence electrons are affected by the ionization of a core electron essentially the same as they would be by the addition of a proton to the nucleus is called the *equivalent cores* approximation. The first use of this approximation in the prediction of chemical shifts of core binding energies was reported in 1970,[3] and since then the approximation has been widely applied in the systemization of core ionization data.[2-7] A method, based on the equivalent cores approximation, for obtaining the heats of formation of gaseous cations from core binding energies has been shown to have an accuracy, in favorable cases, of ±6 kcal/mol or better. This method employs a fundamental relationship involving the core binding energy of a molecule, the heat of formation of the molecule, and the heat of formation of the "equivalent cores" cation. In this research use the method to show that core binding energy data for a series of small isoelectronic molecules can be used to obtain not only heats of formation of gaseous cations but also absolute proton affinities and heats of isomerization. Although the accuracy of the method is perhaps too low to compete seriously with traditional methods for measuring such quantities, the method is valuable because it can give approximate values for species which cannot readily be studied by traditional methods.

Experimental

Gas-phase core binding energies were obtained by using a GCA/McPherson ESCA 36 spectrometer equipped with a magnesium X-ray anode. The Ne 1s, N_2 1s, and Ne 2s photolines were used as calibration standards. Samples were held at a temperature low enough to prevent sample decomposition yet warm enough to maintain a suitable sample pressure in the gas cell.[8] Further procedural details are available elsewhere.[9]

Table I. Recommended Values of Core Replacement Energies

atom X	core level for which E_B is required	Δ_X,[a] eV	uncertainity in Δ_X,[b] eV
C	B 1s	186.91[c]	0.20
N[e]	C 1s	284.90[d]	
N[f]	C 1s	283.68	0.21
O[e]	N 1s	399.63	0.29
O[f]	N 1s	399.04	0.24
F	O 1s	529.60	0.66

[a] Except for Δ_C, values are from ref 6. [b] Standard deviation in Δ_X, as calculated from the data of several molecule/ion pairs for which the required binding energies and heats of formation are known. See ref 5 and 6 for details. [c] Determined from data for BF_3 and CF_3^+, BCl_3 and CCl_3^+, BBr_3 and CBr_3^+, and BH_3CO and CH_3CO^+. [d] On the basis of data for CO and NO^+. [e] High nuclear e$^-$ density. [f] Low nuclear e$^-$ density.

Ketene was prepared[10] by continuously passing acetone vapor through a quartz tube heated to 700 °C. Argon served as the carrier gas. The crude product was repeatedly distilled through a -95 °C trap (to remove acetone) and caught in a -160 °C trap. Final sample purity was verified by infrared spectroscopy and vapor-pressure measurements[11] (358 torr at -63.5 °C).

For the preparation of isocyanic acid, the vapors of recrystallized cyanuric acid were passed through a quartz tube heated to 680 °C.[12] The crude product was purified by fractional condensation with use of -63.5 and -111.6 °C cold traps. The -111.6 °C fraction contained HNCO which was >98% pure. Its infrared spectrum[13] showed no signs of HCN or other likely impurities, and its vapor pressure at -45.2 °C was independent of the extent of sample vaporization.

Borane carbonyl was prepared[14] by the room-temperature reaction of B_2H_6 with CO at 50 atm of pressure. After 24 h the excess CO was pumped out through three -196 °C traps. Slow fractional condensation of the crude product from the -196 °C traps in a -160 °C trap yielded a sample of BH_3CO with a vapor pressure 25.4 torr at -112 °C (lit.[15] vapor pressure is 25.4 torr at -112 °C).

The isocyanides were prepared by standard methods.[16] The vapor pressure of the CH_3NC at 0 °C and the boiling points of $(CH_3)_3CNC$ and C_6H_5NC agreed with the literature values. Cyanamide (Sigma) was

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(8) Sample temperatures for XPS runs were as follows: CH_2CO, -78 °C; HNCO, -60 °C; BH_3CO, -130 °C; CH_3NC, 0 °C.

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sublimed prior to use. Its melting point was 45–46 °C (lit. mp 45–46 °C). Acetonitrile was freshly distilled from P_2O_5. Allene (Matheson) was used without further purification.

Equivalent Cores Method

A full discussion of this approximation has been presented elsewhere;[2-6] for the applications in this research it is only necessary to understand how the approximation is used to obtain the heats of formation of cations. The following general process, in which an atom X (of atomic number Z) in a gaseous cation is replaced by a core-ionized-atom Y (of atomic number $Z - 1$), is referred to as a "core replacement".

$$(\text{element Y})_{\text{std. state}} + MX^+ \rightarrow (\text{element X})_{\text{std. state}} + MY^{*+}$$

(The asterisk denotes a core vacancy.) The energy of this reaction is the "core replacement energy" and is represented by the symbol Δ_X. It has been established that the core replacement energy for a particular element is a constant, essentially independent of the ion, MX^+, containing the element.[5,6] Recommended values for some core replacement energies are given in Table I. It is important to note that the values of Δ_N and Δ_O are dependent on the electron density at the nucleus of the atom of the element in question, i.e., on whether or not the atom has a lone pair of electrons.[5] For example, the Δ_N value of 284.90 eV is appropriate for cations containing nitrogen atoms with lone pairs (e.g., NO^+, the equivalent cores cation of CO).

To illustrate the procedure, consider the data for the following two processes, which enable us to evaluate $\Delta H_f°(BH_3NO^+)$.

$$BH_3CO \rightarrow BH_3C^*O^+ + e^- \qquad \Delta E_1 = E_B(\text{C 1s}) \tag{1}$$

$$\begin{gathered} {}^1/_2N_2 + BH_3C^*O^+ \rightarrow BH_3NO^+ + C_{\text{graphite}} \\ \Delta E_2 = -\Delta_N \end{gathered} \tag{2}$$

The energy of eq 1 is simply the C 1s binding energy of BH_3CO. The energy of eq 2 is the negative of the "core replacement energy", Δ_N, and, according to the equivalent cores approximation, is a constant for all analogous reactions involving C 1s ionized molecules. Addition of eq 1 and eq 2 gives eq 3.

$$\begin{gathered} {}^1/_2N_2 + BH_3CO \rightarrow BH_3NO^+ + C_{\text{graphite}} + e^- \\ \Delta E_3 = E_B(\text{C 1s}) - \Delta_N \end{gathered} \tag{3}$$

The energy of eq 3 is equal to the difference in the heats of formation of BH_3NO^+ and BH_3CO, and we may write:

$$\Delta H_f°(BH_3NO^+) = E_B(\text{C 1s}) - \Delta_N + \Delta H_f°(BH_3CO)$$

Values for the three terms on the right side of the equation are given in Tables I, II, , and III, and using these data, we calculate a heat of formation of 262 kcal mol^{-1} for BH_3NO^+. Incidentally, this heat of formation shows that BH_3NO^+ is unstable with respect to B_2H_6 and NO^+ in the gas phase.

Core Binding Energies

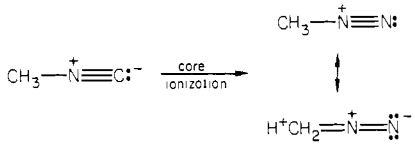
Core binding energies and full widths at half maximum (fwhm) for 7 isoelectronic molecules which have 16 valence electrons and 3 linear heavy atoms are reported in Table III. The assignments of several of the spectra require special comment.

Table II. Heats of Formation at 298 K (kcal mol^{-1})

CO_2	−94.05[a]	CH_3NC	41.3[e]
N_2O	19.6[a]	CH_3CN	17.6[e]
HNCO	−24.3[b]	BH_3CO	−26.6[a]
CH_2CO	−11.4[a]	CH_3CCH	44.3[a]
NCF	5.6[c]	HCCF	30 ± 15[f]
NH_2CN	31.0[d]	CH_2N_2	55 ± 5[g]
HN_3	70.3[a]	$CH_3N_2^+$	209.4[h]
		H^+	365.2[c]

[a] "NBS Tables of Chemical Thermodynamic Properties", *J. Phys. Chem. Ref. Data* 1982, *11*, Supplement No. 2. [b] "JANAF Thermochemical Tables", 1974 Supplement, *J. Phys. Chem. Ref. Data* 1974, *3*, 311. [c] Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* 1977, *6*, Supplement No. 1. [d] Isayan, G. A.; Buchnev, I. F.; Gasparyan, Z. M. *J. Appl. Chem. USSR* 1967, *40*, 230. Also see: "The Merck Index"; 9th ed.; Merck and Co., Inc.: Rahway, N. J., 1976, p 350. [e] Reference 32. [f] "JANAF Thermochemical Tables" *Natl. Stand. Ref. Data Ser.. Natl. Bur. Stand.* 1971, No. 37. [g] Laufer, A. H.; Okabe, H. *J. Am. Chem. Soc.* 1971, *93*, 4137. This value is consistent with the heat of formation of $CH_3N_2^+$ of 209 kcal/mol[22] and the proton affinity of CH_2N_2, ~212 kcal/mol.[27] [h] Reference 22.

The C 1s spectra of CH_3CN and CH_3NC have been deconvoluted into two peaks.[17,18] The CH_3NC spectrum is definitely asymmetric, with a shoulder on the low binding energy side of the band. We assign the lower of the deconvoluted peaks to the carbon atom of the NC group because both ab initio based atomic charges[19] and simple valence-bond formal charges show that the carbon atom is more negatively charged than the carbon atom of the CH_3 group. In addition, the greater half-width of the lower binding energy peak (presumably due to greater vibrational broadening[20,21]) is consistent with the large change in equilibrium geometry expected for the core ionization of the carbon atom of the NC group:



This assignment leads to a heat of formation for the $CH_3N_2^+$ ion at 214 kcal/mol, in fair agreement with the value reported by Foster, Williamson, and Beauchamp,[22] 209 kcal/mol. The binding energies of the deconvoluted CH_3CN peaks lead to $CH_3N_2^+$ heats of formation of 232 or 220 kcal/mol, depending on whether one assigns the lower E_B to the CH_3 or the CN carbon atom, respectively. We have chosen the latter assignment because it gives better agreement with the preceding data. Our assignments for CH_3NC and CH_3CN are in qualitative agreement with the ab initio predictions of Barber et al.[18]

Two peaks were discerned in the N 1s spectrum of NH_2CN. The cyano nitrogen atom is expected to have a lower binding energy (associated with a higher relaxation energy) than the amino nitrogen atom because of the π-donor character of the amino group:

$$H_2N{-}C{\equiv}N \leftrightarrow H_2N^+{=}C{=}N$$

Furthermore, the cyano nitrogen binding energies of CH_3CN and NH_2CN should be of similar magnitude; reversal of the assignment in Table III would make these cyano binding energies differ by 2 eV!

The C 1s binding energy found for BH_3CO is nearly identical with the value for free CO (296.19 eV).[23] However, we are convinced that we were not observing the spectrum of free CO, because the measured O 1s binding energy of BH_3CO differs from the value for free CO by almost 0.5 eV. The significance of the C 1s binding energy of BH_3CO will be discussed in a separate paper.[24]

Proton Affinities

The proton affinity of a base B is defined as ΔH of the reaction.

$$HB^+ \rightarrow H^+ + B$$

As we have shown above, the equivalent cores method can be

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Table III. Core Binding Energies and Full Widths at Half Maximum (eV)[a]

	CO or CN C 1s		other C 1s		O 1s or CN N 1s		B 1s or N 1s	
compd	E_B	fwhm	E_B	fwhm	E_B	fwhm	E_B	fwhm
H_2CCCH_2			290.84 (3)	1.36 (8)				
BH_3CO	296.18 (4)	1.25 (17)			542.05 (2)	1.50 (8)	195.10 (6)	1.73 (16)
CH_2CO	294.73 (3)	1.20 (12)	291.13 (3)	1.48 (10)	540.25 (3)	1.24 (12)		
HNCO	295.89 (6)	1.29 (21)			540.16 (5)	1.29 (12)	406.44 (4)	1.29 (15)
CH_3NC	292.37 (10)	1.38 (20)	293.35 (10)	1.30 (20)	406.67 (4)	1.40 (9)		
CH_3CN	292.44 (8)	1.20 (20)	292.98 (7)	1.20 (20)	405.60 (2)	1.33 (7)		
NH_2CN	293.46 (3)	1.32 (10)			405.40 (4)	1.23 (12)	407.65 (3)	1.22 (11)
$(CH_3)_3CNC$	291.83 (16)	1.55 (20)	291.06 (3)	1.20 (9)	406.05 (2)	1.13 (9)		
			292.84 (8)[b]	1.33 (14)				
C_6H_5NC	291.84 (8)	1.10 (20)	290.84 (3)	1.26 (8)	406.50 (2)	1.24 (6)		
			292.53 (6)[b]	1.35 (15)				

[a] Parenthesized values are twice the standard deviations of Gaussian–Lorentzian fits of the spectra. [b] Carbon atom directly bonded to the NC group.

Table IV. Proton Affinities

molecule for which proton affinity is determined[a]	molecule for which core binding energy is determined[b]	E_B, eV	proton affinity, kcal mol^{-1}	
			from E_B data	lit.
N*NO	HNC*O	295.89	127	
CO^*_2	HN*CO	406.44	138	129[c]
HC*CF	CH_2CO^*	540.25	161 ± 15[d]	
N*CF	HNCO*	540.16	151	
N^*H_2CN	C^*H_3CN	292.98	164	
C^*H_2NN	CH_3NC^*	292.37	207	212[e]
C^*H_2NN	CH_3C^*N	292.44	201	212[e]
HN*CO	C^*H_2CO	291.13	180	181[f]
HN*CO	NH_2CN^*	405.40	177	181[f]
C^*H_2CO	B^*H_3CO	195.10	193	197[g]
HN*NN	NH_2C^*N	293.46	179	
CH_3NC^*	CH_3C^*CH	291.0[h]	193	
CH_3CN^*	CH_3CC^*H	290.4[h]	183	187[c]

[a] Protonated atom indicated by asterisk. [b] Core-ionized atom indicated by asterisk. [c] Reference 26. [d] The large uncertainty is associated with the heat of formation of HCCF. [e] Reference 27. [f] Reference 28. [g] Reference 29. [h] Cavell, R. G. *J. Electron Spectrosc. Rel. Phenom.* 1975, *6*, 281.

employed in conjunction with core binding energies and the heats of formation of neutral molecules to determine the heats of formation of many cations of the type HB^+. Such information, together with the corresponding heats of formation of the bases, B, allows us to calculate the proton affinities. We have used this procedure and the data in Tables I–III to determine the proton affinities of the isoelectronic molecules in Table IV. The proton affinities of N_2O,[25] HCCF, NCF, NH_2CN, HN_3, and CH_3NC are the first values reported for these molecules. We believe these values are within ~7 kcal mol^{-1} of the true values, on the basis of the agreement between our results and the literature values of CO_2,[26] CH_2N_2,[27] HNCO,[28] CH_2CO,[29] and CH_3CN[30] (standard deviation, 7 kcal mol^{-1}). The internal consistency and accuracy of the equivalent cores method is illustrated by the agreement between our two *independently* determined values reported for HNCO.

The proton affinity of HNCO has been determined[28] by ion cyclotron resonance to be 181 kcal mol^{-1}. We have used the core binding energy data for CH_2CO and NH_2CN to obtain estimates of 180 and 177 kcal mol^{-1}, respectively, for PA(HNCO). These results support the suggestion of Wight and Beauchamp[28] that protonation of isocyanic acid occurs on the nitrogen atom.

Recently, photoionization mass spectrometry was used to measure[29] the appearance energies of a series of substituted methyl ketones and to obtain an accurate heat of formation of the acetyl cation CH_3CO^+. This value leads to an absolute proton affinity[29] of 197 kcal mol^{-1} for ketene. From the B 1s binding energy of BH_3CO, we determine the proton affinity of ketene to be 193 kcal mol^{-1}.

Obviously, one useful feature of estimating proton affinities by the equivalent cores method is that values for relatively unstable molecules like HN_3, CH_2N_2, and CNF (see Table IV) may be determined by measuring the binding energies of much more stable molecules.

Isocyanide Isomerization Energies

Core binding energies can be used in conjunction with the equivalent cores approximation to evaluate certain isomerization energies. In this study we apply this technique to the determination of the enthalpies associated with the isomerization of isocyanides to the corresponding nitriles. The method can be illustrated by considering the isomerization of methyl isocyanide to acetonitrile:[31]

$$CH_3NC \rightarrow CH_3CN \qquad \Delta E = \Delta E_{iso}$$

Core ionization of the isocyano carbon of CH_3NC and the cyano carbon of CH_3CN gives the same equivalent cores cation, namely CH_3NN^+. The processes involved in the evaluation of ΔE_{iso} are

$$CH_3NC \rightarrow CH_3NC^{*+} + e^- \qquad \Delta E = E_B(NC^*)$$

$$CH_3NC^{*+} \rightarrow CH_3NN^+ \qquad \Delta E = -\Delta_{N'}$$

$$CH_3C^*N^+ + e^- \rightarrow CH_3CN \qquad \Delta E = -E_B(C^*N)$$

$$CH_3NN^+ \rightarrow CH_3C^*N^+ \qquad \Delta E = \Delta_N$$

Addition of these equations gives an expression for ΔE_{iso} which involves only core binding energies and core replacement energies:

$$\Delta E_{iso} = E_B(NC^*) - \Delta_{N'} - E_B(C^*N) + \Delta_N$$

We have experimentally measured (Table III) $E_B(C^*N)$ to be 292.44 eV and $E_B(NC^*)$ to be 292.37 eV. The core replacement energies for CH_3NC^{*+} and $CH_3C^*N^+$ are 284.90 and 283.68 eV, respectively. The core replacement energy for the isocyanide is greater than that for the nitrile because the isocyanide carbon atom has a lone pair and is expected to have a greater nuclear electron density than the nitrile carbon atom.

From the data we determine the enthalpy of the CH_3NC-to-CH_3CN isomerization to be −30 kcal mol^{-1}. This result is in fair agreement with the thermochemical value of −23.70 ± 0.14 kcal mol^{-1} reported by Pritchard and co-workers.[32] It should be

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(25) The O–H dissociation energy of N_2OH^+ (calculated by using the literature PA of N_2O[26]) is comparable to values found for O-protonated cations; hence the literature PA of N_2O probably corresponds to O-protonation. Our PA(N_2O), calculated from the C 1s binding energy of HNCO, is 9 kcal/mol lower and corresponds to N-protonation.

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emphasized that our estimation of isocyanide isomerization energies does not require knowledge of any heats of formation.

The core binding energies of *tert*-butyl isocyanide, *tert*-butyl cyanide,[33] phenyl isocyanide, and benzonitrile[33] can be used to predict values for the corresponding isocyanide-to-cyanide isomerization enthalpies. The isomerization enthalpy is calculated to be -27 kcal mol^{-1} for *tert*-butyl isocyanide and -28 kcal mol^{-1} for phenyl isocyanide. Given the uncertainty in the core replacement energies (~ 5 kcal mol^{-1}), our results indicate that ΔE_{iso} for the isocyanide RNC is essentially independent of the R group.

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Registry No. CH_2CCH_2, 463-49-0; CH_2CO, 463-51-4; BH_3CO, 13205-44-2; HNCO, 75-13-8; CH_3CN, 75-05-8; NH_2CN, 420-04-2; CH_3NC, 593-75-9; *t*-BuNC, 7188-38-7; C_6H_5NC, 931-54-4; N_2O, 10024-97-2; CO_2, 124-38-9; HCCF, 2713-09-9; NCF, 1495-50-7; CH_2N_2, 334-88-3; HN_3, 7782-79-8.

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[33] To be consistent with our assignment of the CH_3CN spectrum, we assume that the carbon 1s binding energy of the CN carbon atom of a nitrile is always lower than that of the carbon atom directly bonded to the CN group. Thus we take 291.8 and 291.85 eV for the CN carbon atoms of $(CH_3)_3CN$[23] and C_6H_5CN,[34] respectively.

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Structure of the Intermediate Formed in the Reaction of the Styrene Radical Cation and Neutral Styrene

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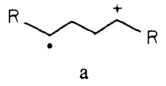
Abstract: The structure of the ion–molecule adduct produced in the gas-phase reaction of the styrene radical cation with neutral styrene has been probed by collisionally stabilizing the adduct and then acquiring its collision-activated decomposition (CAD) spectrum with a tandem mass spectrometer. The CAD spectrum of the adduct is nearly identical with the CAD spectra of the *cis*- and *trans*-diphenylcyclobutane radical cations and with the product ion resulting from a 1,4-regiospecific water elimination from the 1,4-diphenylbutan-1-ol radical cation; therefore the radical cations from all four precursors possess the same structure. The ΔH_f of this radical cation is shown to be ≤ 239 kcal/mol; therefore it cannot have the *trans*-1,2-diphenylcyclobutane structure ($\Delta H_f = 247$ kcal/mol). The results support a two-step mechanism for the [1 + 2] cycloaddition reaction.

Radical cations are thought to play important roles as intermediates in organic cycloaddition reactions.[1-11] The mechanism of the [2 + 1] cycloaddition reactions[12] occurring in solution has not been firmly established, but likely possibilities have been proposed, and they include a concerted process[9] and a two-step process involving an acyclic 1,4-radical cation[13] as an intermediate[6,7] (structure a). A long-bond cyclobutane radical cation



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has been postulated in a recent theoretical study, and it represents a third possible intermediate.[8] Evidence is presented in this report that points to formation of a stable 1,4-radical cation intermediate in the reaction of styrene radical cation and neutral styrene. Although similar structures have been proposed in the literature,[6-8,14] the experiments described herein constitute the first direct evidence of a 1,4-radical cation intermediate in the [2 + 1] cycloaddition of alkene radical cations and alkene neutrals.

Aryl-substituted ethylene radical cations, which are structurally similar to styrene, have been demonstrated to undergo reaction with their corresponding neutrals to produce diaryl-substituted cyclobutane products.[6-9] The gas-phase ion–molecule chemistry of styrene itself has been investigated by ICR spectrometry, and the C_6H_6 elimination mechanism observed for decomposing [styrene radical cation + styrene] adducts was interpreted to involve a 1-phenyltetralin radical cation intermediate.[4] However, this result only applies to an energized intermediate in a collision-free environment and may not pertain to adducts that have been collisionally stabilized.

Accordingly, the structures of the nondecomposing styrene ion–molecule adducts were examined in the present work. Ion–molecule adducts can be stabilized with a high-pressure chemical ionization source and then analyzed with a tandem mass spectrometer (MS/MS). The $C_{16}H_{16}$ radical cation adduct was separated from other ion products by using the first stage of mass analysis of a high-resolution tandem mass sepctrometer[15] and then collisionally activated prior to fragment ion mass analysis by the second stage. The structure of the adduct radical cation was

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[12] This notation refers to the number of electrons involved in the cycloaddition reaction. Thus, [2 + 1] is the number of electrons involved in a [2 + 2] carbon cycloaddition.

[13] The "1,4-radical cation" terminology refers to a structure in which the charge and radical sites are separated. The concept is similar to that of an "ion dipole" proposed recently by Holmes and Radom (see ref 18).

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