(lit.[37,39] mp 214–215 °C); IR (KBr) 3415 (m), 3280 (br), 2990 (w), 1725 (m), 1685 (s), 1645 (s), 1535 (m), 1400 (m), 1375 (w), 1350 (w), 1265 (m), 1230 (w), 1200 (m), 1150 (m), 1100 (m), 1065 (w), 1010 (w), 995 (m), 920 (s), 820 (m), 740 (m), 700 (br), 645 (w) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.60 (s, 6 H, CH$_3$), 8.03 (d, J = 17 Hz, vinyl H), 9.14 (br, 1 H, NH), 9.36 (br, 1 H, NH); ^{13}C NMR (DMSO-d_6) δ 26.4 (CH$_3$), 84.2 (C-5), 103.4 (C-2), 159.0 ($^1J_{CH}$ = 166.8 Hz, C-7, vinyl), 163.5 ($^3J_{CH}$ = 0.0 Hz, C-6, *E*-carbonyl), 163.8 ($^3J_{CH}$ = 9.6 Hz, C-4, *Z*-carbonyl); MS *m/z* 171 ([M$^{\bullet+}$], 52), 156 (33), 114 (66), 85 (10), 70 (28), 69 (100), 59 (56), 43 (42), 41 (17), 28 (10).

4-(Aminophenylmethylene)-3-methylisoxazol-5(4*H*)-one (11). The compound described by Betti[40a] as an amide and by Speroni[40b] as 4-benzoyl-5-imino-3-methylisoxazoline is in fact the title compound **11**.[41] 4-Benzylidene-3-methylisoxazol-5(4*H*)-one (40 g, 0.21 mol) was dissolved with warming in 2.3 L of ethanol, and the solution was saturated with ammonia gas for 30 min. Benzaldehyde (26 g, 0.24 mol) was added, and air was bubbled through the solution at reflux for 30 min, causing a color change from yellow-orange to brown. The presence of benzaldehyde is essential, mediating the air oxidation of the initial Michael addition product. The mixture was left in the open air at room temperature for 2 days, diluted with 300 mL of ethanol, and then stirred for 15 min. The light yellow to rose crystals thus formed were filtered off. The mother liquor was saturated once again with ammonia gas, and the above procedure was repeated four times. The combined crystals were recrystallized from ethanol, giving 5.2 g (12%); mp 262–263 °C dec (lit.[40a] mp 256–257 °C from AcOH); IR (KBr) 3270 (s), 3050 (s, br), 1705 (s), 1650 (s, br), 1560 (s, br), 1490 (s), 1415 (s, br), 1260 (m), 1125 (m), 1010 (s), 890 (m), 860 (s), 760 (s), 700 (s) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.41 (s, 3 H, CH$_3$), 7.43–7.66 (m, 5 H, aromatic), 9.26 (2 H, br, independent of concentration); ^{13}C NMR (DMSO-d_6) δ 13.7 (CH$_3$), 88.6 (C-4), 128.0 (*m*-phenyl), 128.5 (*o*-phenyl), 131.0 (*p*-phenyl), 133.1 (phenyl C-1′), 158.3 (C-3), 167.0 (exocyclic vinyl), 173.9 (C-5); MS, *m/z* 203 ([M + 1]$^+$, 10), 202 ([M$^{\bullet+}$], 100), 201 (5), 183 (8), 144 (21), 130 (5), 117 (5), 104 (17), 77 (12), 66 (11). Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.63; H, 4.89; N, 13.97.

Compound **11** sublimed without decomposition at 220–230 °C (4 × 10^{-5} Torr). Pyrolysis at 850 °C (4 × 10^{-5} Torr) gave benzyl cyanide in 76% yield, identified by IR, ^{1}H NMR, mass spectrometry, and chromatographic comparison with authentic material.

Acknowledgment. This research was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (1977–1985) and the Australian Research Grants Scheme (1986–1987). We are further indebted to H.-J. Wollweber, K.-P. Netsch, and U. Stutz for preparative assistance and to Professor M. Winnewisser for the use of his facilities.

---

(39) Bihlmayer, G. A.; Derflinger, G.; Derkosch, J.; Polansky, O. E. *Monatsh. Chem.* **1967**, *98*, 564.

(40) (a) Betti, M.; Alessandri, L. *Gazz. Chim. Ital.* **1915**, *45* (I), 462. (b) Speroni, G.; Giachetti, E. *Ibid.* **1953**, *83*, 192.

(41) Korte, F.; Störiko, K. *Chem. Ber.* **1961**, *94*, 1956–1965. Jaunin, R. *Helv. Chim. Acta* **1974**, *57*, 209.

Ion/Surface Collisions for Distinction of Isomeric $[C_6H_6]^{\bullet+}$ and $[C_6H_6]^{2+}$ Ions

M. J. Hayward, Md. A. Mabud, and R. G. Cooks*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907.

Received July 20, 1987

Abstract: Ion/surface collisions have been employed to dissociate $[C_6H_6]^{\bullet+}$ ions generated from benzene, 2,4-hexadiyne, and 1,5-hexadiyne. Experiments covering a range of collision energies (25–150 eV) demonstrate that the $[C_6H_6]^{\bullet+}$ ions retain distinct structures under the conditions of this experiment, which preferentially samples ions of low internal energy. Fragmentation efficiencies, as well as associative ion/surface reactions, provide additional means for differentiation of these isomers. It is also shown that high internal energy deposition is not necessarily desirable for isomeric ion distinction. The $[C_6H_6]^{2+}$ ions generated from benzene by electron impact have the same (cyclic) structure as singly ionized benzene.

A widely used method of distinguishing isomeric ions in the gas phase is collision-activated dissociation (CAD).[1-3] CAD is usually implemented in the kiloelectron volt range for high-energy collisions[4,5] or in the energy range below 100 eV.[6,7] The average internal energies deposited in ions upon high- and low-energy collisions can be surprisingly similar.[8] In cases where isomeric ions are particularly difficult to distinguish, it is often beneficial to obtain data under different experimental conditions, e.g., to monitor the dissociation of the ions as their internal energy is systematically varied. This can be achieved by varying the collision energy (energy-resolved mass spectrometry (ERMS))[9,10] or, less frequently, the scattering angle (angle-resolved mass spectrometry (ARMS)).[10,11]

Several authors[12-14] have expressed the view that access to ions of very high internal energy is often desirable in order to maximize differences in dissociation behavior. The use of solid surfaces as collision targets represents one method of achieving high internal energy.[15,16] We present results that show that structural distinction between isomeric $[C_6H_6]^{\bullet+}$ ion are readily made by surface-induced dissociation (SID). Results that demonstrate the value of SID in isomeric ion distinction have recently been reported for several other ions.[17,18]

---

(1) McLafferty, F. W. *Tandem Mass Spectrometry*; Wiley: New York, 1983.

(2) Cooks, R. G. *Collision Spectroscopy*; Cooks, R. G., Ed.; Plenum: New York, 1978.

(3) Levsen, K.; Schwartz, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 509.

(4) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: New York, 1973.

(5) Crow, F. W.; Tomer, K. B.; Gross, M. L. *Mass Spectrom. Rev.* **1983**, *2*, 417.

(6) Dawson, P. H. *Int. J. Mass Spectrom. Ion Phys.* **1970**, *2*, 45.

(7) Yost, R. A.; Fetterolf, D. D. *Mass Spectrom. Rev.* **1983**, *2*, 1.

(8) McLuckey, S. A.; Ouwerkerk, C. E. A.; Boerboom, A. J. H.; Kistermaker, P. G. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *59*, 85.

(9) Jiang, Y.-X.; Wood, K. V.; Cooks, R. G. *Org. Mass Spectrom.* **1986**, *21*, 101.

(10) Verma, S.; Ciupek, J. D.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *62*, 219.

(11) Hemberger, P. H.; Laramee, J. A.; Hubik, A. R.; Cooks, R. G. *J. Phys. Chem.* **1981**, *85*, 2335.

(12) Thorne, L. R.; Beauchamp, J. L. *Gas Phase Ion Chemistry*; Bower, M. T., Ed.; Academic: New York, 1984; Vol. 3.

(13) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: New York, 1973.

(14) Ast, R. *Advances in Mass Spectrometry, Part A*; Todd, J. F. J., Ed.; Wiley: New York, 1985; p 471.

(15) Mabud, Md. A.; DeKrey, M. J.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Proc.* **1985**, *67*, 285.

(16) DeKrey, M. J.; Kenttämaa, H. I.; Wysocki, V. H.; Cooks, R. G. *Org. Mass Spectrom.* **1986**, *21*, 193.

(17) Mabud, Md. A.; Ast, T.; Cooks, R. G. *Org. Mass Spectrom.* **1987**, *22*, 418.

(18) Mabud, Md. A.; Ast, T.; Verma, S.; Jiang, Y.-X.; Cooks, R. G. *J. Am. Chem. Soc.*, in press.

0002-7863/88/1510-1343$01.50/0

Benzene and its acyclic isomers began to receive attention over 20 years ago when the similarity of their electron ionization mass spectra was reported.[19] Since then, the $[C_6H_6]^{\bullet+}$ ion has received much attention, and the topic has been reviewed.[20] The ions $[C_6H_6]^{\bullet+}$ derived from benzene, 1,5-hexadiyne, and 2,4-hexadiyne yield virtually identical CAD daughter spectra at 8 keV,[21] with slightly more pronounced differences appearing at 3 keV.[22] It has been suggested that measurement of charge-exchange efficiencies of doubly charged ions (an exothermic process) as a function of collision gas pressure represents a useful supplementary structural probe, although results obtained for $[C_6H_6]^{2+}$ ions show very little difference between benzene and 1,5-hexadiyne.[23] On the other hand, charge stripping, a highly endothermic process that samples more uniformly the entire parent ion population, provides a clear distinction between ionized benzene and its acyclic isomers.[24] Measurement of kinetic energy releases, which is sometimes a powerful tool in characterizing fragmenting ions, shows that ionized benzene, 1,5-hexadiyne, and 2,4-hexdiyne behave identically.[25-27] Also, ion–molecule reactions under a variety of conditions were unsuccessful in distinguishing these two acyclic isomers from each other.[28] Finally, in a study in which ion/molecule reactions were combined with photodissociation, distinction of the $[C_6H_6]^{\bullet+}$ isomers was accomplished.[29] On the time scale of this experiment, the authors concluded that ionized 1,5-hexadiene isomerized extensively to the cyclic benzene structure. This conclusion has also been reached on the basis of photoion/photoelectron coincidence studies[25] and by trapped ion mass spectrometry.[30]

The structure of the doubly charged benzene molecular ion has also been the subject of interest for a long time. The metastable $[C_6H_6]^{2+}$ ion, which fragments in the field-free region of the mass spectrometer, has been ascribed the acyclic structure $[CH_3C_4CH_3]^{2+}$.[31-33] Gas-phase collisional activation, which preferentially examines internally excited ions,[34] produces similar CAD spectra for the $[C_6H_6]^{2+}$ and $[C_6H_6]^{\bullet+}$ ions derived from benzene; acyclic structures have therefore been postulated for both of these ions.[34] On the other hand, several investigators have proposed[35,36] that the stable ions have a cyclic structure.

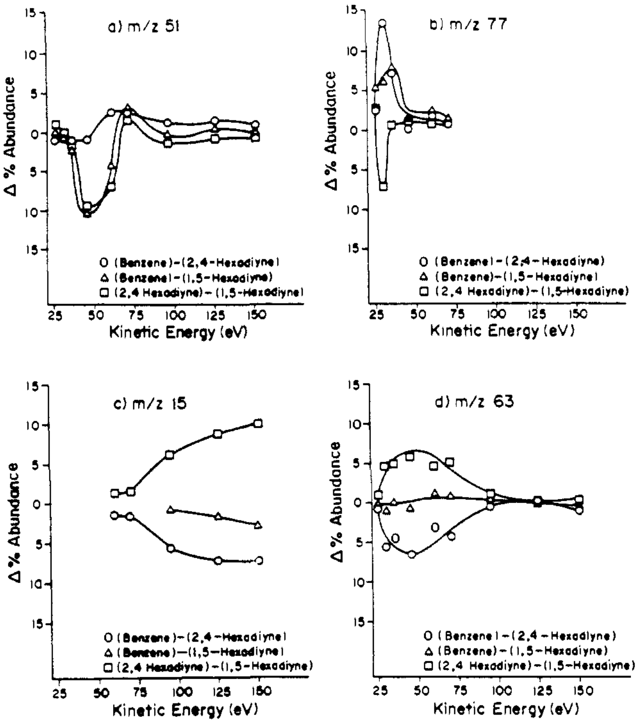

Figure 1. Difference spectra for $[C_6H_6]^{\bullet+}$ isomers: (a) *m/z* 51; (b) *m/z* 77; (c) *m/z* 15; (d) *m/z* 63.

Experimental Section

A hybrid BQ instrument was used to obtain SID daughter spectra. Its construction and operation have been described previously.[15,37] Ions were formed by 70-eV electron impact in a conventional EI source operated at approximately 150 °C. The EI source was held at a potential 21–150 V above ground in order to establish the desired collision energy. The ion beam was accelerated to 6 keV for magnetic mass analysis and then decelerated to ground potential prior to collision with the stainless steel surface. The current due to the primary ion beam striking the surface was monitored continuously during the experiment with a picoammeter. It was typically 0.1 nA. The lenses used for extraction of the emerging beam and its subsequent delivery to the mass-analysis quadrupole were tuned to maximize the total ion current reaching the final detector without significantly reducing the surface current. The angle of incidence was approximately 25 ± 3° with respect to the surface normal, and the emerging beam was extracted at a fixed scattering angle of 121 ± 3° with respect to the incident beam. Diffusion pumps were employed to maintain a constant pressure of 5×10^{-7} Torr in the region surrounding the surface. At this pressure and ambient temperature the surface is assumed to be covered with adsorbed gases. No attempts were made to clean the surface. The data obtained under these conditions were reproducible over a period of months. All isomeric species were examined one after another without adjustment of any instrumental parameters. The spectra are not corrected for ^{13}C isotropic contaminants; in the worst case, that of 1,5-hexadiyne, the $[^{13}CC_5H_5]^{\bullet+}$ isobar (*m/z* 78) contributes 2% to the $[C_6H_6]^{\bullet+}$ ion abundance.

Samples were obtained commercially and purified of noncondensable molecules by using a freeze–pump–thaw cycle.

Results

SID daughter spectra were obtained using a variety of kinetic energies between 25 and 150 eV for $[C_6H_6]^{\bullet+}$ ions generated from the precursors: benzene, 1,5-hexadiyne, and 2,4-hexadiyne. Energy-resolved mass spectra are conveniently presented as plots of normalized ion abundance versus ion kineic energy. However, this procedure has the disadvantage of producing very complicated plots that are difficult to compare, especially when there are large numbers of fragment ions as is often the case with SID daughter spectra. Energy-resolved spectra can be compared more easily by plotting difference spectra as suggested by Mason et al.[38] Difference spectra are simply plots of the differences in normalized ion abundance between pairs of isomers versus ion kinetic energy. Figure 1a illustrates these data for SID of $[C_6H_6]^{\bullet+}$ ions to yield *m/z* 51 (presumed due to $[C_4H_3]^+$ ions). These difference plots clearly distinguish 1,5-hexadiyne from the other two isomers.

---

(19) Momigny, J.; Brakier, M. L.; D'or, L. *Bull. Cl. Sci. Acad. R. Belg.* **1962**, *48*, 1002.

(20) Rosenstock, H. M.; Dannacher, J.; Liebman, J. F. *Radiat. Phys. Chem.* **1982**, *20*, 7.

(21) van Tilbory, M. W. E. M.; van Thuijl, J. *Org. Mass. Spectrom.* **1985**, *19*, 217.

(22) Borchers, F.; Levsen, K. *Org. Mass Spectrom.* **1975**, *10*, 584.

(23) Guilhaus, M.; Kingston, R. G.; Brenton, A. G.; Beynon, J. H. *Org. Mass Spectrom.* **1985**, *20*, 565.

(24) Cooks, R. G.; Beynon, J. H.; Litton, J. F. *Org. Mass Spectrom.* **1975**, *10*, 505.

(25) Baer, T.; Willett, G. D.; Smith, D.; Phillips, J. S. *J. Chem. Phys.* **1979**, *70*, 4076.

(26) Beynon, J. H.; Fontaine, A. E. *Chem. Commun.* **1986**, 177.

(27) Hertel, I.; Ottinger, C. *Z. Naturforsch., A* **1967**, *22*, 40.

(28) Gross, M. L.; Russell, D. H.; Aerni, R. J.; Bronczyk, S. A. *J. Am. Chem. Soc.* **1977**, *99*, 3603.

(29) Vander Hart, W. J.; DeKoning, L. J.; Nibbering, N. M. M.; Gross, M. L. *Int. J. Mass Spectrom. Ion Proc.* **1986**, *77*, 99.

(30) Lifshitz, C.; Gefen, S. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *35*, 31.

(31) Beynon, J. H.; Fontaine, A. E. *J. Chem. Soc., Chem. Commun.* **1966**, *62*, 97.

(32) Ast, T. *Adv. Mass Spectrom.* **1980**, *8A*, 555.

(33) Engel, R.; Halpern, D.; Funk, B.-A. *Org. Mass Spectrom.* **1973**, *7*, 177.

(34) Keough, T.; Ast, T.; Beynon, J. H.; Cooks, R. G. *Org. Mass Spectrom.* **1973**, *7*, 245.

(35) Kingston, R. G.; Guilhaus, M.; Brentron, A. G.; Beynon, A. H. *Org. Mass Spectrom.* **1985**, *20*, 406.

(36) Appling, J. R.; Burdick, G. W.; Hayward, M. J.; Abbey, L. E.; Moran, T. F. *J. Phys. Chem.* **1985**, *89*, 13.

(37) DeKrey, M. J. Ph.D. Thesis, Purdue University, 1985.

(38) Mason, R. S.; Jennings, K. R.; Verma, S.; Cooks, R. G. *Org. Mass Spectrom.* **1985**, *20*, 727.

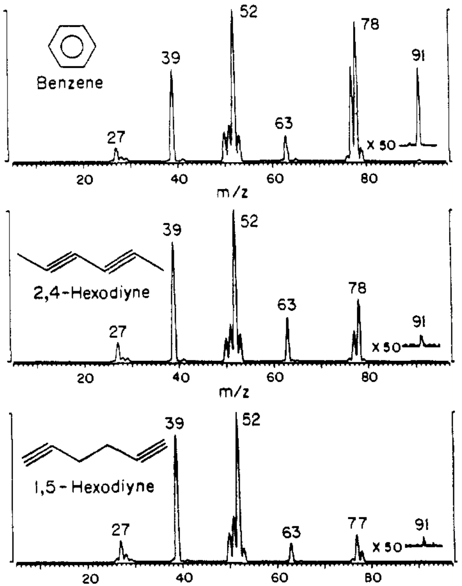

Figure 2. 35-eV SID spectra for $[C_6H_6]^{\bullet+}$ isomers: (a) benzene; (b) 2,4-hexadiyne; (c) 1,5-hexadiyne.

Relative abundances of the *m/z* 51 fragment ions are significantly greater for 1,5-hexadiyne than for its isomers at collision energies near 50 eV. Difference plots for *m/z* 77 fragment ions are shown in Figure 1b. The $[C_6H_6]^{\bullet+}$ ions derived from all three isomers can be distinguished by using this difference plot. The relative $[C_6H_5]^+$ abundances at low kinetic energy (<35 eV) occur in the order benzene > 1,5-hexadiyne > 2,4-hexadiyne.

Spectra 1c and 1d show the difference spectra for *m/z* 15 and 63 fragment ions. 2,4-Hexadiyne is easily distinguished from the other two isomers by using these plots. The foregoing results are consistent with expectations concerning structures of $[C_6H_6]^{\bullet+}$ on the basis of the structures of the neutral C_6H_6 molecules. The greater relative abundance of $[C_5H_3]^+$ (*m/z* 63) and $[CH_3]^+$ (*m/z* 15) for 2,4-hdexadiyne is consistent with the presence of methyl groups in the neutral molecule. These results are also consistent with the expectation that simple bond cleavages will be increasingly favored in ions with high internal energies.

While the energy-resolved spectra presented here provide the most distinctive structural characterization, it is also possible to differentiate the $[C_6H_6]^{\bullet+}$ isomers simply on the basis of the SID spectra recorded at modest collision energy. The data for 35 eV are shown in Figure 2. The spectra illustrate many of the features described above, such as a larger $[C_5H_3]^+$ abundance for 2,4-hexadiyne and larger $[C_6H_5]^+$ and $[C_4H_3]^+$ abundances for 1,5-hexadiyne. The spectra also show some additional features not seen in the difference plots. One case in point is the difference in fragmentation efficiencies, which provides an alternative way to distinguish these isomers. Fragmentation efficiency, the relative amount of dissociation products with respect to the amount of remaining incident ion, is generally not considered in distinguishing isomers by gas-phase collision activation, since all ions do not necessarily undergo collision. In contrast, with SID all ions *must* collide with the target before reaching the detector. Differing fragmentation efficiencies of the isomeric ions in SID can hence be considered when distinguishing isomeric ions. It is seen that the extent of fragmentation follows the order 1,5-hexadiyne > 2,4-hexadiyne > benzene. This is in agreement with what one would expect based on consideration of bond strengths in the neutral molecules.

Another interesting feature of the spectra shown in Figure 2 is the appearance of signals due to association reactions. Such reactive ion/surface collisions have been found in to be isomer specific in other cases.[18] The peaks at *m/z* 79 and 91 can be used to distinguish the benzene molecular ions from those of 1,5-hexadiyne and 2,4-hexadiyne. The *m/z* 79 peak is due to hydrogen atom abstraction from the surface by the incident $[C_6H_6]^{\bullet+}$ ions. $[M + H]^+$ ions have been observed in the SID daughter spectra of many organic ions[7,39] and are believed to involve organic adsorbates, probably hydrocarbons from the pumping system. The product ion of *m/z* 91 is presumed to arise from methylation of benzene ions followed by loss of H_2. A more detailed examination of these associative ion/surface reactions will be the subject of future studies, but their reproducible occurrence here allows their use in structural distinctions.

Table I. 150-eV SID Daughter Spectra of $[C_6H_6]^{\bullet+}$ Ions

m/z	benzene[a]	1,5-hexadiyne[a]	2,4-hexadiyne[a]
14	4	4	5
15	14	11	42
26	61	64	51
27	100	100	100
37	23	25	20
38	50	51	32
39	59	52	47
50	33	31	25
51	11	13	9

[a] Relative abundance given as percent of base peak.

Table II. SID Daughter Spectra of Doubly Charged $[C_6H_6]^{2+}$ Ion Recorded upon Collision with a Gas-Covered Stainless Steel Surface at 42 eV

		intensities (% base peak)		
m/z	benzene[a]	2,4-hexadiyne[a]	1,5-hexadiyne[a]	60 eV benzene[a,b]
50	28	45	20	36
51	100	100	100	100
52	55	45	10	54
53	24	15	10	17
63	12	15		16
65	3			1
77	17	8		14
78	5			1

[a] Only fragment ions above *m/z* 39 are reported. All abundances are given as percent of base peak. [b] The daughter spectrum of singly charged benzene molecular ion recorded at 60-eV collision energy is provided for comparison.

Table I represents the 150-eV SID daughter spectra of the $[C_6H_6]^{\bullet+}$ ions derived from the three precursors examined in this study. The only distinguishing feature at this relatively high collision energy is a large abundance (42%) of the methyl cation in the case of 2,4-hexadiyne-derived $[C_6H_6]^{\bullet+}$ ion. In the other two cases, the abundance of *m/z* 15 is much smaller (15%) at this collision energy. The formation of $[CH_3]^+$ ion via direct bond cleavage reactions during 150-eV collisions of ionized 2,4-hexadiyne with a neutral surface is consistent with large energy deposition in the fragmenting ions. Access to large energy deposition during polyatomic ion/surface collisions has been observed before.[16,40] Although one can distinguish the 2,4-hexadiyne-derived $[C_6H_6]^{\bullet+}$ ions from the other two based on the abundance of *m/z* 15, the major differences in the SID daughter spectra of the $[C_6H_6]^+$ ions observed at lower collision energies (e.g., 35-eV SID) are lost when the ions are highly excited. This indicates that maximization of internal energy in isomeric ions may not always be desirable in order to differentiate them. A similar result has also been encountered recently in a study of bicyclic hydrocarbons.[41]

An investigation of charge exchange of the doubly charged $[C_6H_6]^{2+}$ ions, derived from benzene, 1,5-hexadiyne, and 2,4-hexadiyne, at a stainless steel surface was also carried out. Table II shows the SID daughter spectra of doubly charged benzene, 1,5-hexadiyne, and 2,4-hexadiyne molecular ions, observed at an impact energy of 42 eV (accelerating voltage, 21 V). The parent $[C_6H_6]^{2+}$ ion was selected by adjusting the magnetic sector to pass *m/z* 39. This ion beam may also contain contributions from the singly charged ion of *m/z* 39, which forms in the ion source upon

---

(39) Ast, T.; Mabud, Md. A.; Cooks, R. G. *Org. Mass Spectrom.*, in press.

(40) Bier, M. E.; Amy, J. W.; Cooks, R. G.; Syka, J. E. P.; Ceja, P.; Stafford, G. *Int. J. Mass Spectrom. Ion Processes* **1987**, *77*, 31.

(41) Vainatalo, P.; Kenttämaa, H. I.; Mabud, Md. A.; O'Lear, J. R.; Cooks, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 3187.

dissociation of all the three precursors. However, daughter spectra taken after interaction of this mass-selected ion with the surface show peaks at mass-to-charge ratios of approximately twice its value, and these peaks can only be due to singly charged ions produced from the incident doubly charged $[C_6H_6]^{2+}$ ion. The fragment ions of mass-to-charge ratio 39 and below in the SID daughter spectra may originate from both the doubly charged $[C_6H_6]^{2+}$ ion and the 39+ ion, and hence only the ions above m/z 39 in the SID daughter spectra are considered in the discussion that follows.

Three points are noteworthy: (i) The charge-exchange process gives much more abundant product ions for benzene than for the acyclic isomers; products of charge exchange appear in the relative ratio of 15:2.5:1 for benzene, 2,4-hexadiyne, and 1,5-hexadiyne, respectively. (ii) The daughter spectra are different, although they show the presence of the same fragment ions. (iii) The benzene spectrum is quite similar to the SID daughter spectrum of the benzene molecular ion recorded at 60-eV collision energy. The difference in charge-exchange efficiency suggests that the $[C_6H_6]^{2+}$ ion derived from benzene is quite different from that of the acyclic isomers. This difference might be attributed to the presence of the cyclic structure, which has been proposed as the stable ion structure.[32,33] The similarity to the daughter spectrum of the singly charged benzene molecular ion, which is presumed to have a mixture of structures most of which are cyclic, further supports this interpretation.

Conclusion

It is evident that surface-induced reactions are a useful tool in the distinction of isomeric ions, including the $[C_6H_6]^{\bullet+}$ ions derived from benzene, 2,4-hexadiyne, and 1,5-hexadiyne. The salient findings of this study are as follows: (i) The three $[C_6H_6]^{\bullet+}$ isomeric ions are structurally distinct as is evident, for example, in difference spectra plotted for collision energies that range from 25 to 150 eV. While these results indicate that the three compounds yield distinct isomeric structures, partial isomerization is not excluded. The ions studied in this experiment, like those examined by charge stripping,[24] are stable to fragmentation. Furthermore, because of the large energy deposition,[16,40] they are likely to be drawn from deep in the potential energy well and to be stable also to isomerization. This is probably not the case for the stable ions examined by other methods which consequently do display isomerization, especially cyclization of ionized 1,5-hexadiyne.[25,29,30] (ii) Fragmentation efficiencies of the isomeric ions provide additional information that facilitates distinction between the isomers. (iii) The expected[16,40] high internal energy deposition in SID is evident. At 150 eV, large abundances of methyl cation in the daughter spectra of 2,4-hexadiyne molecular ion and small abundances in the case of benzene and 1,5-hexadiyne molecular ions are observed. It is significant that the only ion among the isomers which has terminal methyl groups is that derived from 2,4-hexadiyne. (iv) However, with the exception of $[CH_3]^+$ (m/z 15), the 150-eV spectra are nearly identical for all three isomers, thus demonstrating that maximization of energy deposition is not always desirable in structural differentiation. (v) Ion/surface reactions provide important additional information in distinguishing isomeric ions. On the basis of the abundances of the peak of m/z 91, presumably due to $CH_3^{\bullet}$ abstraction from the adsorbate by the incident $[C_6H_6]^{\bullet+}$ ions, followed by loss of H_2, benzene-derived $[C_6H_6]^{\bullet+}$ ions can be distinguished easily from the other isomers. (vi) Finally, charge exchange of $[C_6H_6]^{2+}$ from benzene at the surface yields a singly charged ion which has the (presumably cyclic) structure of singly ionized benzene.

Acknowledgment. We acknowledge the support of the National Science Foundation (Grant CHE 85-21634).

Registry No. Benzene, 71-43-2; benzene radical cation, 34504-50-2; benzene dication, 15157-23-0; 1,5-hexadiyne, 628-16-0; 1,5-hexadiyne radical cation, 61369-11-7; 2,4-hexadiyne, 2809-69-0; 2,4-hexadiyne radical cation, 61369-13-9.

Time-Resolved EPR Studies of the Properties of the Triplet-State Enols of Intramolecularly Hydrogen-Bonded *o*-Hydroxybenzaldehyde and Related Molecules

Seigo Yamauchi* and Noboru Hirota*

Contribution from the Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan. *Received July 22, 1987*

Abstract: Time-resolved EPR (TREPR) studies were made on the lowest excited triplet (T_1) states of the intramolecularly hydrogen-bonded molecules *o*-hydroxybenzaldehyde (OHBA), *o*-hydroxyacetophenone (OHAP), 7-hydroxy-1-indanone (7HIN), and salicylamide (SAM) in polar and nonpolar solvents and in single crystals of durene at 77 K. In almost all systems TREPR spectra were obtained. Emission and excitation spectra were also observed in the same systems to assist in the identification of the species involved. Very similar TREPR spectra were obtained for all the molecules studied and were assigned as those of $^3\pi\pi^*$ enols on the basis of the determined zero-field (zf) triplet sublevel schemes, polarization properties, and the emission and excitation characteristics. The triplet sublevel schemes and the $S_1 \rightarrow T_1$ intersystem crossing (isc) ratios were obtained by magnetophotoselection experiments in a methylcyclohexane glass and by the angular dependence of the TREPR signals in a single crystal of durene. Small zero-field splittings (zfs) and unusual isc ratios were obtained for these systems, which was interpreted by considering locations of the higher $^3n\pi^*$ and $^3\sigma\pi^*$ states. A mechanism of the enolization process is discussed by comparing the TREPR spectra of the neutral and anion forms of 7HIN. Different types of TREPR spectra were obtained for OHBA and 7HIN in a mixed solvent of ethanol and toluene (1:1) and were assigned as those of $^3\pi\pi^*$ keto forms.

Excited-state dynamics of intramolecularly hydrogen-bonded molecules is a topic of current interest, and various spectroscopic techniques have been employed to study this problem. The techniques used include picosecond spectroscopy,[1] two-step laser excitation (TSLE) spectroscopy,[2] transient absorption spectroscopy of a nanosecond time scale,[3] and high-resolution fluorescence spectroscopy.[4] Interesting details about dynamics and structures

---

(1) (a) Hou, S. Y.; Hetherington, W. M., III; Korenowski, G. M.; Eisenthal, K. B. *Chem. Phys. Lett.* **1979**, *68*, 282. (b) Smith, K. K.; Kaufmann, K. J.; *J. Phys. Chem.* **1978**, *82*, 2286. (c) Barbara, P. F.; Rentzepis, T. M.; Brus, L. E. *J. Am. Chem. Soc.* **1980**, *102*, 2786. (d) Kosower, E. M.; Huppert, D. *Annu. Rev. Phys. Chem.* **1986**, *37*, 127.

(2) (a) Itoh, M.; Fujiwara, Y. *J. Phys. Chem.* **1983**, *87*, 4558. (b) Itoh, M.; Yoshida, Y.; Takahashi, M. *J. Am. Chem. Soc.* **1985**, *107*, 4819. (c) Tokumura, K.; Watanabe, Y.; Itoh, M. *J. Phys. Chem.* **1986**, *90*, 2362.

(3) (a) Haag, R.; Wirz, J.; Wagner, P. J. *Helv. Chim. Acta* **1977**, *60*, 2595. (b) Scaiano, J. C. *Acc. Chem. Res.* **1982**, *15*, 252. (c) Mordzinski, A.; Grellmann, K. H. *J. Phys. Chem.* **1986**, *90*, 5503.

0002-7863/88/1510-1346$01.50/0