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Examination of Sputtered Ion Mechanisms Leading to the Formation of $C_7H_7^+$ during Surface Induced Dissociation (SID) Tandem Mass Spectrometry (MS/MS) of Benzene Molecular Cations

Mark J. Hayward,[†,‡] Frederick D. S. Park,[†] Lynn M. Phelan,[†]
Steven L. Bernasek,*[,†] Árpád Somogyi,[⊥,§] and Vicki H. Wysocki[⊥,§]

Contribution from the Department of Chemistry, Princeton University,
Princeton, New Jersey 08544, Agricultural Products Research Division, American Cyanamid
Company, Princeton, New Jersey 08544, and Department of Chemistry, Virginia Commonwealth
University, Richmond, Virginia

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Abstract: Recent work reported in the literature has shown new evidence of a sputtered ion mechanism for associative ion surface reactions occurring during surface induced dissociation (SID) tandem mass spectrometry (MS/MS). In the context of a sputtered ion mechanism, we have studied selected routes to the formation of $C_7H_7^+$ during the low-energy collision (ca. 30 eV) of benzene molecular ions with surfaces covered with a hydrocarbon overlayer. A key approach utilized in this work is the use of gas phase ion molecule chemistry to model reactive ion surface collisions. Benzene, $^2H_6$-labeled benzene, and $^{13}C_6$-labeled benzene have been examined by SID and collision activated dissociation (CAD). The CAD experiments have been used to investigate the fragmentation of hydrocarbon adducts of benzene and labeled benzene formed by methane and isobutane chemical ionization (CI) as models of those ions which may be formed via a sputtered ion mechanism during SID. In addition, the thermodynamics of many of the possible sputtered ion routes to the formation of $C_7H_7^+$ have been compared using experimental heats of formation as well as total energies and zero-point vibrational energies (ZPVE) obtained by *ab initio* (MP2 6-31G*//HF 6-31G*) calculations. While there are several seemingly viable sputtered ion routes to the formation of $C_7H_7^+$ during SID of benzene molecular ions, the combination of thermodynamic considerations and experimental results suggest that a likely sputtered ion route involves the reaction of neutralized benzene ions with $C_3H_5^+$ ions (sputtered from the hydrocarbon overlayer) followed by the loss of ethene.

Introduction

The interactions of gas-phase ions with surfaces is an area of growing interest for practical and fundamental reasons. Practical interest in ion surface interactions often involves their use in obtaining analytical information regarding either the ions or the surface. Ion surface collisions are a well-established method for surface analysis[1,2] (i.e. secondary ion mass spectrometry, SIMS). Ion surface collisions also are showing great promise for probing the structures of gas-phase ions via the technique of surface induced dissociation (SID) tandem mass spectrometry (MS/MS).[3,4] Successful use of ion surface interactions in these practical applications is leading to significant interest in improved understanding of the fundamentals of the related processes. However, currently little is known about the fundamentals of polyatomic ion surface interactions, especially at lower ion kinetic energies (20 to 100 eV) where the structures of ions are probed. In this paper, we describe a mechanistic model of ion surface reactions which should contribute to further understanding of the fundamentals of polyatomic ion surface collisions.

Much of what is known about the fundamentals of polyatomic ion surface collisions has been described in reviews of the subject.[3,5,6] In these reviews and elsewhere,[7−11] associative ion surface reactions are described, in which the incident ions react with hydrocarbon surface adsorbates to form ion surface reaction products. Originally, these reactions (hydrogen and alkyl additions) were explained as reactions with radical intermediates[4,5] (presumably sputtered by collision of the incident ions with the hydrocarbon surface overlayer). Later, a convincing description of a concerted mechanism was given.[10] However, recent work has yielded evidence suggesting that these associative ion surface reactions may proceed through a sputtered ion mechanism where the incident ions undergo charge exchange with surface species[6,8] to produce sputtered ions which then react

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* Author to whom correspondence should be addressed: at Princeton University.

[†] Princeton University.

[‡] American Cyanamid Company.

[⊥] Virginia Commonwealth University.

[§] Current Affiliation: Department of Chemistry, University of Arizona, Tucson, AZ.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

(1) Winograd, N. *Anal. Chem.* **1993**, *65*, 622A.

(2) Benninghoven, A.; Hagenhoff, B.; Nieuis, E. *Anal. Chem.* **1993**, *65*, 630A.

(3) Cooks, R. G.; Ast, T.; Mabud, Md. A. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 209.

(4) Dongre, A. R.; Somogyi, A.; Wysocki, V. H. *J. Mass Spectrom.* **1996**, *31*, 339.

(5) Ast, T.; Mabud, Md. A.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1988**, *82*, 131.

(6) Cooks, R. G.; Ast, T.; Pradeep, T.; Wysocki, V. H. *Acc. Chem. Res.* **1994**, *27*, 316.

(7) Hayward, M. J.; Mabud, Md. A.; Cooks, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 1343.

(8) Winger, B. E.; Julian, R. K., Jr.; Cooks, R. G.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1991**, *113*, 8967.

(9) Wysocki, V. H.; Jones, J. L.; Ding, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 8969.

(10) Somogyi, A.; Kane, T. E.; Ding, J. M.; Wysocki, V. H. *J. Am. Chem. Soc.* **1993**, *115*, 5275.

(11) Hayward, M. J.; Park, F. D. S.; Manzella, L. M.; Bernasek, S. L. *Int. J. Mass Spectrom. Ion Processes* **1995**, *148*, 25.

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with the neutralized incident ions to form ion surface reaction products.[11] These three ion surface reaction mechanisms, sputtered radical (i), concerted (ii), and sputtered ion (iii), can be depicted as follows:

$$M^{\bullet +} + SA \rightarrow M^{\bullet +} + S + A^{\bullet} \rightarrow MA^{+} + S \qquad \text{(i)}$$

$$M^{\bullet +} + SA \rightarrow [SA\cdots M]^{+} \rightarrow MA^{+} + S \qquad \text{(ii)}$$

$$M^{\bullet +} + SA \rightarrow M + S + A^{+} \rightarrow MA^{+} + S \qquad \text{(iii)}$$

where $M^{\bullet +}$ is the incident ion which collides with the bulk hydrocarbon covered surface S, A is an individual hydrocarbon group (hydrogen, alkyl, or alkenyl), and MA^{+} is the associative ion surface reaction product (which may undergo fragmentation after formation). Note that short-lived radical species may be left at the bulk surface S for any of the three mechanisms. Regardless of the mechanism, it is likely that these associative ion surface reactions proceed within the Eley−Rideal time frame (i.e. without equilibration at the surface).[12,13] Also, it is now generally accepted that these associative ion surface reactions often involve charge exchange with the surface[6] which is only plausible with the concerted mechanism (ii) and/or the sputtered ion mechanism (iii).

In this paper, thermodynamic and experimental data are examined in the context of the sputtered ion mechanism for a specific associative ion surface reaction, the alkylation of benzene molecular ions to form $C_7H_7^+$ at hydrocarbon surfaces (this reaction was first reported in 1988,[7] then again in 1988 with related work for other compounds,[5] with further study reported in 1991[9] and 1993[10]). Throughout much of the examination, gas-phase ion−molecule chemistry is used to model ion surface reactive collisions and test a wide range of possible sputtered ion reaction routes. The result of this examination is considerable evidence for a specific and perhaps unexpected sputtered ion mechanism leading to the formation $C_7H_7^+$ during the collision of benzene molecular ions with hydrocarbon covered surfaces.

Experimental Section

Instrumentation. Experiments were carried out using four different mass spectrometers (two SID and two CAD) at three locations. Data from each of the instruments were thoroughly compared for each experiment performed. In comparisons between instruments, virtually identical data were recorded. Measurements were repeated several times on different days in order to ensure the repeatability of the results. The instruments and conditions employed were as follows:

One SID instrument (located at Princeton University) was constructed from two Dycor® M2OOM quadrupole mass spectrometers both mounted in a custom 8 in. Conflat® flange. One quadrupole served as a differentially pumped mass selective ion source. The other quadrupole served as a scattered ion detector. The instrument was operated with the standard electron impact (EI) ion source, electron multiplier detector, and Dycor data system. An initial description of the instrument was reported previously.[11] The instrument was mounted in a small vacuum test chamber equipped with an 800 L/s Varian® diffusion pump where experiments were carried out at an approximate pressure of 10^{-8} Torr. The surface employed was a stainless steel rectangle that was polished with 600 grit sand paper and had a thin layer of Inland® 19 pump oil applied with a cotton swab. The surface was held at a position that is specular to the 108° scattering angle.

The other SID instrument (located at Virginia Commonwealth University) has been described in detail.[15] The instrument is constructed from two Extrel 4000 u quadrupoles. The surface is located at a position specular to the 90° scattering angle. The molecular ions of benzene were produced by 70 eV electron impact ionization. The pressure in the analyzer region was approximately 5×10^{-7} Torr. The self-assembled monolayer film was prepared by the spontaneous assembly of octadecanethiol onto vapor-deposited gold. The film was prepared by immersing the UV-cleaned (Boekel, Philadelphia, PA) gold substrate in 1 mM thiol solution for 24 h.[10]

The two CAD instruments utilized (located at American Cyanamid) were the Finnigan TSQ® 45 and the Finnigan MAT 95S. Both were equipped with the standard EI/CI ion source. For both instruments and both CI gases (methane and isobutane), CI gas was held at a pressure of 0.5 Torr in the ion sources. These CI gas pressures yielded reagent ions in the following diagnostic ratios: 3:6:1 for m/z 17, 29, and 41, respectively, for methane CI and 1:5 for m/z 43 and 57, respectively, for isobutane.[14] For both instruments, the collision gas pressure (helium for the MAT 95S and argon for the TSQ 45) was adjusted to attenuate the primary ion beam by 90%. CAD experiments with the TSQ 45 were carried out at 30 eV collision energy. CAD experiments with the MAT 95S were carried out in the first field free region at a collision energy of approximately 4.5 keV. No significant kinetic energy induced differences were observed between the CAD spectra recorded with the MAT 95S and the TSQ 45.

Reagents. Ultrahigh-purity helium, argon, methane, and isobutane were obtained from Matheson®. Methane and isobutane were introduced into the TSQ 45 and MAT 95S ion sources via the standard CI gas inlets. Helium (for the MAT 95S) and argon (for the TSQ 45) were introduced via the standard collision gas inlets. Benzene was obtained from Aldrich®. $^{2}H_6$-labeled benzene, and $^{13}C_6$-labeled benzene were obtained from Cambridge Isotope Laboratories. Samples were introduced through custom batch inlets. Benzene and labeled benzene were cycled through several freeze−pump−thaw cycles just prior to use. Samples were leaked into the ion source using a variable-leak valve.

***Ab Initio* and Thermodynamic Calculations.** *Ab initio* calculations were performed by using the program packages GAMESS[16] and GAUSSIAN 92.[17] Geometries were completely optimized at the Hartree−Fock level with the 6-31G* basis set (HF 6-31G*). Second analytical derivative calculations (zero-point vibrational energies, ZPVE) have also been carried out to check for real minima on the potential energy surface. More accurate total energies were obtained at the second-order Møller−Plesset perturbation level at the appropriate HF 6-31G* equilibrium geometries (MP2 6-31G*//HF 6-31G*) corrected by 0.9 × ZPVE values. Experimental heats of formation were taken from the literature.[18]

Results

A persuading factor in the consideration of sputtered radical[3,5] (i) and concerted[10] (ii) mechanisms for ion surface reactions at hydrocarbon surfaces has been that these mechanisms often require only observation of the ion surface reaction product and usually do not require observation of charged intermediates. After observing an abundant sputtered proton signal (typically 20 to 40% of all ions observed) during SID at hydrocarbon surfaces,[11] we began to reconsider the role of ion sputtering in associative ion surface reactions. The sputtering of protons in high yield is evidence of a sputtered ion mechanism (iii) for

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(12) Eley, D. D.; Rideal, E. K. *Nature* **1940**, *146*, 401.

(13) Williams, E. R.; Jones, G. C.; Fang, L.; Zare, R. N.; Garrison, B. J.; Brenner, D. W. *J. Am. Chem. Soc.* **1992**, *114*, 3207.

(14) Harrison, A. G. Chemical Ionization Mass Spectrometry; CRC Press: Boca Ratan, FL, 1983.

(15) Wysocki, V. H.; Ding, J.-M.; Jones, J. L.; Callahan, J. H.; King, F. L. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 27−32.

(16) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. *J. Comput. Chem.* **1993**, *14*, 1347−1363. Program Package GAMESS, Version: April, 1994.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Ragavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian 92/DFT, Revision F.4; Gaussian, Inc.: Pittsburg, PA, 1993.

(18) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

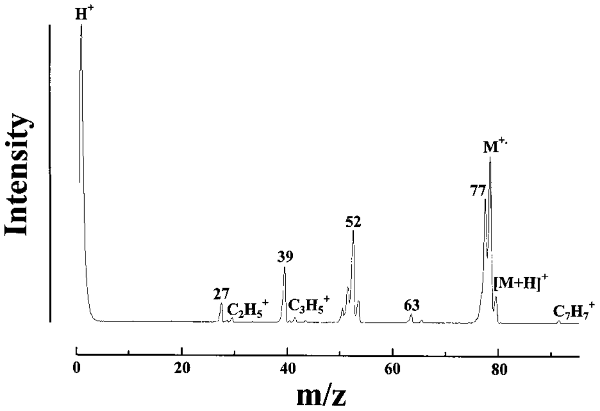

Figure 1. Surface induced dissociation spectrum of benzene molecular ions undergoing 30-eV collisions with a hydrocarbon (pump oil) covered surface. Experiments with $^2H_6$-labeled benzene and $^{13}C_6$-labeled benzene indicate that H^+, $C_2H_5^+$, $C_3H_5^+$, and $C_3H_7^+$ were sputtered from the surface. The labeled experiments also indicate that $[M + H]^+$ ions contain the entire benzene molecule and that $C_7H_7^+$ was formed with six carbons and five or six hydrogens from benzene. Spectra obtained with C_{18} alkanethiolate surfaces are similar and have been published.[10]

hydrogen addition reactions of ions colliding with hydrocarbon covered surfaces.[11] This evidence is illustrated in Figure 1 where a considerable excess of sputtered protons is clearly available for reaction with neutralized benzene molecular ions (approximately 90% of which are neutralized at or near the surface[3,6,10]) to form $[M + H]^+$ (*m/z* 79) ions.[11] It is conceivable that this mechanism (reaction of sputtered species with neutralized molecular ions) also may play an important role in other associative ion surface reactions such as alkylation at hydrocarbon surfaces.[11] As a starting point for further consideration of the plausibility of this mechanism for alkylation reactions, we have examined the alkylation of benzene molecular ions to form $C_7H_7^+$ (*m/z* 91, also shown in Figure 1) in the context of the sputtered ion mechanism (iii).

If the alkylation of benzene molecular ions to form $C_7H_7^+$ proceeds via a sputtered ion mechanism (the plausibility of other mechanisms has been described elsewhere[3,7,10]), then the intermediate benzene-sputtered ion complex also might be observed. Observation (at low abundance) of the $[C_6H_6 \cdots CH_3]^+$ (*m/z* 93) and $[C_6H_6 \cdots C_2H_5]^+$ (*m/z* 107) complexes during SID of benzene molecular ions has been described in the literature.[10] The abundance of the complexes and $C_7H_7^+$ product has been noted to vary with different chain lengths of hydrocarbons at the surface. The increase in abundance for the complexes and $C_7H_7^+$ product with decreasing hydrocarbon chain length is consistent with a sputtered ion mechanism because the sputtered ion yield also increases with decreasing chain length.[10] In an effort to observe the intermediate reaction complexes, additional experiments were carried out to carefully examine the *m/z* 95 to 200 range. Reaction complexes representing C_1 to C_4 addition can be observed when the resolution of the second mass analyzer is reduced to permit maximum sensitivity as shown in Figure 2. Based on these results, we have chosen to examine the possibility that the formation of $C_7H_7^+$ ions during SID of benzene molecular ions at hydrocarbon covered surfaces occurs via the reaction of neutralized benzene ions with the following potential sputtered ions: CH_3^+, $C_2H_3^+$, $C_2H_5^+$, $C_3H_5^+$, $C_3H_7^+$, and $C_4H_9^+$. Additional considerations in the selection of these ions as possible reaction intermediates includes observation of these sputtered ions reported in the literature[3,19] and our ability to provide the gas-phase model which utilizes the thermodynamic and experimental data that follow.

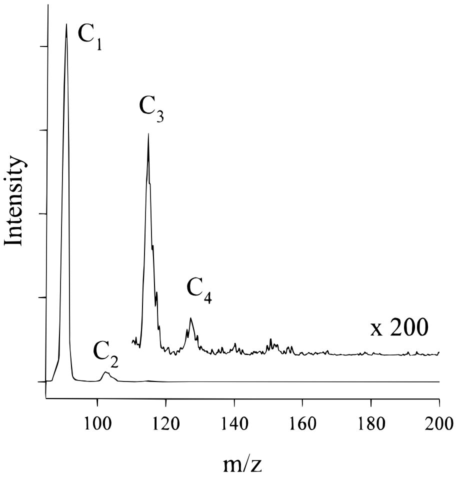

Figure 2. Surface induced dissociation spectrum of benzene molecular ions undergoing 30-eV collisions with a C_{18} alkanethiolate surface. The resolution was reduced in order to observe the C_1-C_4 intermediate reaction complexes with maximum sensitivity. Experiments with pump oil covered surfaces yield similar data.

Thermodynamic Considerations. When considering the thermodynamics of $C_7H_7^+$ formation via a sputtered ion mechanism during SID of benzene molecular ions at hydrocarbon surfaces, the following two key questions should be addressed: (1) how much energy is necessary to create the intermediate alkyl or alkenyl sputtered ions via charge exchange with benzene molecular ions, and (2) what are the energetics of the reaction between *neutralized* benzene and sputtered alkyl and/or alkenyl ions to form the observed $C_7H_7^+$ ions? In the text that follows, these questions are answered by modeling the reactions in the gas phase using available experimental heats of formation[18] and MP2 6-31G*//HF 6-31G* total energies corrected by ZPVE values.

(a) Formation of Sputtered Alkyl and Alkenyl Ions. As suggested previously,[3,5,6,8] positively charged molecular ions can be neutralized at the surface by an electron transfer from the surface to the projectile ion. If sufficient energy is available, the electron transfer also may be followed by sputtering of surface species. In the case of benzene colliding with a hydrocarbon surface, such a reaction might take place as follows:

$$C_6H_6^{\bullet+} + SA \rightarrow C_6H_6 + SA^+ \rightarrow C_6H_6 + S + A^+ \quad \text{(iv)}$$

Thermodynamic data (gas phase) related to reaction iv of benzene molecular ion with n-C_nH_{2n+2} hydrocarbons ($n = 2-11$) are provided in Table 1. The data in Table 1 for n-C_nH_{2n+2} species are intended to model either physisorbed hydrocarbons or the alkyl portion of alkanethiolate self-assembled monolayer (SAM) surfaces (both of which yield SID spectra similar to the one shown in Figure 1). Data are provided for $n = 2-11$ because $n = 18$ (SAM) and $n \geq 24$ (pump oil) data are not readily available in the literature. Columns B−G of Table 1 assume a gas-phase radical neutral species left after reaction (charge exchange and fragmentation). The direct charge exchange between ionized benzene and n-C_nH_{2n+2} (gas-phase data in column A, Table 1) is a slightly endothermic process where the endothermicity decreases with increasing chain length asymptotically approaching a small endothermic value. For example, the energy requirement for the reaction with n-C_8H_{18} is only about 0.6 eV (13.4 kcal/mol). However, charge exchange of ionized benzene and C_nH_{2n+2} may be favorable as the result of the excess internal energy of benzene ions formed

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(19) Kane, T. E.; Somogyi, A.; Wysocki, V. H. *Org. Mass Spectrom.* **1993**, *28*, 1665.

Table 1. Reaction Enthalpies[18] Related to Ions Sputtered from Saturated Hydrocarbon Surfaces via Collisions with Benzene Molecular Ions[a]

	A	B	C	D	E	F	G	H	I
n for C_nH_{2n+2}	charge exchange	CH_3^+	$C_2H_3^+$	$C_2H_5^+$	$C_3H_5^+$ (allyl)	$C_3H_7^+$	$C_4H_9^+$	ΔH_f for C_nH_{2n+2}	ΔH_f for C_nH_{2n}
2	52.3	102.3						−20.0	12.5
3	39.1	100.9	72.4	62.0				−25.0	4.8
4	29.8	102.1	70.8	60.4	77.6	62.6		−30.1	−0.1
5	25.6	100.9	71.6	61.2	75.6	60.6	59.4	−35.1	−5.1
6	20.6	100.9	70.6	60.2	76.6	61.6	57.6	−39.9	−10.0
7	15.4	100.7	70.6	60.0	75.4	60.4	58.4	−44.9	−15.0
8	13.4	101.7	70.6	60.0	74.4	59.4	57.4	−49.9	−20.0
9	11.1	*b*	71.1	60.7	75.1	60.1	57.1	−54.7	−24.9
10	9.2	*b*	*b*	*b*	76.2	61.2	57.2	−59.6	−29.8
11	9.6	*b*	*b*	*b*	*b*	*b*	59.6	−64.6	−34.7

[a] All values are gas phase (kcal/mol) and are calculated with reference to the enthalpy level of $C_6H_6^{\bullet+} + C_nH_{2n+2}$. Data were obtained from ref 18. Column A is the energy for charge exchange with benzene molecular ions. Columns B−G are the energies for charge exchange (column A) followed by fragmentation to yield the indicated ion. Columns H and I are the standard heats of formation for the indicated hydrocarbons. [b] The heats of formation of the complementer radical product were not available.

by electron impact (EI) ionization. The SID efficiency values reported for hydrocarbon surfaces (approximately 90% neutralization) reflect the relative ease of neutralization of benzene molecular ions at these surfaces.[3,6,10,11]

It is possible that the energy required to fragment the ionized alkyl surface chains (i.e. form sputtered ions) can be the result of the excess energy from EI ionization of benzene, and alternatively, the energy can be readily provided by 30-eV SID collision energy (via conversion of the translational energy of the incident ions[3,20−22]). The formation of the methyl cation (i.e., the cleavage of the C−C bond at the end of the ionized chain) requires significantly higher energy than the formation of any of the C_2−C_4 cations. For example, when using C_8H_{18} as a model compound, the endothermicity of these reactions relative to the benzene molecular ion and octane decreases in the order of [methyl]$^+$ (101.7 kcal/mol) $\gg$ [allyl]$^+$ (74.4 kcal/mol) > [ethenyl]$^+$ (70.6 kcal/mol) > [ethyl]$^+$ (60.0 kcal/mol) $\approx$ [propyl]$^+$ (59.4 kcal/mol) > [*n*-butyl]$^+$ (57.4 kcal/mol). This order is not sensitive to the chain length for the gas-phase model (columns B−G, Table 1) and, to some extent, is reflected by the relative intensities of sputtered ions. For example, the intensity of the sputtered [methyl]$^+$ cation is, in general, very low (if detected at all) in SID spectra. The peaks at *m*/*z* 29 ($C_2H_5^+$), 43 ($C_3H_7^+$), and 41 ($C_3H_5^+$) are the most commonly observed sputtered ions during SID[3,7,10,11] and Ar$^+$ sputtering[19] at hydrocarbon surfaces. The most intense sputtered ion (Figure 1) at *m*/*z* 41 ($C_3H_5^+$) is not well explained by these energies (column B−G, Table 1) given that the formation of the unsaturated $C_3H_5^+$ (*m*/*z* 41) allyl[23] cation from the saturated isopropyl cation (*m*/*z* 43) by H_2 loss is endothermic by 15 kcal/mol. The unsaturated $C_3H_5^+$ (*m*/*z* 41) might predominate, however, if formed from a structure other than isopropyl cation or if an initially formed $C_3H_7^+$ contains excess internal energy and further fragments.

Since the sputtered peak at *m*/*z* 41 is relatively intense (compared to the other sputtered hydrocarbons), there may be some additional thermodynamic consideration favoring the sputtering of $C_3H_5^+$. The reaction energies in columns B−G of Table 1 assume that a radical hydrocarbon is left at the surface. However, it seems unlikely that a continual buildup of long-lived hydrocarbon radicals is occurring at the surface. Given that alkylation at hydrocarbon surfaces during SID is generally only observed for incident radical cations (as opposed to even-electron species),[3,5,6] the eventual fate of those radicals may be a driving force for product ion formation in the hydrocarbon sputtering reactions. One possible explanation for the larger abundance of sputtered $C_3H_5^+$ is that the radicals left over from reaction iv combine to produce the more stable hydrocarbon species. In the simplest case, the combination of radicals at the surface might involve mobile H atoms which presumably are mobile enough to combine and form H_2 as depicted in the following reactions:

$$C_nH_{2n+2}^{\bullet+} \rightarrow C_xH_{2x-1} + C_{n-x}H_{2(n-x)+2} + {}^1/_2H_2 \qquad \text{(v)}$$

$$C_nH_{2n+2}^{\bullet+} \rightarrow C_xH_{2x+1}^{\ +} + C_{n-x}H_{2(n-x)} + {}^1/_2H_2 \qquad \text{(vi)}$$

The thermodynamics related to this possibility are illustrated in the trends of gas-phase heats of formation for alkanes versus alkenes in columns H and I of Table 1. While it is 10−15 kcal/mol more favorable to form alkyl versus alkenyl sputtered ions (reaction iv, energies given in Table 1 columns B−G), it is approximately 30 kcal/mol more favorable (difference between columns H and I in Table 1, regardless of chain length) to leave (after fragmentation, i.e. sputtering) a stable neutral alkane rather than an alkene (assuming that the other reaction product is H_2). Assuming that reasonable (stable) end products are formed at the surface via hydrogen loss or transfer (i.e. low probability reaction that significant numbers of long-lived radicals reside at the surface), alkenyl ion sputtering (reaction v) is potentially some 15−20 kcal/mol more favorable than alkyl ion sputtering (reaction vi) thereby providing a possible rationale for the thermodynamic driving force leading to the most abundant sputtered hydrocarbon, $C_3H_5^+$, observed in SID spectra at hydrocarbon surfaces. It should be noted that other more complicated processes, including migration of surface hydrocarbons, other reactions of the surface hydrocarbons with the incident ions, and/or contamination of the surface by residual gases in the high vacuum system, may also contribute to the reactions which eventually stabilize radical species at the surface.

(b) Reaction of Neutralized Benzene with Alkyl and Alkenyl Ions. Assuming the C_1−C_4 sputtered ions considered here are present in the vicinity of the surface, it is reasonable to also assume that they can react with neutralized benzene since approximately 90%[3,6,10,11] of the incident benzene ions are neutralized at the surface. Table 2 provides some energies related to these reactions. The energetics of the reactions of neutral benzene with CH_3^+, $C_2H_3^+$, $C_2H_5^+$, $C_3H_5^+$, $C_3H_7^+$, and $C_4H_9^+$ in the formation of the corresponding ipso-adducts is predicted to be significantly *exothermic* by MP2 6-31G*//HF

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

(21) Burroughs, J. A.; Wainhaus, S. B.; Hanley, L. *J. Phys. Chem.* **1994**, *98*, 10913.

(22) Burroughs, J. A.; Wainhaus, S. B.; Hanley, L. *J. Phys. Chem.* **1995**, *103*, 6706.

(23) Different $C_3H_5^+$ isomers also may exist and/or be formed during the sputtering process. In this work, we only considered the most stable isomer, the allyl cation; see, e.g.: Aue, D. H.; Davidson, W. R.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 6700.

Table 2. Relative Energies for the Formation of Ipso Adducts, $C_6H_7^+$, and $C_7H_7^+$ via the Reaction of Neutral Benzene with Potential Sputtered Hydrocarbon Cations[a]

R^+ reactant ion	X^b (ipso adduct)	Y^c ($C_6H_7^+$)	Z^d ($C_7H_7^+$)
CH_3^+	−81.3	15.9	−78.1
$C_2H_3^+$	−66.3	−27.3	+10.2
$C_2H_5^+$	−49.8	−18.9	−50.3
$C_3H_5^+$ (allyl)	−28.3	3.8	−30.3
$C_3H_7^+$	−34.0	−22.0	−47.9
$C_4H_9^+$	−32.3	−17.7	−43.5

[a] All values are gas phase in kcal/mol. [b] X represents the MP2 6-31G*//HF 6-31G* relative energy (corrected with 0.9 × ZPVE) for the formation of the ipso adduct from neutral benzene and the indicated alkyl or alkenyl ion (R^+). For $C_4H_9^+$, calculations were carried out at a lower level (HF 6-31G*//HF 6-31G*). [c] Y represents the following heats of reactions: $C_6H_6 + R^+ \rightarrow C_6H_7^+ +$ the remaining neutral (CH_2, C_2H_2, C_2H_4, C_3H_4, C_3H_6, and C_4H_8 in the above order). In these calculations, gas phase experimental heats of formation[18] were used. [d] Z represents the following heats of reactions: $C_6H_6 + R^+ \rightarrow C_7H_7^+$ (tropylium) + the remaining neutral (H_2, CH_2, CH_4, C_2H_4, C_2H_6, and C_3H_8 in the above order). In these calculations, gas phase experimental heats of formation[18] were used.

6-31G* calculations with the addition of methyl cation to neutral benzene being the most preferred reaction energetically (see Table 2, column X). Although the addition of propyl cation is predicted to be more exothermic than the allyl addition, the allyl cation can react with either end carbon, which can make the formation of the allyl adduct more favored entropically. Based on experimental heats of formation, the formation of $C_7H_7^+$ (tropylium) ions from neutral benzene and alkyl or alkenyl cations is also predicted to be significantly exothermic in all but one case, $C_2H_3^+$ (see Table 2, column Z). Inherently, all of these reactions could be gas-phase reactions similar to those occurring under chemical ionization (CI) conditions. Therefore, data for the competing reaction, proton transfer (ordinary CI), are provided in column Y of Table 2. Note that in four ($C_2H_3^+$, $C_2H_5^+$, $C_3H_7^+$, and $C_4H_9^+$) of the six routes considered, proton transfer to form $C_6H_7^+$ (an entropically favorable process) is exothermic and can readily compete with $C_7H_7^+$ formation.

Experimental Considerations. The key to considering sputtered CH_3^+, $C_2H_3^+$, $C_2H_5^+$, $C_3H_5^+$, $C_3H_7^+$, and $C_4H_9^+$ ions as intermediates to the formation of $C_7H_7^+$ during SID of benzene molecular ions lies in using a suitable model to experimentally test each of these possibilities. For this set of intermediates, the possibilities were readily tested ***experimentally*** in a gas-phase model using methane and isobutane chemical ionization (CI) of benzene. Figure 3 shows the methane CI and isobutane CI mass spectra for benzene. Clearly, $C_7H_7^+$ is a major product observed in both CI spectra. Furthermore, stable adducts of CH_3^+, $C_2H_3^+$, $C_2H_5^+$, $C_3H_5^+$, $C_3H_7^+$, and $C_4H_9^+$ ions with benzene are also observed as would be predicted from the thermodynamic data (Table 2, column X). Experiments with $^2H_6$-labeled benzene and $^{13}C_6$-labeled benzene showed that each of these adducts contained the entire labeled benzene molecule. In addition, the labeled benzene CI experiments showed that $C_7H_7^+$ was formed with six carbons and five or six hydrogens from benzene, thereby suggesting that $C_7H_7^+$ ions produced by CI were formed via a similar mechanism to those observed during SID of benzene.[9,10] These results indicate that CI of benzene probably is a suitable experimental model for comparison with ion surface interactions of benzene at hydrocarbon surfaces and that at least one of the intermediates being considered is an excellent candidate for the intermediate in the sputtered ion mechanism leading to $C_7H_7^+$ formed during SID of benzene.

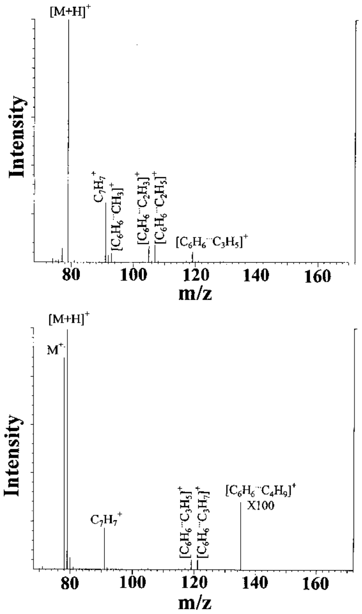

Figure 3. Methane (top) and isobutane (bottom) mass spectra showing C_1-C_4 addition. Experiments with $^2H_6$-labeled benzene and $^{13}C_6$-labeled benzene indicate that the adducts of CH_3^+, $C_2H_3^+$, $C_2H_5^+$, $C_3H_5^+$, $C_3H_7^+$, and $C_4H_9^+$ ions with benzene contain the entire benzene molecule. In addition, the labeled benzene CI experiments showed that $C_7H_7^+$ was formed with six carbons and five or six hydrogens from benzene as is the case with ion surface reactions.

Table 3. Adducts Observed during Chemical Ionization (CI) of Benzene and the Major Collision Activated Dissociation (CAD) Fragments of These Adducts

methane CI adducts	isobutane CI adducts	major CAD fragments[a]
$[C_6H_6\cdots CH_3]^+$ [b]		$C_7H_7^+$
$[C_6H_6\cdots C_2H_3]^+$	$[C_6H_6\cdots C_2H_3]^+$	$C_8H_7^+$, $C_6H_7^+$
$[C_6H_6\cdots C_2H_5]^+$		$C_6H_7^+$, $C_2H_5^+$
$[C_6H_6\cdots C_3H_5]^+$	$[C_6H_6\cdots C_3H_5]^+$	$C_7H_7^+$, $C_3H_5^+$
$[C_6H_6\cdots C_3H_7]^+$	$[C_6H_6\cdots C_3H_7]^+$	$C_6H_7^+$, $C_3H_7^+$
$[C_6H_6\cdots C_4H_9]^+$	$C_6H_7^+$, $C_4H_9^+$, $C_6H_6^{\bullet+}$	

[a] In descending order of abundance. Only fragments with relative abundances greater than 2% are given. [b] $[C^6H^6\cdots CH^3]^+$ was observed to be very stable with a fragmentation efficiency that is at least one order of magnitude lower than the other adducts.

In order to further test the possible sputtered ion routes to $C_7H_7^+$, collision activated dissociation (CAD) experiments were performed to explore the fragmentation pathways of the CI adducts of CH_3^+, $C_2H_3^+$, $C_2H_5^+$, $C_3H_5^+$, $C_3H_7^+$, and $C_4H_9^+$ ions with benzene. Table 3 summarizes the results of these experiments. While almost all of the possible fragments (including $C_7H_7^+$) can be observed at extremely low levels (<2%) in the CAD spectra for each intermediate being considered (except $[C_6H_6\cdots CH_3]^+$), the major fragmentation pathways are very distinct. In the case of $[C_6H_6\cdots CH_3]^+$, the adduct is very stable (i.e. has a low CAD fragmentation efficiency) and forms only the $C_7H_7^+$ ion in low yield. Only two of the adducts, $[C_6H_6\cdots CH_3]^+$ and $[C_6H_6\cdots C_3H_5]^+$, have major fragmentation pathways leading to $C_7H_7^+$. The CAD spectra agree well with the thermodynamic data (Table 2). In each case where $C_6H_7^+$ formation is exothermic, this product is favored, presumably as the result of having a lower activation energy than $C_7H_7^+$ formation which can have extensive rearrangement requirements. Proton transfer from CH_3^+ and/or $C_3H_5^+$ to benzene is endothermic for $C_6H_7^+$ formation and hence the alternative exothermic route to $C_7H_7^+$ becomes the primary reaction channel. As observed with CI and SID, CAD experiments with $^2H_6$-labeled benzene and $^{13}C_6$-labeled benzene showed that $C_7H_7^+$ was formed with six carbons and five or six hydrogens from benzene. These results suggest that $[C_6H_6\cdots CH_3]^+$ and $[C_6H_6\cdots C_3H_5]^+$

are candidates for intermediates leading to $C_7H_7^+$ formed during SID of benzene ions, and that the adducts of $C_2H_3^+$, $C_2H_5^+$, $C_3H_7^+$, and $C_4H_9^+$ ions with benzene are not likely $C_7H_7^+$ intermediates.

The primary sputtered ion mechanism leading to $C_7H_7^+$ formed during SID of benzene ions can be narrowed down to a single pathway by reexamining the data accumulated in this paper. First, the low fragmentation efficiency in the CAD spectra for $[C_6H_6\cdots CH_3]^+$ relative to $[C_6H_6\cdots C_3H_5]^+$ makes it less likely that $C_7H_7^+$ is formed from $[C_6H_6\cdots CH_3]^+$ in CI or SID. Second, in the CI spectra (Figure 3), only methane CI yields significant amounts of CH_3^+ and $[C_6H_6\cdots CH_3]^+$, while *both* methane and isobutane CI have the substantial production of $C_3H_5^+$, $[C_6H_6\cdots C_3H_5]^+$, and the $C_7H_7^+$ product ion in common. This suggests that $C_7H_7^+$ may be produced via $[C_6H_6\cdots C_3H_5]^+$ in the CI experiments. Third, in the SID spectra, observation of an excess of the sputtered ions which react with the neutralized benzene would be expected to be observed[11] as is the case with the protonation of benzene occurring in the presence of an excess of sputtered protons (Figure 1). Sputtered CH_3^+ ions are not observed[3,7,10] for 30-eV collision conditions (also see Figure 1), while sputtered $C_3H_5^+$ ions are seen in a wide variety of SID spectra[3,7,10,19] including those of benzene (Figure 1). Finally, all of these results are entirely consistent with highly endothermic nature of CH_3^+ formation relative to $C_3H_5^+$ (Table 1). Based on these results, we assert that a likely sputtered ion route to $C_7H_7^+$ formation in the SID spectra of benzene ions colliding with hydrocarbon surfaces is the following thermodynamically favorable reaction scheme:

$$C_6H_6^{\bullet +} + \text{hydrocarbon surface overlayer} \rightarrow C_6H_6 + C_3H_5^+ \rightarrow C_7H_7^+ + C_2H_4$$

Conclusions

While convincingly demonstrating the likelihood of a sputtered ion mechanism, the results presented here have not specifically excluded the possibility of other mechanisms leading to the formation of $C_7H_7^+$ during SID of benzene molecular ions (particularly sputtered radical[3,5] (i) and concerted routes[10] (ii)). Thus far, alternative mechanisms (i or ii) have been difficult to thoroughly demonstrate with experimental evidence because these alternatives do not necessarily require observation of charged intermediates. In contrast, the gas-phase ion–molecule model presented here has permitted substantial experimental testing and demonstration of the feasibility of a variety of sputtered ion reaction routes. Given the observation in the SID data of all of the key charged intermediates for the sputtered ion mechanism (involving the sputtering of $C_3H_5^+$ from the hydrocarbon overlayer and then reaction of the neutralized benzene with sputtered $C_3H_5^+$ ions to form $C_7H_7^+$) as well as the good agreement of the gas-phase experimental model and thermodynamic data, it seems likely that the sputtered ion mechanism contributes significantly to the observed $C_7H_7^+$ products of the reaction of benzene ions with hydrocarbon covered surfaces.

Since it is now accepted that these reactions proceed after charge exchange with the surface,[6,8] a possible alternative to a sputtered ion mechanism is the concerted route.[10] When comparing these potential routes (concerted and sputtered ion), there are two key questions: (i) does the surface hydrocarbon fragment before or after bonding to the neutralized benzene ion, and (ii) does the intermediate to $C_7H_7^+$ involve $[C_6H_6\cdots CH_3]^+$ or $[C_6H_6\cdots C_3H_5]^+$? Only very short time scale measurements could address the question of which comes first, fragmentation or attachment to benzene. Additional evidence of the intermediate involved might be obtained by devising an apparatus to monitor the neutrals scattered from the surface during SID or by isotopically labeling the end carbons on a self-assembled monolayer surface. These experiments will be attempted in subsequent investigations.

Based on these findings, we find it useful to view the SID surface reaction chemistry leading to alkylation at hydrocarbon surfaces as being very similar to ion–molecule reactions (specifically methane and/or isobutane CI processes) where the ions corresponding to reagent ions are produced in SID by sputtering the hydrocarbon overlayer and the corresponding neutrals in SID are produced via neutralization of the ions colliding with the surface. This view may be significant to the possible widespread analytical use of SID because it greatly simplifies the understanding of the more commonly observed ion surface reactions at hydrocarbon surfaces by allowing them to be modeled and understood in terms of the well-established techniques of methane and isobutane CI. As done previously,[24] we suggest that the use of gas-phase ion–molecule reactions to model ion surface reactions (particularly those with sputtered ion mechanisms) will facilitate further understanding of other SID processes where associative ion surface reactions are observed.

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[24] Chen, G.; Hoke, S. H.; Cooks, R. G. *Int. J. Mass Spectrom.* **1994**, *139*, 87.