

Reduction Induced by Ion Beams: Hydrogenation of Nitrogen-Containing Heterocycles and Quinones in Molecular Secondary Ion Mass Spectrometry

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Abstract: Hydrogenation of N-containing heteroaromatic compounds occurs when solid samples, in the presence of metals with low work functions (≤ 4.5 eV) and low first ionization energies as the free atoms, are subject to bombardment by low-flux ($\leq 10^{-7}$ A/cm²), high-energy (5 keV) argon ions. The molecules accept two or three hydrogens and are observed as $(M + 2H)^{++}$ or $(M + 3H)^+$ ions. Hydrogenation is observed by using the neat compounds supported on Ti, Ag, Pb, Al, In, Mg, and Gd substrates but is not observed when Pt, Ni, Au, graphite, or Cu substrates are employed. The role of the former metals with low work functions (and low ionization energies) is believed to be the production of low-energy electrons needed to initiate the reductions. Hydrogenation is also observed upon ion bombardment when the compounds are admixed with proton-rich solid matrix (NH_4Cl , *p*-toluenesulfonic acid, $\text{C}(\text{CH}_2\text{OH})_4$, oxalic acid) supported on graphite foil. In these cases, the hydrogen is derived from the matrix as evidenced by abundant $(M + \text{HD})^{++}$ and $(M + 2\text{D})^{++}$ ions when deuterated ammonium chloride matrix is employed. The fact that the extent of reduction depends on the primary ion dose establishes that it occurs in the energized seldge region during ion bombardment. Quinones show behavior similar to that of the heteroaromatic compounds with the important difference that the reduced compound is observed in the protonated $[(M + 2H)^{++}$ and $(M + 3H)^+]$, silver-cationized $[(\text{Ag} + M + \text{H})^{++}$ and $(\text{Ag} + M + 2\text{H})^+]$, and negative ion $[(M + \text{H})^-]$ forms. Proton-initiated (heteroaromatics) and electron-initiated (quinones) reaction mechanisms are proposed to accommodate these results. Hydrogenation is not observed upon bombardment of other heteroaromatics or polycyclic aromatic hydrocarbons. These experiments provide examples of the rich interfacial chemistry associated with desorption ionization mass spectrometry.

Hydrogenation of unsaturated organic compounds can be performed using a variety of reagents,¹ such as platinum and palladium catalysts.²⁻⁷ For example, cyclopentene and cyclooctene are hydrogenated in a batch reactor when adsorbed onto platinum catalysts,⁷ and 1,10-phenanthroline undergoes extensive hydrogenation using either SiHCl_3 ⁸ or Raney nickel catalyst⁹ to yield tetrahydro-1,10-phenanthroline and octahydro-1,10-phenanthroline. Quinones are hydrogenated in the gas phase under electron ionization (EI) conditions to yield $(M + 2H)^{++}$ ions due to adventitious water present in the vacuum chamber.¹⁰⁻¹⁴ Gas-phase hydrogenation of porphyrins¹⁵ as well as other unsaturated organic compounds¹⁶ has been observed in the course of chemical ionization (CI) using ammonia as the reagent. Bimolecular hydrogenation of both RhC_7H_6^+ and C_6H_5^+ cations has also been observed in the gas phase by using appropriate reagents.^{17,18}

Hydrogenation is also known to be induced at solid-gas and liquid-gas interfaces as a result of particle or photon bombardment¹⁹ associated with mass spectrometric techniques such as secondary ion mass spectrometry (SIMS),²⁰ fast atom bombardment (FAB),²¹ plasma desorption (PD),²² and laser desorption (LD).²³ Hydrogenation of both organic and inorganic compounds in liquid matrix (such as glycerol) has been observed to yield $(M + n\text{H})^+$ ions ($n = 2-5$) in FAB and liquid SIMS.²⁴⁻³⁵ In these studies, the hydrogen is derived from the liquid matrix. In a recent FAB study, however, Busch and co-workers demonstrated that reduction of methylene blue to yield $(C + \text{H})^{++}$ (where C = organic cation) need not involve abstraction of hydrogen from the matrix.³⁶ Cerny and Gross³⁷ and Williams and co-workers³⁸ propose that reduction occurs via low-lying molecular orbitals that capture electrons and initiate further reaction. Beam-induced hydrogenation of disulfide bonds in proteins supported in liquid matrix occurs to yield $(M + 3\text{H})^+$ ions, and this interfacial reaction has been used to locate the positions of cysteine amino acids.^{39,40} Reversible reduction of oxazine dyes during FAB has recently been observed. The relative abundances of $(C + 2\text{H})^+$ and $(C + 3\text{H})^{++}$ increase as the primary atom flux is increased from 1 to 10 μA . When the current is subsequently lowered to 1 μA , these ions

quickly disappear.⁴¹ Electrohydrodynamic mass spectrometry (EHD), in which gas-phase ions are generated by the application

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Table I. Positive Ion SIMS Spectra of Compounds 1–9 with NH₄Cl and Silver Powder Matrix^a

ion	1	2	3	4	5	6	7	8	9
(M - H) ⁺	3	1	3	2	8	12	7	6	17
M ⁺⁺	22	6	4	2	3	9	14	12	35
(M + H) ⁺	100	100	100	36	37	100	100	100	100
(M + 2H) ⁺⁺	8	26	8	100		32	2	7	34
(M + 3H) ⁺		4	3	9		5		1	6
(Ag + M) ⁺	8	2	4	5	100	9	6	40	8

^a Prepared as 1:1:1 physical mixtures with NH₄Cl and Ag powder by using Ag supports as 5×10^{-8} A/cm². ^b The contributions from ¹³C and ¹⁵N isotopes have been subtracted out.

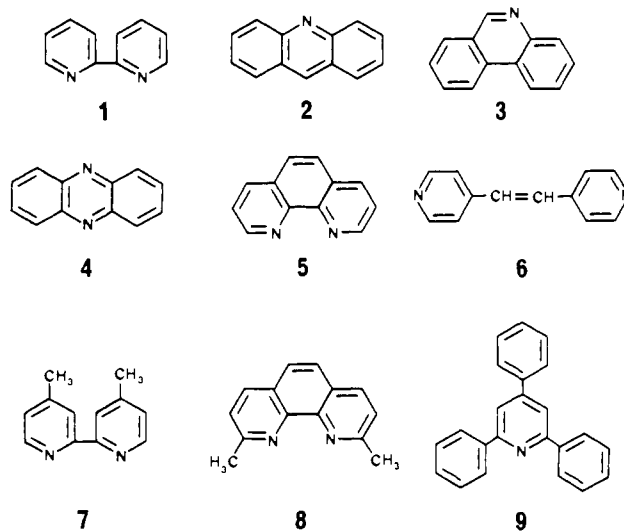
of an electric field to the surface of a liquid, sometimes yields mass spectra displaying ions that result from hydrogenation reactions. This suggests that reduction can occur in glycerol solution in the absence of ion bombardment.⁴² An unusual case of hydrogenation in molecular SIMS was observed when thiophene vapor was passed over a silver foil during argon ion bombardment.⁴³ The resulting SIMS spectrum displayed tetrahydrothiophene, observed in the form of the cationized species (Ag + M + 4H)⁺ and (2Ag + M + 5H)⁺.

In this report, we describe a striking example of hydrogenation of aromatic N-containing heterocycles and quinones, analyzed as *solids*, in which hydrogen incorporation to form (M + 2H)⁺⁺ and (M + 3H)⁺ in the former and in addition (Ag + M + H)⁺⁺, (Ag + M + 2H)⁺, and (M + H)⁻ in the latter occurs in the presence of metals with low work functions or in the presence of proton-rich solid matrices. Reduction reactions are uncommon in conventional molecular SIMS, where the samples are analyzed as solids, and the work reported here represents the first instance where hydrogenation is the *dominant* feature in molecular SIMS spectra.

Experimental Section

All SIMS spectra were obtained with a commercial Riber SQ 156L secondary ion mass spectrometer which has been described elsewhere.⁴⁴ Argon ions of 4.5-keV energy sampled an approximate area of 10 mm² of the solid sample surface. Argon ion fluxes were kept below 5×10^{-7} A/cm² to minimize sample damage. Secondary ions were extracted through a kinetic energy filter, mass-analyzed by using a quadrupole mass filter, and detected with an off-axis Galileo Channeltron electron multiplier. All spectra were recorded on a Hewlett-Packard 7014A *x-y* recorder by using a scan rate of approximately 20 daltons/min. The 70-eV electron impact (EI) mass spectra of both NH₄Cl (MCB Reagents) and ND₄Cl (Cambridge Isotope Laboratories) were obtained with a Finnigan 4000 gas chromatograph/mass spectrometer, and these data were used to estimate the degree of labeling of the commercial ND₄Cl sample.

Neat samples were burnished onto sandpaper-roughened substrates [aluminum, graphite, and indium (Alfa); gold, nickel, platinum, and

Chart I

silver (Aldrich); copper and lead (Fischer); magnesium (Mallinckrodt); and gadolinium (Research Chemicals)]. Other samples were prepared by admixing the compound with matrix in a 1:1 ratio, followed by fine mixing in a commercial pulverizer and burnishing the mixture onto a sandpaper-roughened substrate or by the preparation of 1-mm-thick pressed pellets using a Parr pellet press. Some of these pellets were covered by an overlayer of sputtered metal by using a customized sputtering device in the preparation chamber of the Riber SIMS.⁴⁵

Compounds used in this study included 2,2'-dipyridyl (1), acridine (2), phenanthridine (3), phenazine (4), 1,10-phenanthroline (5), *trans*-1,2-bis(4-pyridyl)ethylene (6), 2,4,6-triphenylpyridine (9), duroquinone (12), phenanthrenequinone (13), 1-hydroxyanthraquinone (15), 1,8-dihydroxyanthraquinone (16), 2,5-dibenzothiofene, phenothiazine, tetraphenylphosphonium bromide, thianthrene, thianaphthene, and triphenylethylphosphonium bromide (Aldrich); 1,4-naphthoquinone (11), anthraquinone (14), and 2,6-dimethylnaphthalene (Chemical Services); 1,2-naphthoquinone (10) (Eastman Organic); tetraphenylarsonium chloride (Eastern Chemical Corp.); anthracene, chrysene, and phenanthrene (Fluka); neocuproine (2,9-dimethyl-1,10-phenanthroline, 8) (Sigma); and 4,4'-dimethyl-2,2'-bipyridine (7) (Strem). Matrices used in this study included pentaerythritol and Ag₂O (Aldrich); Ag, graphite, and Mg powder (Alfa); oxalic acid (Baker); ND₄Cl (Cambridge Isotope Laboratories); NaCl (Fischer); KCl (Mallinckrodt); NH₄Cl and *p*-toluenesulfonic acid (MCB Reagents); and AgNO₃ (Spectropure). All compounds were used without further purification.

Results and Discussion

N-Containing Heteroaromatic Compounds. The positive ion SIMS spectra of compounds 1–9 (Chart I), from use of a mixture of NH₄Cl and silver powder as matrix and silver supports, are given in Table I. This matrix is chosen because NH₄Cl enhances the formation of protonated molecules [(M + H)⁺] and Ag powder enhances the formation of cationized molecules [(Ag + M)⁺]. The spectra are characterized by low-abundance (M - H)⁺ and M⁺⁺ ions, abundant (M + H)⁺ ions, and (Ag + M)⁺ ions of various relative abundances. The large relative abundances of the (Ag + M)⁺ ions displayed in the spectra of compounds 5 and 8 are likely due to the well-known chelating power of these compounds.

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Table II. Positive Ion SIMS Spectra of Compound 4 Supported on Various Substrates^a

substrate	rel abundance, ^b %					work ⁴⁶ funct, eV	ionization ⁴⁷ potential, eV
	(M - H) ⁺	M ⁺⁺	(M + H) ⁺	(M + 2H) ⁺⁺	(M + 3H) ⁺		
Pt	68	100	15	2		5.65	9.0
Ni	44	100	8			5.15	7.635
Au	65	100	17	2		5.1	9.225
graphite	100	47	8			5.0	11.260
Cu	80	100	16	1		4.65	7.726
Ti	28	64	100	15	1	4.33	6.82
Ag	17	16	80	100	10	4.26	7.576
Pb	26	60	100	26	6	4.25	7.416
Al	35	41	100	36	2	4.24	5.986
In	20	47	100	37	6	4.12	5.786
Mg	41	62	100	33	3	3.66	7.646
Gd	29	46	100	40	2	3.1	6.14

^a Using 5×10^{-8} A/cm². ^b The contributions from ¹³C and ¹⁵N isotopes have been subtracted out.

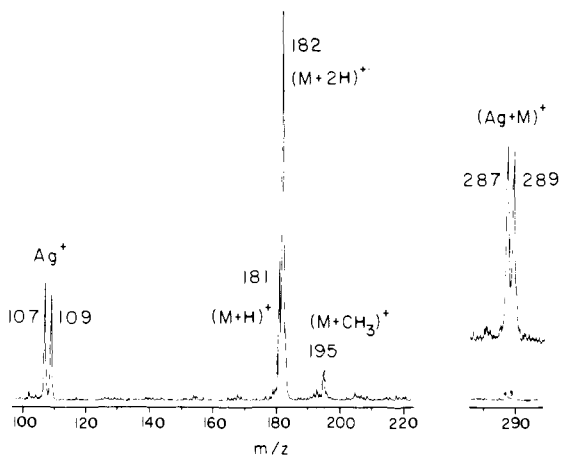


Figure 1. Positive ion SIMS spectrum of phenazine (4) admixed with NH₄Cl and Ag powder supported on silver foil (argon ion flux = 5×10^{-8} A/cm²).

The SIMS spectra of each compound, with the exception of compound 5, also display unexpected ions corresponding to (M + 2H)⁺⁺, which result from the addition of two hydrogens to the molecule. These hydrogenation product ions, as well as (M + 3H)⁺ ions, are most abundant in the SIMS spectra of compounds 2, 4, 6, and 9. The reduced species are not observed in the silver-cationized form. In particular, (Ag + M + 2H)⁺ is not observed in any of the cases studied.

The positive ion SIMS spectrum of compound 4, phenazine, which undergoes the most extensive hydrogenation under these conditions, is shown in Figure 1. The (M + 2H)⁺⁺ ion (*m/z* 182), which is an odd-electron species, is much more abundant than the even-electron (M + H)⁺ (*m/z* 181) and (M + 3H)⁺ (*m/z* 183) ions. An abundant ion is also observed at *m/z* 195, formally corresponding to a methylated ion [(M + CH₃)⁺]. There is no obvious source of a methyl group in the analyte molecule. Therefore it probably is derived from ion/molecule reactions with adventitious hydrocarbons present at the sample surface. The contribution of the matrix in this process will be described later. The negative ion SIMS spectrum of compound 4, obtained by using NH₄Cl and Ag powder matrix and a silver substrate, does not display phenazine ions (e.g., M⁻ or (M - H)⁻).

The SIMS spectrum of neat phenazine has also been obtained by using silver and several other substrates to determine whether reduction occurs in the absence of matrix. The positive ion SIMS spectra of phenazine supported on graphite, copper, silver, and indium substrates are shown in Figure 2. The two most abundant ions displayed in the SIMS spectra of phenazine supported on graphite (Figure 2a) and Cu foils (Figure 2b) are (M - H)⁺ (*m/z* 179) and M⁺⁺ (*m/z* 180). The abundant (M - H)⁺ ion observed when a graphite substrate is employed may be due to hydrogen abstraction from the analyte by organic functional groups at the graphite surface. The SIMS spectrum of phenazine supported on silver foil (Figure 2c) is radically different, however. The ions

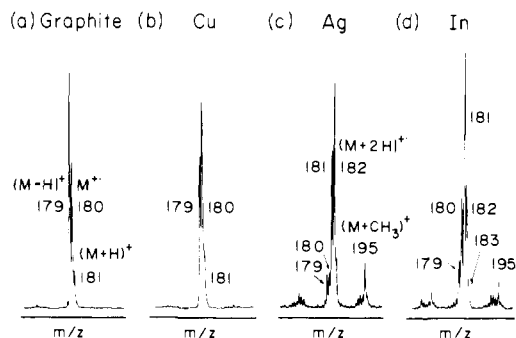


Figure 2. Positive ion SIMS spectra of neat phenazine (4) supported on (a) graphite, (b) copper, (c) silver, and (d) indium foils (argon ion flux = 5×10^{-7} A/cm²).

at *m/z* 179 and 180 are of low relative abundance and (M + H)⁺ is much more abundant than in the previous spectra. The base peak is the ion resulting from hydrogenation of this compound, (M + 2H)⁺⁺. Ions at *m/z* 183 [(M + 3H)⁺] and 195 [(M + CH₃)⁺] are also observed. The SIMS spectrum of phenazine supported on In foil (Figure 2d) also displays hydrogenation product ions but in much lower abundance than when an Ag support is employed.

There is a correlation between the spectra that display hydrogenation and the work functions (the energy required to remove an electron from the metal surface) of the corresponding substrates. The work functions of Ag and In (4.26 and 4.12 eV, respectively) are lower than those of graphite and Cu (5.0 and 4.65 eV, respectively).⁴⁶ To examine this effect over a wider range of metal substrates, eight other metals were used as supports. The corresponding SIMS spectra of phenazine supported on these substrates are listed in Table II. Abundant hydrogenation product ions are displayed in the SIMS spectra when substrates with low work functions (≤ 4.33 eV) are employed. Even though silver does not have the lowest work function of the metals examined, it is associated with the greatest extent of hydrogenation of phenazine. There is also a correlation between the first ionization potentials of the substrates and the spectra that display hydrogenation (see Table II).⁴⁷ The ionization potentials of the substrates associated with reduction are ≤ 7.576 eV, whereas the values are ≥ 7.726 eV for the substrates with which no reduction of the analyte is observed.

In the reduction that occurs upon fast atom or ion bombardment of glycerol solutions,²⁴⁻³⁵ the source of hydrogen typically is the glycerol matrix. To determine if NH₄Cl is the hydrogen source when NH₄Cl and silver powder matrix is employed in the present experiments, samples of compounds 1-9 were prepared by using solid ND₄Cl and silver powder matrix and silver substrates. The positive ion SIMS spectra of these samples are listed in Table III.

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Table III. Positive Ion SIMS Spectra of Compounds 1–9 with ND₄Cl and Silver Powder Matrix^a

ion	rel abundance, ^b %								
	1	2	3	4	5	6	7	8	9
(M – H) ⁺	2	3	2	7	6	9	3	5	9
M ⁺⁺	6	9	4	11	7	6	6	9	7
(M + H) ⁺	33	50	41	27	52	100	59	100	52
(M + 2H) ⁺⁺ , (M + D) ⁺	100	100	100	100	24	61	100	35	100
(M + 3H) ⁺ , (M + HD) ⁺⁺	10	10	2	30	1	18	9	5	14
(M + H ₂ D) ⁺ , (M + 2D) ⁺⁺	1	3	1	77		5	1		3
(M + HD ₂) ⁺				10		1			2
(M + 3D) ⁺				13					1
(Ag + M) ⁺	3	2	4	36	100	10	4	28	12

^a Prepared as 1:1:1 physical mixtures with ND₄Cl and Ag powder by using Ag supports at 5×10^{-8} A/cm². ^b The contributions from ¹³C and ¹⁵N isotopes have been subtracted out.

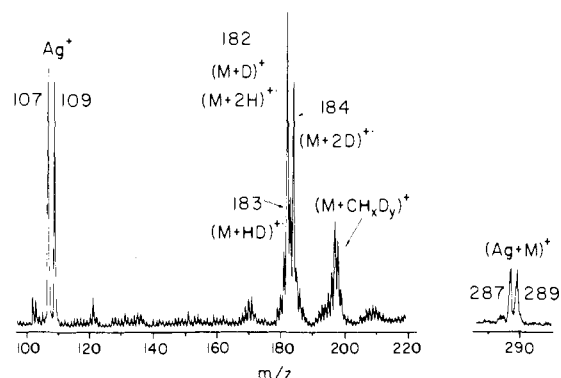


Figure 3. Positive ion SIMS spectrum of phenazine (4) admixed with ND₄Cl and Ag powder supported on silver foil (argon ion flux = 5×10^{-8} A/cm²).

In these spectra, the (M + 2H)⁺⁺ and (M + 3H)⁺ ions are accompanied by (M + HD)⁺⁺, (M + 2D)⁺⁺, (M + H₂D)⁺, (M + HD₂)⁺, and (M + 3D)⁺. The extent of reduction of compounds 1–9 is analogous to that reported in Table I; the SIMS spectra of 2, 4, 6, and 9 display the greatest extent of reduction. The 70-eV electron impact mass spectra of NH₄Cl and ND₄Cl were used to calculate the isotopic purity of ND₄Cl.⁴⁷ The level of deuteration of ND₄Cl is calculated to be approximately 73% (2% d₀, 11% d₁, 20% d₂, 29% d₃, and 38% d₄). On the basis of the relative abundances of the ions in the SIMS spectra listed in Table I, the deuterium incorporation into these compounds is calculated to be 50–60%. This indicates that a majority of the hydrogen incorporated into the analyte during the reduction process is derived from the matrix, although a minor secondary hydrogen source is also implicated. Solid ND₄Cl matrix was also used in a recent study of hydrogen–deuterium exchange, in which exchange of active hydrogens in the analyte was observed.⁴⁸

The positive ion SIMS spectrum of compound 4, phenazine, using ND₄Cl and silver powder matrix and a silver substrate, is shown in Figure 3. Each of the reduction products, as well as the silver-cationized molecule, are displayed. Note that the peak corresponding to the addition of a methyl group (at *m/z* 195 for the neat compound) is replaced by a group of peaks at *m/z* 195–198, corresponding to (M + CH_xD_y)⁺, where *x* + *y* = 3. This indicates that methylation involves participation of the matrix. Cationization of the reduced molecule to give (Ag + M + 2D)⁺ is not observed.

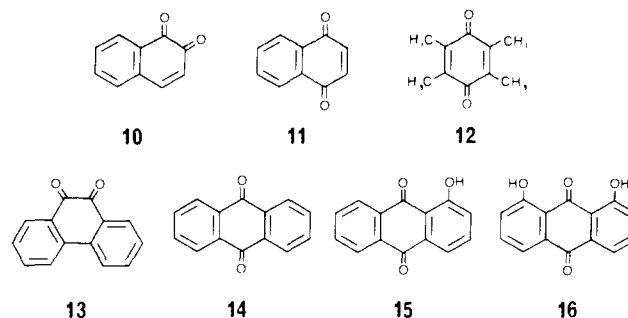
Matrix Effects. The results presented thus far indicate that reduction of compounds 1–9 occurs (i) when NH₄Cl and silver powder matrix is employed and (ii) for the neat compounds in the presence of metals with low work function values. Various other matrices have been examined to determine whether reduction occurs by using proton-rich matrices in the absence of these metals and if metal salts alone can act as reductants.

The positive ion SIMS spectra of compound 4, phenazine, recorded in a variety of matrices and supported on graphite foil, are listed in Table IV. When aprotic matrices (carbon powder, NaCl, KCl) are employed, hydrogenation is not favored; the relative abundances of (M + 2H)⁺⁺ and (M + 3H)⁺ are low,

Table IV. Positive Ion SIMS Spectra of Compound 4 with Various Matrices^a

matrix	rel abundance, ^b %				
	(M – H) ⁺	M ⁺⁺	(M + H) ⁺	(M + 2H) ⁺⁺	(M + 3H) ⁺
carbon powder	13	12	100	6	3
NaCl	93	100	14		
KCl	78	100	57	10	
NH ₄ Cl	13	20	100	70	6
<i>p</i> -TSA	14	8	100	77	2
C(CH ₂ OH) ₄	11	16	100	23	6
oxalic acid	13	18	100	42	8
Ag powder	18	18	100	61	14
Mg powder	10	12	100	44	5
Ag ₂ O	27	27	66	3	1
AgNO ₃	55	86	100	6	1

^a Prepared as 1:1 physical mixtures by using graphite supports at 5×10^{-8} A/cm². ^b The contributions from ¹³C and ¹⁵N isotopes have been subtracted out.

Chart II

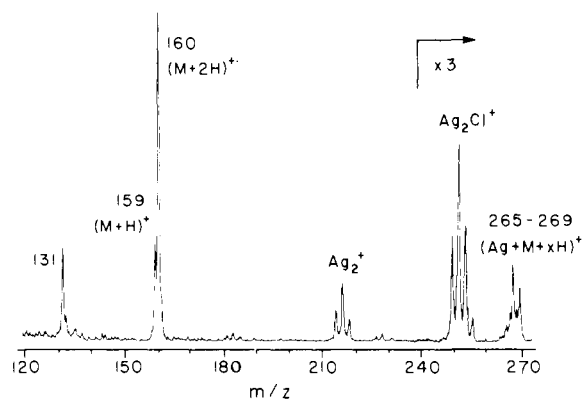
although M⁺⁺ and (M – H)⁺ are favored. When carbon powder is employed as the matrix, the protonated molecule is the base peak, whereas when NaCl and KCl are employed M⁺⁺ is the base peak. When a proton-rich matrix is employed (NH₄Cl, *p*-toluenesulfonic acid (*p*-TSA), pentaerythritol [C(CH₂OH)₄], and oxalic acid), hydrogenation product ions are again observed. This indicates that when there is an abundant proton source available, the reducing metal is not required. When silver or magnesium powder matrix is employed (with the sample supported on a graphite substrate) hydrogenation occurs, as expected. Two silver salts have also been employed as matrices (AgNO₃ and Ag₂O). In neither case is reduction observed. This indicates that *metallic* silver acts as the reductant.

Another method of sample preparation utilized an overlayer of sputtered metal. Hydrogenation of phenazine occurs upon ion beam bombardment in the presence of an overlayer of sputtered silver. The SIMS spectrum of a pressed pellet of phenazine and NaCl (1:1 ratio) was examined and found to be analogous to that for phenazine admixed with NaCl supported on graphite foil; hydrogenation product ions are absent. When an overlayer of silver, approximately 750 monolayers in thickness, is sputtered onto the pellet, the (M + 2H)⁺⁺ ion becomes the base peak in the SIMS spectrum. This again suggests that metallic silver acts as the reductant. In comparison, the SIMS spectrum of a phenazine/NaCl pellet bearing a 750-monolayer overlayer of sputtered

Table V. Positive Ion SIMS Spectra of Compounds 10–16 with NH_4Cl and Silver Powder Matrix^a

ion	rel abundance, ^b %						
	10	11	12	13	14	15	16
$(\text{M} - \text{H})^+$	10		19	8	1	5	8
M^{*+}	11	3	38	9	2	5	3
$(\text{M} + \text{H})^+$	100	21	100	100	44	100	94
$(\text{M} + 2\text{H})^{*+}$	61	100	57	46	100	40	100
$(\text{M} + 3\text{H})^+$	7	4	36	13	10	12	22
$(\text{Ag} + \text{M})^+$	86	2		78	12	69	70
$(\text{Ag} + \text{M} + \text{H})^{*+}$	18	4		18	2	16	14
$(\text{Ag} + \text{M} + 2\text{H})^+$	12	8		26	8	10	35

^a Prepared as 1:1:1 physical mixtures with NH_4Cl and Ag powder by using Ag supports at 5×10^{-7} A/cm². ^b The contributions from ¹³C isotopes have been subtracted out.

**Figure 4.** Positive ion SIMS spectrum of 1,4-naphthoquinone (11) admixed with NH_4Cl and Ag powder supported on silver foil (argon ion flux = 5×10^{-7} A/cm²).

copper does not display hydrogenation products. Beam-induced hydrogenation of N-containing heterocycles therefore occurs when either a metal with a low work function is present or when an abundant proton source is available.

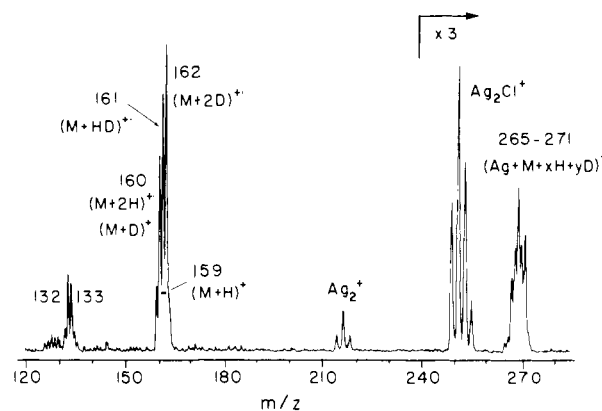
Quinones. In addition to N-containing heterocycles, quinones are also hydrogenated during ion bombardment. The positive ion SIMS spectra of compounds 10–16 (Chart II), taken by using NH_4Cl and silver powder matrix and silver supports, are listed in Table V. These spectra are characterized by low-abundance $(\text{M} - \text{H})^+$ and M^{*+} ions, abundant protonated molecules $(\text{M} + \text{H})^+$, and $(\text{M} + 2\text{H})^{*+}$ and $(\text{M} + 3\text{H})^+$ ions due to hydrogenation. The positive ion SIMS spectrum of compound 11, 1,4-naphthoquinone, is shown in Figure 4. In contrast to the heteroaromatic compounds, hydrogenation product ions are observed in the silver-cationized forms in these spectra; $(\text{Ag} + \text{M} + \text{H})^{*+}$ and $(\text{Ag} + \text{M} + 2\text{H})^+$ ions are displayed. In the spectrum of 1,4-naphthoquinone shown in Figure 4, the most abundant silver-cationized species corresponds to $(\text{Ag} + \text{M} + 2\text{H})^+$ at m/z 267 and 269. Large relative abundances of the silver-cationized molecules are evident for compounds 10, 13, 15, and 16. This is likely to be a result of the chelating ability of these compounds. The total absence of silver-cationized molecules in the spectrum of compound 12 is probably due to steric hindrance from the methyl groups. The negative ion SIMS spectrum of compound 11 obtained by using NH_4Cl and Ag powder matrix and a silver substrate, displays both M^{*-} (m/z 158) and the hydrogenation product ion $(\text{M} + \text{H})^-$ (m/z 159). M^{*-} and $(\text{M} + \text{H})^-$ ions have been observed previously, for example, in a FAB study of quinone antibiotics.²⁵

The SIMS spectrum of neat 1,4-naphthoquinone (11) has been obtained by using graphite, Cu, Pt, Au, and Ag substrates. As is the case for phenazine (4), hydrogenation is observed when a silver substrate is used, as evidenced by $(\text{M} + 2\text{H})^{*+}$, $(\text{M} + 3\text{H})^+$, $(\text{Ag} + \text{M} + \text{H})^{*+}$, $(\text{Ag} + \text{M} + 2\text{H})^+$, and $(\text{M} + \text{H})^-$ ions. The positive ion SIMS spectra of compound 11 supported on the other four substrates display M^{*+} ions as the base peak with $(\text{M} + \text{H})^+$ in low relative abundance. Reduction is not observed. The

Table VI. Positive Ion SIMS Spectra of Compounds 10–14 with ND_4Cl and Silver Powder Matrix^a

ion	rel abundance, ^b %				
	10	11	12	13	14
$(\text{M} - \text{H})^+$	1	38	7	2	
M^{*+}	2	35	5	1	
$(\text{M} + \text{H})^+$	74	23	100	30	12
$(\text{M} + 2\text{H})^{*+}$, $(\text{M} + \text{D})^+$	100	68	95	100	63
$(\text{M} + 3\text{H})^+$, $(\text{M} + \text{HD})^{*+}$	25	85	99	69	100
$(\text{M} + \text{H}_2\text{D})^+$, $(\text{M} + 2\text{D})^{*+}$	3	100	66	36	55
$(\text{M} + \text{HD}_2)^+$	2	3	39	12	8
$(\text{M} + 3\text{D})^+$	1	2	15	3	4
$(\text{Ag} + \text{M})^+$	11	2		8	4
$(\text{Ag} + \text{M} + \text{H})^{*+}$	19	4		4	1
$(\text{Ag} + \text{M} + 2\text{H})^+$, $(\text{Ag} + \text{M} + \text{D})^{*+}$	32	14		19	6
$(\text{Ag} + \text{M} + \text{HD})^+$	11	19		10	16
$(\text{Ag} + \text{M} + 2\text{D})^+$	4	25		15	8

^a Prepared as 1:1:1 physical mixtures with ND_4Cl and Ag powder by using Ag supports at 5×10^{-7} A/cm². ^b The contributions from ¹³C isotopes have been subtracted out.

**Figure 5.** Positive ion SIMS spectrum of 1,4-naphthoquinone (11) admixed with ND_4Cl and Ag powder supported on silver foil (argon ion flux = 5×10^{-8} A/cm²).

corresponding negative ion spectra obtained by using these substrates display low abundance M^{*-} ions. The absolute yield of M^{*-} using a silver substrate, however, is approximately 2 orders of magnitude higher than in the other cases.

The SIMS spectra of these quinones have also been obtained by using a mixture of ND_4Cl (73% isotopic purity) and Ag powder as matrix and Ag as the support (see Table VI). On the basis of the SIMS spectra listed in Table V, the deuterium incorporation into these compounds is calculated to be approximately 50–60%, again indicating that the matrix is the major source of hydrogen. As is the case for compounds 1–9, when using ND_4Cl matrix, the $(\text{M} + 2\text{H})^{*+}$ and $(\text{M} + 3\text{H})^+$ ions are accompanied by $(\text{M} + \text{HD})^{*+}$, $(\text{M} + 2\text{D})^{*+}$, $(\text{M} + \text{H}_2\text{D})^+$, $(\text{M} + \text{HD}_2)^+$, and $(\text{M} + 3\text{D})^+$ ions. This is shown in the positive ion SIMS spectrum of 1,4-naphthoquinone (Figure 5). Deuterium incorporation is also evident in the silver-cationized products. The abundant ions at m/z 269 and 271 in the SIMS spectrum of 1,4-naphthoquinone correspond to $(\text{Ag} + \text{M} + 2\text{D})^+$. The negative ion spectrum of compound 11 displays the reduced species as $(\text{M} + \text{H})^-$ and $(\text{M} + \text{D})^-$. The main difference between the SIMS spectra of the heteroaromatics and the quinones is the $[\text{Ag} + \text{M} + \text{H}(\text{D})]^{*+}$, $[\text{Ag} + \text{M} + 2\text{H}(\text{D})]^+$, and $[\text{M} + \text{H}(\text{D})]^-$ ions present only in the spectra of the latter compounds.

Other Compounds. Other types of organic compounds have been investigated to determine whether reduction occurs upon ion bombardment. Of the compounds examined, only N-containing heteroaromatics and quinones display hydrogen incorporation, however. Analogous experiments using S-containing heterocycles (phenothiazine, 2,5-dibenzothiophene, thianaphthene, and thianthrene), polycyclic aromatic hydrocarbons (2,6-dimethylnaphthalene, phenanthrene, anthracene, and chrysene), and quaternary arsonium and phosphonium salts (tetraphenylarsonium

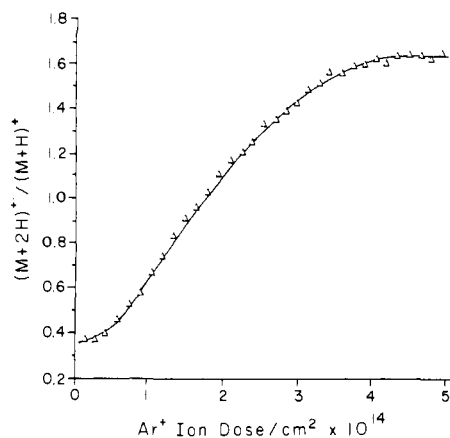


Figure 6. Plot of the $(M + 2H)^{\bullet\bullet} / (M + H)^{\bullet}$ ion ratio versus argon ion dose using neat phenazine (**4**) supported on silver (argon ion flux = 2×10^{-8} A/cm²).

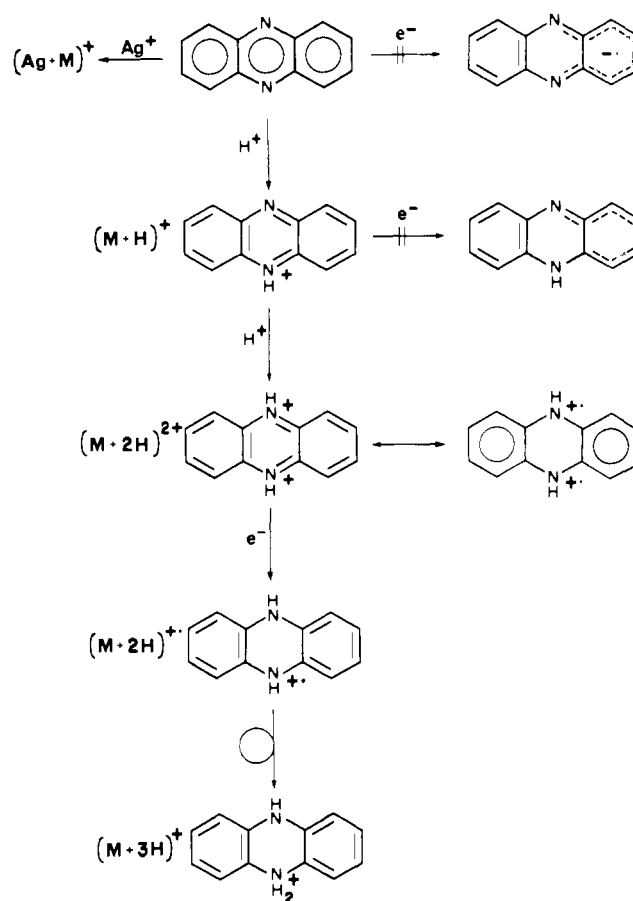
chloride, triphenylethylphosphonium bromide, and tetraphenylphosphonium bromide) resulted in positive ion SIMS spectra that did not display hydrogenation product ions.

Kinetic Studies. The relative abundances of the hydrogenation products displayed in the SIMS spectra in this study are dependent on the primary ion (Ar^+) dose. The ratio of $(M + 2H)^{\bullet\bullet} / (M + H)^{\bullet}$ for neat phenazine (**4**) supported on silver foil, plotted as a function of argon ion dose, is shown in Figure 6. This ratio represents the extent of reduction $[(M + 2H)^{\bullet\bullet}]$ versus that of simple protonation $[(M + H)^{\bullet}]$. The ratio increases until an argon ion dose of 4×10^{14} argon ions/cm² is reached and then levels. At the argon ion flux used for this experiment, 2×10^{-8} A/cm², the leveling time is reached in approximately 45–50 min. The ion dose at which leveling occurs (4×10^{14} primary ions/cm²) corresponds roughly to the point at which one monolayer of the surface has been disturbed (assuming a damage cross section of approximately 25 \AA^2).⁴⁹ This suggests that the reduction occurs at the surface as a result of ion beam bombardment. (A small amount of reduction may occur prior to bombardment, however, since the relative abundance of $(M + 2H)^{\bullet\bullet}$ is initially 20% of the final value.) These data suggest that the reaction is induced by the primary ion and the reaction products are desorbed by subsequent impacts.

The time dependence is observed because the cross section for reduction is lower than that for mixing of the species at the surface. Ion-beam-induced mixing of multilayered samples is well-known from studies employing Rutherford backscattering.^{50–52} Similar leveling effects have been observed in other SIMS studies of interfacial reactions, including reduction of sulfate and nitrate salts⁵³ and hydrogen–deuterium exchange using solid ND_4Cl matrix.⁴⁸ Time dependencies are useful for identifying interfacial reactions.

Reaction Mechanism. Compounds **1–16** are reduced under argon ion bombardment in the presence of metals of low work function (and low ionization potential) or a proton-rich matrix. The fact that reduction of the neat molecules occurs only in the presence of the metal (e.g., Ag) and not the metal salt (e.g., $AgNO_3$ or Ag_2O) suggests that the metal acts as the reductant. The negative ion data for compound **11** supported on the various substrates also suggests that metals with low work functions act as efficient electron donors since the yield of $M^{\bullet-}$ ions is 2 orders of magnitude higher when silver is employed than for metals of

Scheme I



higher work function. This suggests that the metals with low work functions (and low ionization potentials) have in common the ability to provide moderated electrons (i.e., low-energy electrons that can be captured by the molecules with high efficiency). The reducing species might be free electrons or they could be metal atoms or small metal clusters that donate electrons in the energized self-edge region.

The major difference between the SIMS spectra of the N-containing heterocycles and the quinones is that only in the latter case are the hydrogenation products observed in the silver-cationized $[(Ag + M + H)^{\bullet\bullet}]$ and $[(Ag + M + 2H)^{\bullet\bullet}]$ and negative ion $[(M + H)^{\bullet-}]$ forms. This suggests that compounds **10–16** are reduced by a different mechanism than the N-containing heteroaromatics (**1–9**). A model consistent with these findings suggests that ionization occurs in a medium rich in H^+ and e^- (as previously proposed^{37,38}) and that multiple collisions take place (as shown by deuterium incorporation data, including the incorporation into the methylated compound). Although radicals, including H^{\bullet} may be generated, it is not necessary to invoke their involvement to achieve a consistent explanation of the observations.

In the proposed mechanisms, the quinone reductions are initiated by electron addition and the heteroaromatic reductions are initiated by proton addition. These conclusions are supported both by the observations and by thermochemical data. The gas-phase proton affinities of both heteroaromatic compounds (e.g., pyrazine = 874 kJ/mol, phenazine = 936 kJ/mol)⁵⁴ and quinones (estimated to be 800–850 kJ/mol based on data for α,β unsaturated ketones, e.g., methyl vinyl ketone = 838 kJ/mol)⁵⁵ are of similar magnitude. The gas-phase electron affinities of heteroaromatics (e.g., pyrazine = 38 kJ/mol),⁵⁴ however, are much lower than those of quinones (e.g., benzoquinone = 184 and 1,4-naphthoquinone

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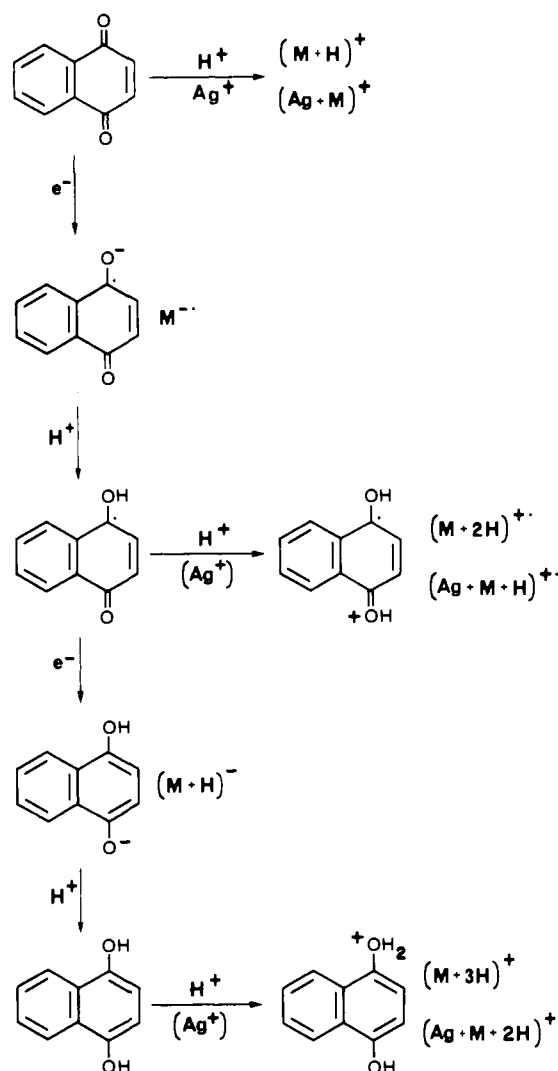
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Scheme II



= 174 kJ/mol).⁵⁴ The proposed mechanisms are outlined below.

The first step in the reduction of the N-containing heterocycles (see Scheme I, using phenazine (**4**) as a model) is the addition of a proton. The addition of an electron to N-containing heterocycles is not likely (based on electron affinity data and the complete absence of $\text{M}^{\bullet -}$ ions in the negative ion spectra). This protonated species likely undergoes the addition of another proton in preference to an electron. Electron addition to the protonated molecule would result in a reduced neutral molecule that is likely to be cationized by silver to yield $(\text{Ag} + \text{M} + \text{H})^{\bullet +}$ ions (as is the case with the quinones). This type of ion is not observed, however.

To determine whether reduced species present in the sample mixture are readily cationized, the SIMS spectrum of a 1:1 physical mixture of 1,4-naphthoquinone (MW = 158) and 1,5-dihydroxy-1,2,3,4-tetrahydronaphthalene (MW = 164) was obtained. The resulting mass spectrum displayed abundant $(\text{Ag} + \text{M})^+$ ions in approximately equal relative abundance from cationization of both species, suggesting that reduced species present in the selvedge are indeed readily cationized.

Addition of a second proton results in a multiply-charged species which can then be reduced by a one-electron addition. The resulting species is the observed reaction product $(\text{M} + 2\text{H})^{\bullet +}$. This cycle can be repeated to yield $(\text{M} + 3\text{H})^{\bullet +}$. During the formation of $(\text{M} + 3\text{H})^{\bullet +}$, protonation likely occurs prior to electron addition. Reduction of multiply charged ions is a favored process upon ion beam bombardment of solids.¹⁹ For example, ion beam bombardment of the diquaternary ammonium salt methylviologen ($\text{C}^{2+}2\text{A}^-$) results in a SIMS spectrum in which the intact cation (C^{2+}) is reduced to yield a singly-charged ion ($\text{C}^{\bullet +}$).⁵⁶

The reduction of the quinones (see Scheme II, with compound **11** as a model) is suggested to be initiated by a one-electron addition. The presence of an abundant $\text{M}^{\bullet -}$ ion in the negative ion spectra and the aforementioned thermochemical data support this conclusion. Alternatively, the neutral molecule can be protonated or argentated to yield $(\text{M} + \text{H})^+$ or $(\text{Ag} + \text{M})^+$ ions which do not undergo hydrogenation. The $\text{M}^{\bullet -}$ ions are then protonated, yielding a reduced neutral compound that can react further by two pathways: (i) addition of H^+ or Ag^+ to yield $(\text{M} + 2\text{H})^{\bullet +}$ or $(\text{Ag} + \text{M} + \text{H})^{\bullet +}$ and (ii) addition of a second electron to yield 1,4-dihydroxynaphthalene. Finally, the addition of H^+ or Ag^+ to the latter product yields either $(\text{M} + 3\text{H})^{\bullet +}$ or $(\text{Ag} + \text{M} + 2\text{H})^{\bullet +}$. Scheme II shows protonation at the hydroxyl site, but ring protonation is also possible.

Conclusions

The hydrogenation reactions reported in this paper represent examples of the increasing number of beam-induced chemical reactions studied by desorption ionization mass spectrometry. The fact that the reactions are ion dose dependent suggests that they are interfacial phenomena and do not occur significantly prior to ion beam bombardment. N-containing heterocycles accept two or three hydrogens and are observed as $(\text{M} + 2\text{H})^{\bullet +}$ or $(\text{M} + 3\text{H})^{\bullet +}$ ions. Quinones are reduced to yield these ions as well as $(\text{M} + \text{H})^+$, $(\text{Ag} + \text{M} + \text{H})^{\bullet +}$, and $(\text{Ag} + \text{M} + 2\text{H})^{\bullet +}$. Hydrogenation occurs for the neat compounds in the presence of metals with low work functions (and low ionization potentials) which act as the reductant. As is the case in liquid SIMS and FAB, the major source of hydrogen is the matrix. Reaction mechanisms based on electron-initiated hydrogenation of the quinones and proton-initiated hydrogenation of the heterocycles are proposed.

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