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Photodissociation Study of $C_6H_6O^{+\cdot}$ Ions in an Ion Cyclotron Resonance Spectrometer

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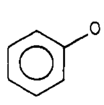
Abstract: Tautomeric phenol and 1,3-cyclohexadien-5-one radical cations exist as distinct, stable species in the gas phase. This is established by a study of the photodissociation spectra of $C_6H_6O^{+\cdot}$ ions generated from four sources. Specifically, the ionized phenol and the $C_6H_6O^{+\cdot}$ from phenetole exist principally as the phenol structure. On the other hand, $C_6H_6O^{+\cdot}$ generated from bicyclo[2.2.2]oct-2-ene-5,7-dione and 2-phenoxyethyl chloride exist as a mixture of keto and enol structures.

In this paper we present spectroscopic evidence that at least two distinct C_6H_6O radical cations exist in the gas phase as ionized phenol and its keto tautomer (A and B). The photodissociation method coupled with trapped ion cyclotron resonance spectrometry has been selected to provide new fundamental information on the nature of these ions. The study is part of our continuing efforts to understand the properties of isomeric isolated species which can interconvert by simple hydrogen shifts, here a 1,3 shift.



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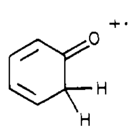
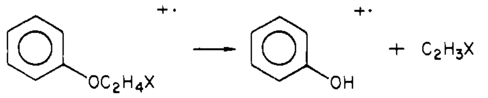


B

Ions of the composition $C_6H_6O^{+\cdot}$ have been investigated by using many different mass spectrometric techniques.[1-19] These studies have involved isotopic labeling,[1-4] ion cyclotron resonance (ICR),[5-8] collisional activation (CA),[9,10] and analysis of the neutral species expelled in the formation of $C_6H_6O^{+\cdot}$ in an electron bombardment flow reactor.[11] Furthermore, the measurements of isotope effects,[2,12] substituent effects,[13,14] appearance potentials,[15-17] and kinetic energy released in decomposition reactions[9,18,19] have been directed at this question. The principal conclusion of all this research has been that two stable ion structures exist in the gas phase: A and B.

In general, the preferred structure of $C_6H_6O^{+\cdot}$ generated in decomposition reactions of ethyl phenyl ether, halogen-substituted ethyl phenyl ethers, alkyl phenyl ethers, and phenyl esters is the phenol structure (reaction 1). The keto form seems to be formed only in the decomposition of bicyclo[2.2.2]oct-2-ene-5,7-dione (reaction 2) and possibly of certain phenoxyethyl halides, although the latter source is uncertain.[19]



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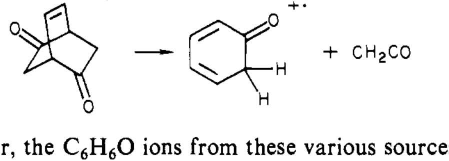

(2)

However, the C_6H_6O ions from these various sources with a lifetime of 10^{-5} s or longer may exist as a mixture of keto and enol forms.[6,8,10] This study was initiated because this has been difficult to test conclusively by using the mass spectrometric methods mentioned above.

Experimental Section

The main features of the ICR spectrometer have been described in a previous paper.[20] The present experiments were performed with a new four-section square cell constructed from molybdenum plates mounted on shielded vespel rods. This cell was used as a McIver-type one-section cell by connecting the marginal oscillator to the source region and applying negative potentials to the drift plates of the reaction region as in the trapped mode of the McMahon-Beauchamp method.[21] Ions were produced by a 10-ms (trapped ICR) or 0.1-s (photodissociation) grid pulse of the electron beam. The ions were trapped for times up to 10 s and brought into resonance by pulsing the source trapping voltage to a higher value. For kinetic measurements at 1.3×10^{-4} Pa (1×10^{-6} torr), the output of the marginal oscillator was connected with a PAR 160 boxcar integrator. For photodissociation experiments, the transient response of the marginal oscillator was integrated and fed into a PDP-11 computer.

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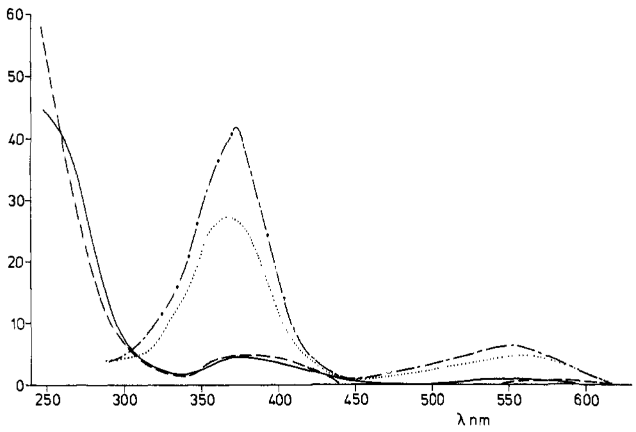


Figure 1. Photodissociation spectra (relative) units) of the m/z 94 ions from phenol (—), phenetole (---), bicyclo[2.2.2]oct-2-ene-5,7-dione (···) and 2-phenoxyethyl chloride (- - -). The spectra of the ions from phenol and phenetole have been multiplied by a factor of 5.

Photodissociation experiments were performed by irradiation with the light of an Osram XBO-900 Xenon arc lamp filtered by a Bausch & Lomb high-intensity monochromator with 6-mm slits (42-nm bandwidth).

For studies of photodecomposition as a function of time, ion intensities after t s were measured alternately with a slow chopper with the light beam on, $N_\lambda(t)$, and off, $N(t)$ (eq 3). For every period of the light beam

$$x_\lambda = [N(t) - N_\lambda(t)]/N(t) \qquad (3)$$

on and off, $x_\lambda(t)$ was calculated and averaged over 10–50 periods. These data were used for the plots of $-\ln(1 - x_\lambda)$ vs. time or wavelength.

The relative value of the light intensity in photons, I_λ, at wavelength λ is defined as $I_{\lambda r}$ and was measured both with an EGG 580/585 spectroradiometer and with an ITT F4000 S-1 photodiode. Photodissociation spectra were then obtained by plotting the relative value of the rate constant for photodissociation, $k_{\lambda r}$, as a function of wavelength (see eq 4 and 5). Strictly speaking, this procedure is only correct for ions of one structural form.

$$1 - x_\lambda = N_\lambda(t)/N(t) = e^{-I_{\lambda r}k_{\lambda r}t} \qquad (4)$$

$$k_{\lambda r} = -[1/I_{\lambda r}t] \ln(1 - x_\lambda) \qquad (5)$$

In most cases, photodissociation spectra were measured with double-resonance or trapping field ejection of part of the ions. Occasionally, a pulsed double-resonance ejection method was used. In that event, all ions except the ion of interest were removed by sweeping the double-resonance frequency. By stopping the pulse when the frequency was of the order of the resonance frequency of the ion of interest, it was possible to prevent ejecting it from the cell.

Ionizing energies were about 15 eV determined by the bias applied to the filament. Pressures were measured by using a Vacuum Generators VIG-21 ion gauge.

The syntheses of the compounds studied have been described previously.[1,19]

Results and Discussion

We begin by assuming that a high proportion of ionized phenol structure (A) can be generated by electron-impact ionization of phenol, whereas the keto isomer (B) can be formed in the decomposition reaction outlined in reaction 2. These assumptions are in accord with evidence of previous studies. Spectra of these two structures formed in the ICR cell are then taken, making use of the photodissociation reaction given in reaction 6. Results of

$$C_6H_6O^{+\cdot} + h\nu \rightarrow C_5H_6^{+\cdot} + CO \qquad (6)$$

double-resonance experiments serve as confirmation that this reaction is occurring. The spectra of $C_6H_6O^{+\cdot}$ from ionization of phenol and decomposition of phenyl ethyl ether, 2-phenoxyethyl chloride, and bicyclo[2.2.2]oct-2-ene-5,7-dione are presented in Figure 1.

It is clear from the appearance of the spectra that at least two structural forms of m/z 94 exist. Ionized phenol and $C_6H_6O^{+\cdot}$ from phenyl ethyl ether have relatively low photodissociation rates in the UV region and two very weak bands in the visible portion of the spectrum. On the other hand, the m/z 94 ions from the 2-phenoxyethyl chloride and the dione are characterized by two relatively strong absorptions in the visible spectrum. Therefore, as a starting point, we attribute the band in the UV region (below 300 nm) to the phenol structure and the two strong photodissociation bands in the visible spectrum to the keto tautomer of phenol (structure B).

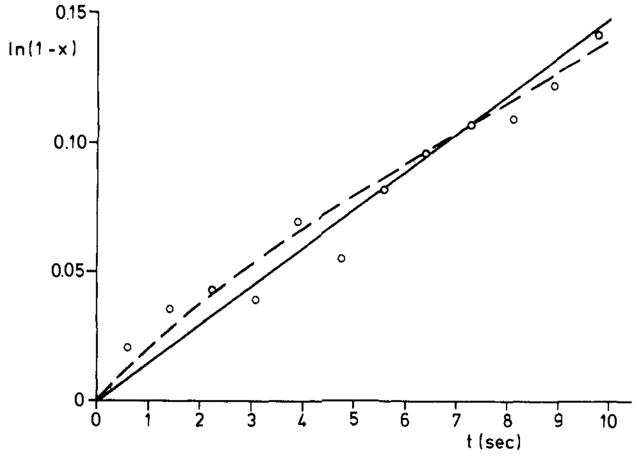


Figure 2. Time dependence of the photodissociation of m/z 94 ions from phenol at 390 nm and at a pressure of 6×10^{-6} Pa.

The next question involves the assignment of the two weak bands in the visible region observed for ionized phenol and $C_6H_6O^{+\cdot}$ from phenyl ethyl ether. They could be attributed to structure A or to a small concentration of structure B because they nearly coincide with the intense absorptions of B. Furthermore, the rate of photodissociation of structure B is so much larger than A (note that the spectra of phenol and phenyl ethyl ether are multiplied by a factor of 5) that a spectrum of a mixture of the two structures will be determined almost completely by structure B. It is necessary, therefore, to collect additional information such as the dependence of the percentage of dissociating ions (x_λ) on irradiation time and the chemical behavior of the two structures in diagnostic ion–molecule reactions. These experiments and specific details of the spectra are discussed for each of the compounds in the following sections.

Phenol. The photodissociation spectra can be ambiguous if ion–molecule reactions compete with the photochemistry. For example, the $C_5H_6^{+\cdot}$ photofragment ion reacts with neutral phenol to produce $C_6H_6O^{+\cdot}$ by charge transfer. In order to suppress this back-reaction, the spectrum of ionized phenol was measured with a continuous double-resonance ejection of $m/z = 66$, $C_5H_6^{+}$.

The two very weak bands in the visible region could signal a small concentration of ion B, as was mentioned previously. To test this possibility, the fraction of photodissociation was monitored as a function of time. An expression for the number of parent ions at time t with the light beam on, $N_\lambda(t)$, is given in eq 7 where

$$N_\lambda(t) = N(t)e^{-I_\lambda k_\lambda t} \qquad (7)$$

k_λ is the rate constant for photodissociation per photon, I_λ is the light intensity at wavelength λ in photons, $N_\lambda(t)$ is the number of parent ions at time t with the light beam on, and $N(t)$ is the number of ions at time t with the light beam off. This expression is true for the case in which all the ions have a single structure. Now, we can write

$$\ln[N_\lambda(t)/N(t)] = -I_\lambda k_\lambda t \qquad (8)$$

and a plot of $\ln(1 - x_\lambda)$, where $x_\lambda = [N(t) - N_\lambda(t)]/N(t)$, as a function of the irradiation time should result in a straight line, both for reactive and for unreactive ions. The relevant data were gathered at 390 nm and at a pressure of phenol of 6×10^{-6} Pa (4.5×10^{-8} torr, see Figure 2). We find that $\ln(1 - x_\lambda)$ varies in a reasonably linear manner with time up to 13% dissociation after 10 s. On the basis of the data, we know that the absorption band centered at about 390 nm is due to, at least in part, the phenol structure. Furthermore, we can rule out a relative population of

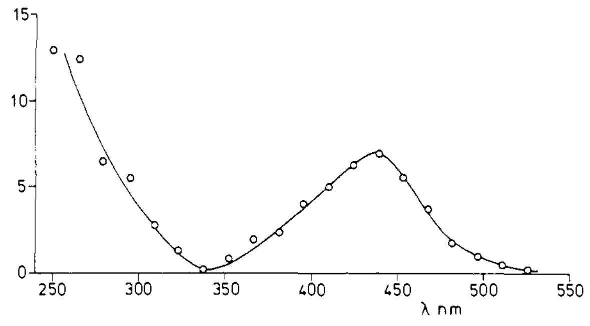


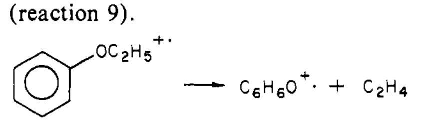
Figure 3. Photodissociation spectrum of $C_6H_5OC_2H_5^{+\cdot}$, the molecular ion of phenetole.

greater than 4–5% of structure B.

We are now in a position to ask whether the data are in accord with the presence of a small amount (1–2%) of B. If B were present, a more rapid initial photodissociation would be observed until it was consumed because B is more photoreactive than A. The curve (Figure 2) would exhibit a sharp onset for the first few seconds followed by a more shallow-sloped line at longer times which corresponds to photodissociation of the less reactive phenol structure. If we assume that 2% of the C_6H_6O ions possess structure B and that the photodissociation rate constants for A and B are 0.0125 and 0.6 s^{-1}, we can calculate the dashed curve in Figure 2. This curve fits the experimental data as well as the straight line decay. Thus, we are unable to distinguish a population of pure A and a mixture of A and a small amount of B.

There are two other indications of the presence of a small amount of structure B. First, the photodissociation spectrum of C_6H_6O ions from bicyclo[2.2.2]oct-2-ene-5,7-dione is interpreted in terms of a mixture of A and B, with a fraction of the ions of structure B capable of isomerizing to A (see below). Accordingly, a small amount of reverse isomerization of A to B is not unexpected. Second, both phenol and its keto isomer exhibit long wavelength bands centered at 550 nm (2.2 eV) and extending to 600 nm (2.0 eV). These energies are too low to cause photodissociation of structure A. This conclusion follows from mass spectrometry appearance energy measurements which yield thresholds of 3.2 and 2.4 eV for production of $C_5H_6^{+\cdot}$ from ionized phenol in the source and metastable regions, respectively. Therefore, the long wavelength band for phenol should be attributed to either a small fraction of structure B or a two-photon dissociation of structure A. The latter has been observed for other substituted benzene ions.[23-26]

Phenyl Ethyl Ether (Phenetole). Phenetole produces abundant $C_6H_6O^{+\cdot}$ by electron impact induced decomposition of the molecular ion (reaction 9).



$$\longrightarrow C_6H_6O^{+\cdot} + C_2H_4 \qquad (9)$$

Measurements of the photodissociation spectrum of *m/z* 94 ions from phenetole are somewhat more difficult. First of all, m/z 94 ions react with phenetole by charge transfer ($k = 1.0 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}); charge transfer to phenol and phenyl ethers seems to be typical for ion A (see below). Moreover, *m/z* 94 ions are also formed by photodissociation of the molecular ions (see Figure 3). Therefore, the photodissociation spectrum of *m/z* = 94 ions has been measured at the lowest possible pressure with either double-resonance or trapping field ejection of the molecular ions of phenetole. Despite ion ejection, we still observe a small photoinduced enhancement of the $C_6H_6O^{+\cdot}$ intensity between 440 and 540 nm, accounting for the weaker band for $C_6H_6O^{+\cdot}$ from phenetole compared to ionized phenol.

Nevertheless, we can still conclude that the vast majority of the $C_6H_6O^{+\cdot}$ ions from phenetole have the same structure as ionized phenol. This conclusion is consistent with the results obtained in previous ICR experiments[5] in which the relative rates of proton transfer from $C_6H_6O^{+\cdot}$ to suitable bases were found to be the same for ionized phenol and $C_6H_6O^{+\cdot}$ from phenetole. However, a small fraction of structure B again cannot be excluded.

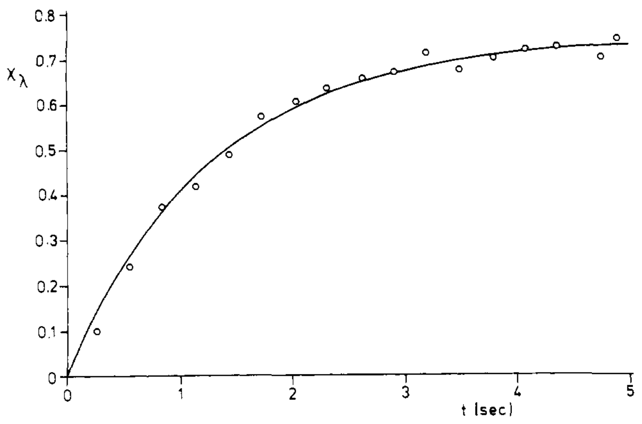


Figure 4. Time dependence of the photodissociation of *m/z* 94 ions from bicyclo[2.2.2]oct-2-ene-5,7-dione at 380 nm and at a pressure of 5.3 × 10^{-6} Pa.

Bicyclo[2.2.2]oct-2-ene-5,7-dione. The molecular ion *m/z* 136 and the *m/z* 94 and 66 fragment ions from bicyclo[2.2.2]oct-2-ene-5,7-dione react very slowly, if at all, with the neutral molecule. The relatively small ion intensity of *m/z* 94 is enhanced upon irradiation of the ion mixture at wavelengths around 450 nm if other ions are not ejected. This effect is almost certainly due to photodissociation of the molecular ion. Therefore, measurements on m/z 94 ions have been performed usually with continuous trap ejection of the molecular ions, *m/z* 136. Occasionally we have also used pulsed double-resonance ejection of all ions except m/z 94 ions.

The *m/z* 94 ions should have the cyclohexadienone structure at times up to 10^{-5} s according to previous reports. Tomer and Djerassi,[6] however, reported that on the ICR time scale the *m/z* 94 ions consist of a mixture of ions with the cyclohexadienone and the phenol structure. In the present experiments, the apparent photodissociation rate has been found to be about 30% lower than in the case of 2-phenoxyethyl chloride (see Figure 1). We do not claim a high accuracy in the determination of relative rates, but this difference might suggest a mixture of ions A and B. Therefore, we have measured the percentage of photodissociating ions as a function of the irradiation time (see Figure 4). Clearly, ln $(1 - x_\lambda)$ at 380 nm is not linear with irradiation time. Instead, x_λ at 5.3 × 10^{-6} Pa can be approximated by

$$x_\lambda = 0.75\,(1 - e^{-0.77t})$$

This result can be interpreted in different ways. If it is assumed that ion B can tautomerize to ion A with a rate k_i, that both A and B do not react with the neutral background, and that the photodissociation of A at 380 nm is negligible, then the reaction scheme is

$$A \xleftarrow{k_i} B \xrightarrow[k_1]{h\nu} C_5H_6^{+\cdot} + CO \qquad (10)$$

and x_λ is calculated to be

$$x_\lambda = [B_0/(B_0 + A_0)][k_1/(k_1 + K_i)][1 - e^{-(k_1 + k_i)t}] \qquad (11)$$

with B_0 and A_0 being the ion intensities at $t = 0$. After 10 s of irradiation, x_λ has been found to be independent of pressure from 4.0 × 10^{-7} to 4.0 × 10^{-6} Pa. This means that a possible tautomerization is not induced by collisions. However, it is impossible to draw further conclusions from the experiments thus far. One cannot distinguish between a slow tautomerization of all ions and a fast tautomerization of part of the ions from the photodissociation results presented here.

We have measured the time dependence of the *m/z* 94 ion intensity in a mixture of bicyclo[2.2.2]oct-2-ene-5,7-dione and pentadeuterated phenol at pressures of about 1.3 × 10^{-4} Pa (see Figure 5) using the usual trapped ICR technique. This was done

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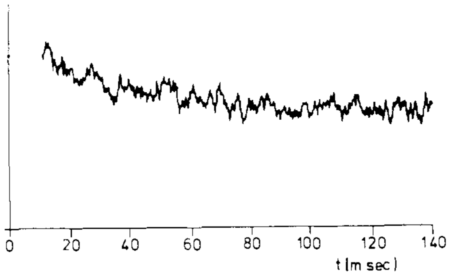


Figure 5. Time dependence of the *m/z* 94 ion intensity in a mixture of bicyclo[2.2.2]oct-2-ene-5,7-dione and pentadeuterated phenol at a pressure of about 1.3 × 10^{-4} Pa.

because the experiments with phenetole and 2-phenoxyethyl chloride have been interpreted to show that the ions A and B can be distinguished by use of charge-transfer reactions with phenol or phenyl ethers. From the reaction scheme

$$B \xrightarrow{k_i} A \xrightarrow[C_6D_5OH]{k_2} C_6D_5OH^{+\cdot} \qquad (12)$$

the *m/z* 94 intensity is calculated to be

$$B + A = [B_o k_i/(k_i - k_2) + A_o]e^{-k_2 t} - [k_2 B_o/(k_i - k_2)]e^{-k_i t} \qquad (13)$$

The time scale is much shorter in these experiments than in the photodissociation experiments. Therefore, a slow tautomerization ($k < 10$ s^{-1}) should not be detected. It follows from the curve in Figure 5 that $k_2 = 1.0 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, k_i is very small, and A_0 and B_0 are about 40% and 60%, respectively. These latter values are in good agreement with the photodissociation experiments which show that A_0 and B_0 are 25% and 75%, respectively, if k_i is small. Therefore, a slow tautomerization can be excluded. Thus, the final conclusion is that if there is a tautomerization of the cyclohexadienone structure to the phenol structure, then this reaction applies only to part of the ions and is complete within a few milliseconds.

2-Phenoxyethyl Chloride. Photodissociation of the molecular ion generates again the *m/z* 94 fragment ion. Because of the two chlorine isotopes, the photodissociation experiments have been performed with continuous trap ejection of both *m/z* 156 and 158 molecular ions.

The spectrum of *m/z* 94 from 2-phenoxyethyl chloride was measured at a variety of pressures. The apparent photodissociation rate constant increases with pressure. This behavior is typical for a mixture of different ions of equal mass having both a different photodissociation rate and a different reactivity with the neutral background, i.e., *m/z* 94 ions consist of a mixture of ions A and B. Furthermore, we conclude, on the basis of the pressure dependence, that phenolic ions react much faster than ions with a cyclohexadienone structure. Double-resonance experiments show that the reaction is charge transfer to the neutral parent molecule. These conclusions have been verified by measurements of the time dependence of the *m/z* 94 and 99 ion intensities in a mixture of 2-phenoxyethyl chloride and pentadeuterated phenol at pressures of about 1.3 × 10^{-4} Pa (see Figure 6). It follows from the curves in Figure 6 that *m/z* 99 ions react rapidly with neutral 2-phenoxyethyl chloride, but the decay of *m/z* 94 ions is not simply exponential. This is in agreement with the conclusion that *m/z* 94 ions consist of a mixture of ions with different structures. The following statements, on the basis of this measurement and similar measurements on pure 2-phenoxyethyl chloride, can be made, provided that the *m/z* 94 ions do not tautomerize:

(1). The C_6H_6O ions exist in two forms as the phenol and the cyclohexadienone structures. The percentage of ions with the phenol structure seems to increase slightly with the energy of the ionizing electron beam from 40–45% at 11 eV up to 60% at 20–25 eV.

(2). Ions with the phenol structure react by charge transfer with neutral 2-phenoxyethyl chloride with a rate constant $k = 0.7 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. For ions with the cyclohexadienone structure the rate constant is 3×10^{-11} cm^3 molecule^{-1} s^{-1}.

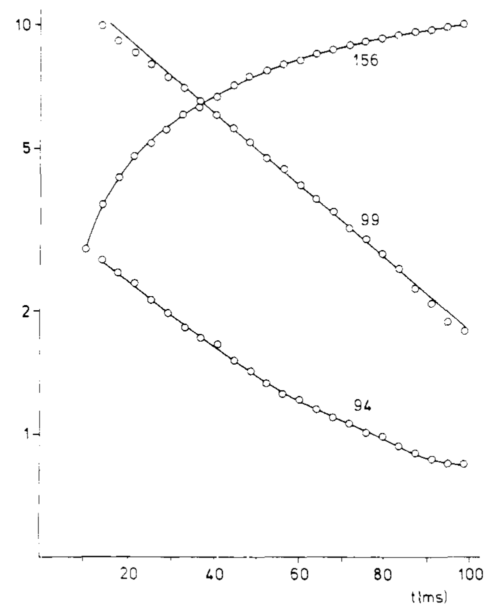


Figure 6. Time dependence of the *m/z* 94, 99, and 156 ion intensities in a mixture of 2-phenoxyethyl chloride and pentadeuterated phenol (*m/z* 99) at a pressure of about 1.3 × 10^{-4} Pa.

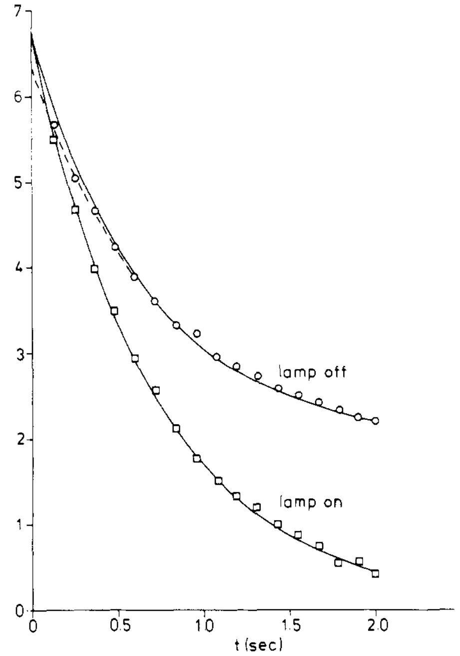
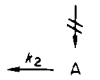


Figure 7. Time-dependent measurements of the *m/z* 94 ions from 2-phenoxyethyl chloride at a pressure of 5.3 × 10^{-6} Pa with and without irradiation at 380 nm.

These results are in reasonable agreement with time-dependent measurements of the *m/z* 94 intensity at low pressure with and without irradiation at 380 nm. An example is given in Figure 7 where the calculated curves are obtained from the following reaction scheme in which k_3 and k_2 are the bimolecular reaction rate constants of B and A with the background



(14)

with $A_0 = 68\%$, $B_0 = 32\%$, $k_3 = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, $k_2 = 1.5 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, and $k_1 = 1.06$ s^{-1}. Therefore, we arrive at the same conclusion as in the preceding case. The *m/z* 94 fragment ions from 2-phenoxyethyl chloride consist of a mixture of ions having the phenol and the cyclohexadienone structures. If tautomerization occurs, it applies only to part of the ions and is complete within a few milliseconds.

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Registry No. Phenol, 108-95-2; phenetole, 103-73-1; bicyclo[2.2.2]-oct-2-ene-5,7-dione, 17660-74-1; 2-phenoxyethyl chloride, 622-86-6; phenol radical cation, 40932-22-7; 1,3-cyclohexadien-5-one radical cation, 34481-01-1.

Secondary Ion Mass Spectrometry of Metal Halides. 2. Evidence for Structure in Alkali Iodide Clusters

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Abstract: Recently, we reported extended-mass secondary ion mass spectrometric data of the alkali iodide (MI) cluster species $[M(MI)_n]^+$, which indicated that certain species in the series (n = 1-22) have different intrinsic stabilities. The cluster ion intensity distribution exhibited anomalies at certain n values rather than the expected monotonic decrease of ion intensity with increasing n. The structures of cluster ions at certain n values, which have enhanced ion intensity, were postulated to have "cubic-like" atomic arrangements. This report presents ultrahigh mass spectral data ($>m/z$ 18 000 and n = 1-70) of CsI clusters, induced by xenon ion bombardment and analyzed by a high-performance secondary ion mass spectrometer. These high-mass cluster ions are the largest mass-resolved ions ever produced and observed using a conventional mass analyzer, and they are more than 20 times more massive than those ions reported with other secondary ion mass spectrometers. These new data support our former hypothesis, which deals with the structures of certain alkali iodide cluster ions, and they confirm predictions based on it. The hypothesis and its relationship to previous work are discussed. The similarity of the body-centered cubic salt, CsI, ion intensity distribution with the ion intensity distributions of the simple cubic salts (NaI, KI, RbI) is also addressed. We conclude from these data that one type of stable configuration of the alkali iodide cluster ions is the "cubic-like" structure, which is reminiscent of the bulk crystal structure.

Introduction

The mechanism of cluster ion formation and the secondary ion emission process of the alkali halides has been the subject of current investigation in this laboratory[1] utilizing a specially designed high-performance secondary ion mass spectrometer.[2] Collision-induced sputtering mechanisms of the metal halides have been studied by the measurement of energy distributions of sputtered neutral species,[3] the recent investigation of sputtered cluster ions by secondary ion mass spectrometry (SIMS),[1,4] bombardment with neutral beams,[5] and theoretical investigation[6,7] including molecular dynamics.[8] The commonality of these studies is the search for the mechanisms of secondary particle emission, ionization, and cluster formation. These phenomena have profound implications in fundamental and applied research in such disciplines as astrophysics, combustion chemistry, materials research, and radiation chemistry. This is a significant field of research because of the direct connection it provides between the transition of gas-phase species to the condensed phase.[9]

Various models for the secondary ion emission process and associated cluster ion formation have been proposed, based on experimental evidence[1,3,4,10] and trajectory computations using molecular dynamics.[8,11] A recent and comprehensive review of molecular SIMS discusses the various models and research trends in this area.[12] The formation of molecular and other polyatomic ions or cluster species by ion bombardment can be broadly viewed either as the direct emission of species originating at the surface or the recombination of sputtered species to form new structures. The direct emission model can include processes such as ejection through momentum transfer in collision cascades,[13] thermal spikes,[14] thermal evaporation,[14] and even agglomeration in the selvedge region[10] or any other unrealized process that can eject species from contiguous sites. On the other hand, the recombination model includes processes like agglomeration, nucleation, or association reactions which form species containing constituents from nonadjacent sites.

Recently, we have reported SIMS spectral evidence for the direct emission of certain high-mass alkali iodide (MI) cluster species during ion bombardment. Positive ions[1,2] of the type $[M(MI)_n]^+$, negative ions[2] $[I(MI)_n]^-$, and metastable ion decompositions of these species have been reported.[1,2] The high-performance instrumental capabilities of the SIMS instrument used in these studies[2] allowed the observation of noteworthy anomalies in the ion intensities at high-mass values in the positive ion SIMS spectra of CsI (n = 19), RbI (n = 16), KI (n = 22), and NaI (n = 22), where n is the largest cluster ions species observed.

Similar anomalies were observed for all of the above alkali iodides. The characteristic features of the mass spectra previously reported[1] are the following: (1) the plot of the log ion intensity vs. log n decreased linearly; (2) the n = 13 species was equal to or more intense than the n = 12 species; (3) the n = 14 and 15 species were dramatically absent or of decreased intensity relative

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