for I_2^- are only slightly less than the 0.52 cm^{-1} I_2 matrix value.[11] As was found for F_2^- and Cl_2^-, the I_2^- fundamental at 115 cm^{-1} is roughly half of the precursor I_2 frequency. The electron transferred from the alkali metal enters an antibonding molecular orbital on iodine and reduces the σ bond order from one to one-half, a bonding change which is in line with the change in fundamental frequency upon reduction of molecular iodine.

The dissociation energies calculated for I_2^- from the ω_e and $\omega_e x_e$ values listed in Table II average 20 kcal/mol. The average value is in reasonable agreement with the thermodynamic value, 24.5 ± 2 kcal/mol, obtained from the following Hess' law calculation, which supports the present spectroscopic analysis and observation of I_2^-.

$I_2^- \rightarrow I_2 + e^-$	59.5 ± 2 kcal/mol[17]
$I_2 \rightarrow 2I$	33.57 ± 0.03 kcal/mol[18]
$I + e^- \rightarrow I^-$	−70.6 ± 0.1 kcal/mol[19]
$I_2^- \rightarrow I + I^-$	24.5 ± 2 kcal/mol

The regularly increasing half-band widths noted here for the resonance Raman progression of I_2^- are typical of solution spectra,[14,20] but this increase was not observed[2] for Cl_2^-, although a slight increase was found for matrix isolated O_3^- and ClO_2.[21,12] The increase in band width for I_2^- was linear with quantum number as illustrated by Figure 3. A reasonably linear plot was found for dissolved I_2 from the second to thirteenth overtones.[14] The band broadening in the solid phase may be due to a guest-host interaction, which is stronger for the more polarizable $M^+I_2^-$ species than for $M^+Cl_2^-$.

The weak Raman bands observed near 162 cm^{-1} in alkali metal-bromine experiments could be due to either Br_2^- or Br_3^-. The latter reddish species[22] has been observed at 162 cm^{-1} in Raman spectra of chloroform solutions of $R_4N^+Br_3^-$ and the former species could reasonably be predicted at half of the Br_2 fundamental, which suggests a band near 160 cm^{-1} for Br_2^-. By analogy with the Cl_2 and I_2 alkali metal studies, the $M^+Br_2^-$ species was probably produced in small quantities from the matrix reaction.

Conclusions

The resonance Raman spectrum of I_2^- has been observed in solid argon for all of the alkali $M^+I_2^-$ species using krypton ion 6471 Å excitation; the $Li^+I_2^-$ species was also observed with 5682 and 5309 Å illumination. The six-membered vibrational progressions beginning near 115 cm^{-1} decreased in intensity and increased in band width in a regular manner with increasing vibrational quantum number. The potassium–iodine reaction products were examined with 3564 Å excitation; an intense 109 cm^{-1} fundamental was observed and presumed to be due to I_3^-, which is not to be confused with the I_2^- fundamentals near 115 cm^{-1} depending upon alkali cation, which required red excitation for resonance Raman observation.

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+*E* Collision Induced Mass Spectra from Negative Ions

J. H. Bowie* and T. Blumenthal

Contribution from the Department of Organic Chemistry, University of Adelaide, Adelaide, South Australia, 5001. *Received August 30, 1974*

Abstract: A new type of mass spectrum is described in which negative ions are converted into decomposing positive ions in the analyzer region of the mass spectrometer. Initial results suggest that these spectra may provide information concerning the structures of both negatively and positively charged ions.

Beynon, Cooks and colleagues have described the application of high-energy ion-molecule reactions occurring in the analyzer regions of the mass spectrometer to effect charge stripping[1] and charge exchange reactions.[2] Such reactions provide information concerning both the structures and fragmentations of ions[1-3] and the energy characteristics and reaction mechanisms of ion-molecule reactions at high energy.[1,2,4] As an extension to this work, Keough, Beynon, and Cooks have reported[5] that particular positively charged ions may be converted to the corresponding negative ions by the collision process

$$M^+ + N \rightarrow M^- + N^{2+}$$

where N is the target gas, generally maintained at a pres-

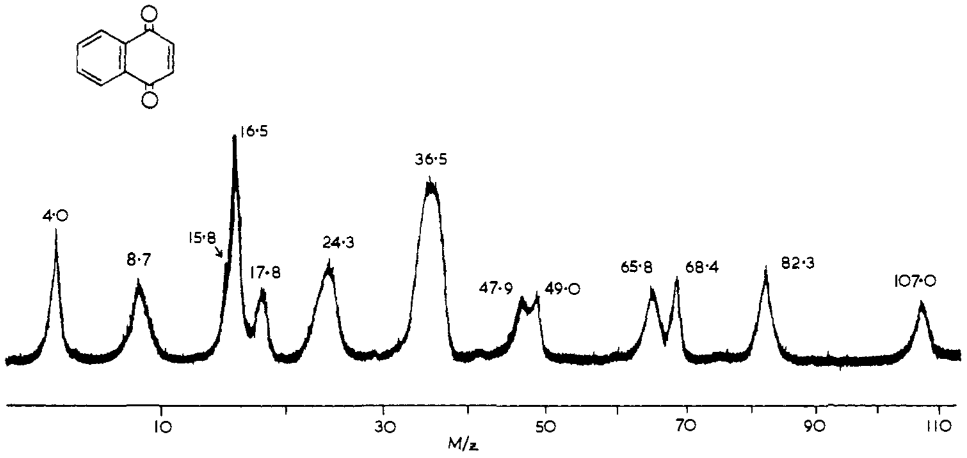

Figure 1. $+E$ mass spectrum derived from the 1,4-naphthoquinone molecular anion. Sample pressure 3×10^{-5} Torr in the second field-free region.

sure of ca. 10^{-4} Torr in the collision region. This is denoted a $-E$ spectrum,[6] and as an example, ionized benzene (with benzene used as target gas) produces abundant $C_n\cdot^-$ and C_nH^- ions ($n = 1$-6).[5]

Negative ions may be formed from suitable organic systems by secondary electron capture[7] and these ions may decompose by unimolecular processes,[7,8] or they may be forced to cleave by collision excitation.[8,9] As part of our negative-ion program, we wished to determine (i) whether an ion m^- can be converted to m^+ by a charge stripping reaction, and (ii) if doubly charged negative ions can be produced by the process

$$M^- + N \rightarrow M^{2-} + N^+$$

To this time we have been unable to detect the formation of doubly charged negative ions by collision processes, in spite of reports[10] of their occurrence in some conventional negative ion spectra.

This paper reports the occurrence of the conversion $M^- \rightarrow M^+$ and describes the decompositions of some positively charged product ions.

Results and Discussion

$+E$ collision induced spectra were measured with an Hitachi Perkin-Elmer RMU 7D mass spectrometer (modified as previously described[9d]) operating at 70 eV, and using a negative accelerating potential of 3.6 kV. The spectra are produced mainly by *decomposition* of the positively charged ions resulting from the charge stripping process. The target gas may be some species which does not furnish negative ions in the source region (e.g., helium, nitrogen, or benzene), or alternatively the sample itself may be used as the target gas (the usual pressure is 3-5 × 10^{-5} Torr in the appropriate collision region). Superior results are usually obtained using the latter technique.

$+E$ spectra may be measured for decompositions occurring in either the first or second field-free regions of the double focusing mass spectrometer. Dissociations occurring in the *second* field region are detected by first accelerating the negative ions, reversing the potential of the electric sector to transmit the negative ions, with the magnet set for positive ions. An automatic magnet scan then produces the $+E$ spectrum. Decompositions in the *first* field-free region are detected using the ion kinetic energy (IKE) technique;[11] i.e., the negative ions are accelerated, the electric sector is set to transmit *positive* ions, and the ion beam is monitored at the β slit as the sector voltage is varied automatically at constant accelerating potential. The $+E$ IKE spectra are not as well resolved as conventional IKE spectra (cf. ref 11).

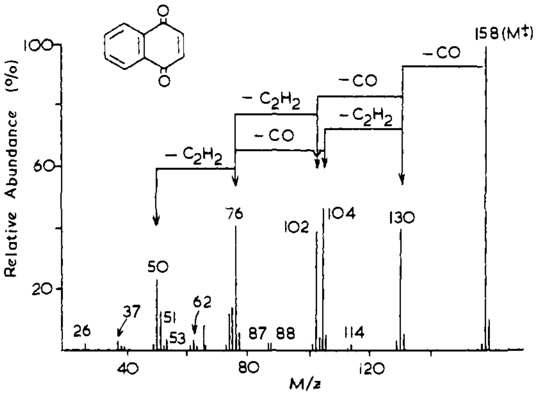

Figure 2. Conventional positive ion mass spectrum of 1,4-naphthoquinone.

$+E$ spectra are best determined by the magnetic scan method. The product and precursor positive ions are then defined uniquely for each decomposition by setting the magnet to $M/z = M_2^2/M_1$ (for a process $M_1^+ \rightarrow M_2^+$, where the charge on any given ion is $q = ze$) reversing the sector potential (from $-E$ to $+E$), then reducing the sector voltage to transmit the particular ion (i.e., to a value $M_2/M_1 \times E$).[12] Examples of $+E$ spectra are illustrated below.

Consider first molecules which yield pronounced molecular anions by secondary electron capture at 70 eV, but which do not contain fragment ions in their spectra. 1,4-Naphthoquinone is such an example,[9a] and its $+E$ spectrum, measured using the sample as target gas, is recorded in Figure 1. The positive ion current is 10^{-4} that produced by the 1,4-naphthoquinone molecular anion. The molecular cation which results directly from the charge stripping process is not detected in the spectrum; instead, 13 processes arising from the decomposing molecular species are present. These are listed in Table I. Analogous $+E$ spectra are obtained using helium, nitrogen, or benzene as collision gases, except that for a given total pressure (say 3 × 10^{-5} Torr) the abundances of all peaks are diminished with respect to those shown in Figure 1. No positive species arising from the collision gases (He, N_2, or C_6H_6) are noted in these spectra. This result, coupled with the nonobservance of doubly charged negative ions in these experiments, leads to the suggestion that the general collision process operating is

$$M^- + N \rightarrow [M^+]^* + N + 2e$$

a process which must be accompanied by the efficient conversion of translational energy to internal energy, in order

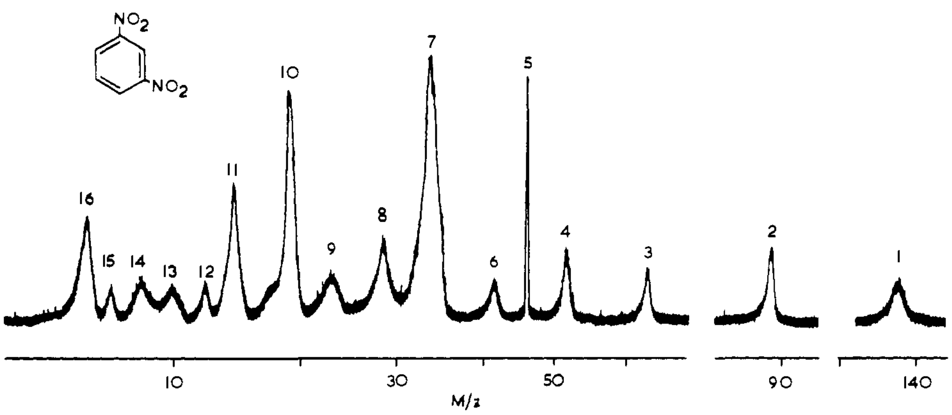

Figure 3. $+E$ mass spectrum of negative ions derived from *m*-dinitrobenzene. Sample pressure 5×10^{-5} Torr in the second field-free region.

Table I. $+E$ Mass Spectrum from the Naphthoquinone Molecular Anion

M_2^2/M_1	M_2/M_1	Process [158(P) →]	Decomposition
107.0	0.822	130	$[P - CO]$
82.3	0.718	114	$[P - CO_2]$
68.4	0.655	104	$[P - (CO + C_2H_2)]$
65.8	0.642	102	$[P - 2CO]$
49.0	0.556	88	$[P - (CO_2 + C_2H_2)]$
47.9	0.550	87	$[P - (CO_2 + C_2H_2 + H^{\cdot})]$
36.5	0.478	76	$[P - (2CO + C_2H_2)]$
24.3	0.397	62	$P \rightarrow C_5H_2^{\cdot+}$
17.8	0.336	53	$P \rightarrow C_4H_5^+$
16.5	0.322	51	$P \rightarrow C_4H_3^+$
15.8	0.318	50	$P \rightarrow C_4H_2^{\cdot+}$
8.7	0.234	37	$P \rightarrow C_3H^+$
4.0	0.160	26	$P \rightarrow C_2H_2^{\cdot+}$

Table II. $+E$ Spectra from Ions in the Negative Ion Spectra of Dinitrobenzenes

Peak	M_2^2/M_1	M_2/M_1	Decomposition	Ortho	Para
1	137.5	0.904	$[P - O]$	–	–
2	88.5	0.721	$[P - NO_2^{\cdot}]$	–	
3	61.5	0.665	$[(P - NO^{\cdot}) - NO_2^{\cdot}]$	–	–
4	50.8	0.545	$[P - (NO_2^{\cdot} + NO^{\cdot})]$	–	
5	46.0	0.996	$NO_2^- \rightarrow NO_2^+$		
6	42.0	0.550	$[(P - NO^{\cdot}) - (NO_2^{\cdot} + O)]$		–
7	34.3	0.450	$[P - 2NO_2^{\cdot}]$		
8	29.0	0.451	$(P - NO^{\cdot}) \rightarrow C_5H_3^+$		
9	23.2	0.375	$P \rightarrow C_5H_3^+$		
10	19.5	0.650	$NO_2^+ \rightarrow NO^+$		
11	14.6	0.299	$P \rightarrow C_4H_2^{\cdot+}$		
12	12.7	0.273	$P \rightarrow NO_2^+$		
13	9.5	0.238	$P \rightarrow C_3H_4^{\cdot+}$		
14	8.3	0.220	$P \rightarrow C_3H^+$		
15	6.5	0.217	$(P - NO^{\cdot}) \rightarrow NO^+$		
16	5.2	0.178	$P \rightarrow NO^+$		

to account for the enhanced energies of the decomposing molecular cations.[13,14]

It is of interest to compare the $+E$ spectrum of 1,4-naphthoquinone (Figure 1 and Table I) with its conventional low-resolution positive-ion mass spectrum[15] (Figure 2), since both spectra, although visually different, yield very similar information. The peaks observed in the conventional spectrum are produced by a series of consecutive and competitive unimolecular decompositions[16] (Figure 2). The 13 fragment ions shown numerically in Figure 2 are also produced in the $+E$ spectrum (cf. Table I), but in the case of the $+E$ spectrum, they are all produced via collision-induced dissociation.

Comparisons between the conventional positive ion spectra and $+E$ spectra of many other molecules which yield abundant molecular anions provide the same general conclusions as those enumerated above for the case of 1,4-naphthoquinone. Phthalic anhydride[17] and benzil[18] further illustrate these features. The $+E$ spectrum of phthalic anhydride shows the following dissociations, $[P - CO_2]$, $[P - (CO_2 + CO)]$, $P \rightarrow C_5H_2^{\cdot+}$, $P \rightarrow C_4H_2^{\cdot+}$, and $P \rightarrow C_3H^+$, while that of benzil exhibits $[P - CO_2H^{\cdot}]$, $[P - PhCO^{\cdot}]$, $[P - PhCO_2^{\cdot}]$, $P \rightarrow C_6H_5^+$, $P \rightarrow C_5H_3^+$, $P \rightarrow C_4H_3^+$, and $P \rightarrow C_3H_3^+$ decompositions. Corresponding ions are present in the conventional spectra.[17,18]

It follows, *for the cases that we have cited,* that the structures of the fragmenting molecular cations produced by direct ionization and from the charge stripping process have the same (or very similar) structures, and that the differences in reactivity between the two species are due primarily to internal energy differences. Similarly, there can be no distinct structural differences between the negative precursor ion and the positive species produced by the charge stripping reaction, as it has been shown[5] that such collision processes are rapid, occurring within the time interval necessary for a molecular vibration.[19] This conclusion has important ramifications in the study of negative ions, as the structures of negative species which do *not* decompose in the negative mode may now be investigated by means of their $+E$ spectra.

Consider now molecules which form both molecular anions and fragment ions. The dinitrobenzenes are appropriate examples; their spectra contain pronounced $P^{\cdot-}$, $(P - NO^{\cdot})^-$, and NO_2^- peaks at 70 eV.[20] The positive ion mass spectra of dinitrobenzenes contain $(P - NO^{\cdot})^+$ and NO_2^+ ions of very small abundance (<1% of the base peak). The $+E$ spectra will therefore show some decompositions yielding ions *not* observed in the conventional positive ion spectra. The $+E$ spectrum arising from negative ions from *m*-dinitrobenzene is shown in Figure 3, and all fragmentations are listed in Table II. The $+E$ spectra of the ortho and para isomers are similar to that of *m*-dinitrobenzene, but they *lack* those decompositions indicated in Table II. Observations arising from these spectra follow.

(i) All three spectra show the presence of an NO_2^+ ion (peak 5 in Figure 3) produced directly from NO_2^-. We have measured the $+E$ spectra of a large number of nitrophenyl systems and the NO_2^+ ion occurs in approximately half of these spectra. This is the only example (to date) where the direct formation of a "stable" positive ion from the collision process has been detected.

(ii) The $(P - NO^{\cdot})^+$ intermediate undergoes four decompositions (peaks 3, 6, 8, and 15 in Figure 3), while NO_2^+ only fragments to NO^+. All other dissociations occur directly from the decomposing molecular species.

(iii) The $+E$ spectra of the isomeric dinitrobenzenes are different (Table II), thus allowing differentiation of the isomers. This can also be achieved using either the positive or negative ion spectra,[20] but in these cases it is necessary to rely solely upon differing abundances of ions in the different spectra.

Conclusions

(1) $+E$ spectra derived from negative ions provide information analogous to that derived from conventional low resolution positive ion mass spectra.

(2) The $+E$ spectrum of a negative ion has the potential to be used to provide information concerning the structure of that negative ion.

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(12) It is not uncommon to obtain a composite IKE signal produced by two (or more) collision-induced dissociations. This is a further reason for determining $+E$ spectra by the magnetic scan method.

(13) We have no facilities available to measure the difference in kinetic energy between the positive and negative ions.

(14) A referee has suggested (i) that a two-stage process involving a neutral intermediate is also possible, and (ii) that the fragmentations may, in part, be due to the high pressures experienced by the ion after stripping.

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(19) A referee has pointed out that the structural relationship applies only during the reaction; subsequently there will be a several microsecond period during which rearrangement can occur. Although rearrangements are not noted for these examples, a further study is planned to investigate the possibility of rearrangements in systems which may be more prone to such reactions.

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Chemical Evolution. XXVI. Photochemistry of Methane, Nitrogen, and Water Mixtures as a Model for the Atmosphere of the Primitive Earth[1]

J. P. Ferris* and C. T. Chen

Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181. *Received August 2, 1974*

Abstract: Methane-water vapor mixtures were irradiated using a low pressure mercury lamp and the reaction products were determined at intervals between 0.5 and 6 hr. Formaldehyde, acetaldehyde, and methanol were observed after 0.5 hr. The presence of ethylene glycol, ethanol, acetone, isopropyl alcohol, *tert*-butyl alcohol, methyl ethyl ketone, isobutyl alcohol, *tert*-amyl alcohol, and neopentyl alcohol was detected in small amounts after 2 hr and the yields increased after 4 and 6 hr irradiation times. Virtually the same product yields were obtained after irradiating a ~2:1 methane-water mixture as were obtained from a ~1:1:1 methane-nitrogen-water mixture demonstrating that nitrogen does not react under these conditions. Furthermore, no amino acids were detected when nitrogen was added to the reaction mixture. The reactions are initiated by the hydroxyl radicals formed by water photolysis. These hydroxyl radicals abstract a hydrogen atom from methane as the first step in the synthesis. The prebiological significance of these photochemically generated compounds is discussed.

Ultraviolet light from the sun offered the greatest potential as the energy source to drive chemical reactions on the primitive earth. It has been estimated that, in the absence of ozone, wavelengths less than 300 nm contributed 3400 cal cm^{-2} $year^{-1}$ and those less than 200 nm contributed 41 cal cm^{-2} $year^{-1}$ to the surface of the primitive earth.[2] The next most abundant energy sources, electrical discharges and shockwaves are estimated to have contributed 4 and 1.1 cal