Reports

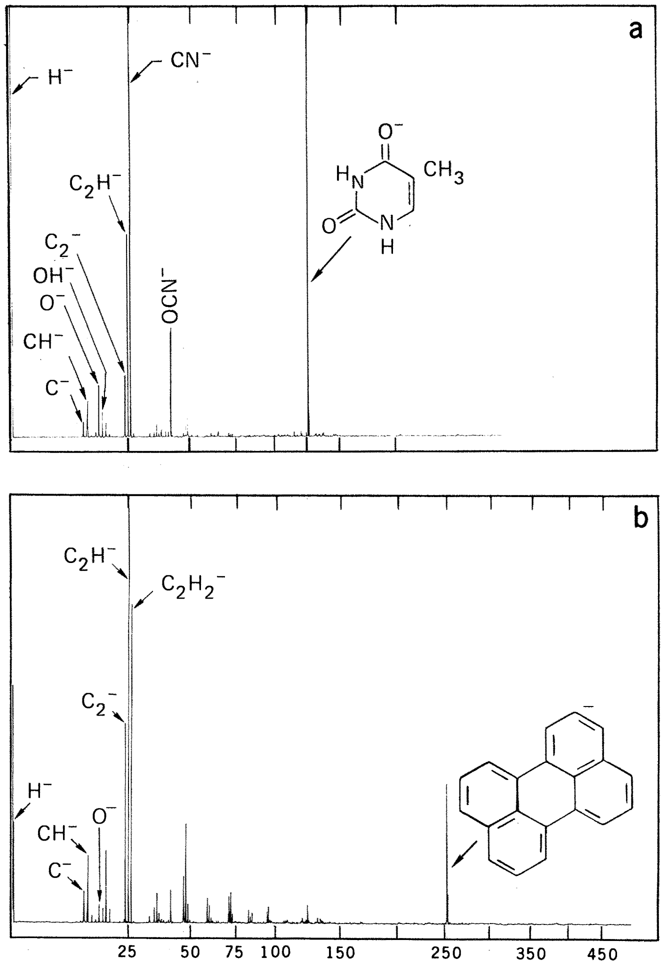
Formation of Negative Ions Under Inverted Field Ionization Conditions

Abstract. *Negative organic ions including those of thymine, perylene, and trinitrotoluene have been produced by subjecting the parent substances on a metal surface to the influence of a high positive electrostatic field. The field produced at highly curved metallic surfaces (below the threshold of field emission) may allow electron uptake by substances that have a sufficient electron affinity. The scope and implications of this novel mass spectrometric technique are discussed.*

Field ionization (FI) has been applied extensively in recent years to many problems in analytical mass spectrometry (*1*, *2*). This ionization process involves electron tunneling from field-polarized molecules into a metallic anode. High enough fields (10^7 to 10^8 volt/cm) may be generated in the vicinity of highly curved surfaces (radius of curvature $\sim 10^{-5}$ cm) of anodes if relatively low potentials (1000 to 2000 volts) are applied between the curved anode and a cathode placed in close proximity to it (0.02 to 0.05 mm away). A related process is field desorption (*3*, *4*) in which absorbed cations are desorbed from an anode under the effect of a strong electrostatic field. The field strength in this case is enough to overcome the electrostatic interaction between cations and anions in an ionic substrate.

We have recently demonstrated (*5*) the analogous phenomenon of desorbing anions from a highly curved cathode under field strengths insufficient to induce field emission (of electrons). Species such as Cl^-, I^-, $NaCl_2^-$, $K_2Cl_3^-$, FeF_4^-, ClO_4^-, and UO_2F^- were demonstrated by mass spectrometry (*5*). It was of interest to find out whether nonionic molecules that possess a positive electron affinity would form negative ions when exposed to a high field in the vicinity of a highly curved cathode. This idea was tested experimentally, and negative ions in a high yield were shown to be produced in this manner.

The experimental setup was identical to that used for conventional FI (*2*). We inverted the polarity of the Stanford Research Institute porous multipoint source (*2*) mounted on a sector magnet analyzer with a low resolution (*3*), the polarity of which was also inverted. The negative ions



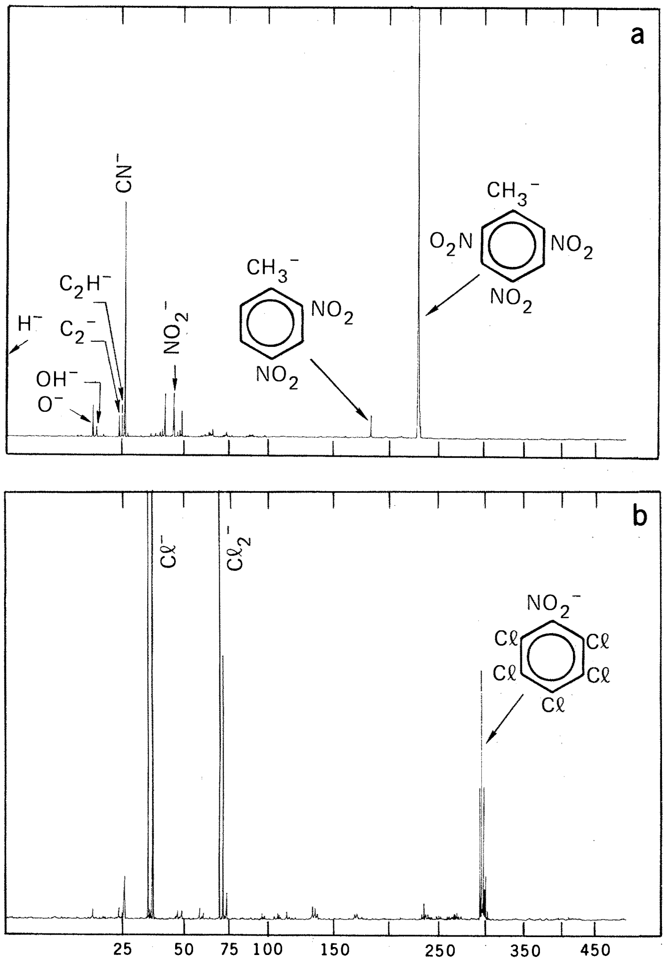


Fig. 1 (left). Negative ion spectra of thymine (a) and perylene (b). Fig. 2 (right). Negative ion spectra of TNT (a) and PCNB (b).

were collected and counted by an electron multiplier. After passing through a preamplifier, the ion pulses were integrated by a rate meter and displayed as a function of the magnetic field on an X-Y chart recorder. The mass spectra of the negative ions were obtained by manual scanning. The points-to-grid voltages were comparable to those used for FI, but the ion current measured for the parent anions (10^{15} ions formed per mole of neutral molecules) was lower by an order of magnitude than that of the corresponding positive molecular ions.

The spectra of several negative ions were obtained. Representative examples are those of thymine and perylene (Fig. 1) and trinitrotoluene (TNT) and pentachloronitrobenzene (PCNB) (Fig. 2). Unlike the virtually unfragmented mass spectra of positive ions obtained from the same compounds under FI (*6*), these spectra show substantial amounts of negatively charged fragmentation products in addition to a high yield of the electron adducts of the parent molecules. However, the peak at a mass-to-charge ratio m/e of 126 in the perylene spectrum (Fig. 1b) may be instead of a fragment a perylene molecule carrying two negative charges, such as F^{2-} or SO_4^{2-} found in field desorption (*5*). Furthermore, the dinitrotoluene (DNT) peak in Fig. 2a is a trace impurity and not a fragmentation product, as evidenced by the fact that the ratio TNT/DNT increased while the sample evaporated into the ionization source.

The mechanism of formation of negative ions under high field conditions is evidently different from that of FI. The strong fields lower the work function of the cathode—even before inducing field emission—so that the electron affinity of molecules in the close vicinity of the cathode induces electron transfer. This electron affinity may be enhanced by the field, which repels electrons of the absorbed polarized molecule away from the cathode. In view of the fact that the electron transfer from the cathode to the polarized substrate is exoergic (positive electron affinity), we may end up with highly excited primary species that will undergo dissociative electron attachment. The negatively charged fragments observed seem to be of species that have a higher electron affinity than the parent molecule, for example, CN^-, OCN^-, C_2H^-, and OH^- in the case of thymine; Cl^- and Cl_2^- in the case of PCNB; and OH^-, CN^-, and NO_2^- in the case of TNT. These entities may break off from the parent molecule at the instant of electron transfer, owing to its exoergic nature, or, more likely, they may be decomposition products of highly excited negative ions formed when an electron is transferred into the highly polarized substrate molecule.

The phenomenon described in this report has not been described before. We shall name this mode of formation of negative ions "field-induced negative ion formation" (FINIF, in short). It has interesting theoretical implications pertaining to the effects of high fields on metals and to the behavior of substrate molecules in high fields. It also has potential analytical applications as it may produce high yields of molecular ions of highly electronegative species that are difficult to field-ionize. Each molecule may have its own characteristic fragmentation pattern, and this pattern may help to elucidate chemical structures of nonvolatile species (when placed directly on the cathode). It may be that FINIF will become a unique tool for the production of previously unknown negative ions that can be investigated for their structures and other properties, for example, electron detachment cross sections, or for their chemical reactivity with neutral or positive species.

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References and Notes

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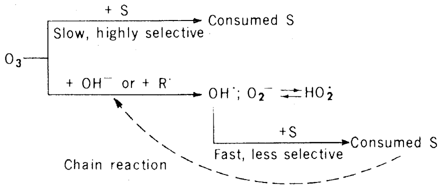
Ozonation of Water: Role of Hydroxyl Radicals as Oxidizing Intermediates

Abstract. *Hydroxyl radicals are the main oxidants formed in the decomposition of ozone in water. This is demonstrated by measuring the relative rates at which different substrates are consumed and comparing them with known reaction rate constants. Knowledge accumulated by radiation chemists and biologists on the reactions of hydroxyl radicals can therefore be used to describe oxidations succeeding ozone decomposition.*

It has long been recognized that O_3, a slowly reacting oxidant, may decompose in water into more reactive intermediates. However, decomposition products have not been identified and a quantitative basis for their subsequent reactions has not been established. In this report we show that (i) O_3 reacts with substrates in water by two different pathways, (ii) OH radicals are important oxidative intermediates formed in the decomposition of O_3, and (iii) it is possible to apply the extensive literature on reactions involving OH radicals in evaluating and optimizing the oxidations initiated by O_3 in water.

Ozone is a widely accepted agent for water treatment processes in many countries. It acts as a bactericide, bleaches many organic chromophores, can improve the taste of water, and oxidizes manganese(II). If O_3 molecules react directly with organic substrates, they will behave selectively in consuming different types of substrates. Styrene, for example, is oxidized 10^5 times faster and xylene 25 times faster than benzene (*1*). Organic chemists take advantage of this group-specific oxidation in the solution of their synthetic and analytical problems. In contrast, when O_3 is to be used to treat refractory organic impurities in wastewater or potable water, conditions are selected which favor a preceding decomposition of O_3 into more reactive oxidants that behave less selectively.

Ozone decomposition is known to be catalyzed by hydroxide ions (*2*). It can also be accelerated by radicals ($R^\bullet$) which act as carriers of a chain reaction. Decomposition of O_3 can therefore compete with direct consumption of O_3 molecules by solutes (S), as shown in scheme 1.



Scheme 1

This reaction scheme is seldom acknowledged in the literature on the application of O_3 to water treatment since the quantitative aspects of the model have not previously been tested by rigorous experiments.

We based our experiments for testing this reaction scheme on the consideration that the types of oxidants involved in the reaction can be identified from the relative rates at which pairs of substrates compete