2 cannot, of course, be excluded by the present data. If such a dimer is formed, its association constant with respect to monomer **2** is less than the association constant for monomer **1**.

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(12) In biochemical applications transference of equilibrium constants for the purine or pyrimidine bases from aqueous solutions to associated bases within nucleic acids could be in error by orders of magnitude. On a more positive note, the demonstration that **2** is 6 kcal/mol more strongly associated in cyclohexane than in dioxane suggests that the energy of enzyme–substrate binding could be strongly influenced by the molecular environment at the binding site. W. P. Jenks, "Catalysis in Chemistry and Enzymology", McGraw-Hill, New York, N.Y., 1962; T. C. Bruice, "The Enzymes", P. R. Boyer, Ed., Academic Press, New York, N.Y., 1970, Chapter 4.

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Exploratory Field Desorption Mass Analysis of the Photoconversion of Adsorbed Polycyclic Aromatic Hydrocarbons

Sir:

Experiments conducted with polycyclic aromatic hydrocarbons (PAH) adsorbed on silica gel, alumina,[1-4] and on surfaces of crystalline PAH[5] demonstrate increased photochemical reactivity over that observed in solution. PAH might similarly undergo accelerated photoconversion when adsorbed on carbon soot.[6-8] In this report, we describe the application of field desorption mass spectrometry (FDMS) to study the photooxidation of PAH adsorbed on carbon. Mass spectra of PAH irradiated directly on carbon microneedle emitters are presented and discussed.

Field ionization mass spectrometry has been used to detect primary, gas-phase, photodecomposition products.[9-11] FDMS, a related technique which is becoming increasingly useful in analytical chemistry,[12] could be similarly applicable to the investigation of surface phase photochemisry. In FDMS the sample is adsorbed directly onto an electrode (the emitter), where it is subsequently ionized and desorbed by application of a high electric field. Although the mechanism of ionization is a subject of current debate, volatilization of the sample prior to ionization is generally believed not to occur. Photochemical reactions of material adsorbed on an emitter take place in the ionization region and, thus, direct analysis of the reaction products is possible. At present, the most commonly used emitter consists of carbon microneedles grown on a thin tungsten wire.[13,14] X-ray studies show the carbon structure of emitter microneedles to be very similar to that of graphite[14] and, hence, soot.[15] Since airborne PAH are principally associated with soot,[8] the results of photooxidation experiments conducted on field desorption emitters should aid in understanding naturally occurring photochemical processes.

A Hitachi-Perkin Elmer RMU-7, single focusing mass analyzer fitted with a field ionization/field desorption ion source, constructed in the authors' laboratory, was used in this work. Similar sources are described elsewhere.[16] The RMU-7 was modified to extend its mass range to *m/e* 500 at an accelerating voltage of 3.6 kV and to provide it with a stable, Hall probe regulated, programmable magnet scan controller. The instrument has a resolution of about 600 at *m/e* 500.

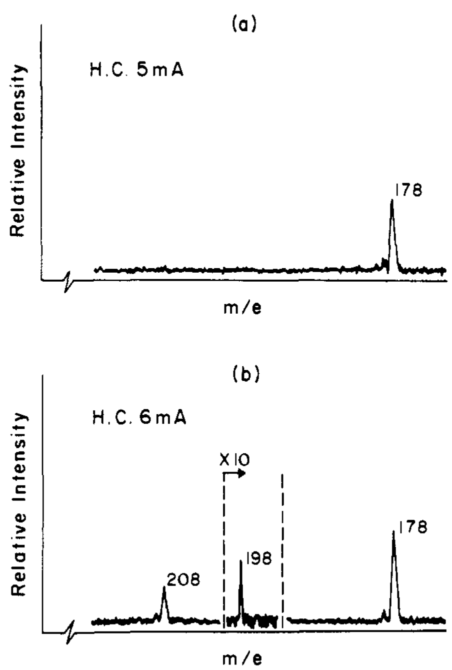


Figure 1. Field desorption mass spectra: (a) anthracene (*m/e* 178), nonirradiated; (b) anthracene, irradiated 1 h.

The sensitivity of the instrument for acetone (*m/e* 58 in the field ionization mode is 2×10^{-8} A/Torr. In the field desorption mode the sensitivity of the RMU-7 to benzo[*a*]pyrene (*m/e* 252), that is the ratio of the total integrated ion current at *m/e* 252 to the amount of sample used (~0.6 ng), is about 5×10^{-14} C/ng. The field desorption limit of detectability for benzo[*a*]pyrene is about 25 pg (0.1 μl of a 10^{-6} M benzene solution deposited on the emitter).

Photooxidation experiments were performed on anthracene, benzo[*a*]anthracene, pyrene, benzo[*a*]pyrene, chrysene, and coronene. Solutions of PAH in bromobenzene (~10^{-3} M) were prepared from reagent grade chemicals after purification by sublimation. Approximately 1 μl of solution was deposited on an emitter, leaving ~0.1 μg of sample adsorbed after solvent evaporation. Field desorption mass spectra of each compound were obtained to establish purity and to provide references for comparison with spectra of the irradiated samples. Reference spectra of all compounds were found to exhibit only molecular ion mass peaks with no evidence of impurities. A typical reference spectrum of anthracene is shown in Figure 1a.

Sample material, adsorbed on an emitter, was irradiated in air with a high pressure mercury arc lamp for 30-60 min. Radiation was filtered with a 5-cm quartz water cell and the emitter support post was immersed in a Dewar containing acetone and dry ice. These measures were taken to prevent thermal reactions and evaporation of surface-adsorbed species. Light intensity at the sample surface was approximately 200 mW/cm^2. Immediately following irradiation, samples were placed in the field desorption ion source for mass analysis.

Photooxidation of anthracene, benzo[*a*]anthracene, pyrene, and benzo[*a*]pyrene on field desorption emitters is observed; photomodification of chrysene and coronene under the same conditions is not observed. All compounds, with the exception of coronene, have been shown to react similarly under exposure to ultraviolet radiation when adsorbed on silica gel.[3]

The mass spectrum of irradiated anthracene is shown in Figure 1b. In addition to the molecular ion mass peak at *m/e* 178, the spectrum exhibits peaks at *m/e* 198 and 208. The peak at *m/e* 208 corresponds to anthraquinone, an expected photooxidation product.[5] The identity of the small peak at *m/e* 198 is unknown. The absence of peaks due to impurities, instrument background, or cluster ions (singly or doubly charged) in the

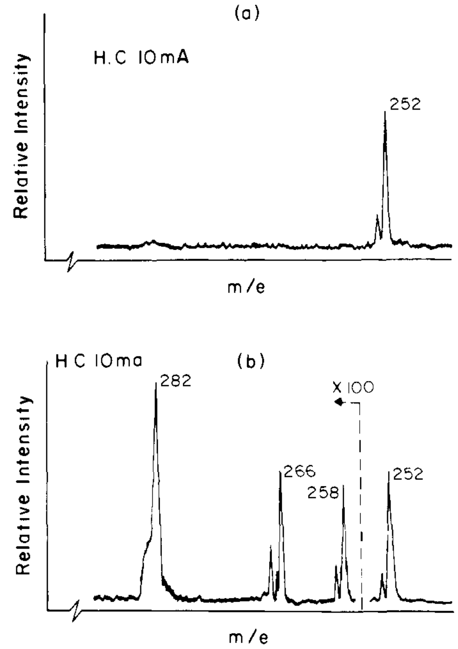
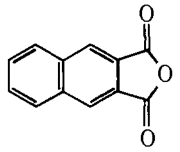


Figure 2. Field desorption mass spectra: (a) benzo[*a*]pyrene (*m*/*e* 252), nonirradiated; (b) benzo[*a*]pyrene, irradiated 40 min.

anthracene reference spectrum (Figure 1a) suggests that the *m*/*e* 198 peak is due to a photoproduct. Although end ring opening is not favorable for anthracene, the production of a dicarboxylic acid may occur under the possibly strong oxidative conditions at the emitter surface during ultraviolet irradiation. Loss of water from the diacid before or during field desorption would lead to the production of naphthalene 2,3-anhydride (**1**) (*m*/*e* 198). A more remote possibility might be the formation of a highly reduced compound (**2**) at the emitter surface.



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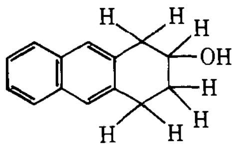

2

Mass spectra of irradiated samples of benzo[*a*]anthracene and pyrene exhibit weak peaks corresponding to diones of the two compounds. No other peaks are evident.

In addition to the parent ion peak at *m*/*e* 252, the mass spectrum of irradiated benzo[*a*]pyrene (Figure 2b) exhibits mass peaks at *m*/*e* 258, 266, and 282. The mass peak at *m*/*e* 282 corresponds to a dione. The mass peaks at *m*/*e* 258 and 266 are not yet identified. As with anthracene, the absence of contaminant or artifact (e.g., cluster ion) peaks in the reference spectrum of benzo[*a*]pyrene (Figure 2a) suggests that the two peaks in question represent photoproducts.

The results of this investigation demonstrate that FDMS can be used to identify photoproducts of PAH adsorbed on carbon. The absence of observed photoproducts in the case of coronene suggests that PAH may not be as reactive on carbon as on silica gel or alumina.

Detection and identification of primary reaction products appear possible with a modified field desorption ion source. The use of conventional mass spectrometry for this task is difficult because of the opposing requirements of high light absorption to generate large numbers of free radicals and of relatively low pressures to enable rapid diffusion into the ionization chamber. By contrast a field desorption sample is introduced into the source in a relatively concentrated, solid phase adsorbed on an emitter. Although reactive gases, such as oxygen, cannot be introduced at pressures greater than 10^{-3} Torr, their partial pressures at the surface of the emitter are greatly increased by the high electric field necessary for ionization.[17] Therefore, adsorbed state photoreactions should proceed under normal field desorption operating conditions. Furthermore, if a free radical production rate of a few picograms per second occurs with about 1 μg of sample, it would be possible to detect and identify the radicals with the instrument used in this study. Plans are currently being developed to conduct in situ experiments.

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Crystal Structure of "Carboxyethylgermanium Sesquioxide"

Sir:

During the past 2 decades the development of the organic chemistry of germanium has been extensive.[1,2] This has been due in part to the semiconducting nature of the element and to the anticipated similarities in chemical and physical properties to silicon.

We wish to report the first crystal structure of a novel "organogermanium sesquioxide" resulting from the hydrolysis of an organogermanium trichloride. It can reasonably be expected that the analogues of organogermanium sesquioxides and organosilicones might have a similar unique crystal structure. As with the alkyl and aryl chlorosilanes, the complexity of the hydrolysis products of organogermanium halides increases with the number of halogen atoms present.[3] The triols derived from the trihalides all dehydrate to form polymeric solids which dissolve like dioxides in hydrohalic acids. The polymeric solids are also soluble in alkalis, from which they may be reprecipitated by carbon dioxide.[4] The general composition of the polymers corresponds to the anhydride formula $(RGe)_2O_3$. The alkyl and aryl germanium oxides are polymeric solids and exhibit no definite melting points. To date, no structures of organogermanium oxides prepared by hydrolysis of a trihalide parent compound have been reported.