

solvent polarity, the TMEDA effect, and the deuterium labeling are all consistent with this interpretation. The presence of adventitious oxygen would have been detected by cyclization at -78 °C from the radical but this was not observed.¹²

In order to show that a valid radical test can be made at -78 °C, the *o*-(3-butenyl)phenyl radical was generated from the corresponding bromide with lithium naphthalene¹⁴ at -78 °C, held at this temperature for 1 h then quenched and worked up to give 52% **3** (X = H) and 46% **2** (X = H). This result indicates the intermediacy of the radical in this reaction because the anion with the same counter ion (Li⁺) and in the same solvent (THF) is stable at this temperature.

Verification of the anionic cyclization at room temperature has been carried out by a series of electrochemical experiments. Electrochemical reduction of *o*-(3-butenyl)bromobenzene carried out at an electrode surface generated an anion which can cyclize to the methylindan derivative.¹⁵ This process was shown to be prevented by introduction of water which protonated the intermediate anion. Alternately, the cyclization was facilitated by use of a mediator to allow reduction to the radical anion which decomposed rapidly to the aryl radical and cyclized before further reduction could occur. These results will be reported in detail shortly.

Radical tests by cyclization of alkene substrates must be carried out at low temperature in nonpolar solvents or under conditions where it has been shown that the anion does not cyclize.

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(12) The possibility that a small amount of oxygen might oxidize the aryllithium reagent to the radical¹³ with subsequent cyclization was examined by introduction of dry air at -78 °C. Quenching after 5 min gave no **3** but ca. 5% of a product which was tentatively assigned the 1-(hydroxymethyl)indan (**4**) structure. On longer treatment more of this product was observed, but no **3**. Thus, the aryllithium reagent was oxidized to the radical which cyclized at -78 °C and was oxygenated leading ultimately to **4**.

(13) Beckwith, A. L. J.; Goh, S. H. *J. Chem. Soc., Chem. Commun.* **1983**, 905.

(14) Garst, J. F.; Barbas, J. T. *J. Am. Chem. Soc.* **1974**, *96*, 3239.

(15) Koppang, M. D.; Ross, G. A.; Woolsey, N. F.; Bartak, D. E. unpublished results.

Mass Spectrometry of Microscale Chemical Reaction Products Produced at the Surface of Organic Solids

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Chemical reactions that take place at the surface of organic solids are of interest in a wide range of fields. We here report a new technique for detecting such reactions. During the course of a ²⁵²Cf ionization¹ mass spectrometric investigation² of the triphenylmethane dye crystal violet,³ we inadvertently exposed a thin solid film⁴ of the dye to light in the presence of air following the essentially nondestructive⁵ mass spectrometric analysis. Subsequent mass spectrometric reanalysis of the dye film demonstrated with great clarity that the compound had undergone extensive chemical transformations.

(1) Macfarlane, R. D.; Torgerson, D. F. *Science (Washington, D.C.)* **1976**, *191*, 920-925. Chait, B. T.; Agosta, W. C.; Field, F. H. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 339-336.

(2) Chait, B. T. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *53*, 227-242.

(3) *N*-[4-[Bis[4-(dimethylamino)phenyl]methylene]-2,5-cyclohexadiene-1-ylidene]-*N*-methylmethanaminium chloride.

(4) The thin film was produced by electro-spraying 1 μg of crystal violet dissolved in methanol onto a circular disk of aluminized polyester with an area of 1 cm² as described by: McNeal, C. J.; Macfarlane, R. D.; Thurston, E. L. *Anal. Chem.* **1979**, *51*, 2036-2039.

(5) We estimate that only 10⁻⁶ of the sample is consumed by the ionization process during a typical measurement.

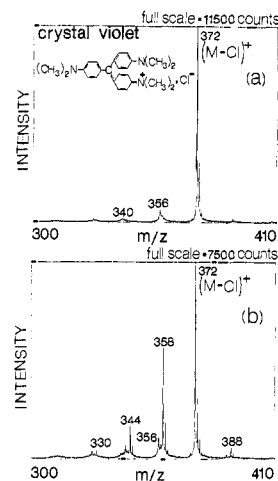


Figure 1. Partial positive ion ²⁵²Cf time-of-flight mass spectra of a film of crystal violet (a) unirradiated and (b) irradiated with visible-wavelength photons.

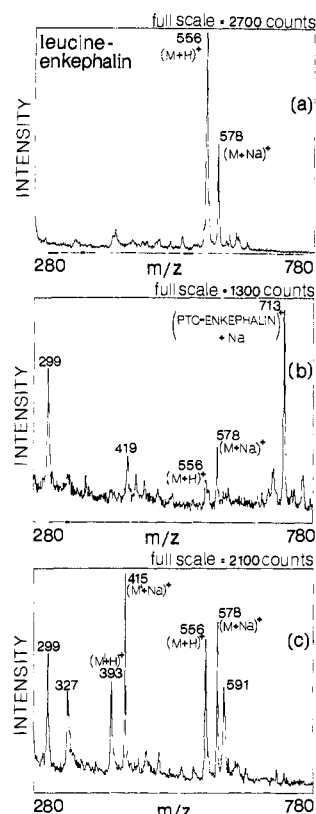


Figure 2. (a) Partial positive ion ²⁵²Cf mass spectrum of a film of untreated leucine-enkephalin. (b) Mass spectrum of the film after exposure to phenyl isothiocyanate, tributylamine, and H₂O vapors. (c) Mass spectrum of the film after subsequent exposure to trifluoroacetic acid vapor. PTC = phenylthiocarbonyl. M denotes the mass of leucine-enkephalin. M' denotes the mass of leucine-enkephalin minus the N-terminal tyrosine residue.

To establish the generality of the procedure the surface reactions of several organic solids were investigated with three major reagent classes:

(1) **Photons.** Figure 1a shows the high-mass portion of the mass spectrum of crystal violet prior to irradiation of the dye film. The spectrum exhibits an intense intact cation peak at *m/z* 372 and several less intense fragment ion peaks (e.g., at *m/z* 356 and 340) arising from successive loss of methane.⁶ Figure 1b shows the spectrum obtained from the same sample film after a brief irra-

(6) Scheifers, S. M.; Verma, S.; Cooks, R. G. *Anal. Chem.* **1983**, *55*, 2260-2266. Pannell, L. K.; Sokolowski, E. A.; Fales, H. M.; Tate, R. L. *Anal. Chem.* **1985**, *57*, 1060-1067.

diation with visible-wavelength photons⁷ in an atmosphere of O₂ with H₂O present.⁸ The peaks at m/z 358, 344, and 330 arise from three photodemethylation products of crystal violet. The small peak at m/z 388 is probably the (M - H)⁺ ion⁶ of the carbinol base of crystal violet, which also appears to be formed as a photoproduct.

Irradiation of rhodamine B⁹ under the same conditions as those for the crystal violet gave analogous deethylation photoproducts with a similar yield. The spectrum of unirradiated diethylstilbestrol¹⁰ exhibits an intense molecular ion peak at m/z 268. Irradiation of the sample with 254-nm photons in air yielded a major product of unknown structure which produces an intense peak at m/z 266.

(2) **Light Gases.** The partial mass spectrum (between m/z 210 and 400) of the sodium salt of vaccenic acid (CH₃(CH₂)₅CH=CH(CH₂)₉COONa) consists of a single peak at m/z 327 (M + Na)⁺. After exposure of the sample to a 1% O₃ in O₂ mixture for a time of 2 s the spectrum exhibits three peaks with m/z 245 (OHC(CH₂)₉COONa·Na⁺), 261 (HOOC(CH₂)₉COONa·Na⁺), and 283 (the (M + 2Na - H)⁺ ion¹ corresponding to the m/z 261 ion). The cleavage in the ozonolysis occurs, as expected, at the double bond.¹¹ Ions from the complementary ozonation cleavage products are not observed because they volatilize rapidly after the sample foil is reinserted into the mass spectrometer. Exposure to O₃ of the vaccenic acid positional isomer petroselinic acid sodium salt (CH₃(CH₂)₁₀CH=CH(CH₂)₄COONa) gave rise to three analogous but distinct products with ions at m/z 175 (OHC(CH₂)₄COONa·Na⁺), 191 (HOOC(CH₂)₄COONa·Na⁺), and 213 (NaOOC(CH₂)₄COONa·Na⁺).

Exposure of a variety of other compounds¹² to O₃, NO, and NO₂ further demonstrated that the production of new materials

(7) Unfiltered tungsten-halogen light source; color temperature = 3100 K; radiant flux on the sample 4×10^6 ergs cm⁻² s⁻¹ for 300 s.

(8) H₂O partial pressure = 15 torr.

(9) *N*-[9-(2-Carboxyphenyl)-6-(diethylamino)-3*H*-xanthen-3-ylidene]-*N*-ethylethanaminium chloride.

(10) α,α' -Diethylstilbene diol.

(11) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. 1.

(12) Compounds exposed to O₃: somatostatin, oxytocin, *S,S*-dimethyl-reduced oxytocin, cystine dimethyl ester dihydrochloride, bilirubin, pregnenolone, 26-hydroxycholesterol, cholesterol, and crystal violet. Compounds exposed to a mixture of NO and NO₂: 26-hydroxycholesterol, 19-hydroxycholesterol, and vaccenic acid sodium salt.

could be sensitively followed and their masses readily identified.

(3) **Complex Vapors.** The data shown in Figure 2 demonstrate the feasibility of carrying out and detecting on a surface film products of a complex reaction, namely, the coupling and cleavage steps of the Edman sequencing reaction for peptides.¹³ Figure 2a shows the partial mass spectrum of leucine-enkephalin¹⁴ prior to treatment. Figure 2b shows the spectrum of the film after it was held in an atmosphere of phenyl isothiocyanate, tributylamine, and H₂O at a temperature of 48 °C for 60 min. The peak at m/z 713 corresponds to the sodium-cationized phenylthiocarbamyl peptide coupling reaction product. The peak at m/z 299 appears to arise from mass spectrometric fragmentation of the protonated phenylthiocarbamyl peptide to give the coupled N-terminal tyrosine fragment ion. Figure 2c illustrates the result of the cleavage step, which was performed with gaseous trifluoroacetic acid at a temperature of 25 °C for 12 min. The phenylthiocarbamyl peptide is fully cleaved yielding the shortened four-residue peptide with mass 392 units. The peak at m/z 299 in Figure 2c corresponds to the protonated thiazolinone derivative of tyrosine. The peaks at m/z 419, 327, and 591 result from products of thus far unidentified side reactions.

The general properties of the mass spectrometric surface reaction probe are summarized as follows:

Sensitivity is high; our experience is that 10⁻⁹ to 10⁻¹⁵ mol of material can be measured in solid-phase particle bombardment mass spectrometry. Low yields (1–2%) of product can be detected reliably (e.g., measured value for the product with m/z 388 in Figure 1 is 1.5%). The method has a high surface specificity since ion bombardment mass spectrometry is highly surface selective. The analysis is essentially nondestructive.⁵ The analyses are rapid since the mass spectra described here required a measurement time of only 1–10 min. In the present system it is not possible to obtain the mass spectra of volatile compounds and volatile reaction products since they are pumped away.

Acknowledgment. This work was supported in part by the Division of Research Resources, National Institutes of Health.

(13) Edman, P.; Henschen, A. In "Protein Sequence Determination"; Needleman, S. B., Ed.; Springer-Verlag: Berlin, Heidelberg, New York, 1975; pp 232–279.

(14) L-tyrosylglycylglycyl-L-phenylalanyl-L-leucine.

Additions and Corrections

Bare Tetranuclear Transition-Metal Cluster Ions in the Gas Phase. Reactivity of Sc₄⁺ with Small Molecules [*J. Am. Chem. Soc.* **1985**, *107*, 1590]. M. B. WISE, D. B. JACOBSON, and B. S. FREISER*

We wish to retract this paper. What was believed to be Sc₄⁺ has been shown subsequently to be Ta⁺. The scandium sample was obtained from Alfa with a purity designation of 99.9% (REO) indicating only that other rare earth oxides are present at <0.1%. Reductive and reaction vessel contaminants such as calcium and tantalum are not included in the (REO) purity designation, nor are any non-rare-earth metals. In fact the scandium sample was determined independently (Galbraith Laboratories, Inc., Knoxville, TN) to be about 5% tantalum by weight. Since we were specifically looking for clusters when the spectrum shown in Figure 1 was obtained, it was wrongly assumed that Sc₂⁺ and Sc₄⁺ were present resulting in a correspondingly incorrect mass calibration. It is evident now from Figure 1 that about a tenfold increase in sensitivity of tantalum relative to scandium is achieved under the specific conditions used. Thus, in summary, one should be aware of the high level of impurities which can be present when obtaining elemental samples from Alfa with an REO purity designation and

of the possibility of observing enhanced impurity peaks when using laser ionization. Finally, on a positive note, this "preliminary study of Ta⁺" demonstrates the extraordinary degree of reactivity of Ta⁺ toward alkanes.

Synthesis and Structures of (C₅H₅)₂Mo₂Fe_xTe₂(CO)₇ (x = 1, 2). Cluster Assembly Mechanisms and the Role of the Tellurium [*J. Am. Chem. Soc.* **1985**, *107*, 3843]. LEONARD E. BOGAN, JR., THOMAS B. RAUCHFUSS,* and ARNOLD L. RHEINGOLD*

Page 3847, Table III, Selected Bond Distances (Å) and Angles (deg) for Cp₂Mo₂Fe₂(μ₃-Te)₂(CO)₇, has been printed incorrectly. A correct copy has been deposited in the Supplementary Material for this article and is available from the authors.

Reactions of Cyclic Cation Radicals with Nucleophiles: A New Route to Distonic Ions [*J. Am. Chem. Soc.* **1985**, *107*, 4562–4564]. THOMAS M. SACK, RONALD L. CERNY, and MICHAEL L. GROSS*

Page 4563: The ratio of the cyclopropane, ammonia, and hexafluorobenzene used in the high-pressure ion-molecule reaction is incorrectly reported as 1:1:0. The proper ratio should be 1:1:10.