

diation with visible-wavelength photons<sup>7</sup> in an atmosphere of O<sub>2</sub> with H<sub>2</sub>O present.<sup>8</sup> 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)<sup>+</sup> ion<sup>6</sup> of the carbinol base of crystal violet, which also appears to be formed as a photoproduct.

Irradiation of rhodamine B<sup>9</sup> under the same conditions as those for the crystal violet gave analogous deethylation photoproducts with a similar yield. The spectrum of unirradiated diethylstilbestrol<sup>10</sup> 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 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CH=CH(CH<sub>2</sub>)<sub>9</sub>COONa) consists of a single peak at *m/z* 327 (M + Na)<sup>+</sup>. After exposure of the sample to a 1% O<sub>3</sub> in O<sub>2</sub> mixture for a time of 2 s the spectrum exhibits three peaks with *m/z* 245 (OHC(CH<sub>2</sub>)<sub>9</sub>COONa·Na<sup>+</sup>), 261 (HOOC(CH<sub>2</sub>)<sub>9</sub>COONa·Na<sup>+</sup>), and 283 (the (M + 2Na - H)<sup>+</sup> ion<sup>1</sup> corresponding to the *m/z* 261 ion). The cleavage in the ozonolysis occurs, as expected, at the double bond.<sup>11</sup> 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 O<sub>3</sub> of the vaccenic acid positional isomer petroselinic acid sodium salt (CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>CH=CH(CH<sub>2</sub>)<sub>4</sub>COONa) gave rise to three analogous but distinct products with ions at *m/z* 175 (OHC(CH<sub>2</sub>)<sub>4</sub>COONa·Na<sup>+</sup>), 191 (HOOC(CH<sub>2</sub>)<sub>4</sub>COONa·Na<sup>+</sup>), and 213 (NaOOC(CH<sub>2</sub>)<sub>4</sub>COONa·Na<sup>+</sup>).

Exposure of a variety of other compounds<sup>12</sup> to O<sub>3</sub>, NO, and NO<sub>2</sub> further demonstrated that the production of new materials

(7) Unfiltered tungsten-halogen light source; color temperature = 3100 K; radiant flux on the sample  $4 \times 10^6$  ergs cm<sup>-2</sup> s<sup>-1</sup> for 300 s.

(8) H<sub>2</sub>O partial pressure = 15 torr.

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

(10)  $\alpha, \alpha'$ -Diethylstilbene diol.

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

(12) Compounds exposed to O<sub>3</sub>: 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 NO<sub>2</sub>: 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.<sup>13</sup> Figure 2a shows the partial mass spectrum of leucine-enkephalin<sup>14</sup> prior to treatment. Figure 2b shows the spectrum of the film after it was held in an atmosphere of phenyl isothiocyanate, tributylamine, and H<sub>2</sub>O 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<sup>-9</sup> to 10<sup>-15</sup> 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.<sup>5</sup> 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.

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(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 Sc<sub>4</sub><sup>+</sup> 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 Sc<sub>4</sub><sup>+</sup> has been shown subsequently to be Ta<sup>+</sup>. 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 Sc<sub>2</sub><sup>+</sup> and Sc<sub>4</sub><sup>+</sup> 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<sup>+</sup>" demonstrates the extraordinary degree of reactivity of Ta<sup>+</sup> toward alkanes.

### Synthesis and Structures of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>Fe<sub>x</sub>Te<sub>2</sub>(CO)<sub>7</sub> (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 Cp<sub>2</sub>Mo<sub>2</sub>Fe<sub>2</sub>(μ<sub>3</sub>-Te)<sub>2</sub>(CO)<sub>7</sub>, 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.