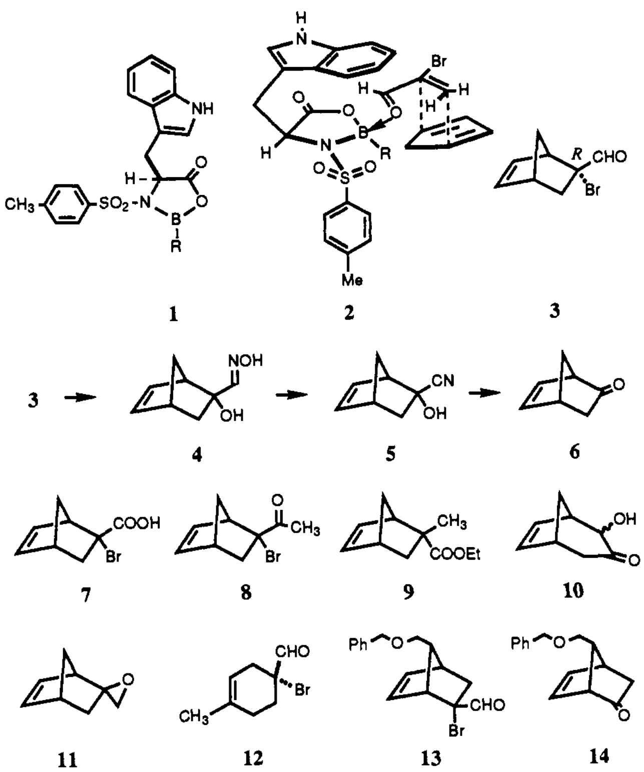
Chart I



Similar results were obtained for the catalyst **1**, R = H, under the same conditions: 98% yield, 98:2 (R/S) enantioselectivity and 97:3 (exo/endo CHO) diastereoselectivity. The minor, endo CHO, diastereomer could be removed to give pure exo adduct **3** by stirring the 94:6 exo–endo mixture with 4 mol % of aqueous $AgNO_3$ at 23 °C for 2 h and subsequent silica chromatography. The absolute configuration of the adduct from catalyst **1** was shown by conversion to the known dextrorotatory ketone **6**, $[\alpha]^{23}_D$ + 980° (*c* 0.3, $CHCl_3$),[10] via the sequence **3** → **4** (aqueous NH_2OH, 23 °C, 8 h, 61%); **4** → **5** → **6** (one flask) (TsCl–pyridine, 23 °C, 2 h; 1 M aqueous NaOH, 23 °C, 1 h, 86%).

2-Bromoacrolein is an outstanding dienophile in this catalytic Diels–Alder process not only because of the observed stereoselectivity (probably a consequence of a high s-cis preference) but also because of the exceptional synthetic versatility of the resulting adducts. To illustrate, **3** can be smoothly converted into **7** (aqueous $NaClO_2$),[11] **8** (CH_3Li; PCC), **9** (**8** with NaOEt-EtOH); **10** (aqueous K_2CO_3, 23 °C) (via the α-hydroxy aldehyde), and **11** ($NaBH_4$-EtOH; NaOH).[8a]

Isoprene and 2-bromoacrolein underwent Diels–Alder addition under catalysis by 5 mol % of **1**, R = H, at −40 °C for 48 h to form **12** (76%) with 96:4 enantioselectivity and complete position selectivity.[12]

The important intermediate for prostaglandin synthesis, **14**, was synthesized with remarkable ease. Reaction of the enantiomer of **1**, R = *n*-Bu or H, (5 mol %), 2-bromoacrolein and 5-(benzyloxymethyl)cyclopentadiene[13] (2.5 equiv) at −78 °C for 8 h in CH_2Cl_2 afforded the adduct **13** with 95:5 (exo/endo CHO) diastereoselectivity and greater than 96:4 enantioselectivity in 81–83% yield.[9,15] After removal of the minor endo aldehyde (stirring with 5 mol % aqueous $AgNO_3$) the product was transformed, by the two-flask sequence described above for **3** → **6**, into **14**, $[\alpha]^{23}_D$ −336° (*c* 0.9, $CHCl_3$) (92% ee; 54% overall yield), chromatographically and spectroscopically identical with an authentic sample of (±)-**14**.[14]

Of great mechanistic significance is the fact that the Diels–Alder reaction of cyclopentadiene and 2-bromoacrolein under catalysis of the oxazaborolidines corresponding to **1** from *N*-tosyl derivatives of (*S*)-valine or (*S*)-hexahydrophenylalanine gave the 2-(*S*)-enantiomer of **3** as major product with ca. 70% enantioexcess.[16] The *dramatically opposite* results for these amino acid derivatives and the (*S*)-tryptophan derivative **1** provide strong evidence for transition-state assembly **2**.

In conclusion, a new concept for the design of enantioselective catalysts has been supported by experiments which demonstrate a very practical and promising methodology for enantioselective synthesis.[17]

Supplementary Material Available: Procedures for the synthesis of **1**, **13**, and **14** together with spectroscopic and physical data (4 pages). Ordering information is given on any current masthead page.

---

[9] Diastereoselectivity was determined by 500-MHz ^1H NMR analysis. Enantioselectivity was determined *both* by 500-MHz ^1H NMR with the chiral shift reagent $Eu(tfc)_3$ (for **3**) or $Eu(hfc)_3$ (for **13**) (Aldrich) in $CDCl_3$ and by reduction with $NaBH_4$, conversion to the Mosher MTPA ester and ^1H NMR measurement. The figure given for enantioselectivity refers to the major (exo CHO) diastereomer.

[10] Paquette, L. A.; Doecke, C. W.; Kearney, F. R.; Drake, A. F.; Mason, S. F. *J. Am. Chem. Soc.* **1980**, *102*, 7228–7233.

[11] Corey, E. J.; Myers, A. G. *J. Am. Chem. Soc.* **1985**, *107*, 5574–5576.

[12] Absolute stereochemistry assigned by analogy with cyclopentadiene.

[13] Corey, E. J.; Koelliker, U.; Neuffer, J. *J. Am. Chem. Soc.* **1971**, *93*, 1489–1490.

[14] Corey, E. J.; Ravindranathan, T.; Terashima, S. *J. Am. Chem. Soc.* **1971**, *93*, 4326–4327.

[15] In this and the other Diels–Alder reactions described herein *N*-tosyltryptophan can be recovered efficiently for reuse.

[16] While the studies described herein were underway, results using various valine- and ethylgylcine-derived oxazaborolidines as Diels–Alder catalysts appeared.[3f,8] In the reported cases the absolute stereocourse of the Diels–Alder addition was *opposite* to that observed for **1**, and the ee's averaged about 60%.

[17] This research was assisted financially by grants from the National Institutes of Health and the National Science Foundation.

Surface Reactions and Surface-Induced Dissociation of Polyatomic Ions at Self-Assembled Organic Monolayer Surfaces

B. E. Winger, R. K. Julian, Jr., and R. G. Cooks*

Chemistry Department, Purdue University
West Lafayette, Indiana 47907

C. E. D. Chidsey

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Received March 6, 1991
Revised Manuscript Received June 13, 1991

Chemical reactions involving molecules confined to specific environments are of growing interest in host–guest chemistry[1] and in surface science.[2] Reactions between gas-phase ionic reagents and molecules constrained to surfaces are potentially interesting and accessible examples of this general phenomenon. They have additional interest given the obvious analogy with conventional ion/molecule chemistry.[3] A few poorly characterized examples of chemical reactions between projectile ions and adsorbates present on surfaces have been reported,[4,5] and this study seeks to unambiguously confirm such reactions by employing self-assem-

---

[1] (a) *Crown ethers and analogs*; Patai, S., Rappoport, Z., Eds; Updates from the Chemistry of Functional Groups; John Wiley and Sons: New York, 1989. (b) Stoddart, J. F. Host Guest Chemistry. In *Annual Reports on the Progress of Chemistry, B*; Royal Society of Chemistry: London, 1988; Vol. 85, Chapter 12. (c) Smalley, R. E. *Sciences* **1991**, *March/April*, 22.

[2] Ceyer, S. T. *Science* **1990**, *249*, 133.

[3] (a) Bowers, M. T., Ed. *Gas Phase Ion Chemistry*; Academic Press: New York, 1979. (b) Graul, S. T.; Squires, R. R. *Mass Spectrom. Rev.* **1988**, *7*, 263. (c) Nibbering, N. M. M. *Adv. Phys. Org. Chem.* **1988**, *24*, 1.

[4] (a) Cooks, R. G.; Ast, T.; Mabud, Md. A. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 209. (b) Ast, T.; Mabud, Md. A.; Cooks, R. G. *Int. J. Mass Spectom. Ion Processes* **1988**, *82*, 131. (c) Bier, M. E.; Vincenti, M.; Cooks, R. G. *Rapid Commun. Mass Spectrom.* **1987**, *1*, 92.

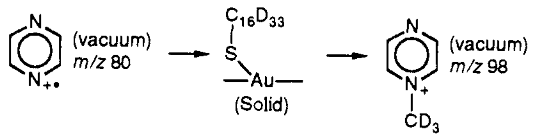
[5] For a similar but independent idea and results, see the accompanying paper: Wysocki, V. H.; Jones, J. L.; Ding, J.-M. *J. Am. Chem. Soc.*, following paper in this issue.

0002-7863/91/1513-8967$02.50/0 © 1991 American Chemical Society

bled monolayer organic films[6] which represent well-characterized organic surfaces. In the experiments discussed, hyperthermal polyatomic ions (5–100 eV laboratory kinetic energy) collide with covalently bound self-assembled monolayers of alkanethiols and fluoroalkanethiols and yield ion/surface reaction products which incorporate atoms from both the surface and the projectile. In addition, (i) elastic or quasielastic scattering and (ii) inelastic scattering followed by dissociation of the activated ion, a process known as surface-induced dissociation (SID),[7] are also observed.

The surface chosen is a self-assembled monolayer[6] of hexadecanethiol covalently bound to a 2000-Å-thick gold film supported on a 100-Å titanium layer on a silicon substrate. These surfaces are prepared by established methods,[8] are cleaned by procedures which allow any residue to be removed under vacuum,[9] and have the advantage of being transportable in air. Spectroscopic and diffraction studies[8,9] of surfaces of the types used here indicate a densely packed, crystalline-like assembly of alkane chains extended away from the surface.

When pyrazine molecular ions, *m/z* 80, are scattered from the self-assembled monolayer surface, the emerging ion beam includes protonated and methylated pyrazine, at *m/z* and 81 and 95, respectively.[10-12] When the deuterated substrate is employed, adduct ions appear at *m/z* 82, $(M + D)^+$, and *m/z* 98, $(M + CD_3)^+$.[13] The quantitative shift in mass on deuteration is a clear indication that the hydrogen and methyl groups which become attached to the projectile are derived from the adsorbate, viz., that the ion/surface methylation reaction can be represented as follows:



The data also indicate that adventitious hydrocarbons on the monolayer surface make a negligible contribution to the scattered ions. In a separate experiment, the monolayer surface was prepared using a mixture of perdeuterated and nondeuterated hexadecyl groups. Methyl adducts appeared at *m/z* 95 and *m/z* 98 but not at intermediate masses, indicating that no H/D exchange occurred. Attempts to reproduce the ion/surface reactions in the gas phase were unsuccessful: ionized pyrazine abstracts $H^\bullet$ from alkanes but does not undergo methyl abstraction.[14]

Ion/surface reactions can be accompanied by dissociation, indicated by the observation of fragment ions at *m/z* 53 and 54 among the scattered ionic products emerging when the pyrazine molecular ion $(M^{\bullet +})$ collides at the unlabeled hydrocarbon surface. These are due to HCN elimination from $M^{\bullet +}$ and protonated pyrazine, respectively, as confirmed by data for the deuterated monolayer surface, for which corresponding fragments are observed at *m/z* 53 and 55. The latter is assigned to loss of HCN from deuterated pyrazine. Fragmentation of both the pyrazine ions $M^{\bullet +}$ and $(M + H)^+$ in the gas phase is also dominated by HCN loss.[15]

While the objectives of this study did not include an examination of the mechanism of the ion/surface reaction, the evidence is consistent with electron transfer from the alkyl group to the incoming ion. The resulting ionized surface-bound hydrocarbon is expected to fragment rapidly, and bond formation between the ionic fragment and the neutralized projectile could then yield the ionic adduct observed. Although the mechanism is speculative, it is consistent with the fact that other odd-electron ions such as the benzene molecular ion $(C_6H_6^{\bullet +})$ undergo $CH_3^\bullet$ abstraction in the collision energy range up to ca. 100 eV (and then fragment by H_2 elimination). Interestingly, the phenyl cation $(C_6H_5^+)$ shows no ion/surface reaction products, its 5-eV spectrum being dominated by elastically scattered ions *m/z* 77 (65% relative abundance) and the SID fragments *m/z* 51 (100%) and *m/z* 27 (10%). The reason for this difference is not known, but it forms a sharp contrast to the gas-phase ion/molecule chemistry of these two ions, where the phenyl cation is highly reactive whereas the benzene radical cation is much less so.[16]

When a hexadecanethiol in which the terminal 14 carbons are fluorinated[9] was employed as the target, the ion/surface reaction channels were shut down and the degree of fragmentation increased. The pyrazine molecular ion was elastically reflected (20% relative abundance) while loss of HCN once (100%) and twice (10%) gave the only other signals. The molecular ion comprised just 15% of the total ion abundance, compared with more than 50% for the alkyl surface, showing that collisions with the fluorinated surface deposit more internal energy in the projectile ion than the nonfluorinated C_{16} surface, perhaps due to the larger target mass. In addition, an increase in total scattered ion abundance from the fluorinated surface is observed and ascribed to elimination of reactive scattering as well as reduction in the degree of neutralization of the projectile ion. (Electron transfer in the reverse direction is known to be highly favored.[17]) This implies that fluorinated self-assembled monolayers might be particularly useful substrates for SID by increasing energy deposition and dissociation efficiency while eliminating ion/surface reactive collisions, although we emphasize that the latter are of great intrinsic interest.

The occurrence of ion/surface reactive collisions is also significant for analytical applications of mass spectrometry because this reaction channel provides an additional method for characterizing gaseous ions.[18] Of equal interest is the possibility that these processes can be used to obtain information on the nature

---

(6) (a) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481. (b) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evail, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321. (c) Porter, M. D.; Bright, T. B.; Allara, D.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

(7) (a) Mabud, Md. A.; Dekrey, M. J.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 285. (b) Aberth, W. *Anal. Chem.* **1990**, *62*, 609. (c) Ijames, C. I.; Wilkens, C. L. *Anal. Chem.* **1990**, *62*, 1295. (d) Bier, M. E.; Schwartz, J. C.; Schey, K. L.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1990**, *103*, 1. (e) Williams, E. R.; Henry, K. D.; McLafferty, F. W.; Shabanowitz, J.; Hunt, D. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 413. (f) Mabud, Md. A.; Dekrey, M. J.; Cooks, R. G.; Ast, R. *Int. J. Mass Spectrom. Ion Processes* **1986**, *69*, 277. (g) Callahan, J. H.; King, F. L.; Ross, M. M.; Wysocki, V. H. *Proc. 38th ASMS Conf. Mass Spectrom. Allied Topics*, Tucson, AZ, June 1990; p 898.

(8) Chidsey, C. E. D.; Liu, G.-Y.; Rowntree, P.; Scoles, G. *J. Chem. Phys.* **1989**, *91*, 4421.

(9) Chidsey, C. E. D.; Loiacono, D. N. *Langmuir* **1990**, *6*, 682.

(10) For earlier data on poorly characterized surfaces, see ref 4. The evidence in these experiments for ion/surface reactions is indirect, largely because metal targets at ca. 10^{-6} Torr vacuum bearing hydrocarbon surface impurities were employed.

(11) The instrument used is described elsewhere.[12] The primary ion beam is created by electron impact, mass and energy selected using the first two sectors, and directed at the surface at a collision energy in the range 5–100 eV and at an impact angle chosen for this experiment as 50° (with respect to the surface normal). The products are collected at a scattering angle of 90° but with low angular resolution and selected using an electric sector to have low kinetic energies (ca. 4 eV). The ion source is some 2 m from the surface, differentially pumped and not accessible by line of sight.

(12) (a) Laue, H.-J.; Amy, J. W.; Winger, B. E.; Cooks, R. G. *Adv. Mass Spectrom.* **1989**, *11*, 148. (b) Winger, B. E.; Laue, H. J.; Horning, S. R.; Julian, R. K., Jr.; Lammert, S. A.; Riederer, D. E., Jr.; Cooks, R. G., to be submitted.

(13) Deuterated pyrazine (100% relative abundance), d_3-methylated pyrazine (3%); the other ions observed are pyrazine molecular ion (60%), its HCN loss fragment (75%), and the HCN loss fragment from protonated pyrazine (25%).

(14) These experiments were done using low energy (0–12 eV) collisions in a Finnigan 4500 triple quadrupole mass spectrometer.

(15) The major fragmentation is HCN loss; triple quadrupole experiments on $M^{\bullet +}$ at 22 eV using multiple collisions on argon show *m/z* 53 (44%) and *m/z* 26 (91%); analogous experiments on $MH^{\bullet +}$ show *m/z* 54 (9%), *m/z* 28 (16%), and *m/z* 27 (4%). In both experiments the selected ion is the base peak.

(16) (a) Holman, R. W.; Gross, M. L. *Int. J. Mass Spectrom. Ion Processes* **1989**, *92*, 79. (b) Miller, D. L.; Gross, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 3783. (c) Gross, M. L.; Russell, D. H.; Aerni, R. J.; Bronczyk, S. A. *J. Am. Chem. Soc.* **1977**, *99*, 3603.

(17) Vincenti, M.; Cooks, R. G. *Org. Mass Spectrom.* **1988**, *23*, 317.

(18) (a) Hayward, M. J.; Mabud, Md. A.; Cooks, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 1343. (b) Cooks, R. G.; Mabud, Md. A.; Horning, S. R.; Jiang, X.-Y.; Paradisi, C.; Traldi, P. *J. Am. Chem. Soc.* **1989**, *111*, 859. (c) Mabud, Md. A.; Ast, T.; Cooks, R. G. *Org. Mass Spectrom.* **1987**, *22*, 418. (d) Mabud, Md. A.; Ast, T.; Verma, S.; Jiang, X.-Y.; Cooks, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 7597.

of the organic functional groups present at an interface. A large variety of reactive ions can be chosen as probes, and this chemical method of surface characterization may prove to be complementary to conventional physical methods which employ electron, photon, or atom beams as probes.[19]

Acknowledgment. We thank W. N. Delgass for valuable discussions and acknowledge support by the National Science Foundation (CHE 87-21768).

---

[19] Walls, J. M., Ed. *Methods of Surface Analysis: Techniques and Applications*; Cambridge University Press: Cambridge, 1989.

Polyatomic Ion/Surface Collisions at Self-Assembled Monolayer Films

Vicki H. Wysocki,* Jennifer L. Jones, and Jian-Mei Ding

Department of Chemistry
Virginia Commonwealth University
Richmond, Virginia 23284-2006

Received March 8, 1991

The chemical and physical properties of ordered molecular monolayers and thin films have been extensively investigated because of their technological potential.[1-11] In solution, 1-alkanethiols are known to spontaneously form highly ordered, covalently bound monolayer films on gold[4-11] or silver.[8] These films have been described in numerous publications[4-10] and are stable, easy to prepare, and useful as electrochemical barriers[4,9-11] in solution. In this report, we discuss the ion/surface chemistry that is detected when gas-phase polyatomic ions, of well-defined mass, structure, and collision energy, collide with a self-assembled monolayer of alkanethiol on gold at collision energies of 10-80 eV.

The experiments described here were performed in a tandem mass spectrometer in which two quadrupole mass analyzers were placed at 90°, with a surface placed to intersect the ion optical path of each quadrupole[12] (angle of incidence 50° with respect to the surface normal). The pressure in the collision region was 10^{-7} Torr. Surfaces utilized include stainless steel, gold, ethanethiol on gold, and octadecanethiol on gold. Gold foil (0.05-0.1 mm thick) was allowed to react with an alkanethiol in ethanol (20 mM) for 15 min[6,9] to produce the self-assembled monolayers.

Several processes can occur when mass-selected polyatomic ions collide with a surface at collision energies in the electronvolt range.[12-22] These include *surface-induced dissociation* (SID) of the mass-selected projectile ion,[13-18] *chemical reaction* between the projectile and surface adsorbates,[13,19,20] and *chemical sputtering*,[13,16,21] i.e., charge exchange between the mass-selected projectile ion and surface adsorbates with the release of ionized adsorbates from the surface. Previously, collisions of mass-selected polyatomic ions with metal surfaces have been investigated primarily by using surfaces that have not been intentionally modified (e.g., stainless steel, gold, silver, and platinum).[13-16,19-22] These reports suggest, however, that adventitious hydrocarbons (e.g., from pump oils) are present at the metal surfaces and that the hydrocarbon adsorbates at the surface can be ionized by charge transfer from certain projectile ions, such as perfluorinated molecules. The spectra recorded in these cases contain chemical sputtering peaks corresponding to typical hydrocarbon ions (CH_3^+, $C_2H_3^+$, $C_2H_5^+$, $C_3H_3^+$, $C_3H_5^+$, $C_3H_7^+$, $C_4H_7^+$, $C_4H_9^+$, ...) and cannot be attributed simply to fragmentation of the incoming projectile ion.

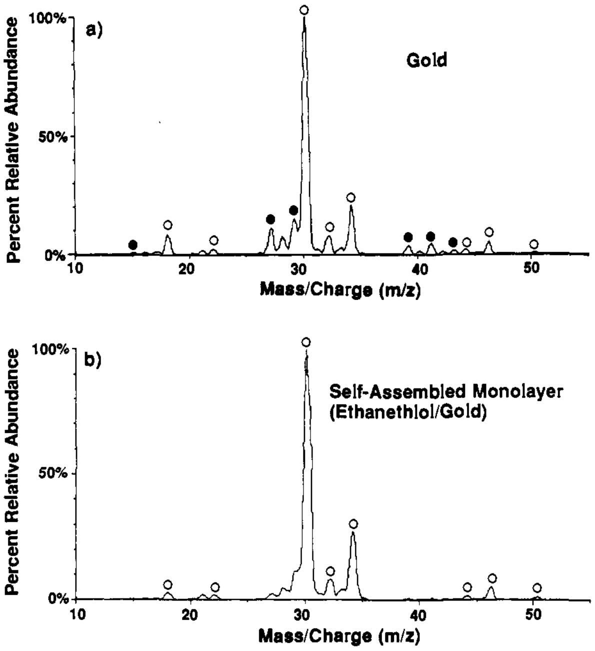


Figure 1. (a) Product ions detected when mass-selected $CD_3CD_2OD^{\bullet+}$ (m/z 52) collides with a gold surface at a collision energy of 60 eV. (b) Product ions detected when mass-selected $CD_3CD_2OD^{\bullet+}$ collides with an ethanethiol/gold surface at a collision energy of 60 eV. For both a and b, the peaks labeled with open circles are direct dissociation products of ethanol-d_6. The peaks labeled with filled circles are sputtered hydrocarbon ions, not dissociation products of ethanol-d_6.

The presence of chemical sputtering products along with diagnostic fragmentation products is illustrated for collision of ethanol-d_6 with an untreated gold surface (Figure 1a). The spectrum indicates product ions that are clearly surface-induced dissociation products of $C_2D_5OD^{\bullet+}$ because they contain combinations of C, D, and O. However, it also shows $C_nH_m^+$ ions that indicate that charge exchange has occurred from the projectile ion to the hydrocarbon adsorbates, with the release of ionized adsorbates.

---

[1] Swalen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Rabolt, J. F.; Wynne, K. J.; Yu, H. *Langmuir* **1987**, *3*, 932-950.

[2] (a) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481. (b) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 45-52.

[3] Tillman, Y. N.; Ulman, A.; Penner, T. L. *Langmuir* **1989**, *5*, 101-111.

[4] Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559-3568.

[5] Strong, L.; Whitesides, G. M. *Langmuir* **1988**, 546-558.

[6] Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. J. *Am. Chem. Soc.* **1989**, *111*, 321-335.

[7] Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558-569.

[8] Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 3629-3637.

[9] Finklea, H. O.; Avery, S.; Lynch, M.; Furtsch, T. *Langmuir* **1987**, *3*, 409-413.

[10] Rubenstein, I.; Steinberg, S.; Tor, Y.; Shanzer, A.; Sagiv, J. *Nature* **1988**, *332*, 426-429.

[11] Li, T. T.-T.; Weaver, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 6107-6108.

[12] Wysocki, V. H.; Ding, J.-M.; Jones, J. L.; Callahan, J. H.; King, F. L. *J. Am. Soc. Mass Spectrom.*, in press.

[13] Cooks, R. G.; Ast, T.; Mabud, Md. A. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 209-265.

[14] Mabud, Md. A.; DeKrey, M. J.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 285-294.

[15] Bier, M. E.; Amy, J. W.; Cooks, R. G.; Syka, J. E. P.; Ceja, P.; Stafford, G. *Int. J. Mass Spectrom. Ion Processes* **1987**, *77*, 31-47.

[16] Schey, K. L.; Cooks, R. G.; Kraft, A.; Grix, R.; Wollnik, H. *Int. J. Mass Spectrom. Ion Processes* **1989**, *94*, 1-14.

[17] Aberth, W. *Anal. Chem.* **1990**, *62*, 609-611.

[18] (a) Ijames, C. F.; Wilkins, C. L. *Anal. Chem.* **1990**, *62*, 1295-1299. (b) Williams, E. R.; Henry, K. D.; McLafferty, F. W.; Shabanowitz, J.; Hunt, D. R. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 413-416.

[19] Ast, T.; Mabud, Md. A.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1988**, *82*, 131-150.

[20] Hayward, M. J.; Mabud, Md. A.; Cooks, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 1343-1346.

[21] Vincenti, M.; Cooks, R. G. *Org. Mass Spectrom.* **1988**, *23*, 317.

[22] DeKrey, M. J.; Kenttämaa, H. I.; Wysocki, V. H.; Cooks, R. G. *Org. Mass Spectrom.* **1986**, *21*, 193-195.

0002-7863/91/1513-8969$02.50/0 © 1991 American Chemical Society