

Reactions of Ions with Organic Surfaces

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Introduction

Mass spectrometry continues to show remarkable growth, both as an analytical technique and as a route to the study of fundamental chemical phenomena.¹ This growth has allowed it to spread from physics and chemistry into many other areas of science, assisted by numerous advances in techniques for creating, mass-analyzing, fragmenting, and reacting ions.

Much of the interesting chemistry associated with mass spectrometry is gas phase ion chemistry; indeed, this is true to such an extent that the two terms are sometimes used synonymously. The collisions of ions with surfaces also fall within the purview of mass spectrometry. One instance is the kiloelectronvolt energy ion bombardment technique of secondary ion mass spectrometry (SIMS), which is used for lateral and depth analysis.² Reduction, ligand transfer, and other reactions can be induced at the surface/vacuum interface, by deposition of energy through collisions of high-energy (kiloelectronvolt) atom and ion beams.³ Technological applications of kilo- and megaelectron-volt energy ion impact on surfaces are particularly significant in materials science, including semiconductor doping by ion implantation and ion beam etching.⁴ At lower and chemically more interesting collision energies, bond formation during ion/surface impact has been of interest for diamond film growth⁵ and other materials science applications, including nitride and oxide formation. Nevertheless, with some notable exceptions,⁶ chemists have paid remarkably little attention to chemical reactions at interfaces in which the ion beam acts as a chemical reagent. This is particularly the case for organic surfaces.

This situation regarding ion/surface reactions is in contrast to the analogous subject of gas phase ion/

molecule reactions, which is an extraordinarily large, well-developed field of chemistry.⁷ The ion/surface reaction experiment is straightforward; beams of low-energy mass-selected ions are allowed to impinge on and react with chemically well-defined surfaces, and either the scattered projectiles or the changes produced in the surface itself are monitored. Center-of-mass collision energies are not too much greater than chemical bond energies when laboratory energies used are in the easily accessible range of a few tens of electronvolts. Studies of ion/surface reactions are further facilitated by the wide variety of chemical structures which are readily available for use as projectiles through various ionization methods and the variety of chemical surfaces available, including self-assembled monolayers,⁸ which are unusual because they can be studied under modest vacuum conditions.

Some of the processes which occur when low translational energy ion beams collide with surfaces have been explored in detail⁹ and are summarized in Table 1. Note that the nature and relative importance of the observed processes are strongly influenced by the choice of the ion and the nature of the surface. Inelastic collisions can lead to dissociation of polyatomic projectiles in a process known as surface-induced dissociation (SID).¹⁰ This process has a gas phase counterpart, collisional activation, which has

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(1) White, F. A.; Wood, G. M. *Mass Spectrometry: Applications in Science and Engineering*; Wiley: New York, 1986. Russel, D. H., Ed. *Gas Phase Inorganic Chemistry*; Plenum Press: New York, 1989. McCloskey, J. A., Ed. *Methods in Enzymology, Vol. 193, Mass Spectrometry*; Academic Press: San Diego, 1990. Shukla, A. K.; Futrell, J. H. *Mass Spectrom. Rev.* **1993**, *12*, 211.

(2) Lee, J. J.; Fulghum, J. E.; McGuire, G. E.; Ray, M. A.; Osburn, C. M.; Linton, R. W. *J. Vac. Sci. Technol. A* **1990**, *8*, 2287. Rüdener, F. G.; Steiger, W. In *Secondary Ion Mass Spectrometry: SIM VI*; Benninghoven, A., Huber, A. M., Werner, H. W., Eds.; Wiley: New York, 1988.

(3) Detter, L. D.; Hand, O. W.; Cooks, R. G.; Walton, R. A. *Mass Spectrom. Rev.* **1988**, *7*, 465.

(4) Wilson, R. G.; Brewer, G. R. *Ion Beams with Applications to Ion Implantation*; R. E. Krieger Publishing Co.: Florida, 1979. Smidt, F. A. *CHEMTECH* **1989**, *19*, 309.

(5) Rabalais, J. W.; Kasi, S. R. *Science* **1988**, *239*, 623.

(6) Kasi, S. R.; Kang, H.; Sass, C. S.; Rabalais, J. W. *Surf. Sci. Rep.* **1989**, *10*, 1. Martin, J. S.; Greeley, J. N.; Morris, J. R.; Jacobs, D. C. *J. Chem. Phys.* **1992**, *97*, 9476.

(7) Bowers, M. T., Ed. *Gas Phase Ion Chemistry*; Academic Press: New York, 1979. Russell, D. H., Ed. *Gas Phase Inorganic Chemistry*; Plenum: New York, 1986. Futrell, J. H., Ed., *Gaseous Ion Chemistry and Mass Spectrometry*; Wiley: New York, 1986.

(8) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481. Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559. Chidsey, C. E. D.; Liu, G.-Y.; Rowntree, P.; Scoles, G. *J. Chem. Phys.* **1989**, *91*, 4421.

(9) Cooks, R. G.; Ast, T.; Mabud, Md. A. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 209.

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Table 1. Processes Which Occur in Low-Energy Ion/Surface Collisions^a

| | |
|--|------------------|
| (i) elastic scattering ^b | |
| $AB^+ \xrightarrow{SX} AB^+$ | |
| (ii) surface-induced dissociation (SID) | |
| $AB^+ \xrightarrow{SX^+} [AB^{++}] \rightarrow A^+ + B$ | |
| (iii) charge-changing reactions | |
| $AB^+ \xrightarrow{SX} AB$ | neutralization |
| $AB^{2+} \xrightarrow{SX} AB^+$ | charge exchange |
| $AB^+ \xrightarrow{SX} AB^-$ | charge inversion |
| (iv) chemical sputtering (charge exchange with surface ion ejection) | |
| $AB^+ \xrightarrow{SX} AB + SX^+ \rightarrow X^+$ | |
| (v) ion/surface reactions | |
| $AB^+ \xrightarrow{SX} ABX^+$ | |
| $AB^+ \xrightarrow{SX} AX^+ + B$ | |
| $AB^+ \xrightarrow{SX} AX^+ + SB$ | |

^a AB^+ is a polyatomic projectile. S is the surface, and X represents a functional group bound to it. All polyatomic product ions can be formed with excess internal energy leading to further fragmentation. ^b Elastic scattering is taken to include mildly inelastic processes which do not lead to fragmentation or reaction.

long been a centerpiece in mass spectrometry, where it is used for the characterization of mass-selected ions and the analysis of mixtures.¹¹ SID offers a complementary means of acquiring this structural information. Reactive collisions take a number of forms as indicated in Table 1. They include charge-changing reactions, among them the interesting charge reversal processes,¹² as well as simple charge exchange.^{13,14} This last process is usually undesirable, since it leads to projectile ion loss through neutralization, but it can also be a method of choice to cause efficient neutralization when fast neutrals are desired.¹⁵ Another charge transfer process is chemical sputtering,¹³ in which neutralization of the projectile ion leads to ionization and release into vacuum of a surface-bound group. This reaction channel provides an alternative to high-energy, momentum transfer sputtering processes as a means of surface analysis. Atom or group transfer, rather than charge exchange, is the defining characteristic of the most important of the reactive collision processes, grouped as (v) in Table 1.

Ion/surface collisions at low energy promise to extend the scope of mass spectrometry through utilization of the new methods of characterizing ions implicit in the processes summarized in Table 1. They

proffer information on the chemical nature of the outermost layers of surfaces, including functional group information, through chemically specific ion/surface reactions. The same collision processes offer the prospect for chemical modification of the outermost monolayers of surfaces in a highly controlled fashion. At this early stage in the development of this area of research, interest is focused on the types and mechanisms of ion/surface reactions, the utility of the SID process, and the effects of target surface and projectile chemical structure on reactivity.

Reactive Collisions of Ions with Surfaces

A rich chemistry accompanies the collisions of ions of translational energy of some tens of electronvolts with organic surfaces. Reactions occur which are highly specific to the projectile/surface combination, and some occur in high yield. The variety of processes available is a consequence of ready access to an enormous variety of projectile ion structures and the fact that they can be given well-defined and easily controlled translational energies.

Consider the following reactions, which are representative of this new chemistry:

(i) Transition metal ions and ions of group IIIA–VIIA elements abstract multiple fluorine atoms from fluorocarbon surfaces.^{16,17} For example, a 60-eV Mo^+ beam is scattered principally as MoF_n^+ ($n = 1-4$).¹⁷ This is the dominant ionic scattering channels for Mo^+ and is estimated to occur for at least 10% of all projectile ions.¹⁷

(ii) Halogen exchange between fast-moving projectiles and fluorinated surfaces is observed. Chlorine- and bromine-containing cations abstract fluorine atoms from fluorocarbon surfaces and simultaneously transfer halogens to the surface; e.g., $SiCl_4^+$ is reactively scattered as $SiCl_2F^+$. The ion CF_2Cl^+ is ejected when the modified surface is examined in an independent sputtering experiment, a result which is interpreted as demonstrating the presence of covalently bound Cl on the surface.¹⁸

(iii) Polynuclear aromatic hydrocarbons induce C–C bond cleavage when they impact hydrocarbon surfaces as molecular cation radicals; they scatter from the surface carrying away the released alkyl groups.^{19,20} This reaction, which is believed to proceed by electron transfer from the surface to the ion, also occurs for radical cations of heteroaromatic compounds like pyrazine,²¹ but does not occur for related even-electron ions.

(iv) Abstraction of hydrogen is the most common process for typical organic radical cations impinging on hydrocarbon surfaces.²² Highly unsaturated ions can undergo multiple hydrogen abstractions; for ex-

(10) Mabud, Md. A.; Dekrey, M. J.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 285.

(11) Cooks, R. G., Ed. *Collision Spectroscopy*; Plenum Press: New York, 1978. McLafferty, F. W., Ed. *Tandem Mass Spectrometry*; Wiley: New York, 1983. Busch, K. L.; Glish, G. L.; McLuckey, S. A. *Mass Spectrometry/Mass Spectrometry*; VCH Publishers: New York, 1988.

(12) Bier, M. E.; Vincenti, M.; Cooks, R. G. *Rapid Commun. Mass Spectrom.* **1988**, *1*, 92.

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

(14) Mabud, Md. A.; Dekrey, M. J.; Cooks, R. G.; Ast, T. *Int. J. Mass Spectrom. Ion Processes* **1986**, *69*, 277.

(15) Chorush, R. A.; Vidavsky, I.; McLafferty, F. W. *Org. Mass Spectrom.* **1993**, *28*, 1016.

(16) Pradeep, T.; Ast, T.; Cooks, R. G.; Feng, B. *J. Phys. Chem.*, in press.

(17) Pradeep, T.; Riederer, D. E., Jr.; Hoke, S. H., II; Ast, T.; Cooks, R. G.; Linford, M. R. *J. Am. Chem. Soc.*, in press.

(18) Pradeep, T.; Feng, B.; Ast, T.; Patrick, J. S.; Cooks, R. G.; Pachuta, S. J. *Int. J. Mass Spectrom. Ion Processes*, submitted.

(19) Schey, K. L.; Cooks, R. G.; Kraft, A.; Grix, R.; Wollnick, H. *Int. J. Mass Spectrom. Ion Processes* **1989**, *91*, 1.

(20) Williams, E. R.; Jones, G. C.; Fang, L.; Zare, R. N.; Garrison, B. J.; Brenner, D. W. *J. Am. Chem. Soc.* **1992**, *114*, 3207.

(21) Morris, M. R.; Riederer, D. E., Jr.; Winger, B. E.; Cooks, R. G.; Ast, T.; Chidsey, C. E. D. *Int. J. Mass Spectrom. Ion Processes* **1992**, *122*, 181.

ample, HCCN^{++} undergoes abstraction of up to four hydrogen atoms from hydrocarbon surfaces. At least two of these come from the same alkyl chain.²³

(v) XeF^+ cations are produced when Xe ions collide with fluorinated surfaces,²⁴ while bromine cations abstract difluorocarbene to give BrCF_2^+ scattered ions.¹⁶

(vi) Metal carbonyl cations, such as $\text{W}(\text{CO})_6^{++}$, undergo deeply inelastic collisions at fluorinated organic surfaces to produce lower carbonyl ions, as well as the naked metal ions, each of which can undergo concerted halogen abstraction.¹⁷

(vii) C_{60} cation radicals, upon collision with fullerene surfaces, undergo fusion to give C_{120}^{++} , accompanied by products due to C_2 loss and gain.²⁵

(viii) Silicon cluster ions Si_{12}^{++} undergo reactive collisions at a graphite surface to give Si_9C^+ and Si_3C^+ products. If, however, the graphite surface is oxygen passivated, the same projectile yields Si_3O^{++} products.²⁶

(ix) Nickelocene $[\text{Ni}(\text{C}_5\text{H}_5)_2]$ molecular ions, when generated in an appropriate internal state, undergo a dissociative rearrangement upon collision with a surface to give the catalytically interesting (and theoretically much studied) metal hydride, NiH_2^+ , as the scattered ion. The hydrogens are derived from the projectile ion, not from the surface!²⁷

(x) An ion/surface reaction of the benzene molecular ion (pickup of H^+ followed by loss of H_2) has been shown to represent a sensitive probe as to the degree of order of alkanethiol self-assembled monolayer (SAM) surfaces. Ordering was shown to depend on the carbon chain length and commences in the range of 7–10 carbons.²⁸

It is of great interest that the above reactions occur in the course of a collision of a fast-moving projectile (component of velocity normal to the surface on the order of 10^5 – 10^6 cm/s). The spectrum of scattered products is illustrated in the case of $^{186}\text{W}^{++}$ ions colliding at a fluorinated long-chain alkanethiol surface in Figure 1. Note the low abundance of the scattered projectile itself, compared with that of the fluorinated product ions. The ion/surface reaction yield (scattered ion current vs projectile ion current) is at least 10%. Note, too, that WF^+ formation is endothermic, while WF_2^+ formation is exothermic (assuming it to be accompanied by carbon–carbon bond formation). There is a correlation between the extent of fluorine abstraction and thermochemistry in that metals which form stronger metal–fluorine bonds are more reactive and pick up more fluorine atoms.¹⁶

Many halogenated projectiles, like SiCl_3^+ (Figure 2), yield abundant fluorine atom abstraction products upon collision with fluoroalkane surfaces. In a dif-

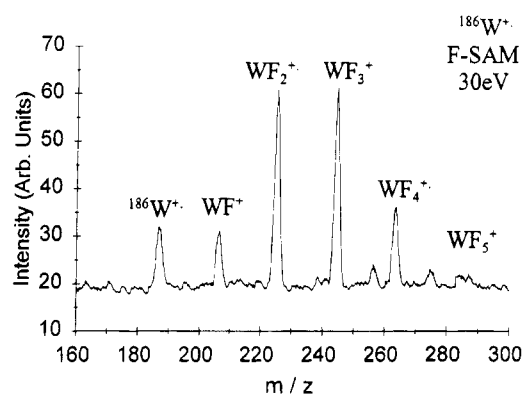


Figure 1. Partial scattered ion mass spectrum obtained upon 30-eV collisions of W^+ ions at a fluorinated self-assembled monolayer (SAM) surface. Adapted from ref 16.

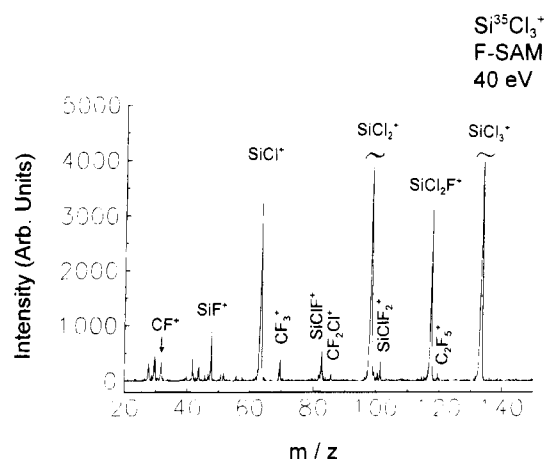
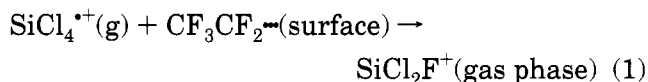
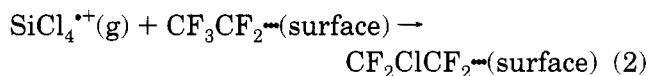


Figure 2. Scattered ion mass spectrum obtained upon 40-eV collisions of $\text{Si}^{35}\text{Cl}_3^+$ ions at a fluorinated SAM surface. The peaks marked ~ are slightly off-scale.

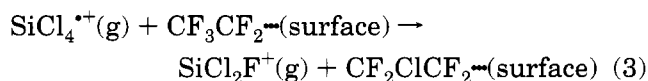
ferent case, that of the tetrachlorosilane radical cation, both the scattered ion spectrum and the resulting modified surface have been examined. In this case the main gas phase ionic product is that shown in reaction 1:



Following bombardment, the surface has been examined by SIMS, and the observation of the fragment CF_2Cl^+ points to the fact that it was modified according to reaction 2:



The remarkable result is that transhalogenation (reaction 3) between the gaseous ion and the surface has occurred in the course of a high-velocity collision process, although it is not possible to say whether the reaction occurs in a concerted fashion.



There are at least two mechanisms by which ion/surface reactions occur, and they are distinguished chiefly by whether or not they involve electron trans-

(22) Ast, T.; Mabud, Md. A.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1988**, *82*, 131.

(23) Riederer, D. E., Jr.; Cooks, R. G.; Linford, M. R. *Org. Mass Spectrom.*, submitted.

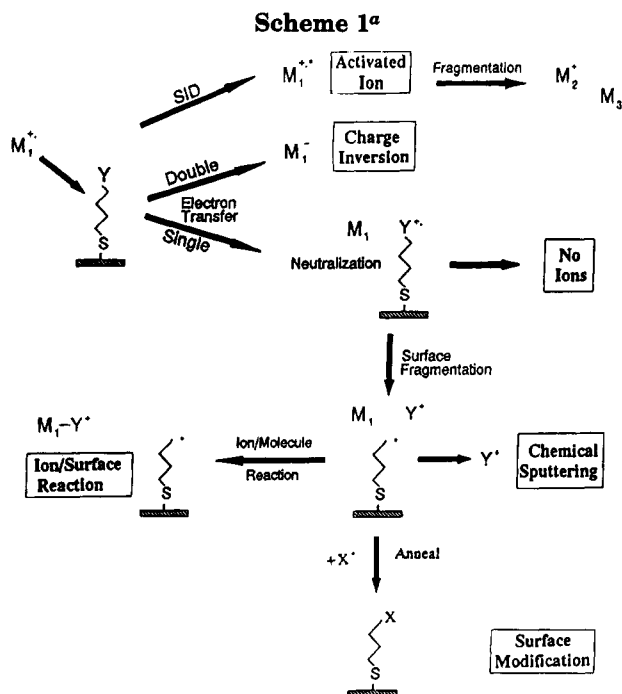
(24) Riederer, D. E., Jr.; Miller, S. A.; Ast, T.; Cooks, R. G. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 938.

(25) Busmann, H.-G.; Lill, Th.; Lacher, F.; Hertel, I. V. *Materials*, Tokyo, September 1993. Compare: Pradeep, T.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes*, in press.

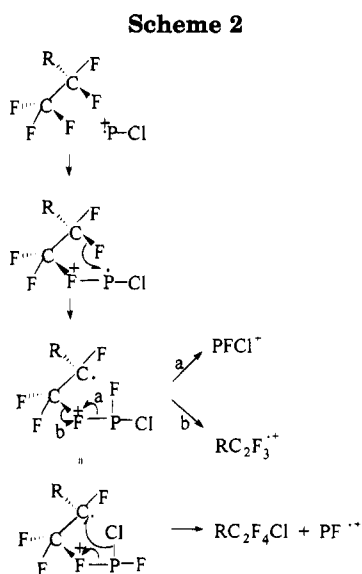
(26) Whetten, R. L.; St. John, P. M. Pittsburgh Conference, Chicago, IL, Feb 27 to March 3, 1994.

(27) Pradeep, T.; Patrick, J. S.; Feng, B.; Miller, S. A.; Ast, T.; Cooks, R. G. *J. Phys. Chem.*, submitted.

(28) Franklin, R. L.; Kane, T. E.; Somogyi, A.; Angelico, V. J.; Wysocki, V. H. 42nd ASMS Conference on Mass Spectrometry and Allied Topics, Chicago, IL, May 30 to June 3, 1994.



^a Adapted from ref 23.



fer. In the first, typified by alkyl group abstraction by the radical cations of heteroaromatic compounds, the incoming ion undergoes charge exchange as it approaches the surface, producing a surface-bound radical cation. If sufficient energy is transferred in this step, the surface-bound ion will fragment, yielding an ion, e.g., a carbenium ion, which can attach to the arriving and now neutralized projectile in an interfacial ion/molecule reaction. This mechanism is illustrated in Scheme 1. It is supported by data which show that it occurs efficiently when the projectile is a radical cation. The co-occurrence of the chemical sputtering process, which is also illustrated in Scheme 1, provides additional evidence for this mechanism.²⁴

The second general mechanism can be illustrated in the particular case of the reaction of a $\text{PCl}^{+\bullet}$ projectile with a fluorinated SAM surface. The process in general involves oxidative addition, probably via a fluoronium ion intermediate (Scheme 2). Note that dissociation (ligand loss, for example) may accompany formation of new bonds. The overall reaction may be

endothermic, in which case it is driven by the translational energy of the projectile ion.^{16,17} In the case of metal ion projectiles, angle resolved data support a single-collision, multiple atom abstraction mechanism.¹⁷ The threshold collision energy for the reactions is often below that for chemical sputtering, one indication that electron transfer is not involved.

Both of the prototypical ion/surface reactions presented above have counterparts among ion/molecule reactions. Furthermore, in both types of ion/surface reactions, the scattered ion leaves the surface with a low translational energy. Single-collision events are proposed in which the ion loses energy to the surrounding atoms and groups on the surface while undergoing bond-forming processes. Note the similarity of this proposed mechanism to that which occurs in the gas phase collisional activation of large biomolecule ions by small targets such as N_2 or CO_2 ,²⁹ in the capture of CH_2 by biomolecule ions upon collisions with methane,³⁰ and in the capture of rare gases by kiloelectronvolt fullerene molecular ions.³¹ In all these cases the projectile is either temporarily or, in the fullerene reaction, permanently captured by the target. It is not suggested that ion/surface reactions involve equilibration of the ion on the surface, but rather that sufficient time is spent for multiple bond formation, before the cooled products drift away.

Surface-Induced Dissociation

Tandem mass spectrometry has become increasingly important in solving problems in areas such as biological and environmental science. This experiment commonly employs collisions of mass-selected parent ions (m_1^+) with target gases to generate product ions (m_2^+) by the process of collision-induced dissociation (CID) or, less frequently, through gas phase ion/molecule reactions. The experiment forms the basis for annual sales of tandem mass spectrometers which are in the tens of millions of dollars. In spite of its great usefulness, collision gas has deleterious effects on mass spectrometer performance, and gaseous collisions do not efficiently activate larger ions. These are reasons to explore complementary methods of ion activation.

Collisions with surfaces represent one alternative to gas phase collisions for conversion of translational to internal (T-V) energy and fragmentation of the excited projectile. Systematic studies on SID have shown that (i) the energy transferred in the collision process is readily controlled by varying the impact energy; (ii) T-V energy transfer is relative efficient, often ca. 20% of laboratory energy (depending on choice of target and scattering geometry), and hence highly excited ions are readily produced; and (iii) good ion yields (up to 50%) can be obtained by the use of organic monolayer or multilayer surfaces, which limit the degree of neutralization of the projectile beam.

The characteristic narrow distribution of internal energy deposited in an ion in the course of a collision with a surface (vs gas phase collisions) is best seen

(29) Mazluff, E. M.; Campbell, S.; Rodgers, M. T.; Beauchamp, J. L. *J. Am. Chem. Soc.*, in press.

(30) Cheng, X.; Fenselau, C. *J. Am. Chem. Soc.* **1993**, *115*, 10327.

(31) Weiske, T.; Böhme, D. K.; Hrusák, J.; Krätschmer, W.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 884. Caldwell, K. A.; Giblin, D. E.; Hsu, C. S.; Cox, D.; Gross, M. L. *J. Am. Chem. Soc.* **1991**, *113*, 8519. Ross, M. M.; Callahan, J. H. *J. Phys. Chem.* **1991**, *95*, 5720.

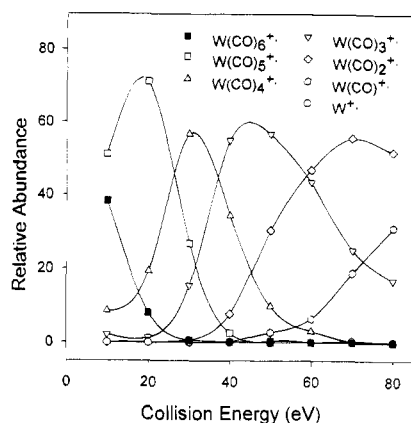


Figure 3. Relative abundances of fragment ions obtained upon collisions of $W(CO)_6^{+}$ at a hydrocarbon-covered stainless steel surface as a function of collision energy. Adapted from ref 32.

by considering the behavior of a "thermometer" ion such as $W(CO)_6^{+}$. Thermometer ions fragment by a simple sequence of reactions of known internal energy requirement, and the energy deposition can be judged by the extent to which these consecutive reactions (in this case CO losses) occur.³² Figure 3 shows data taken for a hydrocarbon surface with a tandem quadrupole instrument.³³ The fragmentation pattern varies dramatically with small changes in laboratory collision energy, illustrating the narrow energy deposition (see also peptide data below). $W(CO)_2^{+}$, the formation of which requires an internal energy of 7.5 eV, becomes the major product ion at collision energies above 60 eV. On the basis of this and similar data for other thermometer ions such as the ferrocene radical cation, it is determined that the fraction of the laboratory translational energy partitioned into internal energy of the projectile upon collision at a fluorinated alkane surface is about 20%, while about 13% is partitioned into internal energy at a hydrocarbon surface.^{21,34}

The fragmentation reactions observed when *organic* ions are excited in collisions with surfaces depend on the internal energy deposited, but otherwise match the processes observed after gaseous collisional activation. It is concluded that the activation and dissociation steps are well separated in time in both experiments; fragmentation occurs after the organic ion has moved some distance away from the surface and is controlled by statistical partitioning of energy among internal modes. However, there is evidence that this description does not apply to some organometallic ions, including PCl^{+} (Scheme 1). In these cases ion/surface reactions accompany fragmentation, suggesting that the two processes are concerted and that fragmentation occurs at the surface.¹⁶

The degree to which ion/surface reactions compete with surface-induced dissociation is of interest for applications of SID. Many reactions can be prevented by minimizing the chance of electron transfer, and this can be achieved by choice of an ion of low recombination energy and a surface of high work function. In practical terms, this requires a comparison of the

ionization energies (IE) of the neutrals from which the projectile ion is generated with those from which the surface coating is constituted. (Note that the identity of the surface coating, not the underlying substrate, has proven to control neutralization as comparisons of various SAM surfaces has shown.) The case of ferrocene ions (IE of the neutral 6.75 eV) colliding upon alkane surfaces (IE of neutral monolayer ca. 11 eV) is particularly striking, since there is very little neutralization. Consistent with this, protonated ferrocene is not observed as a scattered product, in spite of the very high proton affinity of ferrocene. This is a clear indication that electron transfer is involved in the proton transfer processes seen with other projectiles.³⁴ Many large organic ions for which structural information is desired have ionization energies that are lower than those of the surface coatings commonly used, and SID processes dominate the spectra, with minimal neutralization and little or no ion/surface reaction detected.

Applications of SID to problems of ion structure have become quite common. SID spectra have been reported for numerous compound classes including small organic ions,^{9,35} aromatic and polynuclear aromatic compounds,^{19,20} fullerenes,³⁵⁻³⁷ silicon clusters,³⁸ alkali halide clusters,³⁹ furocoumarins,⁴⁰ and metalloporphyrins.⁴¹ The large energy transfer results in fragmentation by easily interpretable bond cleavage reactions thus assisting in isomer characterization.⁴² Extensive dissociation (e.g., to C2 and C3 units) can be produced for compounds such as the polynuclear aromatic hydrocarbons or large cluster ions which are otherwise difficult to fragment.

Applications of SID to characterization of biomolecules represents a new field of study. CID is well-established for studies of biopolymers, particularly peptides and proteins. Even so, there are reasons for seeking a complementary method to CID to sequence peptides. These include (i) the cost of four-sector and other high-performance mass spectrometers; (ii) the fact that the key spectra produced are complex, with limited backbone cleavage and extensive side chain cleavage often being detected; (iii) the fact that triple quadrupole mass spectrometers do not produce the charge-remote side chain cleavages (d and w ions) that can be used to differentiate leucine from isoleucine and glutamine from lysine; and (iv) neither low- nor high-energy CID deposits a narrow internal energy distribution. Several groups, using a number of different instrument types, have recorded SID spectra of peptides.⁴³⁻⁴⁶ A systematic study of a number of peptides showed that SID results in extensive frag-

(35) Kane, T. E.; Somogyi, A.; Wysocki, V. H. *Org. Mass Spectrom.* **1993**, *28*, 1665.

(36) Busmann, H.-G.; Lill, Th.; Reif, B.; Hertel, I. V.; Maguire, H. G. *J. Chem. Phys.* **1993**, *98*, 7574.

(37) Beck, R. D.; St. John, P. M.; Alvarez, M. M.; Diederich, R. L.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 8402.

(38) St. John, P. M.; Whetten, R. L. *Chem. Phys. Lett.* **1992**, *196*, 330.

(39) Beck, R. D.; St. John, P. M.; Homer, M. L.; Whetten, R. L. *Science* **1991**, *253*, 879.

(40) Bier, M. E.; Cooks, R. G.; Horning, S.; Brusini, G.; Traldi, P.; Guitto, A.; Rodighiero, P. *Adv. Mass Spectrom.* **1989**, *11*, 966.

(41) Castoro, J. A.; Nuwaysir, L. M.; James, C. F.; Wilkins, C. L. *Anal. Chem.* **1992**, *64*, 2238.

(42) Mabud, Md. A.; Ast, T.; Verma, S.; Jiang, Y.-X.; Cooks, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 7597. Mabud, Md. A.; Ast, T.; Cooks, R. G. *Org. Mass Spectrom.* **1987**, *22*, 418. Hayward, M. J.; Mabud, Md. A.; Cooks, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 1343.

(43) Bier, M. E.; Schwartz, J. C.; Schey, K. L.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1990**, *103*, 1.

(32) Wysocki, V. H.; Kentamaa, H. I.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1987**, *75*, 181.

(33) Wysocki, V. H.; Ding, J.-M.; Jones, J. L.; Callahan, J. H.; King, F. L. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 27.

(34) Miller, S. A.; Riederer, D. E., Jr.; Cooks, R. G.; Cho, W. R.; Lee, H. W.; Kang, H. *J. Phys. Chem.* **1994**, *98*, 245.

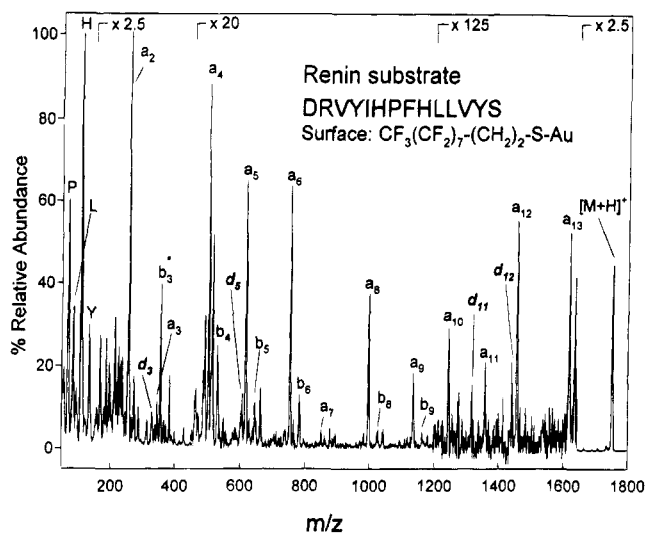


Figure 4. Surface-induced dissociation spectrum of the $[M + H]^+$ ion (m/z 1758) of renin substrate obtained upon 50-eV collisions at a fluorinated SAM surface. MH^+ ions were formed by Cs^+ bombardment; 80–100 pmol of sample in thioglycerol matrix were loaded onto the probe tip. Adapted from ref 46, which see for definition of peptide fragments (d_3 , a_4 , etc.).

mentation that can be used to sequence the peptides, that the structurally diagnostic type d and w ions can be produced by SID (e.g., see Figure 4), and that low detection limits can be achieved (10 pmol of sample).⁴⁶

More recently, Wysocki and co-workers have used SID to investigate peptide fragmentation as a function of peptide sequence.⁴⁷ These experiments illustrate and exploit the narrow energy distribution associated with SID: plots of percent fragmentation vs collision energy show sharp onsets for fragmentation, consistent with deposition of a narrow distribution of internal energies. These fragmentation efficiency plots have shown that changes in sequence lead to different onset energies for fragmentation, reflecting differences in stability of the different structures investigated. When peptides differ in the identity of a single residue, the peptide with the more basic residue shows the highest onset energy for fragmentation. The results are consistent with fragmenting structures in which a mobile proton is transferred among basic sites in the peptide, promoting charge-directed fragmentation. An additional interesting feature of the fragmentation efficiency study is that it clearly highlights differences in the energy deposition associated with the ionization methods used to produce the ions (electrospray vs Cs^+ ion bombardment, LSIMS). This, too, is a result of the narrow energy distribution associated with SID; because SID deposits a narrow distribution of energies in the activation step of the MS/MS experiment, differences in energy deposition associated with the ionization method are readily apparent. (Note that differences in LSIMS/SID fragmentation efficiency curves relative to ESI/SID curves are too large to be explained by the small differences in kinetic energy distributions as-

sociated with the two ionization methods.) In addition to peptides, work is in progress on a number of other compound types including disaccharides⁴⁸ and cisplatin-related drugs bound to nucleosides.⁴⁹ It is expected that continued application of SID to biomolecules will not only assist in structure elucidation problems but also help solve many fundamental questions regarding mechanisms and energetics of dissociation of large molecules.

Instrumentation for the Study of Ion/Surface Collisions

Surface-induced dissociation was attempted with limited success in the 1970s using grazing incidence of high-energy ion beams.⁵⁰ It was first demonstrated unambiguously using a hybrid instrument which employed a magnetic sector for the initial mass selection step, a deceleration system to control the impact energy, and a quadrupole mass analyzer for mass analysis of products scattered through large angles.¹⁰ This instrument is representative of one of the main types of SID instruments: those in which the collision occurs between the analyzers in a beam-type tandem mass spectrometer. In addition to hybrids, tandem quadrupoles^{51,52} and tandem time-of-flight (TOF/TOF) instruments^{48,53} have been successfully applied.

In order to avoid having to reorient two analyzers of a mass spectrometer at large angles, the ion beam can be directed so as to achieve large angle scattering while maintaining the normal in-line ion optical design. A whole series of beam deflection and surface collision devices have been tested using ion trajectory simulation programs and incorporated into existing mass spectrometers.^{43,52} In these cases the scattering angles and velocities are more difficult to characterize, but good SID performance is nevertheless obtained. Another form of in-line device is the use of narrow capillary tubes, typically of conductive glass,⁵⁴ but also of metal.¹⁵ In-line collisions are also used in multiple sector instruments, using deceleration to achieve collision energies in the range of tens of electronvolts.⁵⁵

A completely different approach to achieving ion/surface reactions is to employ a single mass spectrometer and to achieve two steps of mass analysis and a surface collision within the one instrument. This has been accomplished in ion cyclotron resonance^{44,56} and quadrupole ion traps⁵⁷ by directing the ions toward the walls, and in TOF instruments by allowing collisions to occur with a surface placed within the reflector electrode assembly.³⁷

(48) Dongré, A. R.; Wysocki, V. H. *Org. Mass Spectrom.*, in press.

(49) Schaaff, T. G.; Wysocki, V. H. 42nd ASMS Conference on Mass Spectrometry and Allied Topics, Chicago, IL, May 30 to June 3, 1994.

(50) Cooks, R. G.; Ast, T.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *16*, 348.

(51) 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.

(52) Wysocki, V. H.; Ding, J.-M.; Jones, J. L.; Callahan, L. H.; King, F. L. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 27.

(53) Schey, K. L.; Cooks, R. G.; Grix, R.; Wollnik, H. *Int. J. Mass Spectrom. Ion Processes* **1987**, *77*, 49.

(54) Aberth, W. *Anal. Chem.* **1990**, *62*, 609.

(55) Despeyroux, D.; Wright, A. D.; Jennings, K. R.; Evans, S.; Riddoch, A. *Int. J. Mass Spectrom. Ion Processes* **1992**, *122*, 133. Schey, K. L.; Thornburg, K. R. *Proceedings 41st ASMS Conference on Mass Spectrometry and Allied Topics*; American Society for Mass Spectrometry: Santa Fe, NM, 1993; p 269.

(56) James, C. F.; Wilkins, C. L. *Anal. Chem.* **1990**, *62*, 1295. Nuwaysir, L. M.; Castoro, J. A.; Wilkins, J. A. *Org. Mass Spectrom.* **1991**, *26*, 721.

(57) Lammert, S. A.; Cooks, R. G. *J. Am. Soc. Mass Spectrom.* **1991**, *2*, 487.

(44) Williams, E. R.; Henry, K. D.; McLafferty, F. W.; Shabanovitz, J.; Hunt, D. F. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 413.

(45) Cole, R. B.; LeMeillour, S.; Tabet, J.-C. *Anal. Chem.* **1992**, *64*, 365. Despeyroux, D.; Wright, A. D.; Jennings, K. R. *Int. J. Mass Spectrom. Ion Processes* **1993**, *126*, 95.

(46) McCormack, A. L.; Somogyi, A.; Dongré, A.; Wysocki, V. H. *Anal. Chem.* **1993**, *65*, 2859.

(47) Jones, J. L.; Dongré, A. R.; Somogyi, A.; Wysocki, V. H. *J. Am. Soc. Mass Spectrom.*, in press.

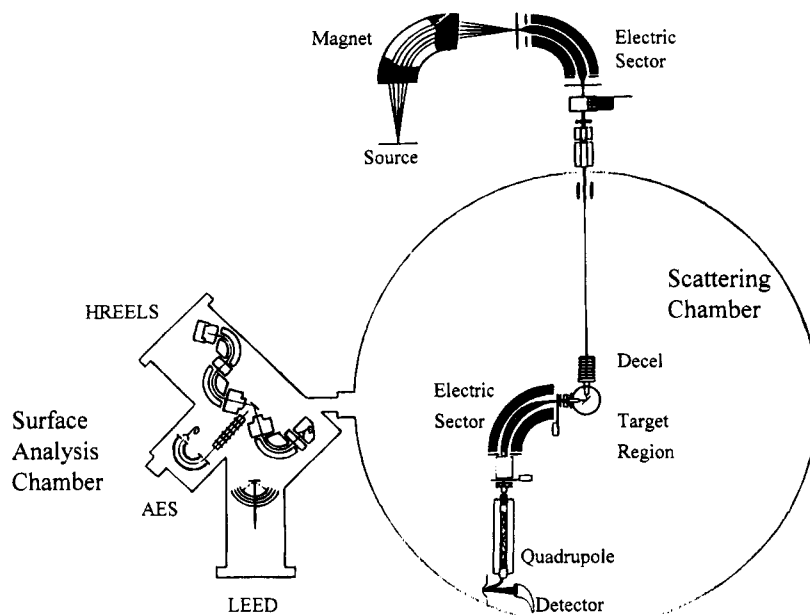


Figure 5. Instrument used for study of ion/surface collisions of mass-selected ions and the characterization of the chemical modified surfaces using electron spectroscopy. The surface characterization chamber connected to the scattering chamber housing the target region contains LEED (low-energy electron diffraction), AES (Auger electron spectrometer), and HREELS (high-resolution electron energy loss spectrometer).

The VCU ion/surface studies utilize a tandem quadrupole instrument with a 90° interquadrupole angle and a 90° scattering angle. It is equipped to allow fine control of the collision energy and utilizes a cartridge system to select any of a number of preloaded surfaces for analysis. The Purdue work utilizes an instrument (Figure 5) designed to allow selection of the mass, kinetic energy, and incident direction of the primary ion beam and to select for the corresponding properties in the scattered ion beam. Capabilities are being finalized to allow the surface to be examined in situ, using standard surface science techniques of LEED, HREELS, and AES. Primary ion doses used on both instruments are such that damage to the surface occurs slowly on the time scale required to record the mass spectra of scattered ions (typically 1 nA or less on an area of 3 mm^2).

Surfaces for Ion/Surface Collision Studies

Surfaces of known chemical composition are required for fundamental studies of ion/surface collisions. This normally requires characterization using standard ultrahigh vacuum techniques, and important work on ion/surface reactions is being done in this way.⁵⁸ As an alternative, self-assembled monolayer surfaces have proven excellent substrates for SID and other ion/surface processes. They reduce ion neutralization by keeping the minimum distance between the projectile ion and the underlying metal substrate at 1 nm or so. They are easily prepared and cleaned and long-lasting under low-flux, low-energy ion beam impact. After washing with an appropriate volatile solvent, they can be used even at 10^{-8} Torr, where they display no surface impurities. They also can be prepared with a variety of terminal head groups which can be used to examine functional-group-specific ion/surface reactions.

(58) Wainhaus, S. B.; Burroughs, J. A.; Wu, Q.; Hanley, L. *Anal. Chem.* **1994**, *66*, 1038.

In a recent study,⁵⁹ it has been shown that the choice of surface can affect the nature of the excitation process in studies aimed at characterizing ion structures by SID (vide supra). Low collision energies (20–30 eV) populate an electronically excited state of the C_3F_6^{+} projectile, which fragments preferentially to give C_3F_5^+ , after collision at an alkyl thiol SAM surface. Under the same experimental conditions, a fluoroalkyl thiol surface promotes vibrational excitation of C_3F_6^{+} and different products are generated.⁵⁹

Liquid polymer films can be used as collision surfaces in molecular beam studies if they have sufficiently low vapor pressures.⁶⁰ This is the case for the commercial perfluorinated polyether, Krytox, which has been shown to behave almost identically in inelastic and reactive ionic collisions to the fluorinated self-assembled alkyl thiolate surface.⁶¹ This liquid surface can be used in macroscopic thicknesses without charge buildup due to its adequate electrical conductivity. Many other insulating surfaces are of interest but could not be studied until the recent demonstration that an electron flood-gun can be used to effect continuous neutralization of the surface.⁶² This development is expected to cause a significant increase in the variety of reactions encountered. Another novel surface is rhenium oxide, which has an unusually high work function, and which therefore limits the degree to which neutralization of a positive ion beam occurs. In agreement with expectation, SID data taken from rhenium oxide surfaces show orders of magnitude greater scattered ion intensity, when compared with metal surfaces.⁶³

(59) Ast, T.; Riederer, D. E., Jr.; Miller, S. A.; Morris, M. R.; Cooks, R. G. *Org. Mass Spectrom.* **1993**, *28*, 1021.

(60) Saecker, M. E.; Govoni, S. T.; Kowalski, D. V.; King, M. E.; Nathanson, G. M. *Science* **1991**, *252*, 1421.

(61) Pradeep, T.; Miller, S. A.; Cooks, R. G. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 769. Schevy, K. L. 42nd ASMS Conference on Mass Spectrometry and Allied Topics, Chicago, IL, May 30 to June 3, 1994.

(62) Kane, T. E.; Wysocki, V. H. *Int. J. Mass Spectrom. Ion Processes*, submitted.

(63) Amirav, A.; Dagan, S. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 869.

The significant issue of surface damage during ion bombardment has been addressed.^{35,58} The somewhat surprising result, from a variety of low-fluence experiments, is that while considerable damage of the surface can take place after extended times, and there are corresponding changes in the ion/surface reactions, the scattered dissociation spectra remain largely unchanged.

Future Directions

Collisions of low-energy ions with organic surfaces represent a recent area of activity, which is yielding useful results and raising interesting questions of reaction mechanism and dynamics. The observation that polyatomic ions fragment upon surface collisions, viz., undergo SID, widens the scope of tandem mass spectrometry. For example, the characterization of biological compounds is a problem to which the SID experiment brings new capabilities. The interesting mechanistic and dynamical questions are legion, since the chemical reactions accompanying collisions of ions at surfaces are still very little explored, although recent work has led to the recognition of the oxidative addition and electron transfer induced mechanisms discussed above. The discovery of many additional reactions is anticipated as more types of surfaces are examined. Certain probe beams, notably fluorinated ions and rare gas ions, cause charge exchange and efficient desorption of the surface groups, and further study of this chemical sputtering process is needed. In addition, the systematic discovery of ion/surface reactions which are functional group specific will allow

tests to be developed to identify functional groups at interfaces. Other questions awaiting exploration include the following: (i) In which cases does dissociation occur in isolation, and when is it surface-mediated? (ii) Can state-selected reactions be observed? (iii) What is the effect of thermal activation of the surface? (iv) What is the angular dependence of scattering and of reactive collisions? (v) What is the residence time of ions at the surface?

The type of chemistry described here may ultimately allow chemically selective modification of surfaces with control of the lateral modification pattern. The energies of the projectile ions are low enough to ensure that ion/surface reactions are limited to the outermost monolayers of the surface. Moreover, it is relatively straightforward to cause the projectile ion beam to impinge upon selected regions of the surface.¹⁸ These features seem sure to result in a form of chemical writing on the surface which is at once highly chemically specific and also highly localized, both in depth and in spatial extent. Such a capability would have immense implications for optoelectric and computational devices.⁶⁴ The simple observation of halogen transfer between a chlorinated ion beam and a fluorinated surface represents a starting point on this journey.

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(64) MacDonald, S. A.; Willson, C. G.; Frechet, J. M. J. *Acc. Chem. Res.* **1994**, *27*, 151.