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Letter

Surface-induced chemical reactions of cluster ions: competitive processes of protonated acetone formation in acetone dimer–surface collisions

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Abstract

In low energy collisions (10–50 eV) of acetone dimer ions with a stainless steel surface (covered with hydrocarbons) we have been able to observe the occurrence of two different chemical reactions initiated by the surface impact and leading to the protonated acetone ion, namely (1) an intracluster ion–molecule reaction, and (2) a hydrogen pick-up reaction of the cluster ion with the surface material. In accordance with predictions from molecular dynamics simulations, this appears to be the first observation of competitive chemical reactions of a cluster ion driven by energy transfer in a surface collision. (Int J Mass Spectrom 188 (1999) L1–L6) © 1999 Elsevier Science B.V.

Keywords: Cluster ions; Surface induced reactions; Acetone; Tandem mass spectrometry

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1. Introduction

Ion-surface collisions is an area of research rapidly growing in an effort to identify and explore new methods for both characterizing gaseous ions and the nature of the surface [1,2]. In addition to being of fundamental importance, ion–surface interactions are also relevant to technological applications [2] encompassing such diverse fields as (1) secondary ion mass spectrometry, (2) reactive scattering for surface analysis, (3) surface-induced dissociation for structural analysis, (4) surface modifications for the preparation of new electronic materials (including the large area of plasma processing) and, quite importantly, (5) plasma–wall interactions in electrical discharges [3] and fusion plasmas [4]. Surface induced dissociation (SID) processes and surface induced reactions (SIR) have been identified and investigated in the past years for collisions in the laboratory energy range of tens of electron volts.

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A particular interesting and exciting subfield in the area of ion–surface collisions is the interaction of clusters with surfaces [5]. Depending on the initial kinetic energy of the impinging cluster projectile, the interaction with a surface may lead either to cluster deposition, to cluster fragmentation, or even to cluster ionization or the emission of electrons (see [5] and references given in [6]). Experimental studies concerning cluster-ion/surface "reactions" have been mainly restricted to SID reactions; nevertheless, in case of singly charged fullerene ions also SIR (surface pick-up reactions [7,8]) have been observed.

Recently, Cleveland and Landman [9] have investigated theoretically the structure, energetics, and dynamics of shock conditions generated in a nanocluster upon impact on a sodium chloride crystalline surface using molecular dynamics simulations for a 561 atom argon cluster incident with a velocity of 3 km/s (energy of ≈9 eV per atom). Their findings demonstrated that the impact of this cluster on the surface results in a piling-up phenomenon leading to high-energy collision cascades and the development of a new transient medium in the cluster environment characterized by extreme density, pressure, and temperature conditions. In their conclusions they suggested that in the presence of reactants embedded in this colliding cluster, such collisions could promote chemical reactions between cluster constituents as well as between cluster constituents and the surface material. In a follow-up paper, Levine and co-worker suggested, on the basis of molecular dynamics calculations, a possible existence of intracluster reactions such as "burning air" in mixed nitrogen/oxygen clusters [10].

For a quantitative investigation of SID and SIR processes (for instance to determine activation energies [11]) it is of utmost importance to control and determine accurately the collision energy and to achieve energy spreads as small as possible. The usual energy resolution in studies of SID processes of polyatomic ions was about 2–4 eV [11] [full width at half maximum] (FWHM), whereas in cluster ion studies energy distributions of several tens of electron volts (FWHM) have been the state of the art in the past few years [6–8,12,13].

In a recent effort to improve this situation we have constructed a tandem mass spectrometer apparatus consisting of a B-sector field combined with an E-sector field, a Surface, and a Time-Of-Flight mass spectrometer (BESTOF), which enables investigation of ion–surface reactions with a high projectile mass and energy resolutions [14–17]. Results of studies using BESTOF on SID and SIR of acetone [14] and benzene [16] molecular ions and benzene clusters [15] have been reported earlier. In this article we report on studies using BESTOF, where we have been able to observe experimental evidence for intracluster reactions initiated upon (hydrocarbon covered stainless steel) surface impact in competition with a surface pick-up reaction for size selected acetone dimer ions A_n^+ (with A for CH_3COCH_3). Besides typical fragmentation patterns, we observe protonated reactant ions (e.g. AH^+) produced by both intracluster reactions and reactions with the surface adsorbates.

2. Experiment

Briefly, the experimental apparatus BESTOF [16] consists of a double-focusing two-sector-field mass spectrometer (reversed geometry) in combination with a linear time-of-flight mass spectrometer. Neutral acetone clusters were produced by supersonic expansion through a 20 μm nozzle in a continuous cluster source. The pressure of the expanding gas was about 2.5 bar and the temperature in the expansion vessel was set to 300 K. After passing through a skimmer, the neutral acetone cluster beam entered transversely a Nier-type electron impact ion source. The ions produced by an impact of 70 eV electrons were extracted from the ion source region and accelerated to about 3 keV for mass and energy analysis by a high-resolution double-focusing two-sector-field mass spectrometer allowing for the production of isotopically pure projectile ions. After passing the mass spectrometer exit slit, ions were refocused by an Einzel lens and decelerated to the desired collision energy before hitting the stainless steel surface. The collision energy of ions impacting on the surface was defined by the potential difference between the ion source and the surface. The potential difference (hence, the collision energy) could be varied from zero to about 2 keV with a typical energy resolution better than about 200 meV (FWHM). Field penetration effects were minimized by shielding the surface with conical shield plates. The incident angle of the projectile ions on the surface was set at 45° and the scattering angle was kept at 90° (defined as a deflection from the incident beam direction). A fraction of the product ions formed at the surface exited the shielded chamber through a 1 mm diameter orifice. These ions were then subjected to a pulsed extraction and acceleration field, which initiated the time-of-flight analysis of these ions. The mass selected ions were detected by a double stage multichannelplate connected with a fast scaler (of a time resolution of 5 ns per channel) and a laboratory computer.

In the initial stage of our present studies, experiments were carried out using a stainless steel surface under ultrahigh vacuum conditions (10^{-9} to 10^{-10} Torr) maintained in our bakeable turbopumped surface collision chamber. However, even these conditions did not exclude the production of monolayers of hydrocarbon contaminants (pump oil, etc.) on the surface.

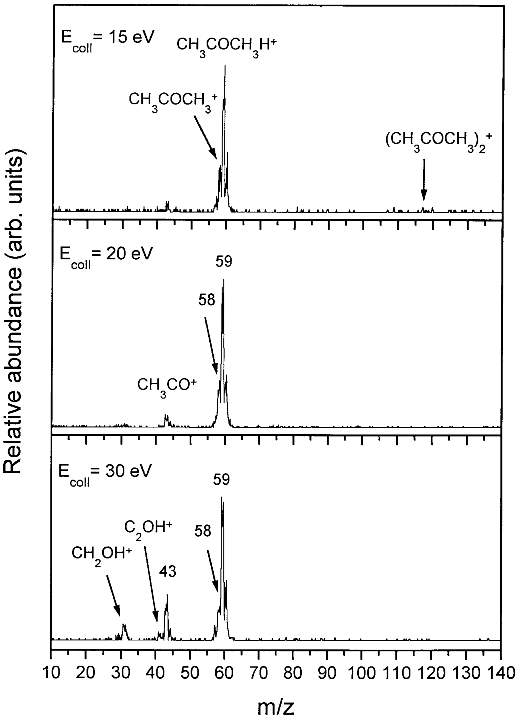

Fig. 1. Product ion mass spectra for the impact of the acetone dimer ion $(CH_3COCH_3)_2^+$ for collision energies of 15, 20, and 30 eV, respectively.

3. Results and discussion

The positive ion mass spectrum after ionization of an acetone cluster beam by 70 eV electrons shows a rather complicated fragmentation pattern: Besides the monomer acetone parent ion peak and the monomer fragment ions (mass 43 and smaller), known from electron impact ionization of the acetone molecule, additional series of cluster ions are present such as the stoichiometric cluster ions $(CH_3COCH_3)_n^+$, the protonated cluster ions $(CH_3COCH_3)_nH^+$ and the acetylated ion series $(CH_3COCH_3)_nCH_3CO^+$. The mass spectrum is dominated by the stoichiometric cluster ion series, but the abundance of the nonstoichoimetric ions, which are readily identified as ion–molecule reaction products in the acetone system, is of the same order of magnitude.

In the present investigation we concentrated only on the interaction of slow (10–40 eV) stoichiometric cluster ions [18] with the stainless steel surface and this article reports specifically on the dimer ion.

Fig. 1 illustrates the surface collision reaction products for the impact of mass selected dimer ions $(CH_3COCH_3)_2^+$ at the collision energy of 15, 20, and 30 eV, respectively. Fig. 2 shows the corresponding relative abundances of the product ions in dependence on the collision energy. At around 20 eV, the major product ions are the protonated monomer ion $(CH_3COCH_3)H^+$ and the monomer ion $(CH_3COCH_3)^+$. Both types of product ions are observed at collision energies as low as 10 eV. The abundance of the acetyl cation, which is a minor fragment product ion at 20 eV, increases monotonically with collision energy. The acetyl ion is the major collision-induced decomposition product for the acetone molecular ion in the gas phase [19]; it is also a major dissociation product formed in low energy surface-induced reactions upon

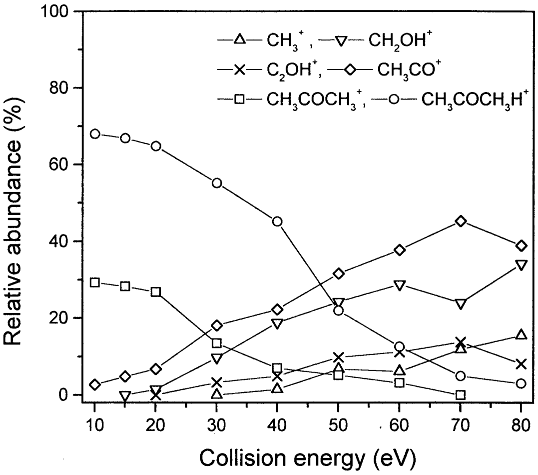

Fig. 2. Dependence of the relative abundances of product ions on impact energy of the acetone dimer ion $(CH_3COCH_3)_2^+$.

impact of the acetone molecular ion on a surface [14]. Consequently, we identify the acetyl cation with the breakup of molecular acetone ions after surface impact of the dimer ion. In addition to the acetyl ion several fragment ions, CH_3^+ and CH_2OH^+, are observed in appreciable amounts at higher collision energies. CH_3^+ is known to be a fragment ion of the acetone monomer ion (similar to the acetyl case, see prior discussions), whereas the CH_2OH^+ ion is known from our previous studies to be a dissociation product of protonated acetone cations, produced in the surface collision, when the collision energy is increased [14]. As both the acetone monomer ion and the protonated acetone ion are present in the product ion mass spectrum and both are decreasing in relative abundance as the relative abundances of the other fragment ions, i.e. CH_3^+, CH_2OH^+, and CH_3CO^+, are increasing with increasing collision energy, the production pathways of these fragment ions appear to be straightforward. However, as will be discussed, the production route(s) of the protonated acetone monomer ion, $(CH_3COCH_3)H^+$, is the real interesting point in this study.

Surface reactions of the acetone monomer cation give as a major product ion the protonated acetone ion formed exclusively by H abstraction from hydrocarbons chemisorbed on the surface [14]. As shown in Figs. 1 and 2, below 50 eV this protonated acetone ion is also the most prominent reaction product from the surface reaction of acetone dimer ions (and also for higher cluster analogues discussed in [20]). Thus, in line with the aforementioned it is conceivable that, in principle, this ion may be produced by two competing reactions of the impacting dimer ion, i.e.

$$(CH_3COCH_3)_2^+ + S \rightarrow (CH_3COCH_3)_2^{+*}$$

$$\rightarrow (CH_3COCH_3)H^+ + CH_2COCH_3 \qquad (1a)$$

$$(CH_3COCH_3)_2^+ + S/RH \rightarrow (CH_3COCH_3)H^+$$

$$+ CH_3COCH_3 + R \qquad (1b)$$

where reaction (1a) represents a surface collisional activation of the impinging dimer ion followed by an intracluster ion–molecule reaction between the acetone ion and its neighbouring neutral molecule (discussed above in the context of electron impact ionization of neutral acetone clusters), and reaction (1b) represents a reaction with surface hydrogen-containing adsorbates (dissociative H-atom pick-up reaction).

Important insight into the origin of the protonated acetone formation can be gained by performing an additional experiment using fully deuterated acetone dimer ions, $(CD_3COCD_3)_2^+$, as projectiles. In this case, the product ion mass spectrum (see Fig. 3) of the monomer group consists of three peaks, identified as the deuteronated acetone ion $(CD_3COCD_3)D^+$, the protonated acetone ion $(CD_3COCD_3)H^+$, and the acetone monomer “fragment” ion $CD_3COCD_3^+$. It is clear that in this case the deuteronated acetone ion is produced, in analogy to reaction (1a), via a surface induced intracluster ion–molecule reaction, whereas the protonated acetone ion is produced, in analogy to reaction (1b), via a reaction of the impinging dimer ion with hydrogen containing surface adsorbates.

In order to rationalize the formation of these two reaction products in the interaction of the acetone dimer ion with the surface, we adopt the double-well model of ion–molecule reactions as proposed by Brauman [21]. The acetone dimer ion, relaxed by monomer evaporation from larger acetone cluster ions to low internal energies [18], exists before the interaction with the surface in two different configurations, $(CD_3COCD_3)D^+.(CD_2COCD_3)$

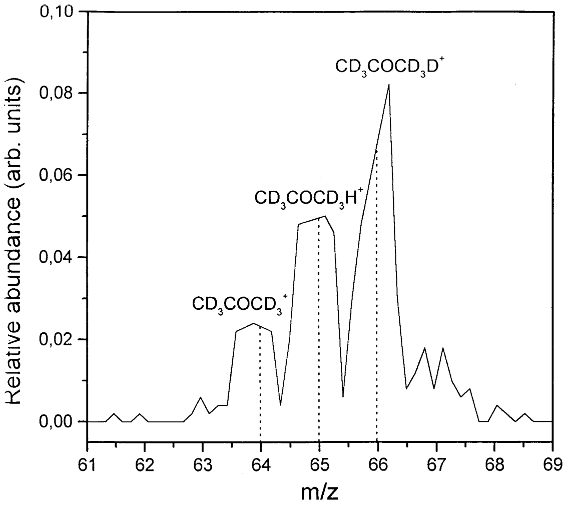

Fig. 3. Section of the product ion mass spectrum (at around the monomer mass) for the impact of the fully deuterated acetone dimer ion $(CD_3COCD_3)_2^+$ at the collision energy of 30 eV.

and $(CD_3COCD_3).(CD_3COCD_3)^+$, separated by a barrier. In the surface collision part of the projectile translational energy is converted into the internal energy of the dimer ion and this leads to the dissociation of the two moieties to ions $(CD_3COCD_3)D^+$ and $(CD_3COCD_3)^+$. In the latter case, most of the molecular acetone ions may react with the surface hydrocarbons to give, by hydrogen abstraction, the protonated acetone as a major product. The intact molecular ions $(CD_3COCD_3)^+$, are also observed as a less abundant reaction product. Some of these may be ions which, after dissociation at the surface, could not react to $(CD_3COCD_3)H^+$, but some may have been formed in slow unimolecular dissociations of the receding dimer ion to $(CD_3COCD_3)^+ + (CD_3COCD_3)$, after the interaction with the surface.

In conclusion, in extension of several pioneering studies involving surface induced dissociation of cluster ions [6–8,12,13,22], we have been able to observe and analyse surface induced reactions of cluster ions. In these reactions, the energy necessary to make the reaction go is supplied by the surface collision. In particular, we have been able, as predicted by Cleveland and Landman from molecular dynamics simulations [9] (see also [10,24]), to detect, for the interaction of the deuterated acetone dimer ion $(CD_3COCD_3)_2^+$ with the surface, two different channels of a surface reaction, on the one hand, the intracluster chemical reaction leading to the production of the deuteronated acetone monomer ion $(CD_3COCD_3)D^+$ (in "collisions which catalyze chemical reactions between cluster constituents" [9]) and, on the other hand, the reaction of hydrogen pick-up leading to the formation of the protonated acetone monomer ion $(CD_3COCD_3)H^+$ (in "collisions between the cluster ion and the surface material" [9]). Similar surface induced reactions have been observed in interactions of larger acetone cluster ions with the surface. The results will be reported separately [20].

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