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Transient ISEELS: a new probe of chemical reactions

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Abstract

An inner shell electron energy loss spectrometer (ISEELS) has been adapted as a probe of chemical reactions by coupling its gas phase interaction region to the output of a variety of chemical reactors including thermolysis, gas phase reaction, and heterogeneous reaction systems. Three examples of transient ISEELS studies are presented: in situ generation of a reactive carbene by thermolysis of its stable dimer, reaction of a silylene with N_2O in the gas phase, and the heterogeneous reactions of H_2S and H_2O with crystalline boron in a heated quartz tube. In the latter example, temperature dependent inner shell excitation spectra, mass spectrometry and ab initio calculations were used to show that in the high temperature limit the reaction of H_2S (g) and B (s) over SiO_2 (s) gives rise to borine (HBO), a species previously un-detected from this reaction chemistry. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Photoelectron spectroscopy has long been used as a probe of transient species [1] generated by a variety of means, such as thermolysis, photolysis, plasma decomposition, and homogeneous or heterogeneous chemical reactions. The detailed information on occupied electronic structure provided by transient PES helps identify novel species and understand reaction mechanisms, and thus transient PES has an honored place among transient spectroscopies [2]. Site specific core excitation, with either electron impact or X-rays, probes unoccupied electronic structure in ways which are very complimentary to photoelectron spectroscopy. Thus it is reasonable to consider applying core excitation spectroscopy to transient studies. In several of our earlier studies we have coupled reaction chemistry to our spectrometer either for purification [3] or for generation of a novel species [4]. Recently we have begun systematic application of gas phase inner shell electron energy loss spectroscopy (ISEELS) [5,6] as a probe of transient species. Here we give a general discussion of the transient ISEELS technique, its advantages as a probe of chemical reactions, and outline some examples. The first two examples: thermolysis of a carbene dimer, and the reaction of a stable silylene with N_2O, are presented for the first time; the transient ISEELS study of the reactions of

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H_2S and H_2O with boron and quartz has been published in detail elsewhere [7].

2. Experimental

The apparatus is a non-monochromated inelastic electron scattering spectrometer, operated in constant final energy mode [6,8]. It is optimized for dipole regime studies of gases, and thus provides spectra similar to those from X-ray absorption [9]. All spectra were acquired using 2.5 keV final energy, an average scattering angle of 2° and an energy resolution of 0.7 eV fwhm. The collision region can be heated to 200°C, while the rest of the apparatus is protected by water cooled plates located above and below the gas cell section. The variable temperature collision region can be coupled in line-of-sight fashion to chemical reactors by means of a 6-mm vacuum port. The distance from the electron beam to the exterior vacuum wall is less than 5 cm. This short distance is important to maximize the solid angle for direct transport and to minimize wall collisions which often destroy highly reactive intermediates or products. As an example, in the HBO system we were able to place the output of a furnace at 1200°C less than 2 cm from the vacuum wall and thus the reaction center was less than 7 cm from the ISEELS measurement site.

3. Results and discussion

Our first transient ISEELS experiments involved exploration of reactions involving divalent, dicoordinate carbon and silicon. The divalent oxidation state for group IV is highly reactive due to the thermodynamic driving force to form the much more stable tetravalent system. However, isolable carbenes and silylenes can be obtained by electronic stabilization and the use of sterically demanding substituents that prevent dimerization [10–15]. The core excitation spectra of carbenes, silylenes and germylenes have been used to study electronic and structural aspects of this stabilization [16,17]. Transient studies of related but unstable carbene or silylene species help to extend our understanding of the origin of stabilization. Fig. 1 compares the C1s and N1s spectra of a tetra-amino ethylene compound, which is the dimer of the saturated-ring methyl-substituted carbene of interest, with those of the product of a thermally induced decomposition reaction (induced by passing the reactant gas through a 1-m long stainless steel coiled tube heated to 290°C), and with the C1s and N1s spectra of the stable, saturated-ring *t*-butyl substituted carbene. The C1s spectrum of the thermolysis product has a low lying peak attributed to C1s→C2p excitation at the C^{II} carbene site. The N1s spectrum has a strong low-lying peak which is attributed to N1s excitation to a π^* orbital delocalized in the $N–C^{II}–N$ region. We conclude the dimer is dissociated into the indicated saturated-ring methyl-substituted carbene. Relative to the stable *t*-butyl counterpart, the low-lying C1s and N1s spectral features occur at considerably lower energy, consistent with a smaller HOMO–LUMO gap and thus a more reactive molecule.

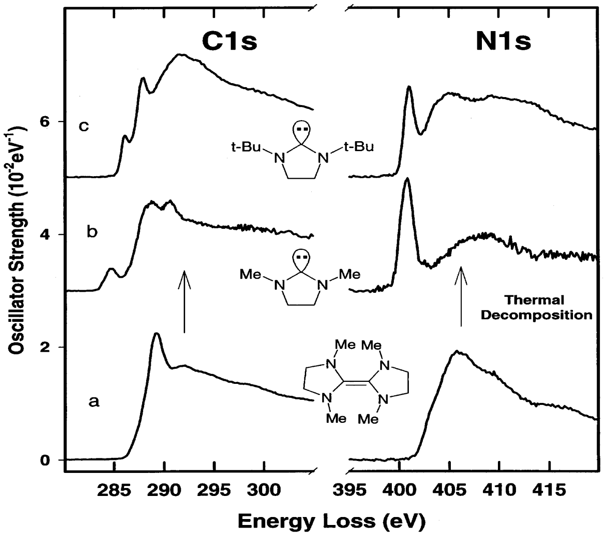

Fig. 1. C1s and N1s ISEELS spectra of (a) the indicated tetra-aminoethylene species at room temperature; (b) the thermal decomposition product from heating the tetra-aminoethylene species to 290°C, believed to be the indicated saturated-ring, methyl-substituted carbene; and (c) the corresponding saturated-ring, *t*-butyl substituted carbene [13].

Stable but highly reactive carbenes and silylenes have tremendous potential as synthetic reagents [18–21]. Transient studies of the reactions of these species with other compounds can help develop this potential by helping understand reaction mechanisms. One synthetic goal has been the generation of other unstable Si^{II} compounds, such as SiO, from the stable unsaturated-ring, *t*-butyl silylene. The gas phase reaction of silylene and N_2O is expected to generate SiO cleanly. Such a reaction could be useful for use of the highly reactive SiO species as an in situ reagent. The Si1s spectrum of SiO shows a strong Si1s→π* peak [22]. An analogous feature should appear in the Si2s spectrum if significant SiO exists in the collision region after reaction, but this was never detected. While we were not able to detect the inner shell spectra of SiO, the ISEELS results (Fig. 2) clearly demonstrate that a gas phase reaction does occur under the conditions used. If SiO was generated, as expected, it is likely that it reacted further to form a non-volatile product which condensed on the walls of the long coiled stainless steel tube before reaching the collision region. The long, coiled stainless steel tube was used as the gas phase reactor to ensure sufficient contact of the silylene and N_2O.

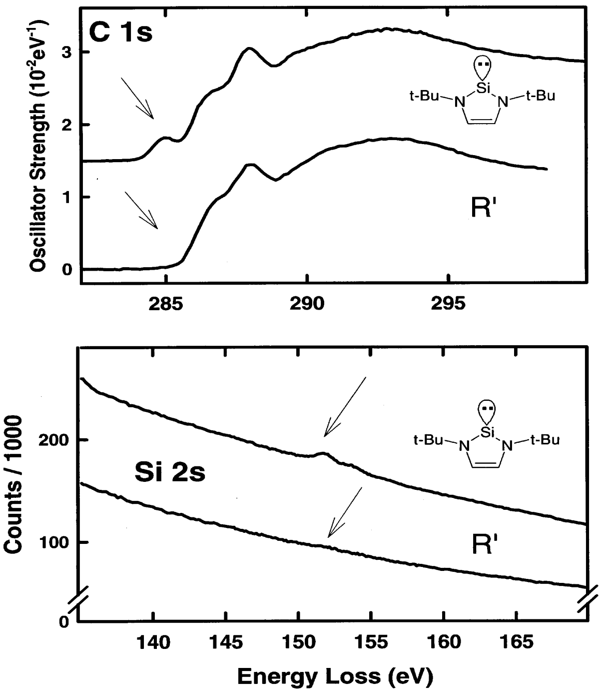

Fig. 2. Transient ISEELS study of the reaction of an unsaturated-ring, *t*-butyl silylene with nitrous oxide. The low lying feature in the C1s spectrum, which is related to delocalization in the heterocylic ring, and signal at the Si2s edge are lost when the silylene mixed with N_2O at ~10^{-2} Torr pressure is passed through ~1 m coiled stainless steel tube at 290°C.

In the third example, transient ISEELS has been used to probe a reaction system previously studied by transient PES, namely the heterogeneous reaction of hydrogen sulfide and boron [23,24], which is a well-known route to HBS. The ISEELS results [7] fully reproduced the chemistry tracked by transient PES. In addition, we were able to identify a new product in the reaction, one which has never been detected with transient PES of the H_2S/B reaction, although it had been identified as a trace component by mass spectrometry and investigated with other transient spectroscopies from different reactions. As with other ISEELS investigations, we have used quantum chemistry, in this case ab initio GSCF3 calculations [25,26], to support our interpretation of the transient chemistry, to assign the ISEELS spectra, and to better understand the spectral–structure relationships. Fig. 3 presents ISEELS spectra recorded on the gas phase output (~10^{-5} Torr) of a heated quartz tube through which H_2S is passed over boron crystals. At a furnace temperature of 1100°C the H_2S S2p and S2s signals disappear and new S2p, S2s and B1s signals are detected, consistent with complete conversion to HBS. This is the expected reaction product based on the transient PES studies [23,24]. However, further heating to 1200°C results in almost complete loss of S2p signal, introduction of an O1s signal (see insert to Fig. 3), and a modified B1s spectrum. We interpret this new species, which was not detected in the transient PES studies, as that of HBO. One alternate possibility is formation of boroxine ($H_3B_3O_3$), which is the thermodynamically most stable compound of $(HBO)_x$ stoichiometry. However we were able to rule that out by showing that the B1s and O1s spectra of boroxine, made by passing water over hot boron in the same apparatus [27,28], is distinct from the high temperature species of the H_2S/B reaction. In addition, the mass spectra of the vapor in the spectrometer during these reactions [7] fully support our interpretation of the transient chemistry, although the ISEELS spectrum is a much more sensitive probe, since much of the HBO is destroyed by wall collisions before entering

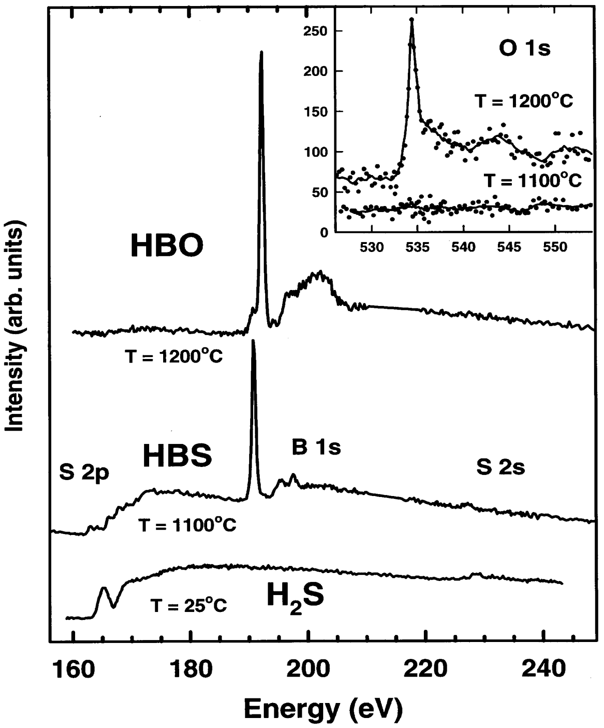

Fig. 3. ISEELS spectra of the output of the reaction of H_2S (g) and crystalline boron in a quartz tube heated to the indicated temperatures [7]. The inset plots the O1s spectra from the two regimes of the (H_2S/B(s)/quartz) high temperature reaction.

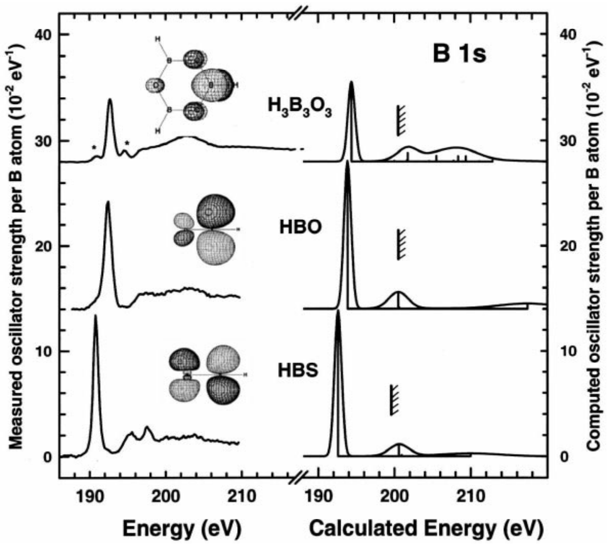

Fig. 4. Comparison of experimental and computed B1s spectra of HBS, HBO and $H_3B_3O_3$. All data is presented on an absolute oscillator strength per B atom scale, with offsets. The MO diagrams are those of the computed $\pi^*_{B=S}$ and $\pi^*_{B=O}$ orbitals which are populated to form the most intense low-lying peak in each molecule. The features indicated by * on the $H_3B_3O_3$ plot are believed to be from minority species for which computed spectra are given elsewhere [7].

the mass spectrometer. A detailed interpretation of the S2p, S2s, B1s and O1s inner shell spectra, based on comparison of the spectra of all three species, and with simulated spectra based on GSCF3 ab initio calculations, has been published elsewhere [7]. Fig. 4 compares the experimental and computed B1s spectra of HBS, HBO and $H_3B_3O_3$. The B1s spectrum of HBO is distinct from that of $H_3B_3O_3$ and there is good agreement with calculated spectra for all three species, although there is evidence for minority species in the H_2O/B reaction. The novel chemistry revealed by transient ISEELS suggests that attack of quartz by H_2S at high temperature could be a useful means to produce small amounts of reactive oxygen. This could be developed as a means for controlled partial oxidation for use in transient studies or even synthetic applications.

In view of the significant synthetic potential of the stable silylenes and carbenes [18–21], in situ spectroscopic investigations such as those described above may be crucial to develop a refined mechanistic understanding of their unique reactivity. These reactions may be used not only to generate similarly stable products that are otherwise difficult to obtain, but may also serve to generate reactive intermediates, for example the transient SiO from a stable silylene and N_2O.

4. Summary

This work demonstrates the utility of ISEELS as a gas phase probe of homogeneous and heterogeneous chemical reactions. Further developments might include coupling the spectrometer to DC, or microwave plasma sources, or to laser induced reactions. As with many transient spectroscopic probes, both creative optimization of the chemistry and correct coupling of the reactor to the spectrometer are critical to success. Gas phase inner shell spectroscopy studies of reactions can provide complementary information to other transient techniques, with potential for superior performance in some aspects. The ability to look at a number of different core edges quasi-simultaneously provides elemental analysis. When combined with in situ mass spectrometry, this can be very helpful when studying a poorly characterized reaction. ISEELS has better sensitivity to low yield processes than PES since the gas density required is several orders of magnitude lower. Finally, but perhaps most important, the insight into bonding and electronic structure provided by core excitation, a site- and symmetry-specific probe of unoccupied electronic structure, is highly complementary to that of PES, which probes the occupied valence levels.

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