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Bimolecular photoreaction of adsorbates: 2 HX→H2+X2 (X=Cl, Br)

C.C. Cho, J. C. Polanyi, and C. D. Stanners

Citation: The Journal of Chemical Physics **90**, 598 (1989); doi: 10.1063/1.456460
View online: http://dx.doi.org/10.1063/1.456460
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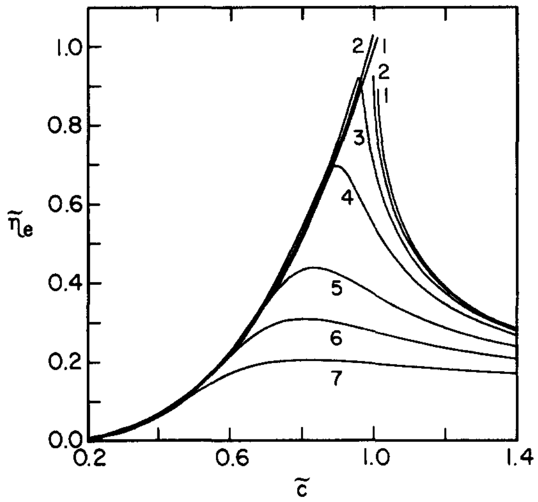

FIG. 1. Reduced elongational viscosity $\tilde{\eta}_e \equiv \eta_e/\eta_e^*$ vs reduced concentration $\tilde{c} \equiv c/c^*$, for each of successively larger values of the dimensionless flow strength $\tilde{h} \equiv \gamma/2D_r^*$. (See the text for definitions of η_e^*, c^*, and D_r^*.) Curves 1 through 7 refer to $\tilde{h}$ = 0,0.02, 0.067, 0.2, 0.67, 1.33, and 2.67, respectively.

$[= (\gamma/2D_r^*)_c] = 0.045$ corresponds to an easily realizable velocity gradient. In particular, for macromolecular dimensions of $d \approx 200$ Å and $L \approx 3000$ Å (e.g., tobacco mosaic virus) estimates of D_r^* suggest that $\gamma \approx 10\ \mathrm{s}^{-1}$ will be more than sufficient to suppress the phase transition in rod alignment and hence to give the $\tilde{\eta}_e$ vs $\tilde{c}$ plots shown in Fig. 1. Accordingly, experimental measurements of the elongational viscosity for these systems can be expected to test the theoretical predictions presented here from our general treatment of orientational structure and dynmaics in interacting rod fluids.[15]

[a] Work supported in part by NSF Grant No. CHE85-42620.

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Bimolecular photoreaction of adsorbates: 2 $HX \rightarrow H_2 + X_2$ (X = Cl, Br)

C.-C. Cho, J. C. Polanyi, and C. D. Stanners
Department of Chemistry, University of Toronto, Toronto M5S 1A1, Canada

(Received 16 September 1988; accepted 26 October 1988)

There is a growing interest in the photolysis of adsorbates.[1] Atomic photoreaction, PRXN(*A*), has been observed in which *A* reacts with co-adsorbed *AB*(ad).[2,3] This constitutes "surface aligned photochemistry" (SAP). The dynamics depend on alignment.[4,5]

We report a new category of PRXN, bimolecular photoreaction. PRXN(*B*), in which photodissociation does not occur, nonetheless the reaction $2HX(ad) \rightarrow H_2(g) + X_2(g)$ (X = Cl, Br), is observed in good yield.

Experiments were performed in UHV on LiF(001) at 85K.[3] The surface was dosed with HBr (99.95%) or HCl (99.5%), (H_2 and X_2 removed). PRXN(*B*) was observable from 0.1–10 monolayers coverage.

Unpolarized excimer radiation at 193 and 248 nm was used with fluences ~25 mJ/cm^2. Each pulse photodesorbed > 50% of the HX adsorbate.[2,3] Species leaving the surface were detected by time-of-flight (TOF) mass spectrometry.

Figure 1(a) shows the mass 2 (H_2) TOF spectra resulting from 193 and 248 nm irradiation of a 1.5 L (langmuir) dose of HBr. Peak A was observed at 193 nm only; we ascribe it to PRXN(*A*) following HBr photodissociation.[3]

Peak B in the H_2 TOF appears for both 193 and 248 nm irradiation of HBr(ad), and also for 193 nm irradiation of HCl(ad). This peak can be identified by its time of arrival as due to H_2 leaving the surface, rather than a larger molecule desorbing and cracking in the ionizer. The H_2 translational energy for B peaks at 0.018 eV for HBr(ad) independent of laser wavelength, and at 0.012 eV for HCl(ad).

At 193 nm the Br_2 translational energy distribution from HBr(ad) peaks at 0.058 eV; at 248 nm it peaks at 0.075 eV [Fig. 1(b)]. The Cl_2 from HCl(ad) at 193 nm peaks at 0.042 eV [Fig. 1(d)]. These energies are comparable with those for photodesorption.[2,3]

The amount of H_2 and X_2 desorbing from the surface is roughly equal at each wavelength and for all coverages; approximately 5% of the yield of photodesorbing HX. Since

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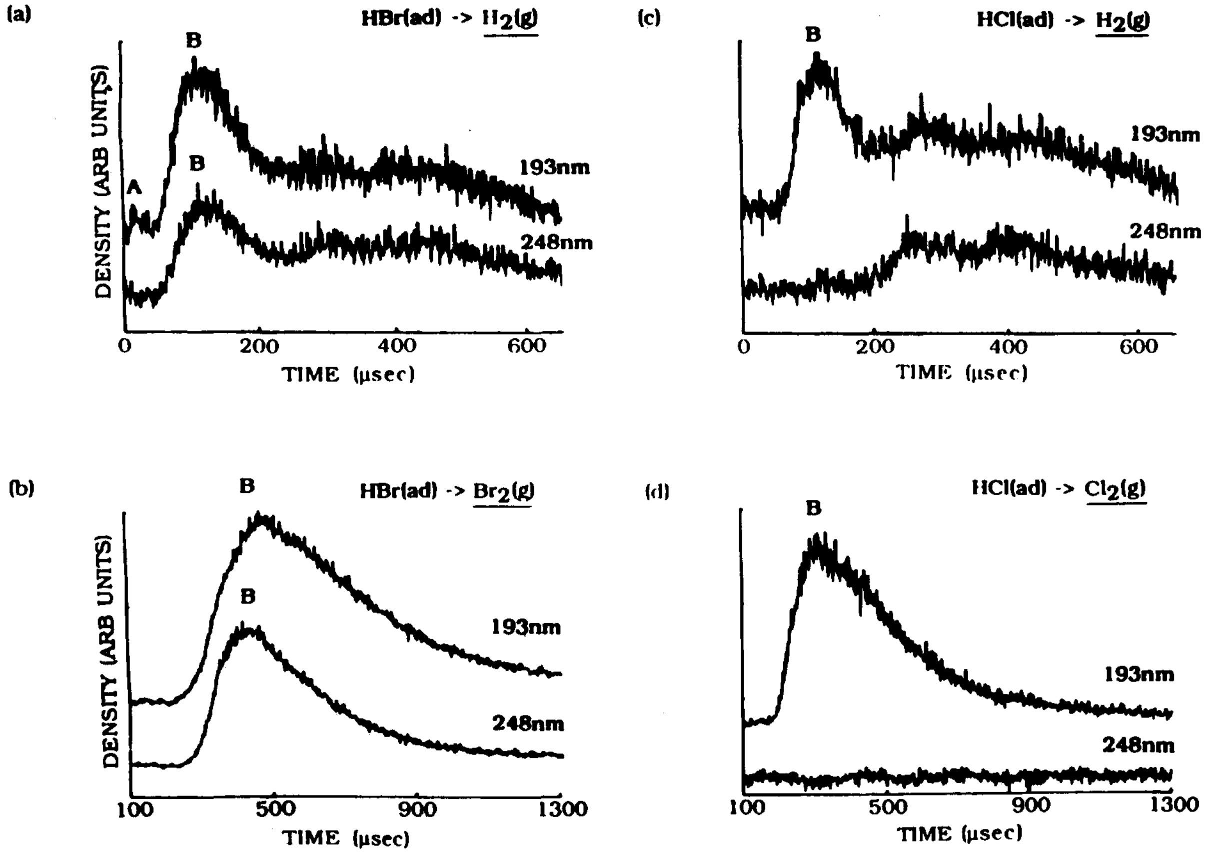

FIG. 1. TOF spectra (a) H_2 from HBr; (b) Br_2 from HBr;(c) H_2 from HCl;(d) Cl_2 from HCl.

H_2 can be an impurity in HX, we tried adding pure H_2 while dosing HBr. This did not increase the peak B H_2 signal, confirming that B is reaction product.

Adding H_2 concurrently with HX increased the amount of H_2 arriving at late times [>300 μs in Figs. 1(a) and 1(c)]. If this H_2 was released from the crystal concurrently with illumination, it would have the improbable peak energy of 0.002 eV or less (<23 K). We believe instead that this H_2 is desorbed by a delayed heating process. There is no corresponding X_2 desorption, consistent with its greater heat of adsorption and desorption.

The yield of H_2 (peak B) from adsorbed HBr at 248 nm is the same as the yield at 193 nm for coverages up to a monolayer, in spite of the fact that the yield of H atoms from photodissociated HBr(ad) is approximately two orders of magnitude smaller at 248 nm.[3] *A process producing equal yields of H_2 and X_2 without photodissociation of HX is the bimolecular reaction between adjacent HX*: $2HX \rightarrow H_2 + X_2$. We have evidence for HBr island formation down to low coverages,[3] hence aligned adjacent HX will always be present in the adsorbed state. The same products could be formed by exoergic hydrogen atom abstraction ($\rightarrow H_2$) and endoergic halogen atom abstraction ($\rightarrow X_2$) but the yields of H_2 and X_2 would then be very different.

Although the ground state four-center reaction of hydrogen halide molecules is symmetry forbidden,[6] the reaction of electronically excited species would be allowed. The comparable yield of product from HBr(ad) irradiated at 193 or at 248 nm suggests that electronic excitation of the monomer is not involved. However, the mechanism could involve the excitation of HX dimer leading to direct formation of H_2 and X_2. The absorption cross-section for the HCl dimer at 248 nm is presumably too small to produce detectable H_2 and Cl_2 [lower curves, Fig. 1(c) and 1(d)].

Assuming that for absorbed photons the quantum efficiency is unity for production of $H_2 + X_2$, a cross section of ~ 0.006 Å^2 is obtained for PRXN(B) of HBr (193 nm, 1.5 ML). This is roughly twice the cross section we measure for photodissociation of adsorbed HBr (193 nm). The cross section for PRXN(B) of HCl (193 nm) is ~ 0.0015 Å^2. This is an order of magnitude larger than the cross section we measure for photodissociation of HCl(ad); PRXN(B) is an efficient process.

The endothermicity of $2HX \rightarrow H_2 + X_2$ is 0.99 eV for X = Br, and 1.92 eV for X = Cl. For PXRN(B) of HCl at 193 nm there is a possible 4.5 eV of excess energy available to the products. Since the translational energy distributions of the Cl_2 and Br_2 are similar, resembling the translational energy distribution for photodesorption,[2,3] we believe X_2 product is trapped and subsequently photodesorbed.

The 193 nm H_2 photoproduct from HCl(ad) has the same translational energy as from 193 nm on HBr(ad), in

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spite of endothermicities differing by 0.93 eV. Furthermore, 193 nm on HBr(ad) gives the same translational energy distribution of H_2 as at 248 nm, despite 1.42 eV less photon energy. The translational temperature of the desorbing H_2 is close to the surface temperature; interaction is strong.

Efficient bimolecular photoreaction, PRXN(B), at a surface may well have implications for the chemistry of atmospheric ozone. In modeling, HCl is treated as being inert.[7] However, Cl_2, which is reactive, could be produced by PRXN(B) of HCl at the surface of ice particles. [We coated our LiF with ice and still observed efficient PRXN(B) in HBr(ad)].

Supported by NSERC Canada, University of Toronto, Venture Research Unit of BP Canadian Holdings, and Ontario Laser and Lightwave Research Centre. We thank A. L. Arduini and F. S. Rowland for discussions.

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Absorption spectroscopy of mass-selected ions in neon matrices[a)]

Daniel Forney, Michael Jakobi, and John P. Maier
Institut für Physikalische Chemie, Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

(Received 14 September 1988; accepted 31 October 1988)

Considerable progress has been made in the spectroscopic characterization of polyatomic ions in recent years. In particular, IR laser absorption, emission and laser excitation techniques have been successfully developed and applied to yield a wealth of details on ions.[1] Invariably in all these approaches the identification of the carrier is the major obstacle. Thus there have been several laser absorption experiments reported using mass-selected ion beams,[2] relying usually on predissociation[3] or occasionally on charge exchange[4] or fragmentation following further photon absorption.[5] However, these methods have not been proven to be generally applicable. In addition, in all the laser based methods, prior knowledge of the wavelength region of the expected transition is usually crucial.

We present here the demonstration of a new technique aimed at obtaining the first spectral information on mass selected ions embedded in a neon matrix by direct absorption spectroscopy.

Neon matrices have been demonstrated to be useful media for the study of the electronic,[6] IR,[7] and ESR[8] spectra of ions. Nevertheless, as in the gas phase, unambiguous assignment of any observed signals is difficult especially as a mixture of species is always generated when producing the ions by photoionization, electron impact, or in discharges.

We have, therefore, combined the gas phase method of ion production and mass selection with the matrix isolation technique. Thus, Ne matrices containing the ion of choice can be prepared and then subjected to already available spectroscopic methods. In our case this is the measurement of the electronic absorption spectrum of the ion. The 220–1200 nm wavelength region can be scanned to locate the transition and this in turn provides the necessary information for the application of high resolution laser techniques in the gas phase. The case of C_2^+ vindicates this tandem approach; its $\tilde{B}\,^4\Sigma_u^- \leftarrow \tilde{X}\,^4\Sigma_g^-$ transition was first observed in the neon matrix[9] and subsequently in the gas phase.[10]

We report here the demonstration of this, in principle general, technique. The experimental arrangement consists of a differentially pumped quadrupole mass spectrometer, with a conventional electron impact ion source, coupled to a closed-cycle helium cryostat system within which absorption spectra can be measured by the waveguide technique.[11] The experimental details of the latter have been given.[6,12] In these first measurements the exit of the quadrupole was located ≈ 2 cm from the 1.5×1.5 cm rhodium-coated copper substrate held at 5 K. The matrix was grown to a thickness of $\approx 130\ \mu$m over a period of 2–3 h by mixing neon with the stream of mass-selected ions coming out of the quadrupole with kinetic energies of 50–350 eV. Typically 10^{-8}–10^{-9} A ion currents were used.

The following results illustrate the potential of the technique. Cyanogen (or acetylene) was introduced into the ionization chamber, C_2^+ ions were mass selected and the matrix was grown with ≈ 150 eV ions ($\approx 5 \times 10^{-9}$ A) exiting from the quadrupole. Figure 1(a) shows a portion of the absorption spectrum recorded. In the 220–1200 nm spectral region only the 0–0 and 1–0 bands of the recently discovered $\tilde{B}\,^4\Sigma_u^- \leftarrow \tilde{X}\,^4\Sigma_g^-$ electronic transition of C_2^+ are observed.[9,10]

When $C_2N_2^+$ ions were mass selected (≈ 150 eV, $\approx 2 \times 10^{-8}$ A) not only signals due to the known $\tilde{C}\,^2\Pi_{3/2,u} \leftarrow \tilde{X}\,^2\Pi_{3/2,g}$ transition of cyanogen cation[13] but also absorption features of C_2^+ [Fig. 1(b)] as well as N_2^+ and CN are

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