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Citation: The Journal of Chemical Physics **94**, 4282 (1991); doi: 10.1063/1.460614 View online: http://dx.doi.org/10.1063/1.460614 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/94/6?ver=pdfcov Published by the AIP Publishing

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Kinetic energy release in thermal ion-molecule reactions: The Nb²⁺ (benzene) single charge-transfer reaction

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(Received 1 July 1988; accepted 1 August 1990)

We have adapted the techniques originally developed to measure ion kinetic energies in ion cyclotron resonance (ICR) spectrometry to study the single charge-transfer reaction of Nb²⁺ with benzene under thermal conditions in a Fourier transform ion cyclotron resonance mass spectrometer (FTICRMS). The partitioning of reaction exothermicity among the internal and translational modes available is consistent with a long-distance electron-transfer mechanism, in which the reactants approach on an ion-induced dipole attractive potential and cross to a repulsive potential at a critical separation of ~7.5 Å when electron transfer occurs. The reaction exothermicity, 5.08 eV, is partitioned to translation of Nb⁺, 0.81 ± 0.25 eV, translation of C₆H₆⁺, 1.22 ± 0.25 eV, and internal excitation of C₆H₆⁺ to produce the la_{2u} electronic state, which is ~3 eV above the ground state of the ion. We have also studied the kinetics of the reaction of Nb²⁺ with benzene and determined the rate constant, $k = 1.4 \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹, and the efficiency, 0.60, of the process. These also support the proposed charge-transfer mechanism. In addition to the charge-transfer pathway, which accounts for 95% of the reaction products, Nb²⁺ is observed to dehydrogenate benzene to form Nb²⁺ (benzyne). This process implies $D(Nb^{2+}-benzyne) \ge 79$ kcal/mol.

INTRODUCTION

The detailed study of gas-phase ion-molecule chemistry continues to be an area of intense interest. In particular, the investigation of gas-phase transition metal ion chemistry has grown very rapidly during the last decade.¹ Much of this study has focused on identifying the products of thermal reactions of transition metal ions with organic neutrals, interrogating product ion structures through various activation techniques, and determining reaction kinetics in an effort to elucidate reaction mechanisms. However, a thorough understanding of the encounter collision between a transition metal ion and a neutral partner must include information on the reaction dynamics, ideally, a full potential energy surface complete with details of state-to-state reaction cross sections and energy disposal into the available modes of the products. Toward this goal, several groups have studied the effects of electronic excitation on the course of transition metal ion-molecule reactions.^{2,3}

Central to our ability to effectively study reaction dynamics is the development of experimental techniques for monitoring the partitioning of energy among the available modes during the course of a reaction. Recent advances in ultrafast spectroscopy permit the use of femtosecond laser pulses to directly probe the transition state during the course of a number of dissociative half-collisions.⁴ Short of this direct approach, powerful spectroscopic methods can be employed to examine the energy deposited in the products of an ion-molecule event, and details of the reaction dynamics can be inferred from the observed distribution of energy. In particular, infrared chemiluminescence and laser-induced fluorescence have emerged as ideal techniques for the determination of product internal energies, but these approaches can be applied only in those limited cases in which the products are formed in luminescent states or can be laser excited to an appropriate fluorescent state.⁵ Clearly, these emission techniques also require a significant density of excited product ion if measurable luminescence intensities are to be produced. For researchers studying the thermal and near-thermal chemistry of transition metal ions in an ion cyclotron resonance mass spectrometer, this requirement makes routine measurement of luminescence and laser-induced fluorescence spectra quite difficult; however, Marx and coworkers have demonstrated that these experiments can be successfully performed in a number of cases.⁶

An alternative method for exploring the dynamics of ion-molecule processes in an ion cyclotron resonance mass spectrometer has been developed. By studying the trapping voltage dependence of product ion intensities, the kinetic energy deposited in those product ions during the course of a reaction can be measured. Kinetic energy release measurements performed in reversed-geometry sector instruments have been used to advantage in describing the dynamics of metastable ion dissociations.^{7,8}

The ICR technique is based on the anisotropic fields employed to store ions in the instrument: Ions are trapped by a magnetic field in two dimensions and by an electrostatic field in the third. This trapping environment was first exploited by Dunbar and co-workers, who used it to assign the electronic transition in their studies of CH_3Cl^+ photodissociation.⁹ Using polarized light they observed a minimum in

0021-9606/91/064282-09\$03.00

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the CH₃⁺ photoproduct ion intensity when the optical vector was oriented such that the dissociating C–Cl bond was aligned with the magnetic field. Under these conditions, the recoil velocity permitted some of the methyl cations to escape the electrostatic potential well. When the recoil direction was oriented perpendicular to the magnetic axis, the kinetic energy of the methyl cation was insufficient to escape the magnetic field. By studying the analogous phenomenon for H₂⁺, while continuously varying the polarization angle and the depth of the electrostatic trapping well, Dunbar and co-workers were able to quantify the kinetic energy of H ⁺ formed during the photodissociation of H₂⁺ and the anisotropy β in the angular distribution of the photoproducts.¹⁰

Marx^{6(d),6(e),11} and Bowers¹² further developed the technique and applied it to measure the kinetic energy of the product ions formed in a number of thermal charge–transfer reactions involving monatomic and small polyatomic ions and neutrals. Only one study has been reported to date on the kinetic energy released during a charge–transfer reaction involving a doubly charged ion.^{11(c)}

Indeed, there have been few studies of thermal ion-molecule reactions involving doubly charged ions.¹³ Most of these have focused on the chemistry of doubly charged rare gas, alkali, and alkaline earth ions. The chemistry of these species is dominated by charge-transfer pathways, including single charge transfer, often with subsequent autoionization or Penning ionization of the singly charged products to generate doubly charged products, double charge transfer, and, in some cases, radiative charge transfer. The other major pathway reported has been clustering reactions of Mg^{2+} , Ca^{2+} , Ba^{2+} , and Xe^{2+} . Many of the observations in these studies were rationalized on the basis of long-distance electron transfer modeled by avoided crossings of reactant and product potential energy curves.

Studies of the thermal ion-molecule reactions of multiply charged transition metal ions have been even fewer. While these species have highly exothermic charge-transfer pathways available with virtually all organic molecules, four recent studies have demonstrated that other interesting pathways are competitive with charge transfer. Ti^{2 + 14} and Nb^{2 + 15} participate in a number of pathways to produce doubly charged transition metal-ligand species. In addition, LaFe²⁺ has been successfully generated in a Fourier transform ion cyclotron resonance mass spectrometer through the reaction of La^{2+} with Fe(CO), followed by collisioninduced dissociation to remove CO ligands and produce the bare metal dimer dication.¹⁶ In light of the interesting chemistry associated with these doubly charged transition metal ions, we report on the chemistry of Nb²⁺ with benzene and the kinetic energy deposited in the ionic products of the charge-transfer pathway.

EXPERIMENTAL

Kinetic energy measurements were performed by using a Nicolet FTMS-2000 Fourier transform ion cyclotron resonance mass spectrometry (FTICRMS) data station interfaced to a single-cell ICR mass spectrometer. The details and methodologies of FTICRMS have been extensively reviewed.¹⁷ The 5.2 cm cubic trapping cell is situated between the poles of a Varian 15 in electromagnet, which was operated at a field of 0.85 T. Typical base pressures on this instrument are $\sim 10^{-8}$ Torr as measured with an uncalibrated Bayard-Alpert ionization gauge. For these experiments, benzene (Baker, spectral grade) was maintained in the cell at a pressure of $\sim 5 \times 10^{-6}$ Torr and argon (Airco) was maintained at $\sim 10^{-4}$ Torr. Benzene was used as provided except for multiple freeze-pump-thaw cycles to remove noncondensible gases from the sample. Varian controlled leak valves were used for reagent introduction.

Reaction kinetics were studied by using a complete FTMS-2000 FTICRMS equipped with a single rectangular analysis cell (4.76 cm imes 4.76 cm imes 9.52 cm) situated in the bore of a 3 T superconducting magnet. Typical base pressures on this system are $\sim 10^{-9}$ Torr. The Bayard-Alpert ionization gauge was calibrated by observing the self-protonation reaction of acetone and using the observed decay rate with a previously determined rate constant¹⁸ to calculate the actual pressure of acetone and effect an instrument geometry correction. This process was studied over a range of pressures to generate a pressure-dependent calibration curve. The absolute pressure of benzene used in the kinetics experiments was determined by using the R_x ion gauge sensitivity factors reported by Bartmess and Georgiadis¹⁹ in conjunction with this calibration curve. The benzene pressure measured in this manner was 3.3×10^{-8} Torr, and argon was maintained in the cell at 2×10^{-6} Torr.

Singly and doubly charged niobium ions were generated by laser desorption/ionization of a pure block of niobium (Alfa) using the fundamental output of a Quanta Ray Nd:YAG laser.²⁰ Laser-desorbed metal ions, especially multiply charged ions, are produced with high kinetic and internal energies.²¹ Therefore, in an effort to cool the ions, they were stored for 150 ms in the kinetic energy release experiments and 500 ms in the kinetics experiments prior to subsequent study to permit thermalizing collisions with argon.²² During this thermalization, the trapping voltage was dropped to 0.5 V to assist in eliminating kinetically excited ions. After the cooling period, Nb²⁺ was isolated by swept double-resonance ejection²³ of Nb⁺ and any products resulting from reactions of the hot metal ions with background benzene.

The principles of kinetic energy release studies using ICR spectrometry have been discussed in detail.^{6(d),6(e),9-12} Briefly, two regimes of ICR operation can be defined in terms of an ion trapping criterion. Assume a single-valued kinetic energy distribution for the products of an ion-molecule reaction and define that the magnetic field is oriented along the z axis of the trapping cell (i.e., the electrostatic potential constrains the ions along the z axis). When the depth of the electrostatic trapping well V is greater than this ion kinetic energy E_k , the fraction of the ions trapped f will be unity,

$$V > E_k : f = 1.$$

However, when the well depth is less than the ion kinetic energy, ions will only be trapped if the z-axis component of their kinetic energy is less than the depth of the trapping well. Clearly, in this regime, ion trapping is a function of the angle between the ion's kinetic energy vector and the magnetic field vector. Assuming an isotropic distribution of ion-molecule reaction products and integrating this criterion over the possible angles gives

$$V < E_k : f = (V/E_k)^{1/2}$$

This analysis also assumes a flat trapping well in which all of the ions produced experience the same trapping potential. The implications of this assumption for cubic trapping cells are discussed below.

Based on this analysis, four situations can be envisioned.^{11(c)} Product ions with no kinetic energy should show no trapping voltage dependence in their trapped fractions. Ions with a single-valued distribution of kinetic energies should show a sharp break in plots of f vs $V^{1/2}$. Ions with several distinct kinetic energies should show several sharp breaks. Finally, ions with a broad continuum of kinetic energies should show a smoothly changing slope in their f vs $V^{1/2}$ plots. As described above, f should decrease linearly with decreasing $V^{1/2}$ to f = 0 at $V^{1/2} = 0$. For single-valued kinetic energy distributions, the slope of this line will be $E_k^{-1/2}$. However, the slope of the lowest energy linear portion of the plots for multivalued or continuous distributions will be a weighted function of the distribution of kinetic energy releases given by

$$m = \sum f_i (1/E_{k,i})^{1/2}$$

where f_i is the fraction of the ions possessing kinetic energy $E_{k,i}$.

The pulse sequence used in the kinetic energy release experiments is depicted in Fig. 1. Following the quench, ion formation (laser), ion thermalization (cool), and Nb^{2 +} isolation (reisolation) pulses described above, thermalized Nb^{2 +} was permitted to react with benzene for 0.3 s. In a series of experiments, the trapping voltage during this reaction time was adjusted from 0.5 to 7.0 V in steps of 0.1 V. Finally, ion detection was achieved under broadband excitation conditions during the excite and receive pulses. The trapping voltage was 8 V at all times, except during the quench, cooling, and reaction pulses.

Shot-to-shot variation in ion yield from the laser ionization source produced large scatter in the raw intensity data. In addition, increasing the trapping voltage led to increased raw intensities of thermalized and kinetically excited ions



FIG. 1. FTICRMS experimental pulse sequence for the determination of kinetic energy released during thermal ion-molecule reactions.

since more space charge can be accommodated with deeper trapping wells. The scatter in the data and the kinetic energy independent changes in the ion intensity with increasing trapping voltage were effectively eliminated by measuring the ratio of the intensities of the singly charged (kinetically excited) product ions, Nb⁺ and C₆H₆⁺, to the intensity of the doubly charged (thermalized) ion, Nb²⁺.

RESULTS

Nb²⁺ has previously been observed to activate C–H and C–C bonds in small alkanes.¹⁵ Nb²⁺ reacts with benzene by reactions 1 and 2. Clearly, the chemistry is dominated

$$Nb^{2+} + C_6H_6 \rightarrow Nb^+ + C_6H_6^+ 95\%$$
 (1)

$$\rightarrow \text{NbC}_6\text{H}_4^{2+} + \text{H}_2 \qquad 5\% \qquad (2)$$

by single charge transfer. Dehydrogenation of benzene, as observed in reaction (2), places a lower bound on the Nb²⁺ (benzyne) bond strength of $D(Nb^{2+}-benzyne) \ge 79$ kcal/mol.²⁴ Ideally, a kinetic energy analysis of reaction 2 could be used to improve this limit; however, the neutral H₂ product is expected to carry away the major fraction (169/171) of the kinetic energy released, making the kinetic energy of the ionic product too low to be measured with our technique. Interestingly, the chemistry of Nb⁺ with benzene also proceeds by dehydrogenation to form Nb⁺ (benzyne) and Nb⁺ (benzyne)₂.²⁵

A typical pseudo-first-order kinetics plot for the reaction of Nb²⁺ with benzene is displayed in Fig. 2. Based on the calibrated benzene pressure and the slope of this plot, the rate of this reaction was determined to be 1.4×10^{-9} cm³ molecule⁻¹s⁻¹. Replicate studies gave a very reproducible rate; the absolute error in this rate constant is probably no larger than \pm 30%. Based on a Langevin collision rate of 2.32×10^{-9} cm³ molecule⁻¹s⁻¹ calculated using a polarizability for benzene of 10.4 Å³,²⁶ the efficiency of this reaction k/k_L is quite high at 0.60. The excellent linearity of this decay is encouraging, but not conclusive, evidence for cooling of the Nb²⁺ population to its ground state.



FIG. 2. Pseudo-first-order kinetics plot for the decay of the Nb²⁺ signal during the reaction of Nb²⁺ with benzene.

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The raw intensity ratios Nb^+/Nb^{2+} and $C_6H_6^+/Nb^{2+}$, collected in the kinetic energy release studies were processed by normalization to produce a trapping efficiency of one above the highest break point in the f vs $V^{1/2}$ plots. Then eight data sets, each consisting of the normalized intensity ratios obtained by signal averaging 10 transients at each of 66 trapping voltages, were used in a weighted average to produce the kinetic energy plots for Nb⁺ and $C_6H_6^+$ in Figs. 3 and 4, respectively. The weighting factor was the variance of the data in the regime of unit trapping efficiency above the highest energy break.

The fraction of ions trapped shows the expected dependence on $V^{1/2}$; however, three aspects of the data merit further discussion. First, there is a small but noticeable positive slope in the region above the highest energy break. Ideally, fshould be unity throughout this region. To determine if this slope was associated with the kinetic energy of the ions, the following experiment was performed. Argon was admitted to the cell and ionized by electron impact ionization to produce Ar $^+$ and Ar²⁺. Using a double-resonance pulse, the majority of the Ar + was ejected and the intensities of the Ar + and Ar² + were made approximately equal. This methodology gave a reproducible ratio of Ar^{+}/Ar^{2+} . Then this ratio was studied under the kinetic energy release conditions as a function of trapping voltage. Neither the singly nor the doubly charged ions should have a significant amount of kinetic energy. In addition, single charge transfer of Ar²⁺ with Ar to produce Ar⁺ which could possess significant kinetic energy has been observed to proceed with a very slow rate constant, $k = 4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \frac{13(g)}{13}$ making this process unimportant on the timescale of this experiment. Under these conditions, the ratio Ar^{+}/Ar^{2+} should be independent of trapping voltage. However, as depicted in Fig. 5, this ratio does show a positive slope very similar to that observed in the kinetic energy release measurements. Studies of the diffusional loss of nonreactive ions from trapping cells²⁷ do not account for this voltage-dependent, charge-dependent behavior. A tentative explanation



FIG. 4. Kinetic energy plot for $C_6H_6^+$ (fraction of $C_6H_6^+$ trapped as a function of $V_{172}^{1/2}$) generated during the reaction of Nb²⁺ with benzene.

might be based on the spatial distribution of the singly charged vs doubly charged ions in the trapping cell and the extent to which those distributions and the associated signals produced are affected by space charge and trapping well depth. In any event, having effectively modeled this slope and demonstrated that it is not associated with the kinetic energy of the ions, we can confidently correct the data.

A second striking aspect of the data is the fact that the fraction trapped extrapolates to zero at a positive value of $V^{1/2}$. This positive x intercept has been noted in previous kinetic energy studies using ICR spectrometry²⁸ and has been traced to surface charging of the trapping plates due to cell contamination, changing the effective trapping potential the ions experience. Extensive and regular cleaning of the trapping plates has been shown to reduce this problem; however, the most effective approach, and the one adopted in this and previous studies, is simply to shift the data to force the linearly decreasing portion of the plot through the origin.

A final significant aspect of the data is the smoothness of the breaks in the plots. As discussed in the Experimental



of $V_{trap}^{1/2}$) generated during the reaction of Nb²⁺ with benzene.

FIG. 5. $[Ar^+]/[Ar^{2+}]$ as a function of $V_{tran}^{1/2}$

sie is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: J, Chem. Phys., Vol. 94, No. 6, 15 March 1991, -36 section, a smooth break is usually indicative of a broad distribution of kinetic energies in the product ions. However, a careful analysis of the derivation of the ion trapping criterion when applied to cubic cells explains this smooth curvature. Ions formed in a trapping cell readily relax to the center of the cell with respect to the z dimension through thermalizing collisions. Diffusional loss models show that this process is fast while the loss of ions out the sides of the cell is relatively slow, since the magnetic field constrains the ions in the xy plane. Therefore, the derivation described above in which all of the ions experience the same trapping voltage holds provided that the potential is essentially constant throughout the xy plane at z = 0, where x = y = z = 0 is defined as the center of the cell. However, solution of Laplace's equations for the ICR trapping cell shows that the electrostatic trapping well is actually quadrupolar in shape.²⁹ In fact, ions relaxed to z = 0 and located at the center of the xy plane in a cubic trapping cell experience a trapping well depth that is only half that of ions relaxed to z = 0 and located at the edges of the xy plane in the cell, as depicted in Fig. 6. Clearly, if the ions are distributed throughout the cell, a deconvolution process must be used to account for this effect.

This problem was not nearly as important in earlier kinetic energy studies by ICR for two reasons. First, rectangular cells $(1 \times 1 \times 2)$ were used in those studies, and the trapping well is nearly flat in a rectangular cell; the well depth in the center of the cell is 89% of that at the edges in x or y, as depicted in Fig. 7. Second, ions were generated by electron impact ionization in these studies using an electron beam which produced the majority of the ions in the center of the cell. Therefore, the ions were assumed to be localized in the center of the cell, and all were expected to experience the same trapping voltage.

The complications introduced by our cubic cell are obvious. In addition, our ions were generated by laser desorption, which probably distributes ions throughout the cell,

Potential

FIG. 6. Quadrupolar electrostatic trapping well for a cubic $(1 \times 1 \times 1)$ ICR cell. The magnetic field is oriented along the z axis.



FIG. 7. Quadrupolar electrostatic trapping well for a rectangular $(1 \times 1 \times 2)$ ICR cell. The magnetic field is oriented along the z axis.

producing a much greater spatial distribution in the cell than is expected from electron impact ionization. To account for these effects, we reasoned that, after thermalizing collisions, this broad distribution of ions in the cell would collapse to the xy plane at z = 0, producing a uniform distribution of ions across the x and y dimensions of the cell at z = 0. Convolution of a single-valued kinetic energy release with the shape of the trapping potential predicted by Laplace's equations at z = 0 accounts for the smooth break in the kinetic energy plots without requiring a broad continuum of kinetic energy releases.

Correction for the slope and intercept produces the data depicted in Figs. 8 and 9. In each case, the solid line is a single-valued kinetic energy release convoluted with the



FIG. 8. Corrected kinetic energy plot for Nb⁺ (fraction of Nb⁺ trapped as a function of $V_{eff}^{1/2}$) generated during the reaction of Nb²⁺ with benzene. The solid line represents a single-valued kinetic energy (0.81 eV) convoluted with the shape of the trapping well and fit to the experimental data.

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FIG. 9. Corrected kinetic energy plot for $C_6H_6^+$ (fraction of $C_6H_6^+$ trapped as a function of $V_{eff}^{1/2}$) generated during the reaction of Nb²⁺ with benzene. The solid line represents a single-valued kinetic energy (1.22 eV) convoluted with the shape of the trapping well and fit to the experimental data.

trapping potential function and fit to the experimental data by least squares methods. Based on these fits, the kinetic energy of Nb⁺ is assigned as 0.81 eV and the kinetic energy of $C_6H_6^+$ is assigned as 1.22 eV. Thus the total reaction exothermicity channeled into product ion kinetic energy is 2.03 eV. The total exothermicity of the reaction assuming thermal reactants is simply the difference in the ionization potentials of Nb⁺ and C₆H₆, 5.08 eV. Given the measured kinetic energy and the calculated total exothermicity, the internal energy deposited in the products is calculated as

$$IE(Nb^+, C_6H_6^+) = IP(Nb^+) - IP(C_6H_6)$$

- KE(Nb^+, C_6H_6^+)
= 14.32 - 9.24 - 2.03 = 3.05 eV.

The ionization potentials for Nb⁺ and $C_6 H_6$ were obtained from Refs. 30 and 31, respectively. The results of the reaction kinetics studies, kinetic energy release experiments, and curve-crossing analysis (*vide infra*) are summarized in Table I.

A thorough error analysis is difficult for the kinetic energy release studies, given the extensive data manipulation required to obtain the results. Certainly, the systematic error

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associated with the experiment and data correction, particularly the error in the effective trapping voltage due to surface charging and any errors in our assumed spatial distribution of ions, outweighs the statistical error associated with measuring the intensity ratios. The positive x intercepts are a good indicator of our uncertainty in the effective trapping voltage. Based on those measured intercepts, a liberal error bar of ± 0.25 eV is assigned to the kinetic energies measured above. In a very real sense, this substantial uncertainty makes the results of our analysis qualitative or semiquantitative at best. However, despite this uncertainty, interesting conclusions about the mechanism of this single chargetransfer reaction can be drawn based on the measured kinetic energies.

DISCUSSION

Two straightforward points can be employed as a first order analysis of the measured kinetic energy releases. First, momentum conservation requires that the kinetic energies of the two product ions $E_{k,1}$ and $E_{k,2}$ are related by the expression

$$E_{k,2} = (m_1/m_2)E_{k,1},$$

where m_1 and m_2 are the respective masses of the first and second product ion. Based on the kinetic energy measured for Nb⁺, 0.81 ± 0.25 eV, a kinetic energy release of 0.97 ± 0.30 eV is expected for C₆H₆⁺. The measured C₆H₆⁺ kinetic energy, 1.22 ± 0.25 eV shows reasonably good agreement with this expected value. Therefore, the kinetic energy release measurements are consistent with momentum conservation.

Second, the observed kinetic energies are supported by the chemistry. Reaction 3 is predicted to be exothermic by

$$Nb^{2+} + C_6H_6 \rightarrow NbH^+ + C_6H_5^+$$
 (3)

~3.5 eV based on ΔH_f (NbH⁺) = 330 kcal/mol calculated using a recent ion-beam determination of D(Nb⁺– H) = 53 \pm 3 kcal/mol^{2(g)} and supplemental thermochemical values.³² Furthermore, reaction 4 is expected to be 1.2 eV

$$Nb^{2+} + C_6H_6 \rightarrow Nb^+ + C_6H_5^+ + H$$
 (4)

exothermic. In fact, neither process is observed. Reaction 4 would be driven by the recombination of Nb^{2+} to form

TABLE I. Summary of reaction kinetics, energy partitioning, and curve-crossing results for the thermal single charge-transfer reaction of Nb^{2+} with benzene.

Reaction rate, k	$1.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
Langevin rate, k_L	$2.32 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
Reaction efficiency, \tilde{k} / k_L	0.60
2nd ionization potential (Nb)	14.32 eV
lst ionization potential (C_0H_0)	9.24 eV
Charge-transfer reaction exothermicity	5.08 eV
Kinetic energy, Nb ⁺	$0.81 \pm 0.25 \text{ eV}$
Kinetic energy, $C_0 H_0^+$	$1.22 \pm 0.25 \text{ eV}$
Total product kinetic energy	2.03 + 0.50 eV
Total product internal energy	3.05 + 0.50 eV
Calculated curve crossing	7.5 Å

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son.

 Nb^+ , but 2.03 + 0.50 eV of this energy is partitioned into translational modes, effectively making reaction 4 endothermic. The situation can be envisioned in another way. Assume that charge transfer takes place and 2.03 + 0.50 eV of the reaction exothermicity is partitioned to product ion translation. Even if all of the remaining energy, 3.05 ± 0.50 eV, is deposited into $C_6H_6^+$ internal modes, it is insufficient to access the benzene ion's lowest energy dissociation process, reaction 5, which has an activation energy of 3.8 eV.³²

$$C_6H_6^+ \to C_6H_5^+ + H$$
 (5)

No $C_6H_5^+$ is observed, so the chemistry supports the measured kinetic energy release values.

A deeper analysis of the kinetic energy release measurements raises some important questions. Gerlich has discussed the limitations of these ICR measurements in the context of his general model for the effects of target motion on kinetic energy measurements.³³ He concludes that the ICR technique is unsuited for the study of product ion kinetic energy in nonthermal systems. We believe that our efforts to thermalize the Nb^{2+} population were successful as supported by the kinetics observed. Furthermore, Gerlich demonstrates that for large kinetic energy releases, such as those determined in this study, the thermal distribution has little effect on the measured average kinetic energy; however, his results predict that energy resolution decreases with increasing kinetic energy and sharp breaks are not expected for high kinetic energy releases. Of course, this system exhibits a smoothly changing break due to the effects of the quadrupolar trapping well described above. But Gerlich's contention has an important consequence: At high kinetic energies, many kinetic energy distributions will fit the observed f vs $V^{1/2}$ data. Indeed, we fit a range of kinetic energies to our data with some success, but the best fits were always produced by a single-valued kinetic energy, and a single-valued kinetic energy is consistent with the mechanism we propose below. However, the possibility of a distribution of product kinetic energies clearly exists, especially when the high density of low-lying states for Nb²⁺, Nb⁺, and $C_6H_6^+$ is considered.30,34

As mentioned above, much of the chemistry of doubly charged ions can be rationalized in terms of a simple curvecrossing model. In particular, it has been applied successfully to describe qualitatively the chemistry of Ti^{2+14} and $Nb^{2 + 15}$ with small alkanes and to estimate the curve-crossing distance in the Ar^{2+} -CO single charge-transfer system based on the measured kinetic energy release.^{11(c)}

Briefly, the model describes the doubly charged ion and neutral collision partner approaching on an ion-induced dipole curve, $-\alpha q^2/2r^4$, where α is the polarizability of the neutral, q is the ion's charge, and r is the separation of the two species. At some critical distance, an electron is transferred from the neutral to the doubly charged ion generating two singly charged ions, which exit on a Coulombic repulsive curve q^2/r (Fig. 10). If the energy difference between the curves at infinite distance is known, the point at which the curves cross defines the critical distance at which electron transfer can take place. Curve-crossing distances of about 2 to 6 Å have been observed to lead efficiently to

-2 $(q^{2}/r) - 5.08$ $-\alpha q^2/2r^4$ 3 5 Separation (Å) FIG. 10. Potential energy curves for the Nb²⁺-benzene charge-transfer reaction. The reactants approach on an attractive ion-induced dipole potential, $-\alpha q^2/2r^4$. Long-distance electron transfer occurs at ~7.5 Å, and the singly charged product ions exit on a repulsive Coulombic potential, q^2/r .

charge-transfer products.^{13(c)} The total kinetic energy released in the Nb²⁺-benzene charge-transfer reaction is consistent with a curve-crossing distance of \sim 7.5 Å. The uncertainty in the total kinetic energy permits curve crossings as close as 6.2 Å and as far away as 9.6 Å.

The ground-state curves, which cross at ~ 3.9 Å, are included for compari-

This model provides the basic framework for the full Landau-Zener treatment of curve-crossing probabilities.³⁵ Unfortunately, the utility of the full Landau-Zener treatment is limited in this study for a number of reasons. Most notably, the Landau-Zener approach requires that the mixing, H_{12} , of the crossing states be small with respect to the relative kinetic energy of the collision partners, and the low collision energies which are characteristic of thermal ionmolecule reactions often violate this requirement.^{13(q)} Furthermore, the model assumes s-orbital interactions and only applies for particular types of orbital coupling;^{13(0),36} given the extensive state density of transition metal ions it is unlikely that these conditions are met in this system. In any case, it is quite improbable that the results of this study could be used with the Landau-Zener model to extract coupling parameters in light of the uncertainty in the measured kinetic energies and the qualitative nature of the potential energy curves.

However, some information on the curve-crossing probability can be obtained based on the kinetics data and this simple model. For a process such as reaction 6, the

$$A^+ + B^- \to A + B \tag{6}$$

curve-crossing model can be used to determine the probability for neutralization during a collision. As the reactants approach the critical distance, the probability that no curve crossing occurs is P and the probability that crossing does occur is 1 - P. In either case, the species continue to approach until they reach their turning point and begin to move away from one another. If an overall change in surface is to take place, those pairs which crossed curves on the way in (probability 1 - P) must not cross on the exit channel

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(probability P), and those which did not cross on the way in (probability P) must cross on the exit channel (probability 1 - P). Clearly, the overall probability for curve crossing during a single collision is 2P(1 - P). This model limits the maximum efficiency of the curve-crossing process to 0.5.³⁷

The doubly charged situation is somewhat different. If the curve crossing occurs on the entrance channel (probability 1 - P), the ionic products immediately access a repulsive surface, and many of the resulting trajectories for the scattered ionic products may not have an opportunity to sample the critical region a second time. The likelihood of sampling the critical region a second time under these circumstances will be very sensitive to the initial impact parameter. If, on the other hand, no crossing occurs on the way in (probability P), a net curve crossing is achieved only if a switchover takes place on the exit channel (probability 1 - P). So, the overall probability for curve crossing in the doubly charged system is given by an impact parameter dependent sum of the (1 - P) case and the P(1 - P) case. Thus, the reaction efficiency in the doubly charged model is not necessarily limited to 0.5, in keeping with the relatively high efficiency, 0.60, observed in this system.

The reaction kinetics and measured product ion kinetic energies permit a qualitative assessment of the charge-transfer mechanism in this system. In general, charge-transfer processes have been discussed in terms of electron jumps with and without momentum transfer.^{6(d)} Charge transfer proceeding by long-distance resonant electron transfer should proceed without momentum transfer in the case of a singly charged ion encountering a neutral partner. The resonant mechanism is allowed when the neutral collision partner possesses an ionic state with an energy which is equal to the recombination energy of the ionic collision partner. The fact that significant kinetic excitation of the products is observed in some cases is direct evidence for non-resonant charge transfer proceeding through intimate collisions with momentum transfer. In either case, vibrational energy analysis of the product ion often shows non-Franck-Condon distributions, presumably because the neutral may be distorted by the field of the ion during the course of the thermal charge-transfer event.

Single charge transfer during a collision between a doubly charged ion and a neutral collision partner must produce ions with significant kinetic energies due to Coulombic repulsion, even if the transfer proceeds in a long-distance "resonant" fashion. Thus, the charge–transfer reaction will proceed efficiently via a long-distance mechanism if the neutral collision partner possesses an ionic state with an energy equal to that liberated when the doubly charged ion picks up an electron less the kinetic energy of the products.

Our results indicate that charge transfer in the Nb²⁺ – benzene system proceeds by a curve crossing at ~7.5 Å, generating product ions with a total of 2.03 eV kinetic energy and depositing 3.05 eV into internal modes of the products. Examination of the photoelectron spectrum of benzene shows that the molecular ion's $1a_{2u}$ excited electronic state is centered ~3 eV above its $1e_{1g}$ ground electronic state.³⁴ The state immediately above the $1a_{2u}$ is the $3e_{1u}$, which is ~4.6 eV above the ground state. As the reactants approach on the

ion-induced dipole curve, a curve crossing could take place to populate the $3e_{1\nu}$ state of the benzene ion; however, this crossing would partition only about 0.5 eV into kinetic energy and would therefore have to occur at a critical distance of 29 Å based on the curve-crossing model. This distance is quite large, and it is likely that the orbital overlap at this distance is very poor, making charge transfer to populate this state an inefficient process. As the reactants continue along the attractive surface, they have another chance to cross at ~7.5 Å and populate the $1a_{2\mu}$ state of the benzene ion. Given that this situation is totally consistent with the energy partitioning observed, it is quite likely that this is the charge-transfer mechanism. In addition, the ground state of neutral benzene is a singlet, while the $1a_{2u}$ state of the ion is a doublet. Since the ground state configurations of Nb²⁺ and Nb⁺ are a^6D and a^5D , respectively,³⁰ the proposed chargetransfer mechanism also conserves spin.

Clearly, internal excitation of the Nb⁺ product is also possible. However, it is quite likely that the electronic structure of the benzene ion dictates the charge-transfer dynamics. This charge-transfer reaction is driven by the intense field associated with the doubly charged metal ion, which is similar to the fields responsible for ion formation in field ionization or photoionization of neutral benzene.

CONCLUSIONS

This study demonstrates, once again, that valuable information concerning thermal ion-molecule reactions, particularly charge-transfer reactions, can be obtained through the measurement of ion kinetic energies in an ICR spectrometer. The reaction kinetics and product kinetic energies observed in the single charge-transfer reaction of Nb²⁺ with benzene support a long-distance electron-transfer mechanism resulting in significant product ion kinetic energies (total kinetic energy = 2.03 ± 0.50 eV) and population of the $1a_{2u}$ excited electronic state of C₆H₆⁺.

Further advances in our knowledge of thermal ion-molecule chemical dynamics will depend on the development of rigorous models for the collision event. Clearly, thermal and near-thermal charge transfer is a very interesting process which warrants extensive additional study, both theoretical and experimental.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (CHE-8920085) and the Division of Chemical Sciences in the Department of Basic Energy Sciences in the United States Department of Energy (DE-FGO2-87ER13766). J. R. G. gratefully acknowledges the National Science Foundation, the American Chemical Society, and the Eastman Kodak Company for fellowship support. We would also like to acknowledge Extrel for the cell assembly currently installed in our FTMS-2000. The successful completion of this project would not have been possible without the help of Dr. Denise Parent, Dr. R. Graham Cooks, Don Phelps, and Lance Safford. Finally, we wish to thank the referee for a thorough and thought-provoking review.

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