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Probing Chemical Reactions: Evidence for Exploration of an Excited Potential Energy Surface at Thermal Energies

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The reaction K + NaBr → KBr + Na is probed during the reactive collision by a continuous wave laser tuned to frequencies not resonant with excitation in either reagents or products. Transient [K··Br··Na] absorbs a laser photon giving [K··Br··Na]*, which can decompose to Na* + KBr. Emission from excited Na* at the sodium *D* lines provides direct evidence of laser absorption during the reaction. Different excitation spectra were observed, depending on which sodium *D* line was monitored. This difference is explicable if, in the absence of the laser, the reaction flux partially bifurcates to a second potential energy surface during the reaction.

Over the last few years we, among others (*1*), have developed methods that permit the spectroscopic probing of simple systems during chemical reaction. We report here evidence that suggests that during the reaction, K + NaBr → KBr + Na, the system can hop onto an excited electronic potential energy surface, remain there for several vibrational periods, and then return to the ground electronic surface. This process takes place in parallel with the normal reaction confined to the ground-state surface. Thus, the flux partially bifurcates so that part traverses a path on the ground-state surface and part traverses a path on an excited-state surface before returning to the lowest surface. In very energetic systems, such as those arising from photodissociation, chemiluminescence, or electronically excited reagents, electronic surfaces are closely spaced and products are often produced in different electronic states (*2*). In contrast, reactions starting and ending on the ground electronic state are normally presumed to occur on only that one potential energy surface. However, we believe that the results of the present experiments provide evidence of a reaction in which this is not the case.

The system under investigation is the bimolecular chemical reaction K + NaBr → KBr + Na. This reaction has negligible activation energy; the reagents approach each other to within bonding distance and react on nearly every collision. In our experiments, which are carried out with crossed molecular beams of NaBr and K, the reaction is not artificially restricted, as it would be if the reaction were initially bound in a van der Waals complex. The reaction process is thus representative of normally occurring processes that include the entire array of thermal collision energies, impact parameters, and orientations. The reaction is probed spectroscopically by placing the molecular beam crossing region inside the cavity of a continuous-wave dye laser that is tuned to wavelengths not absorbed by either reagents or products. The transient species undergoing reaction, denoted as [K··Br··Na], absorb laser light, producing excited [K··Br··Na]*. These excited species can decompose reactively to give KBr and Na*. The "laser-assisted" reaction is thus monitored by the *D* line emission from the Na* atomic levels $^2P_{1/2}$ and $^2P_{3/2}$, at 589.6 and 589.0 nm, respectively. This emission is passed through an interference filter and monitored by a photomultiplier as the excitation wavelength is varied. Typical laser-assisted signals from Na* are ≈200 s^{-1}, in rough agreement with estimates (*3*) that are based on the assumption of molecular beam densities, zero activation energy for the dark reaction, a collision lifetime of ≈3 ps, and a circulating intracavity power of ≈200 W. The signal size is thus consistent with the excitation of a minute fraction (*3*) of the transient reacting species ($\approx 5 \times 10^{-6}$), and the highly rarified molecular beam conditions minimize other interferences.

Previous measurements (*4*) were made with the use of an interference filter that passed only the sodium D_2 line at 589.0 nm, which corresponds to the transition $^2P_{3/2} \rightarrow {}^2S_{1/2}$. Because different molecular electronic states of the reaction intermediate or transition region species correlate with different atomic fine structure states of the product, we also investigated the emission from the D_1 line at 589.6 nm ($^2P_{1/2} \rightarrow {}^2S_{1/2}$) using a different interference filter. The measured excitation spectra are differ-

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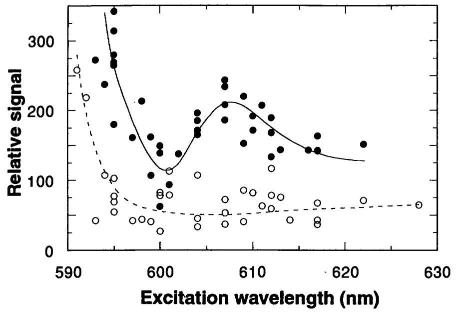

Fig. 1. Excitation spectra for [K··Br··Na]. The wavelength of the excitation laser was varied during observation of the emission from excited Na* atoms produced in the laser-assisted reaction. Filled circles (solid trace) represent emission observed through a filter passing only the D_2 line at 589.0 nm, corresponding to the $^2P_{3/2} \rightarrow {}^2S_{1/2}$ transition; empty circles (dotted trace) represent emission observed through a second filter passing only the D_1 line at 589.6 nm, corresponding to the $^2P_{1/2} \rightarrow {}^2S_{1/2}$ transition.

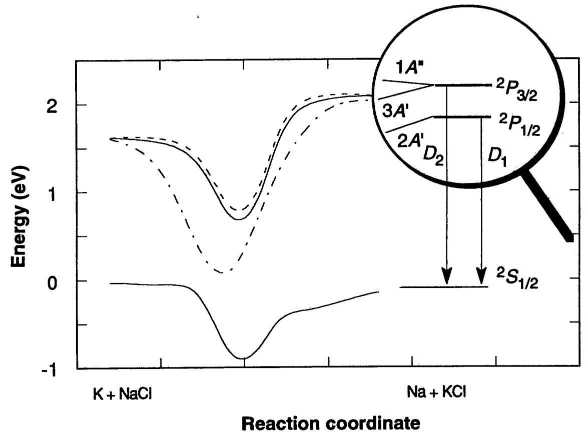

Fig. 2. Calculated minimum potential energy paths (angle not restricted) on the Yamashita and Morokuma surface for the 1 $^2A'$ (bottom solid trace) and 3 $^2A'$ (top solid trace) states. The paths shown for the 2 $^2A'$ (alternating dotted and dashed trace) and 1 $^2A''$ states (dashed trace) are approximated. Detail to the right shows that the $^2P_{3/2}$ level (589.0 nm) correlates adiabatically with the 1A'' and 3A' surfaces and that the $^2P_{1/2}$ level (589.6 nm) correlates adiabatically with the 2A' surface. (This representation is necessarily an oversimplification; four dimensions are needed to represent fully the potential surfaces for this three-atom system.)

ent from those of the D_2 line (Fig. 1). The signal (corrected for filter transmission) is that obtained with all three beams on, after the subtraction of contributions from, for example, dark current and laser scattering (*4*). These data were obtained by the alternation of the filters to observe the different *D* lines at a given wavelength. To minimize the effects of signal drift, the wavelengths were varied at random after each comparison of *D* line intensities.

Despite the negligible energy difference between the *D* lines (17 cm^{-1}), the excitation spectra depend strongly on which of the two *D* lines is observed (Fig. 1). Not only is the intensity ratio not statistical ($\neq$2:1) (*5*), but the "red" spectral feature observed in D_2 emission near 608 nm is absent in D_1 emission. In addition, the "blue" feature (the rise near 595 nm) has a lower energy onset in D_2 emission, although D_1 is the lower energy asymptotic atomic line. The excitation spectrum reflects the probability of electronic excitation of the transition region species and the resulting decomposition of the excited species to give Na*. This process differs depending on which of the atomic fine structure states is formed.

Yamashita and Morokuma (*6*) have calculated ab initio surfaces (neglecting spin-orbit interactions) for the KClNa system and performed trajectory calculations on those surfaces. Some features of their surfaces are shown in Fig. 2, in which curves are plotted that represent the minimum energy path through the reaction. The potential wells (Fig. 2) can be understood as the result of avoided crossings of the ($M^+ \cdots M'X^-$) surfaces with the ($M \cdots M'^+X^-$) surfaces. The existence of a stable KClNa has been verified experimentally (*7*).

Yamashita and Morokuma found for the K + NaCl → KCl + Na reaction that the first excited 2A' surface dips close to the ground 1A' surface. They further reported that excitation in the visible region of the spectrum (near 590 nm) would access the 3A' (or 1A'') surface in a 3$A' \leftarrow 1A'$ transition (*6*). Using the trajectory surface hopping model for this system, they calculated a spectrum that shows only a gradual monotonic decline with wavelength. This calculation does not reproduce our chloride system data (*4*). To treat the bromide system, we assumed, to first approximation, that the potential energy surfaces would be similar to those of the chloride and used the trajectory-surface hopping model to calculate an excitation spectrum for the heavier bromide system. Again no structure was found (*4*). Thus, the trajectory-surface hopping calculations provide no mechanism for the origin of the red feature seen in the 3$A' \leftarrow 1A'$ spectrum for the three halide (bromide, chloride, and iodide) systems we have studied. Because of the similar topology of the 1A'' and 3A' surfaces, it is unlikely that the red feature arises from an excitation of the 1$A'' \leftarrow 1A'$ transition, because similar results would be expected from such a surface hopping calculation.

The experimental D_1-D_2 emission spectra and the correlation diagram (Fig. 2) help to explain the observed behavior. The 2A' surface is predicted to lie within ≈3 kcal mol^{-1} of the 1A' surface for certain orientations in the entrance channel. In earlier hyperthermal collision experiments on the MX + M′ system, Na* or K* was produced (*8*). A transition from the ground 1A' surface onto an excited surface clearly occurred. To explain this result a diabatic transition from the ground 1A' surface onto the 2A' surface was postulated. We believe that the same sort of diabatic transition gives rise to the red feature at 608 nm. In the dark reaction, the reacting species can hop diabatically from the ground surface to the low-lying, first-excited electronic surface. In the absence of a photon, there is not enough energy for the reactive system to climb out of the well on the 2A' surface, and the trajectory can be localized on the 2A' surface for a number of molecular vibrations before it hops back to the 1A' surface. While temporarily trapped on the 2A' surface, the reacting species can be excited by the laser to either the 3A' or 1A'' surface, both correlating with emission on D_2. Because the geometry would be somewhat restricted on the 2A' surface, a quasibound-free spectral feature becomes plausible near the wavelength of good Franck-Condon overlap (*9*).

The atomic $^2P_{1/2}$ level correlates adiabatically with the 2A' surface. No red feature is predicted for the emission on the D_1 line by the quasibound-free mechanism just described, because this feature would indicate a 2$A' \leftarrow 2A'$ transition and the transition moment for an excitation remaining within the 2A' manifold should be very weak. As shown in Fig. 1, no red feature is found on D_1. Thus, emission on the D_1 line probably arises from direct 2$A' \leftarrow 1A'$ excitation. Both *D* lines display a blue feature (rise near 595 nm), which we interpret as an exit-channel excitation of a perturbed Na atom. Subtle differences in the shapes of the surfaces near the product asymptote probably account for the differences in the onset of the blue feature for the excitation spectra observed on the two *D* lines.

Thus, the 2A' state seems to play a major role in these spectra because reactive flux that has hopped onto that surface can be excited by the laser, leading to a red feature observable only on the D_2 line. Although the laser interrogates the 2A' population during its transient existence, the laser plays no role in diverting the flux to the 2A' surface. The reactive system explores part of the 2A' surface during the course of a normal bimolecular reaction: the reaction flux bifurcates between the two surfaces and, in the dark reaction, eventually returns to the ground-state surface.

In the dark reaction, the flux that reaches the ${}^2A'$ surface must evolve to either ground-state products or ground-state reagents because there is not enough energy to form an asymptotic excited state (*10*). No information is yet available about the relative proportions of reagents or products formed from the flux leaving the $2A'$ surface, although the reagents might be reformed by a reversal of the initial hop. Perhaps some evidence that this reversal is taking place is that experimental reactive branching fractions for similar systems tend to be lower than statistical estimates, suggesting that some of the flux could be diverted to a nonreactive surface (*11*). However, these measurements of branching fractions are a blunt probe of the fate of the $2A'$ flux because they are dominated by the contributions of paths restricted to the ground-state surface.

We thus believe that this reaction normally occurs through two complementary pathways. One path is confined to the ground-state electronic surface, and the second is a path that includes a hop onto an excited electronic surface for several molecular vibrations and then a return to the ground surface. Normal "state-to-state" methods of chemical dynamics, which only probe the asymptotic states of either the reagents or products, are unlikely to yield evidence of this behavior. The current approach, which directly probes the intermediates of the reaction by transition species spectroscopy, offers direct evidence for a transient population of an excited state in a ground-state chemical reaction. One might describe the system as "stopping off for a beer" on the way to reaction; it may or may not lose its way after leaving the bar.

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Why Silicon Is Hard

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Compared with pure metals and ionic salts, covalent solids such as silicon are hard and brittle because dislocations do not move in them except at high temperatures. A satisfactory explanation for this behavior has been lacking in spite of its great importance for the mechanics of materials and structures. It is shown here that the critical atomic process leading to the observed brittleness is analogous to a chemical substitution reaction. Analysis of this analogy with the aid of a correlation diagram yields the observed high resistive stress and high activation energy. When a kink on a dislocation line moves, it breaks the atomic bonding symmetry, a forbidden process.

Pure metals are often quite soft (even at very low temperatures), whereas covalent solids such as silicon are hard and brittle at all temperatures below their Debye temperatures. This difference in behavior has not been properly explained by current theories of dislocations. The standard Peierls-Nabarro theory gives the stress needed for a dislocation line to overcome the maximum crystal potential (with the assistance of thermal activation) (*1*). The equation it gives for this stress has the form: $3G[\exp(-10a/b)]$, where G is the shear modulus, a is the glide plane spacing, and b is the Burgers displacement. For the diamond structure, $a/b \simeq 1.8$ and so the stress is about 10^{-3} G, which is two orders of magnitude smaller than observations. Furthermore, metals such as copper and aluminum have nearly the same shear moduli as silicon but are three orders of magnitude softer at the same purity level.

The technical difficulties of the Peierls-Nabarro theory have been discussed by Nabarro (*1*) and by Hirth and Lothe (*2*). Its general deficiency is that it is a classical theory, so it should not be expected to be applicable at the atomic scale of chemical bonds. The fundamental nature of a dislocation's motion is that of a chemical substitution reaction of the type described by Woodward and Hoffmann (*3*) as a disconcerted process (that is, a forbidden one). The motion of a dislocation can be analyzed in a simple way by means of a Walsh correlation diagram.

Dislocation lines do not move concertedly; rather, they move through kinks that lie along their lengths. If the average kink velocity along a line is v_k and the kink concentration is c_k, then the dislocation line velocity v_d is given by $\alpha c_k v_k$, where α is a geometric factor of order unity. The conventional theory is based on the idea that the rate-determining step is the rate of formation of kink pairs and that kink mobilities are high (*4*). However, this theory is quite tenuous for both theoretical (*1, 2*) and experimental reasons. Direct measurements of kink formation rates have not been possible, and theoretical estimates are not reliable. Also, the behavior of crystals is inconsistent with the model. According to kink nucleation theory, if a crystal were flowing plastically at a high temperature and the temperature were quickly decreased, there should be a transient period during which the crystal would continue to flow. This is not observed. The activation energies that are observed for dislocation motion are sharply defined and independent of the applied stress (*4, 5*). If kink pair formation were controlling the rate, there should be a spectrum of activation energies. Furthermore, at low stress levels the activation length for kink pair formation is too large for a dominant thermal activation process because the phonon wavelengths are short and their phases are random above the Debye temperature. Therefore, the probability of reaching the activated transition state is very small. Consequently, kink mobility must control the overall rate.

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