Dynamics of Nonadiabatic Reactions. 2. $F + Na_2 \rightarrow NaF + Na^*$

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Chemiluminescence from the reaction $F + Na_2 \rightarrow NaF + Na^*(i)$ has been measured for six electronically excited states of Na: the upper state of the D line, 3^{2} P, and the more energetic states i = 3^{2} D, 5^{2} S, 4^{2} D, 6^{2} S, and 5^{2} D. The reaction is excergic by 49 kcal/mol for formation of sodium in the 3²P state, and slightly endoergic for the three highest energy channels. Measurements were made by recording visible chemiluminescence from the crossing region of partially collimated beams of reagents. The relative rate constants to form successively higher electronic states, i, decreased exponentially. These rates could be fitted approximately by statistical models following averaging over the breadth of thermal reagent energies.

Introduction

There is continuing interest in reactions leading to electronically excited products that can be detected by chemiluminescence.¹ The chemiluminescent reactions of halogen atoms, X, with alkali-metal dimers, M_2 , to yield the lowest excited states $({}^2P_{3/2}, {}^2P_{1/2})$ of the alkali-metal atom have been studied for over half a century since the "diffusion flame" experiments of M. Polanyi and co-workers.² These experiments led to the development of the harpooning model, in which the forces that give rise to the reaction are governed by the switch from a covalent to an ionic potential.³⁻⁵ The production of the lowest excited state of M was initially explained by a vibrational-to-electronic (V-E) energy transfer process:64

$$M + X_2 \rightarrow MX^{\dagger} + X \tag{1}$$

$$X + M_2 \rightarrow MX^{\dagger} + M(^2S)$$
 (2)

$$MX^{\dagger} + M \rightarrow MX + M^{*}(3^{2}P)$$
(3)

The same process was used to account for the small amount of emission observed from highly excited states of Na (i.e., Na*(i)) in the Na, Na₂, Cl₂ system.^{6b} Subsequently, Magee⁴ used symmetry arguments to suggest that the reaction

$$X + M_2 \rightarrow MX + M^*(i) \tag{4}$$

to yield $M^{*}(3^{2}P)$ should be as rapid as (2), due to the existence of adiabatic pathways.

More recently, Herschbach and co-workers showed that reactions 3 and 4 were fast processes, the latter having a cross section of 10–100 Å² for X = Cl and $M_2 = Na_2$, K_2 .⁷⁻⁹ They were also able to show that other electronically excited $M^*(i)$ states could be formed directly via reaction 4 with energies up to the collision allowed limit, i.e., with the total exothermicity plus relative translational energy of the reagents appearing as electronic excitation in the atom M*.

Two theoretical approaches have been used to predict the partitioning of available energy over electronically excited states in the product of reaction 4. In the work of Krenos and Tully¹⁰ the relative cross sections for the allowed product channels were calculated using the statistical phase space theory. The emission intensities predicted in this way were found to be in satisfactory agreement with observation. The applicability of this statistical theory to the $X + M_2$ reaction systems was rationalized in terms of the multitude of curve crossings giving rise to nonadiabatic transitions into states correlating with electronically excited products.¹⁰ The unrestricted flow of electronic energy could thus be a sign of extremely complex dynamical behavior occurring within a manifold of potential energy surfaces. Subsequently Faist and Levine¹¹ calculated the same distribution by the simpler method of information theory and obtained still better agreement with the experimental results. We reexamine these calculations in part 3 of this series.12

Implicit in the use of statistical models for the electronic excitation of M* was the fact that the electronic orbital angular momentum of the product did not affect its rate of formation. This was found to be the case for the formation from reaction 4 of the 7^2 S and 5^2 D states of potassium.¹³ These states, with almost identical energies, have different electronic angular momenta. Their rate constants k(i) were found to be identical to within experimental error.

The Rydberg series, $M^{*}(i)$, for a number of reactions of type 4 were also observed in diffusion flames,¹⁴ but relative intensities observed in this case differed significantly from the beam results. This was explained¹³ in terms of quenching processes in the relatively high-pressure flame studies (~10 Torr of Ar).

Recently, Figger and co-workers¹⁵ observed chemiluminescence from the excited states, Cs*(i) formed in the reaction

$$O + Cs_2 \rightarrow CsO + Cs^*(i) \tag{5}$$

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Figure 1. Schematic of the apparatus. The components shown are as follows: SO, sodium oven; A, heated aperture; F, sodium beam flag; D, discharge tube outlet; BA, sodium beam axis; CB, copper baffles; MB, monel box; AL, achromatic lens; BS, beam splitter; S, slit; L, lens; ISA, low-resolution spectrometer; PM1 and PM2, signal and monitor photomultipliers, respectively.

The relative emission intensities were comparable to those predicted by information theory in the rigid rotor-harmonic oscillator approximation.

The Rydberg series of $Na^{*}(i)$ has also been observed in beam-gas experiments,¹⁶ in an Na, Na₂, F₂ system. The formation of highly excited sodium atoms was ascribed to reaction 4. In these studies the relative emission intensities of the electronically excited products were not measured.

Paper 1 of this series¹⁷ was concerned with nonadiabatic effects in product branching occurring in the reaction $F + HBr \rightarrow HF$ + $Br(^{2}P_{3/2}, ^{2}P_{1/2})$. In the present work we report the first measurements of the intensity of the chemiluminescence from the excited sodium atoms obtained from

$$F + Na_2 \rightarrow NaF + Na^*(i)$$
 (6)

The reaction was carried out by crossing an uncollimated effusive beam of F atoms with a partially collimated alkali-metal beam. The relative emission intensities extended over a range of 6 orders of magnitude. The results were compared with the predictions obtained from the phase space theory and information theory. Both statistical models were found to account satisfactorily for the observed distribution over electronically excited product states when averaged over a 500 K thermal distribution of reagent collision energies.

In the following paper¹² we report on experiments in which a seeded supersonic jet of F was used to vary the collision energy for the same $(F + Na_2)$ reaction.

Experimental Section

The experimental arrangement was similar to one described earlier.¹⁸⁻²⁰ The apparatus consisted of a crossed-beam reactor (reagent pressure $\sim 10^{-4}$ Torr) housed inside a high-vacuum chamber (background pressure $< 10^{-6}$ Torr). The reaction vessel is shown schematically in Figure 1. The Na + Na₂ beam source was a two-chamber stainless steel oven with a circular nozzle orifice of diameter 0.2 mm. The reservoir and nozzle sections of the oven were resistively heated by separate circuits so that their temperatures could be controlled independently. The oven was wrapped in tantalum reflection shielding to minimize heat loss and reduce the contribution of black-body radiation to the measured signal. Prior to a run the oven was loaded with 1.5 mol of freshly cut sodium (ACS reagent grade).

The Na + Na₂ beam was partly collimated by a heated aperture plate held at a temperature of 600 K. The aperture had a diameter

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TABLE I: Atomic Line Emission Intensities

transition	wavelength, Å	upper state energy, ^a kcal/mol	obsd rel int	approx rel rates
$3^2 P \rightarrow 3^2 S$	5890	48.5	1.00	1.00
$3^2 D \rightarrow 3^2 P$	8195	83.4	7.5×10^{-2}	7.5×10^{-2}
$5^2 S \rightarrow 3^2 P$	6161	94.9	7.7×10^{-4}	1.4×10^{-3}
$4^2 D \rightarrow 3^2 P$	5688	98.8	4.7×10^{-4}	7.4×10^{-4}
$6^2 S \rightarrow 3^2 P$	5154	104.0	1.6×10^{-6}	3.2×10^{-6}
$5^2 D \rightarrow 3^2 P$	4983	105.9	1.0 × 10 ⁻⁶	1.9 × 10 ⁻⁶

^aEnergy of the upper state relative to the ground state of sodium, $3^2S_{1/2}$.

of 6 mm and was located 5 mm downstream from the nozzle. A beam flag situated immediately after the collimating aperture was used to interrupt the beam for measurements of background signals. The sodium beam traversed the reaction chamber and condensed on water-cooled surfaces suspended inside the vessel. The surface opposite the sodium source was equipped with an array of fins that acted as a sodium trap. The distribution of the sodium deposits showed that little scattering of this beam occurred after the collimating aperture. The axis of the optical detection system intersected the sodium beam center-line at a point 50 mm downstream from the sodium beam nozzle and perpendicular to the sodium beam.

The F atoms were produced by a 2450-MHz microwave discharge (60-80 W of power) in pure CF₄, used as supplied (99.7% pure, Matheson Co.). Gas flows were measured with displacement-type flowmeters and were controlled by using a Teflon needle valve operated at a fore-pressure of 50-100 Torr of CF₄. The F atoms were produced in a quartz tube of 8-mm i.d. The microwave cavity was located upstream of a 45° bend in the inlet tube, to eliminate background signals due to light from the discharge.

Before an experiment the inside of the atomic halogen inlet tube was cleaned with a 10% HF solution and coated with a 1:1 mixture of orthophosphoric acid and methanol. The tube was then baked to form a surface of P_2O_5 , which served to reduce atomic recombination. The end of the discharge tube was centered 20 mm above the orthogonal intersection of the sodium beam axis and the optical axis. The length of the inlet tube from the microwave cavity to its tip was 35 cm. The pressure inside the tube was in the range 10^{-2} -1 Torr.

Visible radiation was collected from the reaction zone and focused onto the entrance slit of a double monochromator by a lens mounted outside the vacuum chamber. The transmitted light was focused onto a cooled photomultiplier tube. The intensity of the reference state, given by the D lines, was observed continuously by splitting about 15% of the collected light onto a second photomultiplier tube equipped with a narrow bandpass interference filter. The output of both the detectors was amplified and measured by using pulse-counting electronics. The resulting signal and monitor channel count rates were processed by using an on-line computer. The monitor channel was calibrated by measuring the D line with both detectors, using a neutral density filter (OD 3.0) in the signal channel optics. This detection system allowed the measurement of line intensities relative to the emission at the D lines.

Two spectrometers were used in this study. High-resolution spectral scans and kinetic studies were performed with a 1-m focal length double monochromator (Jarrel-Ash, Model 25-100, f/8.7). Relative atomic line intensity measurements were made using a 10-cm focal length double monochromator (I.S.A., Model DH10 VIR, f/3.5). This low-resolution instrument (60-Å fwhm) provided a gain in sensitivity needed for the measurement of the weakest lines. In the case of the experiments employing the Jarrel-Ash spectrometer, the monitor optics were located on the opposite side of the reaction vessel, aligned with the viewing region of the signal channel optics.

All measured intensities were corrected for the relative sensitivity of the detector and the transmission of the optics by comparison with standard sources. For the region 370-730 nm a Photo Research (Model PR2303) visible lamp was used as a

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standard. At wavelength >700 nm a 1100 K black body was employed.

Results and Discussion

The atomic emission intensities observed are summarized in Table I. The temperature of the liquid sodium in the body of the oven was 960 K and the nozzle was held at a constant temperature of 1010 K. The flow of CF_4 was 10 μ mol/s. The intensities were taken from the peak heights above background, with use of 60-Å resolution. The peak intensity was determined by scanning the spectrometer over the line center. Reagent densities were estimated to be as follows: $[F] = 6 \times 10^{12} \text{ cm}^{-3}$ $[F_2] = 4 \times 10^{11} \text{ cm}^{-3}, [Na] = 8 \times 10^{11} \text{ cm}^{-3}, [Na_2] = 7 \times 10^{10}$ cm⁻³. The densities calculated for atomic and molecular fluorine are based on a previous study of the products from a discharge in CF_4^{21} and on measurements previously performed with this flow system.^{19,20} The sodium monomer and dimer densities were calculated by using the published vapor pressure²² and thermochemical data.²³ The product of the backing pressure and the orifice diameter was 2.7 Torr.cm, resulting in a supersonic expansion of sodium vapor (Mach number ~ 8). Under these conditions collisional association occurring in the expansion results in an increased dimer mole fraction. The results obtained by Aerts et al.²⁴ indicate that the final dimer concentration is $\sim 15\%$ of the alkali-metal beam density.

We have observed six atomic transitions in all, as shown in Table I, with the maximum product electronic energy located 105.9 kcal/mol above the ground state of sodium. As noted in the Introduction, previous studies of similar reaction systems have shown that the process $X + M_2 \rightarrow MX + M^*$ accounts for the electronic excitation of M. The observation of a similar chemiluminescence spectrum under the low-density conditions of our experiment leads us to consider the reaction

$$F + Na_2 \rightarrow NaF + Na^*(i)$$
 (6)

as the primary source of excitation.

Kinetic studies were carried out to confirm that the electronically excited atoms were formed via reaction 6. Previous experiments carried out using this reaction system under similar flow conditions had established it as the major source of emission at the D lines.¹⁸ The contribution attributed to secondary processes, as described by reaction sequence (1), (2), and (3), was found to be less than 20% of the total intensity. Accordingly we have employed the intensity of the $3^2P \rightarrow 3^2S$ emission (I_D) as a measure of the F + Na₂ reaction rate and hence as a guide to changing Na₂ and F concentrations.

The kinetic studies were performed for emission from the 3^2D , 5^2S , and 4^2D states to the 3^2P state. The effect of changing the nozzle temperature with constant oven-body temperature is shown in Figure 2; this procedure varies the equilibrium dimer mole fraction in the stagnation region by changing the dissociation equilibrium Na₂ \rightleftharpoons 2Na. The equilibrium constant for dissociation increases as the nozzle temperature increases and hence leads to lower D-line intensity at higher nozzle temperatures by lowering the Na₂ density.

The intensity of the D-line emission was followed continuously by using the monitor channel signal for each of the three scans shown in Figure 2. The monitor channel signal is directly proportional to the D-line intensity provided both detectors view the same region of the reaction cell. A slight optical misalignment can lead to an offset between the zeroes of the monitor and signal channels. Parts b and c of Figure 2 show evidence of this type of systematic error: the best linear fits to the data for the 4²D \rightarrow 3²P and 5²S \rightarrow 3²P transitions have slightly negative intercepts with the D-line coordinate (abscissa). The lines shown in Figure 2 have been forced to pass through the origin, and hence the offset



Figure 2. Plots of emission intensities: (a) I_{IR} (infrared lines), (b) I_R (red lines), and (c) I_G (green lines), as functions of I_D (D lines) with varying [Na₂]. The transitions are shown in the upper right of each graph. The density of Na₂ was varied by changing T_{N} , the oven nozzle temperature. (Oven reservoir temperature $T_R = 950$ K; $P_{vap} = 81$ Torr.)

error is indicated as a distortion of the slope of the experimental data.

Figure 3 shows the result of varying the total backing pressure in the oven by simultaneously changing the nozzle and body temperatures. In these experiments the nozzle temperature was maintained 60–100 K above the liquid temperature. The last series of studies presented in Figure 4 show the effect of changing the flow of CF₄. In all cases the intensities for the higher energy product states are proportional to the intensities of the D lines, indicating that all of these excited states come from the same source as the 3²P state. Hence we attribute the higher energy electronically excited product to reaction 6. Kinetic studies were not possible for the two weakest emission lines ($6^{2}S \rightarrow 3^{2}P$ and $5^{2}D \rightarrow 3^{2}P$ transitions); we have assumed that they are populated by the same reaction as is responsible for the formation of the other three high-energy states Na*(3²D, 5²S, 4²D).

The thermochemical value for the bond dissociation energy of NaF(g) is currently accepted as the best experimental determi-

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Figure 3. Plots of (a) I_{IR} , (b) I_R , and (c) I_G , as functions of I_D with varying [Na₂]. The backing pressure of sodium vapor was varied by changing T_R in the range 850-950 K, keeping $T_N \cong T_R + 100$ °C.

nation available:²⁵ $D^{\circ}(0 \text{ K}) = 114.2 \text{ kcal/mol.}^{26}$ Combining this value with the spectroscopic dissociation energy for Na₂ (16.99 \pm 0.01 kcal/mol)²⁷ gives an enthalpy change of -97.2 kcal/mol for formation of ground-state products. This implies that the three highest energy states observed (the 4²D, 6²S, and 5²D terms) are endoergic. We will adopt the nomenclature used by Struve et al.9 and distinguish the "reaction-allowed" product states from the "collision-allowed" states, these being excergic and endoergic, respectively. The highest collision-allowed state observed is endoergic by almost 9 kcal/mol, considerably more than the average reagent energy of approximately 3 kcal/mol. We are thus in a position to compare reaction rates for products formed over



Figure 4. Plots of (a) I_{IR} , (b) I_R , and (c) I_G , as functions of I_D with varying [F]. The F-atom concentration was varied by changing the total flow of CF₄ over the range 0.1-3.5 μ mol/s (sodium oven conditions: T_R = 940 K; T_N = 1000 K; P_{vap} = 71 Torr).

a wide range of reagent energies.

High-resolution spectra of the multiplet structure were obtained for the four most intense lines. These showed all the spin-orbit components to be in their statistical ratios, implying statistical population of the components of the 3²P, 3²D, and 5²S terms. This finding is in agreement with the earlier flame^{14b} and beam studies.⁸

This observation makes possible the preliminary analysis of the data, as presented in the final column of Table I. Here we have employed the Einstein A factors,²⁸ statistically averaged over the spin-orbit multiplets, to compute the relative rates of product formation. For steady-state reaction conditions the rate of formation of product in state i is given by

$$k(i) = N_i \sum_{k} A_{i \to k} - \sum_{h} N_h A_{h \to i}$$
(7)

where N_i is the population in the emitting state and the constants

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Figure 5. Relative rates of formation of Na*(i) (from eq 8) as a function of electronic energy of the product atom. All rates normalized to the rate of formation of Na*(3²P). The downward arrow indicates the total reaction energy available to the products, $-\Delta H^{\circ}$.

 $A_{i \rightarrow k}$ are the A factors for the depletion transitions $i \rightarrow k$. The second term on the right-hand side of eq 7 accounts for the radiative population of state i from levels at higher energy with populations $N_{\rm h}$. Equation 7 can be simplified by omitting this cascading term, giving

$$k(\mathbf{i}) = \frac{I_{\mathbf{i} \to \mathbf{j}}}{A_{\mathbf{i} \to \mathbf{j}}} \sum_{\mathbf{k}} A_{\mathbf{i} \to \mathbf{k}}$$
(8)

where $I_{i \rightarrow j}$ are the observed emission intensities. Calculations discussed later in this section have shown that the maximum contribution expected from cascading is $\sim 20\%$ of the total rate of formation. A plot of the approximate rates as a function of the electronic energy of the product atom is presented in Figure It is evident that k(i) diminishes rapidly with increasing 5. electronic energy, E(i); the decrease is particularly steep for the states in excess of the 4^2D that must be accessed through reagent energies in the tail of the 500 K reactant Boltzmann distribution.

In what follows we compare statistical models of chemical reaction with experiment. In phase space theory the probability of reaction along a particular channel is simply proportional to the number of states available, taking account of energy and angular momentum conservation.^{29,30} Phase space theory was applied by Krenos and Tully¹⁰ to the reactions $X + K_2 \rightarrow KX$ + K*(i) for which chemiluminescence spectra are reported in ref 9. These reactions closely resemble the title reaction of this paper. These authors found that the theoretical cross section for the formation of excited atoms was well approximated by

$$\sigma_{\rm ps}({\rm i}) \propto g_{\rm i}(\epsilon + E({\rm i}))^2$$
 (9)

In this expression g_i is the degeneracy of channel i and $\epsilon + E(i)$ represents the sum of reagent energy and exothermicity for channel i, respectively. The energy dependence of the microscopic rate constants is therefore given by

$$k_{\rm ps}(i) \propto g_{\rm i} \epsilon_{\rm T}^{1/2} (\epsilon + E(i))^2 \tag{10}$$

where ϵ_T is the relative translational energy of the reagents in the center-of-mass frame.

Information theory has also been successfully applied to the problem of estimating statistical product energy distributions.^{31,32} For the case of atom-plus-diatom in the rigid rotor-harmonic

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oscillator approximation, the energy dependence of the prior rates $k_{it}(i)$ is given by¹¹

$$k_{\rm it}({\rm i}) \propto g_{\rm i}(\epsilon + E({\rm i}))^{5/2}$$
 (11)

where g_i , ϵ , and E(i) have the same definition as in relation 9. It is important to note that the phase space theory result (eq 9) represents a statistical approximation to the reaction cross section; in contrast, the prior rate expression given by eq 11 is based solely on products being formed in a uniform distribution over available states.³² Previous studies have dealt with the differences between these two statistical approaches.^{33,34} We compare the two approaches in the following paper.12

For the purpose of comparison with experimental results in this work, we have calculated thermally averaged rate constants by integrating over a distribution of collision energies. In the case of the phase space theory the averaged rate expression based on eq 10 is written as

$$\bar{k}_{ps}(i) \propto g_i \int_E^{\infty} d\epsilon_T \epsilon_T (\epsilon_T + E(i))^2 \exp(-\epsilon_T / kT^*)$$
 (12a)

where the lower limit of integration is given by

$$E = \begin{cases} -E(i) & \text{for } E(i) < 0 \text{ (endothermic channels)} \\ 0 & \text{for } E(i) > 0 \text{ (exothermic channels)} \end{cases}$$
(12b)

and T^* is the effective collision temperature:³⁶

$$T^* = \frac{m_1 m_2}{m_1 + m_2} \left(\frac{T_1}{m_1} + \frac{T_2}{m_2} \right)$$
(13)

This last equation provides an average temperature, given reagent gases of masses m_1 and m_2 at temperatures T_1 and T_2 . In (12a) we have assumed, as a first approximation, zero internal energy in the diatom (Na₂) and Maxwell-Boltzmann distributions for both reactant species. We have ignored the energy contributed by the flow velocity of Na₂ in the supersonic beam. The expression resulting from the averaging of the information-theoretical prior rates (c.f. eq 11) is

$$\bar{k}_{it}(i) \propto g_i \int_E^{\infty} d\epsilon_T \ \epsilon_T^{1/2} (\epsilon_T + E(i))^{5/2} \exp(-\epsilon_T / kT^*)$$
 (14)

where the terms have the same meaning as in eq 12a.

Relative rate constants were calculated for all the atomic sodium levels up to the 6²D state (E(i) = -13 kcal/mol) by numerical evaluation of the integrals. An effective temperature of 505 K was employed, corresponding to a fluorine atom temperature of 300 K and a sodium dimer temperature of 1000 K, equal to the source temperatures. This choice results in an average collision energy of 1.5 kcal/mol. For each set of rate constants eq 7 was used to calculate the steady-state population distribution, to give the relative intensities of the observable transitions.

Comparisons of the observed and calculated intensities are shown in Figure 6 for the phase space theory and in Figure 7 for information theory. All intensities have been normalized to that obtained for the $3^2D \rightarrow 3^2P$ transition since this emission contains no contribution from other processes, such as the reaction F_2 + $Na_2 \rightarrow F + NaF + Na^*(3^2P)$ (see ref 12), and the V-E energy transfer described by reactions 1-3.

In each of Figures 6 and 7 the broken lines show the limits of uncertainty in the theoretical prediction, corresponding to uncertainty in the bond dissociation energy of NaF. Recent ab initio calculations (near the Hartree-Fock limit, SCF and SCF+Cl)²⁵ place a lower limit on D(NaF) of 113.5 kcal/mol. Comparison of the thermochemical bond dissociation energies for the alka-

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Figure 6. Comparison of observed intensities with those predicted by phase space theory, as a function of the energy of the emitting state. Intensities have been normalized to the $3^2D \rightarrow 3^2P$ transition. The circles are experimental points. The dashed lines connect the corresponding intensities calculated from phase space theory by eq 12a and 7. $(T(Na_2) = 1000 \text{ K}, T(F) = 300 \text{ K})$. The uncertainty in the reaction energy is indicated by the range between the upper and lower dashed curves.



Figure 7. Comparison of observed relative intensities with those predicted by information theory (otherwise as for Figure 6).

li-metal halides²⁶ with values from recent photofragmentation experiments^{36,37} shows overall agreement to be within the limits ± 1.5 kcal/mol. The upper limit of error of the thermochemical value (114.2 kcal/mol) is therefore taken as ± 1.5 kcal/mol and the lower limit as -0.7 kcal/mol. Inspection of Figures 6 and 7 shows the phase space results are in adequate agreement with experiment while the intensities calculated from information theory are low for the higher energy states. One interesting feature revealed in both theoretical approaches, as in the experiment, is the "shoulder" occurring between the ²S and ²D states for the four highest energy levels observed. This effect is seen to be a consequence of the 1:5 ratio in the degeneracy factors for these levels.

Calculations were also performed with the inclusion of 0.98 kcal/mol of vibrational energy in the Na₂ ($T(Na_2) = 600$ K) and 1.7 kcal/mol from the flow speed of Na₂, thereby increasing the mean reagent energy $\bar{\epsilon}$ to 3.8 kcal/mol. Assuming that this reagent energy is fully available for electronic excitation of the products leads to an approximate 12-fold increase in the predicted yield of the highest electronic states (6^2S and 5^2D) for phase space theory and 20-fold in the case of information theory. In view of the fact that information theory underestimates these populations



Figure 8. Comparison of corrected relative rates with those predicted by the full phase space theory (solid line). The approximate phase space treatment yields the broken line. The experimental points indicated by circles correspond to the best estimate of the available energy, based on the thermochemical bond dissociation energy of NaF, whereas the points shown as squares and triangles correspond to upper and lower limits for the available energy, respectively.

in Figure 7, it then gives a better fit to the experimental findings than does phase space theory.

Another interesting feature revealed in the comparison of Figure 6 is the slight upward displacement of the D-line intensity compared with the value predicted by phase space theory. To test the significance of this observation, we have performed a full phase space calculation using the mean collision energy of 1.5 kcal/mol. This calculation is described more fully in part 3 of this series;¹² the original formulation of the theory of Pechukas and $Light^{30b}$ is followed, with the number of available product states at a given exoergicity computed using a realistic potential for NaF. In addition, no approximations are made regarding the angular momentum restrictions, beyond those inherent in the estimation of the range of total angular momentum available to the collision complex. This treatment thus yields a more exact phase space prediction than that given by the approximate relation used above (eq 9). The full calculation results in a change in the exponent of the available energy given in eq 9, with the approximate value 2 replaced by 1.65, as estimated by linear regression of the theoretical relative cross-sections.

In Figure 8 this result is compared with the observed relative rates for the reaction-allowed states, normalized to $k(3^{2}P)$. The log-log plot is employed to linearize the theoretical rates, with the reduced energy defined by $[E_{TOT} - e(i)]/[E_{TOT} - e(3^{2}P)]$, where E_{TOT} is the total energy available and e(i) is the energy found in electronic excitation of Na. The reduced energy represents the energy in product channel i that goes into nuclear motion, divided by the corresponding energy for the $3^{2}P$ product. The collision energy is $\epsilon = 1.5$ kcal/mol.

Two corrections have been applied to the experimental relative rates: (a) the D-line intensity was decreased by 20% to correct for contributions from other processes,¹⁸ as discussed above; (b) the cascade contributions to the populations, as calculated from the rates obtained by using the approximate phase space theory, were subtracted. The latter correction, which has a significant effect on $k(3^2P)$, is discussed in more detail in ref 12. The error bars shown in Figure 8 reflect the maximum resulting uncertainty in $k(3^2P)$.

The effect of the uncertainty in the reaction exothermicity is indicated in Figure 8 by two additional sets of points for the 3^2D and 5^2S states. These additional points (given by open squares and open triangles) represent the experimental rates with the value of the reduced energy coordinate determined by using the upper and lower error limits for the total reaction energy (i.e., E_{TOT} +1.5/-0.7 kcal/mol). We observe that the reduced energy coordinate is not greatly affected by the uncertainty in the reaction energy for these two states. The solid line in Figure 8 follows the rates predicted by the full phase space calculation, while the broken

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Figure 9. Adiabatic state correlation diagram for the reaction $F + Na_2$ $NaF + Na^{*}(i)$. For simplicity only a few electronically excited product states are shown. The correlations correspond to C_s symmetry.

line represents a fit to the approximate results from eq 12a. In the absence of thermal averaging, the slope of the approximate phase space result would be given by the exponent in eq 9, which is exactly 2. The thermal averaging of this expression, given by eq 12a, enhances the rates predicted for the higher electronic states and hence causes the slope of broken line to be lowered slightly.

We observe that the relative rates for formation of the 3²D and 5²S states fall slightly below the full phase space result. Since thermal averaging causes a slight increase in the predicted rates for these states, as noted in the paragraph above, averaging of the full phase space result would show even greater disagreement with experiment. For the case of increased collision energy discussed above ($\bar{\epsilon} = 3.8$ kcal/mol) the predicted relative rates for the higher energy states would be increased further, again leading to greater disagreement with experiment. We conclude that a marginal disagreement exists between phase space theory and the observed formation of the reaction-allowed states.

It is interesting to note that the phase space predictions¹⁰ of the atomic line intensities obtained by Struve et al.⁹ were not in complete agreement with their experimental data. The phase space theory underestimated the potassium and rubidium D-line intensities in comparison with those observed for the higher electronically excited states, by a factor of 2-3 for all reactions analyzed. This deviation is in the same direction as we find here for the $F + Na_2$ system.

In summary, the uncertainty in the reaction exothermicity, combined with the uncertainty in the internal energy of the Na₂ in our experiment, leads to a range of predicted relative rates for the collision-allowed states. Within these error limits, both the phase space and information theory could adequately account for the observed rates.

The effects of the uncertainties in exothermicity and internal energy on the predicted rates are not as pronounced in the case of the reaction-allowed states, where a more detailed comparison between experiment and theory is possible. For the 3²P, 3²D, and 5²S states, the information theory results showed good agreement with experiment. A slight discrepancy was noted for these same states in the case of phase space theory. We thus conclude (a) that either phase space theory or information theory can be used to obtain an adequate set of k(i) for the collision-allowed states and (b) that the distribution over electronically excited states of Na in the product of $F + Na_2$ reaction is close to statistical.

The same findings can of course be pictured deterministically. The statistical or near-statistical outcome documented above would suggest that the microscopic behavior is complex. An examination of the potential energy surfaces gives qualitative grounds for this.

The adiabatic state-correction diagram for the F + Na₂ reaction is indicated in C_s symmetry in Figure 9. It gives the qualitative picture of the probable curve crossings intermediate between reagents and products, shown schematically in Figure 10.

The 3-fold degeneracy of the halogen atom p orbital gives rise to three potential energy surfaces (pes) that correlate adiabatically with NaF + Na.^{4,38} Figure 10 shows these correlations for a few



Figure 10. Qualitative diagram showing ionic and covalent potential "curve crossings" for the reaction $F + Na_2 \rightarrow NaF + Na^*(i)$. Reagent and product separations are shown for electron jumps in the entrance and exit channels, respectively. The state symmetries correspond to C_s symmetry. The circles indicate avoided crossings. The horizontal dashed line in the exit channel indicates the ionization limit for the excited Na states.

excited product states. This figure was obtained by using the rules given by Shuler.³⁹ The Na*(i) + NaF product states (of which the two lowest 4²S and 3²D are shown in the figure; 3²D being the lowest observable in our spectral region) correlate adiabatically with reagent states $F + Na_2^*$, well separated from the ground-state reagents.⁴⁰ It follows that under the conditions of the present experiment, any reaction leading to the higher electronic state products (states i above 3²P) is nonadiabatic. Adiabatic pathways from the ground electronic states $F({}^{2}P_{u}) + Na_{2}({}^{1}\Sigma^{+}_{g})$ lead only to $Na(3{}^{2}S_{g}) + NaF({}^{1}\Sigma^{+})$ and $Na^{*}(3{}^{2}P_{u}) + NaF({}^{1}\Sigma^{+})$. It is interesting to note that the deviation of rates predicted by the full phase space theory from those observed in this study may be visualized in terms of enhanced production of the Na(3²P) product with respect to the higher energy electronic states.

As has long been realized,⁴ an important feature of the halogen plus alkali metal reactions is the possibility of crossing (i.e., nonadiabatic behavior) between pes. At moderate internuclear separations adjacent to configurations at which adiabatic pes approach one another, the Born-Oppenheimer approximation fails, and electronic states can be coupled as a result of nuclear motions. For the entrance and exit valleys of the various pes it is possible to infer what crossings of energy states will be involved. For the intermediate strong-interaction regions, shown in Figure 10, we have used Balint-Kurti's calculated pes.⁴¹

The locations of the crossing points (circled in Figure 10) were calculated from the customary expression for the ionic-covalent degeneracy:5

$$r_{\rm c} = \frac{14.38 \text{ eV} \cdot \text{\AA}}{\text{IP} - \text{EA}} \tag{15}$$

where IP denotes the ionization potential and EA the electron affinity. The EA of atomic F, needed in the entry valley, was 3.40 eV.⁴² The IP used in the same coordinate for $Na_2(X^1\Sigma^+_g) \rightarrow Na_2^+(^2\Sigma^+_g)$ was 4.8. eV,⁴³ which is the adiabatic value (according to the calculations of Bardsley et al.44 and Car et al.46 this differs little from the vertical IP). The remaining vertical IP's, to Na_2^+

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states higher in energy than ${}^{2}\Sigma^{+}_{g}$, where obtained from the calculations of Bardsley et al.⁴⁴ In the exit channel the IP was that for Na (5.139 eV)⁴⁵ and the vertical EA for NaF was 0.42 eV.⁴⁷

The substantial number of curve crossings shown in Figure 10 provide a possible rationale for a statistical outcome. If the speeds of approach to these intersections, v, the changes in slopes of the pes at the intersections, ΔF , and the adiabatic splitting parameters, ΔE , were such that the probability of staying on an adiabatic curve, P_{stay} , were comparable with the probability of hopping, P_{hop} (= $1 - P_{\text{stay}}$), where⁴⁸

$$P_{\rm hop} = \exp\left[\frac{-\pi^2 (\Delta E)^2}{h \Delta F v}\right] \tag{16}$$

then the presence of many regions of close approach between the pes could lead to a free flow of energy between the electronic degrees of freedom (Na*(i)) and the nuclear motion of the system (translation, rotation, and vibration).

On these grounds it appears reasonable to suppose that the outcome of these reactions is only marginally and approximately statistical and that either a reduction in the substantial averaging over reagent energies (eq 12a and 14) or a decreased lifetime of XM₂^{*} brought about by enhanced reagent collision energy could give rise to significant deviations from statistically in the distribution over product electronic states.

The following paper in this series was designed to test this hypothesis. Significant deviation from a statistical outcome was indeed observed in this further study, though the qualitative trend toward decreased population in the states of increased electronic excitation continued to hold.

Acknowledgment. S.H.P.B. and P.C. are indebted to the Natural Sciences and Engineering Research Council of Canada (NSERC) for the award of scholarships. We thank NSERC for generous support of this research in all its phases. We also thank Roy Josephs for technical assistance in this work.

Registry No. F⁻, 14762-94-8; Na₂, 25681-79-2.

Dynamics of Nonadiabatic Reactions. 3. Effect of Enhanced Collision Energy in F + Na₂ → NaF + Na*

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A crossed-molecular-beam study has been performed of the three-center reaction $F + Na_2 \rightarrow NaF + Na(i)$. The relative cross sections for producing many of the electronic states of Na (states i ranging from 3^2P to 7^2P) have been measured at two collision energies, 4.7 and 12.8 kcal/mol. The cross sections decreased rapidly with increasing electronic excitation, the falloff being less steep at higher collision energy. The excitation function for populating the 3²P state was measured and found to increase with increasing collision energy, suggesting the presence of a barrier to the production of this lowest electronically excited state. The barrier height for this pathway was 4.5 kcal/mol. The excitation functions for the 3^2D , 5^{2} S, and 4^{2} D states could be inferred from the measured relative cross sections; they also increased with increasing collision energy. We have performed phase space and information theory calculations at the same level of approximation to obtain distributions over electronically excited states of the sodium reaction products and have compared these with the experimental results. Information theory predicts a much more rapid decrease in the cross sections with increasing electronic excitation than does the phase space theory. Comparing the experimental results with phase space theory, we find that, for enhanced reagent collision energy, the distribution of reaction product over electronically excited states is nonstatistical. In particular the first excited state (3^2P) is populated at a rate an order of magnitude greater than would be expected from statistical considerations. Higher states are formed in an approximately statistical distribution. The observed dynamical bias may originate in the fact that only the 3²P state can be accessed by an adiabatic pathway.

Introduction

In paper 2 of this series,¹ the branching into electronically excited states of the product Na*(i) for the reaction

$$F + Na_2 \rightarrow NaF + Na^{*}(i)$$
 (1)

was studied by using a crossed-molecular-beam apparatus. In paper 2,¹ the relative intensities from Na* product states were measured for the first time and found to be in approximate

agreement with the statistical outcome. This experiment was performed with a near-thermal distribution of energy for reactants, having an average energy of approximately 3 kcal/mol. The question arose as to whether or not this apparent agreement with the statistical model could be a consequence of the substantial thermal averaging over reagent energies. In the present work we have suppressed this energy distribution through the use of supersonic jets and have made the collision energy a variable. At increased collision energy the lifetime of the intermediate might be further reduced, thereby resulting in measurable deviations from the statistical distribution.

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