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.

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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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Figure 1. Experimental setup (see text); O1 is the fluorine oven, O2 is the sodium oven, and W is a Pyrex window.

As discussed in the Introduction to paper 2, the statistical phase space theory of chemical reaction²⁻⁴ has previously been applied to the $X + M_2$ reaction systems studied by Herschbach and co-workers.⁵⁻⁷ It was found that the population distributions in the electronically excited states of the alkali-metal product atoms were adequately described by phase space theory.8 Interestingly, this statistical outcome was not associated with the formation of a long-lived complex, since Herschbach's laboratory found that the alkali-metal halide product was backward scattered rather than symmetrically distributed. (A simple RRK calculation⁹ indicates that a complex of three atoms with 4-5 kcal/mol of excess energy would only exist for 0.1 ps.) The large exothermicity of reaction 1 might be expected to give a shorter lifetime for the FNa2^{*} intermediate and consequently give rise to deviations from the statistical results found for the other reactions.

Faist and Levine¹⁰ have performed an information theory calculation that gave a better fit to the experimental data than did the phase space calculation. Since the phase space theory considered both energy and angular momentum conservation, while the information theory took account only of energy conservation, it was suggested¹⁰ that the better fit using information theory resulted not from the theoretical approach but from a more precise treatment of the density of states. This implies that if the phase space calculation were to be redone with a more accurate accounting of the vibrational and rotational levels in the diatomic species, an equally good or better account of the experimentally determined population distributions of M* over electronically excited states would be obtained. This calculation was not performed at that date but will be presented here.

Using a seeded supersonic beam of atomic and molecular fluorine crossed with a beam of sodium, we have measured the electronic distribution of Na* atoms at two different collision energies: 4.7 and 12.8 kcal/mol. We have shown that the reaction $F + Na_2 \rightarrow NaF + Na^*$ is the major source of the observed chemiluminescence. At both collision energies the distribution over electronically excited states of Na* is shown to deviate from that predicted by statistical theories, though the distribution of

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states higher than the first excited state (3²P) may be approximately described as statistical. We have also performed a phase space calculation with a more accurate treatment of the rovibrational states of the NaF product than was done previously and have compared the two statistical theories, phase space and information theory, at the same level of approximation.

Experimental Section

Equipment. The experimental arrangement is shown in Figure The main vacuum chamber contained the reaction zone, the alkali-metal beam source, and the alkali-metal beam trap. It was pumped by an N.R.C. HS-32 32-in. diffusion pump backed by a Stokes 212H-10 rotary mechanical pump with a capacity of 150 cfm. The fluorine beam source was produced in a separate chamber, pumped by a Stokes 150-9 16-in. ring jet booster pump backed by an N.R.C. 100-S rotary mechanical pump with a capacity of 100 cfm.

The Na beam source was a double-chamber oven arrangement described in detail elsewhere.¹¹ The body of the oven contained a charge of approximately 10 mol of sodium metal. A thermocouple well extended into this reservoir for the accurate measurement of the sodium temperature. The oven body was used in the temperature range 800-950 K. The nozzle section was kept 50 K hotter than the body to prevent sodium metal from distilling into the nozzle section and clogging the 0.23-mm diameter orifice from which the beam emanated. The entire oven was surrounded by a double sheet of stainless steel foil and was inserted into a stainless steel can. This in turn was surrounded by a water-cooled copper can with an opening through which the Na beam emerged. A thin brass mask, thermally isolated from the cooled copper can, was positioned around the perimeter of this opening. It was heated radiatively to 500 K by the Na oven; this prevented the buildup of Na metal at the opening. Without this mask the condensed sodium metal blocked the beam after a few hours of operation.

Further downstream along the Na beam was a liquid nitrogen cooled shield with a thermally isolated inverted conical opening (2.5-cm diameter; 8 cm from the nozzle) heated by thermo-coax wire to around 400 K to prevent clogging with solid sodium metal. Between this cone and the nozzle orifice was a solenoid-actuated flag, used to interrupt the sodium beam during measurement of the background radiation. After passing through the reaction zone, the sodium beam was condensed in a liquid nitrogen cooled can.

The fluorine atoms were produced by thermal dissociation inside a nickel oven maintained at temperatures around 980 K. The oven consisted of a nickel tube 6 cm long and 0.5 cm in diameter clamped in water-cooled copper jaws. An electrical current of about 400 A at 4 V passed through the oven, heating it resistively. The temperature was measured by a thermocouple spot welded to the oven opposite the nozzle opening. The opening was a 0.20-0.40-mm hole drilled into the side of the tube. The fluorine oven assembly was positioned in front of a nickel skimmer with an opening of 2.0 mm positioned 15 mm from the nozzle. The F atom beam then emerged into the main chamber.

The reaction zone in the main chamber was some 6 cm downstream from the skimmer. The fluorine beam backing pressure was several hundred Torr of 5% F_2 in either He or Ar. Before use of the beam at peak operating temperatures, it was necessary to passivate the oven against attack by fluorine. The technique is described in detail elsewhere11 and follows a procedure suggested by Lee.12

The reaction zone comprised a region approximately 1 by 2 cm. The chemiluminescent radiation from a small central part of this zone was imaged onto the entrance slit of an Interactive Technology CT-103 1-m spectrometer and was dispersed by a 600 lines/mm grating blazed at 1.6 μ m. All of the observed radiation lay in the range 450-900 nm, so that our experiments were performed in the second and third orders of the grating. We used slit widths of 1 mm corresponding to a reciprocal linear dispersion of ~ 15 Å/mm.

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The dispersed radiation was focused onto a cooled Hamamatsu GaAs photomultiplier (Model R943-02) followed by a P.R.A. preamplifier and a P.R.A. amplifier/discriminator. An Apple II+ computer was used to count the pulses from the discriminator as well as to control the spectrometer and perform the data reduction. Just above the entrance slit to the spectrometer a beam splitter directed about 4% of the incident radiation into a Hamamatsu R928P multi-alkali-metal photomultiplier tube. This latter signal constituted the monitor channel.

Sodium Beam Characteristics. The concentration of dimer molecules in the sodium vapor varied with pressure and temperature. As the temperature of the body section of the oven increased, the pressure in the nozzle chamber increased; this higher pressure produced a greater concentration of sodium and thence a larger mole fraction of dimers. On the other hand, as the temperature of the nozzle section was increased, the concentration of dimers decreased due to thermal dissociation. These two temperatures could be independently varied, and hence the dimer mole fraction could be controlled. Knowing the vapor pressure for sodium¹³ and its molecular constants,¹⁴ we could predict the sodium dimer mole fraction inside the oven by standard thermodynamics.15

In the beam, an additional contribution to the concentration of sodium dimers resulted from condensation of sodium atoms in the supersonic expansion. This effect has been studied by Aerts et al.¹⁶ in the case of Na₂. We have used their data to predict the most probable velocity and the concentration of dimers in our sodium beam. We calculated that our beam typically consisted of 1-5% sodium dimer molecules (depending on the conditions) of which 10-50% originated from condensation. Herschbach and co-workers⁷ found that under similar conditions, their alkali dimers had velocity distributions corresponding to a Mach number of ~ 10 , i.e., $\Delta v/v = 0.11$.

Fluorine Beam Characteristics. The conditions in the fluorine beam have been studied previously in this laboratory¹⁷ under similar conditions. The beams were found to have a velocity distribution corresponding to a Mach number of 14 ($\Delta v/v = 0.08$) in the helium-seeded case and to a Mach number of 10 ($\Delta v/v =$ 0.11) in the argon-seeded case. The most probable velocities determined from that study were used in this work to determine the collision energy between the sodium and fluorine beams (Ar-seeded beam, $E_{COLL} = 4.7$ kcal/mol; He-seeded beam, E_{COLL} = 12.8 kcal/mol). It was also found in the earlier study that the mole fraction of F atoms measured in the beam followed precisely that predicted by thermodynamic arguments, as for sodium. With this information it was straightforward to determine the density of F atoms and F_2 molecules in the reaction zone. In these experiments, the percent dissociation of fluorine molecules was about 50%.

Procedure. We have recorded, by photon counting, the intensities of each atomic line and subtracted from that the background radiation, the latter being measured by setting the spectrometer to a wavelength between spectral lines. In addition we recorded in a separate counting system the signal from the monitor channel, which measured the total chemiluminescence. This channel was used to correct for drift in the signal during the experiment due, for example, to changing reagent flow with time. Both channels were corrected for pulse pileup as follows.

The random behavior of photons arriving at the photodetector was assumed to be a Poisson distribution. Following the arrival of a photon, there is a dead time before the electronics can detect another photon. The probability that a photon will be missed¹⁸ is given by

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$$Z = 1 - \exp(-t/\tau) \tag{2}$$

where t is the dead time of the electronics, $\tau = 1/P$, and P is the average count rate. We define a maximum count rate, F, which is the rate at which the electronics could just count every pulse if they were uniformly distributed, instead of randomly distributed. This expression then gives us a relation between the actual count rate, P, and the measured count rate, R:

$$R/F = (P/F) \exp(-P/F)$$
(3a)

This equation cannot be analytically inverted to give P. We have therefore rewritten it to read

$$y = xe^{-x}$$
 or $y - xe^{-x} = 0 = G(x)$ (3b)

For a measured value of y (= R/F), we used a Newton-Raphson (N-R) routine to find the zero of the function G(x) and thus the value of x (=P/F) that corresponds to the measured y. For all values of R/F, the correct P/F could be found in less than six iterations of the N-R routine. The correct value for F was determined for each channel separately with a pulse generator. This procedure was tested and found to be accurate for count rates as high as twice those measured in the experiment.

The rates for populating each state i cannot be directly extracted from the line intensity data and then compared with the cross sections obtained from the statistical theories, since correction must be made for radiative cascading from the higher electronic states into the lower states. The intensity of a transition is related to the population in the upper state that gives rise to that transition by

$$N(i) = \frac{I_{i \to j}}{A_{i \to j}g_i} \tag{4}$$

where N(i) is the population per magnetic sublevel of state i, $I_{i\rightarrow j}$ is the intensity of the transition between states i and j, $A_{i\rightarrow j}$ is the Einstein A factor for that transition, and g_i is the degeneracy of state i.

This population arose from two sources, the reaction and radiative cascading. In a continuous-wave experiment such as ours, the population of each state maintained a steady-state value. Therefore, the rate for populating each state i and its decay rate were equal and given by

$$R_{\text{TOT}}(i) = N(i) / \tau(i) = R(i) + \sum_{u} g_{u} N(u) A_{u \to i}$$
 (5)

where $\tau(i)$ is the lifetime of state i and the summation extends over all upper states u of degeneracy g_u , which are populated by the reaction and connected to state i with the stated A factor. The R(i)'s, i.e., the reactive rate constants, are the quantities of interest in this study.

As the reagents are common to all final states i, the relative rates, R(i), simply correspond to the relative rate constants, k(i). For well-defined reagent energy, as in these experiments, we can report the relative rate constants, k(i), as $\sigma(i)$, the relative cross sections. The sum in eq 5, which is the radiative cascading contribution to the population of state i, needs to be determined and subtracted from the total measured rate R_{TOT} .

If the intensity of a transition is measured for each state populated by the reaction and if we know the A factors¹⁹ for all of the transitions, the population for every state can be obtained. The cascading contribution can then be calculated exactly for each state and can be subtracted from the total rate to determine R(i). However, in our experiment, there were several states that could not be observed because of our limited spectral range. To estimate the cascading contribution to each total rate $R_{TOT}(i)$, we assumed a complete set of reactive rates, R(i)'s. Using these to solve the set of eq 5, we obtained a complete set of populations that allowed us to calculate the cascading contribution for each state. The actual R(i) for each observed level was then determined by subtracting the estimated cascading contribution from the measured total rate.

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Figure 2. Grotrian diagram for sodium. The energy scale is in units of electronvolts. The number beside each term level is the principal quantum number, n. The arrows connecting certain terms represent the transitions that were observed in these experiments. The two double-headed arrows represent the total exothermicity available at the two collision energies.



Figure 3. Plot of the logarithm of the relative cross sections as a function of electronic excitation. Filled squares are for the low collision energy experiment, open squares for the high collision energy. The two arrows on the horizontal axis correspond to the exothermic limit for the two collision energies. The two curves are scaled to show the increase in cross section with increased collision energy.

By using simple statistical models for the initial R(i)'s, we found that the R(i)'s subsequently determined from the measured data were not significantly model dependent, since the correction for cascading was in general small. The correction was most pronounced for the ²S states, amounting to about 30% for the 5²S and 6²S states. The measured intensity for the 3²P state had a 10% contribution from cascading. We are therefore satisfied that the determination of our R(i)'s is not sufficiently model dependent to affect the conclusions of our study.

Results and Discussion

Experimental Distributions. The low collision energy experiment (4.7 kcal/mol) was energetic enough to excite up to the $5^{2}P$ state of the Na atom. At this collision energy four levels of the Na atom were observed: $3^{2}P$, $3^{2}D$, $5^{2}S$, and $4^{2}D$. All other transitions of the nine accessible states (see Figure 2) occurred outside of our spectral range. In contrast, the high collision energy experiment at 12.8 kcal/mol, which excited 20 levels up to the $7^{2}P$ state, resulted in 10 states being observable, those seen at the low collision energy plus $6^{2}S$, $5^{2}D$, $6^{2}P$, $7^{2}S$, $6^{2}D$, and $7^{2}P$. For

the highest levels where the signal is weakest, the signal-to-noise ratio was about 2.5. Figure 3 shows the experimental cross sections for populating each electronic level as a function of the electronic energy. The effect of radiative cascading has been taken into account, as explained in the Experimental Section. The arrows show the upper limit of energy available for each collision energy. We observe electronic states of Na up to these limits. The relative cross sections decrease with increasing electronic excitation by over 4 orders of magnitude.

Kinetics Experiments. In this section we report the results of experiments designed to determine the kinetic behavior of processes giving rise to Na^{*}. In addition to reaction 6, other reactions known

$$F + Na_2 \rightarrow NaF + Na^* -\Delta H = 97.2 \text{ kcal/mol}$$
 (6)

to produce electronically excited sodium atoms include V-E (vibrational-to-electronic) energy transfer from vibrationally excited NaF^{\dagger} formed in any one of reactions 7–9:

$$Na + F_2 \rightarrow Na^{\dagger} + F -\Delta H = 77.4 \text{ kcal/mol}$$
 (7)

$$Na_2 + F_2 \rightarrow 2 NaF^{\dagger} -\Delta H = 174.4 \text{ kcal/mol}$$
 (8)

 $F + Na_2 \rightarrow NaF^{\dagger} + Na - \Delta H = 97.2 \text{ kcal/mol}$ (9)

all of which are followed by the V-E process

$$NaF^{\dagger} + Na \rightarrow NaF + Na^{*}$$
 (10)

Another reaction expected to form Na* directly⁷ is

$$Na_2 + F_2 \rightarrow F + NaF + Na^* -\Delta H = 60.1 \text{ kcal/mol}$$
(11)

Reaction 11 is only exothermic enough to produce sodium atoms in the 3^2P state. Reaction 7 is just able to produce the 4^2S state in addition to 3^2P , but 4^2S is not observable in this experiment. Reactions 8 and 9 are more exothermic and can populate still higher levels.

If the process giving rise to our radiation is the result of reaction 6, $F + Na_2$, then the radiation should change linearly with the concentration of [F] and [Na₂]. Reaction sequence (7) + (10) will follow $[Na]^2[F_2]$ kinetics, sequence (8) + (10) $[Na][Na_2][F_2]$, sequence (9) + (10) $[Na][Na_2][F]$, and (11) will behave as $[Na_2][F_2]$. It should, therefore, be possible to distinguish reaction 6 from other possible sources of Na^{*}.

Two separate temperatures have been scanned in these kinetic studies, that of the sodium oven nozzle and that of the fluorine beam source. We have measured the intensity of various atomic lines as a function of these two temperatures. We calculated the flux of each component as a function of the temperature in question and compared the changing line intensity with this change in flux. In the following graphs, the lines represent theoretical calculations of the fluxes of stated atomic and molecular species, and the data points are the experimental determinations of the line intensities.

The first experiment involved changing the Na nozzle temperature. These data are shown in Figure 4. The temperature of the F/F_2 beam and that of the body of the sodium oven were held constant throughout the experiment. The Na nozzle temperature ranged from 830 to 990 K. Since the body temperature was unchanged, the pressure of sodium in the nozzle was constant, but as the temperature increased in the nozzle section the mole fraction of dimers decreased while that of the atomic species increased correspondingly. Since the initial mole fraction of dimer was small (<0.02) the fractional increase in the atomic mole fraction was minimal. The sodium beam flux decreased since it depended on temperature as $T^{-1/2}$. A further term of $T^{-1/2}$ came from the fact that the density of particles in the reaction zone decreased with increased particle velocity. Therefore, in addition to any change in signal resulting from a change in mole fraction, we expect the signal to decrease linearly with temperature as a result of the two terms mentioned above.

This experiment can distinguish only between reactions that follow $[Na]^2$, i.e., sequence (7) + (10) and the remainder. The three transitions shown in Figure 4 are those originating from the



Figure 4. Comparison between experiment and theoretically determined line intensities as a function of the sodium oven nozzle temperature. The data points are experimentally measured; circles for 3^2P , triangles for 3^2D , and open squares for 4^2D . The lines are the theoretical expectations assuming the following kinetic behavior: the curves are for $[Na]^2$ kinetics, $[Na][Na_2]$ kinetics, and $[Na_2]$ kinetics, as indicated.

 $3^{2}P$ state (the D line), the $3^{2}D$ state, and the $4^{2}D$ state. It is evident that the intensities of these lines do not follow the [Na]² dependence. Therefore, reaction 7 followed by reaction 10 is excluded as the source of this radiation. The experiment does not allow us to distinguish between [Na₂] kinetics and [Na][Na₂], since [Na] changes so little. We discount the sequence (9) + (10) for the following reason. It involves the same reactants as the direct $F + Na_2$ reaction 6, which is known to give rise to Na^{*} chemiluminescence, but in addition it requires a second collision to produce Na^{*}. At the densities in these beams, $\sim 10^{-4}$ Torr, this secondary process will be much less probable than the single-step reaction 1. Assuming a reasonable set of reaction cross sections for these processes (reactions 6, 9 and 10) and lifetimes for the various species, we calculated a 100-fold greater signal from the direct process (6) than from the indirect process (9) + (10). We therefore discount the contribution of (9) and (10) and conclude that our signal depends directly upon the concentration of [Na₂].

Figure 5 shows the results for the fluorine oven temperature scans. The electronic transitions shown originate from the 3^2D , 5^2S , and 4^2D states. The intensity variation of these transitions follows closely the behavior expected for a process involving atomic F. This observation excludes reaction schemes (7) + (10) and (8) + (10) and also reaction 11, thereby indicating that the signal we are observing originates from the reaction F + Na₂.

For this same kinetic experiment (variation of fluorine oven temperature), we observed that the D-line radiation, in contrast to emission originating in higher excited states, was not dependent only on [F]; at low fluorine oven temperature, corresponding to negligible [F], the D-line emission remained substantial. This was particularly marked in the low collision energy experiments. Results of further kinetic experiments reported elsewhere²⁰ indicate that the source of the D-line radiation at low fluorine oven temperature is the bimolecular reaction $F_2 + Na_2$, yielding directly $Na^{*}(3^{2}P)$ (i.e., reaction 11). At the fluorine oven temperatures employed in the present study the dissociation of F₂ was such that the fraction of D-line radiation resulting from this four-center reaction was 31% in the Ar-seeded beam experiment (low collision energy) and 16% in the high collision energy experiment. A proportionate correction was applied to the D-line intensity in arriving at the data reported here for reaction 6.

Dissociation Energy of NaF. A major source of uncertainty in comparing theoretical results for the $F + Na_2$ reaction with data obtained experimentally is the dissociation energy of NaF. A thermochemical determination of this bond energy²¹ gave a value of 114.2 kcal/mol. Ham²² found that reaction 8 yielded Na* in



Figure 5. Comparison between experiment and theoretically determined line intensities as a function of the fluorine oven temperature. The data points are experimentally measured; circles are for the 3^2D state, triangles for the 4^2D state, and open squares are for the 5^2S state. The curves represent theoretical [F₂] kinetics and [F] kinetics, as indicated.

electronically excited states of sufficient energy to suggest a larger bond energy, $123 \pm 3 \text{ kcal/mol}$. It now appears more probable that these highest states derived their energy from the tail of the Boltzmann distribution of reagent collision energy. Recent ab initio computations²³ have confirmed the thermodynamic measurement, leading to acceptance of the value 114.2 kcal/mol (-0.7 kcal/mol, +1.5 kcal/mol; see also ref 1). As we shall show in the following section, the residual uncertainty in bond dissociation energy represents by far the largest error in comparing the yields of the highest electronic states of Na* with the statistical expectation.

Statistical Theories. The $X + M_2$ family of reactions has previously been interpreted with considerable success in terms of statistical models. The first such calculation was by Pechukas, Light, and Rankin.² On the assumption that phase space theory^{3,4} was applicable, they examined the plausibility of the direct mechanism (reaction 1) and the vibrational-to-electronic energy-transfer mechanism (reactions 1–3 in the preceding paper) as a source of the 3²P state of Na in the reaction Cl + Na₂. They found that the indirect process could occur to a significant extent but that the high quantum yields observed experimentally²⁴ required that the direct process play an important role. This is in qualitative accord with crossed-molecular-beam findings.⁷ The electronic-state distributions were first calculated from phase space theory by Krenos and Tully.⁸

The phase space theory assumes the formation of an intermediate complex that dissociates with equal probability into all states accessible, under the constraints of conservation of total energy and angular momentum. By determining the volume of phase space occupied by the alternative outcomes, one obtains the relative cross sections for populating the various electronically excited states. Krenos and Tully applied this procedure to the reaction of K_2 with various halogen atoms. They fitted their data to a simple power law:

$$\sigma(i) \propto g_i [E_{\text{TOT}} - E_i]^{\beta}$$
(12)

where $\sigma(i)$ is the cross section for populating electronic state i of the alkali atom, g_i is its degeneracy, E_{TOT} is the total energy available to the products, and E_i is the electronic energy of state i above the ground electronic state. The quantity $E_{TOT} - E_i$ represents the total energy available for distribution over all degrees of freedom *other* than the specified electronic excitation. The value of β was found to depend slightly upon the reaction partners and the assumptions made concerning the interaction. The average value of β was found to be 2.0.

Subsequently, an information theory approach was advanced by Faist and Levine¹⁰ and applied to the same experimental data.

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Information theory, as applied to chemical reaction dynamics, makes a statistical assumption similar to that found in phase space theory, i.e., that each accessible state has equal probability. An important difference between the two is that information theory incorporates conservation of energy but not conservation of angular momentum.

In the paper by Faist and Levine, an analytical expression is given for the "prior" electronic-state distribution, treating the rovibrational levels of the diatomic species exactly. The relative cross sections, $\sigma(i)$, for populating each state i are then given by

$$\sigma(i) \propto g_i \sum_{v} \sum_{j} (2J+1) (E_{TOT} - E_i - E_{vj})^{1/2}$$
(13)

where $E_{v,j}$ is the energy of the rovibrational level (v,j), and the sums are over all rotational and vibrational levels accessible with the given energy. This distribution has been called the vj prior. One can simplify this expression by assuming a rigid rotor for the rotational levels of the diatomic. By integration over these rotational levels, eq 13 becomes

$$\sigma(i) \propto g_i \sum_{v} (E_{TOT} - E_i - E_v)^{3/2}$$
 (14)

This distribution is referred to as the RR-v distribution. Further simplification is possible by assuming an harmonic oscillator for the vibrational levels of the diatomic. Integration then leads to the RRHO distribution

$$(i) \propto g_i (E_{\text{TOT}} - E_i)^{5/2}$$
 (15)

This equation has the same form as that for the phase space theory (see eq 12) except that the exponent has the value of 2.5 instead of 2.0.

These prior distributions were used by Faist and Levine to measure the agreement between information theory and the experimental distributions. The authors found that even their most approximate (the RRHO) prior distribution was in better agreement with the experimental results than was that obtained from the more rigorous phase space theory. Faist and Levine¹⁰ suggested that the reason for the difference was to be found not in the different theoretical approaches but instead in the precision with which the calculations had been performed in the two cases. They suggested that if a more exact treatment of the density of vibrational states were to be performed for phase space theory, as had been done for information theory, then the phase space data would agree with the information theory results.

Accordingly, we have undertaken a comparison of phase space theory and information theory at the same more exact level of approximation. This will now be described. Since spectroscopic constants were not available for the high states of product vibration relevant to this highly exothermic process, we used the Rittner potential of Brumer and Karplus²⁵ to describe the NaF interaction. The vibrational levels were calculated by using a Numerov–Cooley procedure.²⁶ Phase space theory and information theory were then compared in this same level of approximation by using the calculated rovibrational levels in each case.

The phase space calculation required an estimate of the potential forces for all of the accessible levels. We followed Krenos and Tully⁸ in assuming that the interaction could be described by a single van der Waals C_6 constant for each electronic level. These constants were obtained from the expression

$$C_6(i) = D(i) + \alpha(i) \,\delta(i)^2$$
 (16)

where D(i) is the dispersion coefficient,²⁷ $\alpha(i)$ is the polarizability of the atom,²⁸ and $\delta(i)$ is the diatomic dipole moment.²⁵

The results of these calculations of the relative cross sections for populating the various electronic states of Na from the reaction $F + Na_2$ were fitted to an equation of the form of (12), and the exponent was determined. The energy argument was modified so as to be the fraction of the total energy that went into all degrees of freedom except electronic. This argument, called the reduced



Figure 6. Comparison between experiment and phase space statistical theory for the low collision energy (4.7 kcal/mol) experiment. The data are normalized to the 3^2P state (filled-in point). States of higher electronic excitation lie to the left of this point. The solid line represents the phase space predictions for the system. The NaF bond dissociation energy, $D_0^{\circ}(NaF)$, used here was the median value, 114.2 kcal/mol.



Figure 7. Data analogous to Figure 6 except for the high collision energy (12.8 kcal/mol) experiment. The data are presented for the median $D_0^{\circ}(\text{NaF})$ value of 114.2 kcal/mol (square) and also for extreme values of 113.5 (triangle) and 115.7 kcal/mol (circle). The figure is normalized to the filled-in point (square). The points shown as + indicate superimposed data points for \Box , Δ , and O.



Figure 8. Same data as in Figure 7 but normalized to the 3^2D state (filled triangle). The data at the left representing states of electronic excitation higher than the 3^2P state tend to follow the phase space predictions, but the 3^2P state has an observed cross section >10-fold that predicted statistically. The dashed line gives the information theory prediction.

energy, $E_{red} = (E_{TOT} - E_i)/E_{TOT}$, is used in its logarithmic form in Figures 6-8.

The previous work of this nature,⁵⁻⁷ as has been explained, did not involve the reaction $F + Na_2$ but was instead concerned with other members of the class, specifically K, Rb, Br₂, and Cl₂. The

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exponent from the information theory work was found to be 2.5 while in the phase space theory work, the exponent was 2.0.

The current reaction is more exothermic than its counterparts due to the increased bond energy of NaF. We have fitted the results of our calculations to the same equation as previously. By using the more accurate description for the density of internal states in the NaF molecule, we obtain the result that the two theories are more divergent rather than less. The exponent arising from our information theory calculation (using the vJ prior distribution) is 2.59, while our phase space calculations give exponents of 1.43 ± 0.15 in the high collision energy case and 1.75 ± 0.04 for the low collision energy. The overall average exponent from the phase space theory is 1.59.

A clear difference between information theory and phase space theory lies in the treatment of the angular momentum of the system. Our calculations are for a system that is more exothermic than those studied previously, and it appears that there are a substantial number of states that, though energetically accessible, are forbidden by conservation of angular momentum. Therefore, states of low electronic excitation will have many more states of internal excitation associated with them in the case of information theory than in the case of phase space theory. If this interpretation is correct, we are seeing that in a highly exothermic process, angular momentum constraints can be significant.

Comparison with Phase Space Theory. In light of the above, we have compared the results of our experiments with the predictions of phase space theory. Figure 6 is a log-log plot of the relative cross sections as a function of the reduced energy, all normalized to the $3^{2}P$ state.

In plots of this type, the data points corresponding to those states of highest electronic excitation are located in the lower left-hand portion of the graph. These points are subject to some uncertainty, which warrants explanation. As mentioned, the bond energy of NaF is uncertain by about 1.5 kcal/mol. This uncertainty is reflected in the reduced energy parameter. For states of high electronic excitation, there is very little energy left for distribution among the internal energy states; an uncertainty of 1.5 kcal/mol may be larger than the energy left for internal degrees of freedom, thereby leading to substantial uncertainty along the abscissa. We shall give an estimate of the effect of this uncertainty below.

Figures 6 and 7 show the results of the phase space theory compared with the experimentally determined cross sections. These data were plotted assuming a bond energy for NaF of 114.2 kcal/mol. Figure 6 shows the results for the low collision energy experiment and Figure 7 shows the results for the high collision energy experiment. The straight line is the phase space predictions as indicated above. In both cases it should be noticed that the relative cross sections fall off with increasing electronic excitation (moving from right to left) more quickly than is predicted by the statistical theory. Figure 7 also presents the same experimental data (for the high collision energy experiment) plotted assuming the two extremes for the NaF bond energy of 113.5 and 115.7 kcal/mol. The general trend of a more rapid decrease in cross section than predicted by statistics holds true despite the uncertainty in $D_0^{\circ}(NaF)$.

In Figure 7 the data have been normalized to the 3^2P state. Figure 8 shows the experimental data of Figure 7 renormalized to the higher energy state, 3^2D . The rate of decrease of the relative cross sections for the states higher than the 3^2P state follow closely the predictions of the statistical theory, but now the 3^2P state has over an order-of-magnitude greater cross section than predicted. The information theory prediction is also shown in Figure 8 as a dashed line. The slope of this line gives a significantly larger change in the relative cross section than is observed over this range of available energy.

A plausible explanation for this dynamical skewing, i.e., nonstatisticality, is the fact that all of the electronically excited states of sodium with the exception of the first excited state (3^2P) can be accessed only by the reaction by nonadiabatic pathways—the system must jump to some other adiabatic curves during the course of the reactive event to be able to reach these higher states. It has been argued previously²⁹ that the adiabatic pathway to the lowest excited state, 3^2P , should permit it to be populated with a rate similar to, if not greater than, that associated with the product ground electronic state, 3^2S . The existence of an adiabatic pathway to 3^2P may explain its anomolously large cross section as compared with the statistical outcome.

Excitation Function. Up to this point we have determined the relative distribution of the cross sections at two collision energies for populating a number of the electronically excited states of Na. What has not been reported is the way in which the cross section for a particular state changes with collision energy.

As noted above, the observed radiation from the 3^2P state stems from two reactions, the one currently being considered and the four-center reaction designated reaction 11. In the next paper in this series,²⁰ we show how we have deconvoluted these two reactions for the 3^2P state and obtained the excitation functions for both reactions. Since the data analysis is described in detail in the following paper, we simply report here the results for the three-center reaction relevant to the present study, $F + Na_2$.

Relative to the reaction at low collision energy (4.7 kcal/mol) the production of the 3²P state by the three-center reaction at 12.8 kcal/mol is increased by a factor of 32. We emphasize that this is for the production of the 3²P state only (the enhancement in the higher states can be inferred from the relative distributions reported here; there is no information regarding the ground electronic state). These two points do not, of course, fully describe the excitation function; nevertheless, they tell us that it is definitely a rising function of collision energy. This indicates the presence of a barrier to the reaction. Since the reaction is readily observed at 4.7 kcal/mol collision energy, we conclude that the barrier is less than approximately 4.5 kcal/mol in height. The variation of cross section with collision energy is reflected in the two curves in Figure 3.

Conclusion

We have measured the population distribution for the electronic states of sodium atoms produced in the reaction $F + Na_2 \rightarrow NaF$ + Na* at two collision energies, 4.7 and 12.8 kcal/mol, in a crossed-beam experiment. These distributions were compared with the predictions of a statistical theory (phase space theory). Considering all of the electronic states together, it was found that this three-center reaction did not produce a statistical population distribution over the full manifold of states. Electronic states higher than the first excited state (3²P) may be populated statistically, but the 3²P state is biased dynamically away from the statistical value.

We have performed both phase space and information theory calculations for this system using a more accurate description for the density of vibrational states than has been used heretofore. The two theories disagree more markedly in their predictions at this improved level of computation, suggesting that the angular momentum constraints embodied in phase space theory play a significant role in determining the outcome for highly exothermic processes such as this one.

Finally, we observe that the excitation function for the production of the 3^2P state is a rising function with increasing collision energy, indicating the presence of a significant barrier to this reaction with a height of $\lesssim 4.5$ kcal/mol.

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