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State-specific low temperature reactions of $DBr^{+2}\Pi_i(v^+) + (D_2, DBr) \rightarrow D_2Br^+$

Andrey E. Belikov¹, Mark A. Smith^{*}

Department of Chemistry, University of Arizona, 1306 E. University Dr., Tucson, AZ 85721, USA

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Abstract

State-specific reactions of $DBr^+({}^{2}\Pi_{i}, v^+)$ with D_2 and DBr were studied in a low temperature free jet flow reactor. The selected spin-orbit and vibrational states of the DBr^+ ion were prepared by resonance-enhanced multiphoton ionization. All of the reactant and product ions were monitored using time-of-flight mass spectrometry. Rate coefficients for the DBr^+/DBr reaction are $\sim 1.4 \times 10^{-9}$ cm³ s⁻¹ independent of the ion internal state, similar to those for the HBr^+/HBr reaction. Rate coefficients of the DBr^+/D_2 reaction rise from 0 (lower spin-orbit-vibrational states) to 2×10^{-11} cm³ s⁻¹ (highest energy states) and are observed to follow a mass independent threshold function similar to the HBr^+/H_2 reaction. © 2002 Published by Elsevier Science B.V.

1. Introduction

Control of chemical reaction efficiency through selection of reactant state remains a primary goal of the field of reaction dynamics. It is anticipated that state-specific behavior of chemical reaction systems will reveal information concerning reactive potential energy surfaces difficult to obtain by other means and that state selective dependence of branching between competitive collision pathways (inelastic and reactive) will elucidate the nature of coupling between multiple channels on these surfaces. In this regard, recent developments in reso-

*Corresponding author. Fax: +1-520-621-8407.

E-mail address: msmith@u.arizona.edu (M.A. Smith).

nance enhanced multiphoton ionization (REMPI) of HCl and HBr have demonstrated fine internal state selection of the $HX^+(^2\Pi_i, v^+)$ cation amenable to reaction study [1]. We have recently explored fine structure (*i*) and vibrational (*v*) state dependence for the reactions [2]

 $HBr^{+2}\Pi_i(v^+) + HBr \to H_2Br^+ + Br$ (1a)

$$HBr^{+2}\Pi_i(v^+) + H_2 \rightarrow H_2Br^+ + H$$
(1b)

Reaction (1a) is an ion-dipole driven reaction on a completely attractive potential energy surface for which the model of reactive capture appears to hold. In this case reaction efficiency appears to remain fixed at the collision ion-dipole capture limit for all temperatures and for all internal HBr⁺ states probed. In contrast, Reaction (1b) is 0.35 eV endothermic and occurs on a potential surface for which little is directly known. Reaction (1b) is

¹ Permanent address: Institute of Thermophysics, Novosibirsk, 630090, Russia.

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observed to increase in rate when internal energy in excess of the thermodynamic barrier is placed in the HBr⁺ reactant (for example in the i = 1/2, $v^+ = 1$ state) however, even in this case, the rate coefficient is measured to be a small fraction of the collision limit indicating either a low propensity for reactivity or rapid inelastic relaxation of the prepared state. In order to further elucidate the nature of these observations and perhaps lend insight to other important reactions such as the isoelectronic radical reactions [3]

$$OH + HBr \rightarrow H_2O + Br \tag{2a}$$

$$OH + H_2 \rightarrow H_2O + H \tag{2b}$$

we have investigated the state selected reactions

$$\mathbf{DBr}^{+2}\Pi_i(v^+) + \mathbf{DBr} \to \mathbf{D}_2\mathbf{Br}^+ + \mathbf{Br}$$
(3a)

$$\mathbf{D}\mathbf{B}\mathbf{r}^{+2}\Pi_i(v^+) + \mathbf{D}_2 \to \mathbf{D}_2\mathbf{B}\mathbf{r}^+ + \mathbf{D}$$
(3b)

at the low translational temperatures within a free jet expansion [4]. This study has not only increased the number of available internal energy states presented to these reaction systems, but also explores the role of isotope effects [5–8] within both the reactive and inelastic pathways.

2. Experiment

A detailed description of the free jet flow reactor, including preparation of reagent ions using REMPI and the monitoring of products by timeof-flight mass spectrometer, can be found in [9]. A pulsed axisymmetric nozzle with an orifice diameter of 0.4 mm was used as a gas source employing D₂ buffers seeded with 0.4–2.8% DBr. The REMPI laser beam was focused onto the center streamline of the subsequent jet at some distance, z_i , from the nozzle. The laser radiation in the range of interest, $\lambda = 250-270$ nm ($\Delta\lambda \leq 0.01$ nm), was produced from the frequency doubled (BBO) output of a Nd/YAG pumped dye laser (Coumarin 503). The newly prepared DBr⁺(${}^{2}\Pi_{i}, v^{+}$) cations contained in the field free core of the free jet flow moved and interacted with free jet core species until at some distance, $z_{\rm f}$, they were extracted into the time-offlight mass spectrometer. Typical experimental values were: $z_i = 1 \text{ cm}$; $z_f = 3 \text{ cm}$; and $p_0 = 80-300$ Torr. The low DBr fractions were used to better isolate reaction (3b), which was much slower than reaction (3a). An additional reason to use low density and low DBr concentration flows was to minimize clustering that may affect both gas-dynamic properties and chemistry. Appearance of clustered ions was monitored and thereby controlled through mass spectrometry.

State selection of DBr⁺(²Π_i, v⁺) cations was achieved via (2 + 1) REMPI of DBr through the f^3 $\Delta_2(v = 0), f^3\Delta_2(v = 1), F^1\Delta_2(v = 0)$ and $F^1\Delta_2(v =$ 1) Rydberg intermediates, using the R(1) line in all cases (the corresponding wavelengths were $\lambda = 269.18, 263.30, 259.44, 253.98$ nm). According to investigations by Xie and Zare [1], REMPI through these states produces DBr⁺(²Π_i, v⁺) ions almost exclusively (greater than 98%) in a single spin–orbit and vibrational state, namely, (*i* = $3/2, v^+ = 0$), (*i* = $3/2, v^+ = 1$), (*i* = $1/2, v^+ = 0$), and (*i* = $1/2, v^+ = 1$), respectively. In all cases, we chose laser wavelengths, which led to equal efficiency of D⁷⁹Br⁺ and D⁸¹Br⁺ production.

Loss of DBr^+ ions along the free jet axis is caused by the reactions (3a) and (3b), as well as by geometric expansion of the flow

$$-d[\mathbf{DBr}^+]/dt = k_a[\mathbf{DBr}][\mathbf{DBr}^+] + k_b[\mathbf{D}_2][\mathbf{DBr}^+] + [\mathbf{DBr}^+]f(t).$$
(4)

Here k_a and k_b are the rate coefficients of reaction (3a) and (3b) and the function f(t) describes the geometric expansion of the flow and is assumed to be equal for charged and neutral particles [4]. Inputting α as the fraction of DBr molecules in the D₂ + DBr mixture, $\alpha = [DBr]/([DBr] + [D_2]); N_1^+$ as the fraction of DBr⁺ ions, $N_1^+ = [DBr^+]/([DBr^+] + [D_2Br^+]);$ the total gas density $n = [DBr] + [D_2];$ and an effective rate coefficient

$$k_{ab} = k_a \alpha + k_b (1 - \alpha). \tag{5}$$

Eq. (4) can be simply expressed in a first order linear form:

$$-dN_1^+/dt = nk_{ab}N_1^+.$$
 (6)

Integration of Eq. (6) over the distance along the free jet axis from the point of ionization, z_i , to the point of extraction, z_f , gives the final expression that was used for data analysis

$$\ln(N_1^+) = k_{ab}(1/z_i - 1/z_f)n_0 z_0^2/u,$$
(7)

where n_0 is the stagnation density, $z_0 = aD$, where D is the nozzle diameter, a is a constant, which is dependent on the heat capacity ratio $\gamma = C_p/C_v$ and is equal to 0.401 or 0.298 for $\gamma = 5/3$ and 7/5, respectively. Here we used a model of spherical expansion [10]: $n = n_0(z/z_0)^{-2}$, which works very well in a hypersonic region of the flow and is confirmed for measurements along the center streamlines of the jet flow.

The ratio between DBr⁺ and D₂Br⁺ concentrations was measured by their corresponding time-of-flight signals while varying the stagnation gas density, n_0 , for a number of DBr concentrations in the mixture, α . The effective rate coefficient k_{ab} was derived via a best fit to Eq. (7) for each particular value of α . Finally, dependence of k_{ab} on α allowed for determination of the rate coefficients k_a and k_b , according to Eq. (5).

3. Results

The rate coefficients of the reactions (1a), (1b) and (3a), (3b) are presented in Table 1. The results for both isotopes are very similar in all cases. There is no apparent kinetic isotope effect for either reaction. The rates of the reactions (1a) and

Table 1

Rate coefficients^a of the state-specific ion-molecule reactions

$$(\mathrm{H}_2,\mathrm{HBr}) + \mathrm{HBr}^{+2}\Pi_i(v^+) \rightarrow \mathrm{H}_2\mathrm{Br}^+ + (\mathrm{H}, \mathrm{Br})$$

and

Ionic state	$^{2}\Pi_{3/2},v^{+}=0$	$^{2}\Pi_{3/2},v^{+}=1$	$^{2}\Pi_{1/2},v^{+}=0$	${}^{2}\Pi_{1/2}, v^{+} = 1$	
Neutral reactant		For HBr ^{+b}			
HBr	$13.8\pm1.6^{\rm c}$	15.0 ± 1.3	16.6 ± 0.9	12.8 ± 1.6	
H_2	0.016 ± 0.021	0.047 ± 0.017	0.084 ± 0.010	0.207 ± 0.019	
		For DBr ^{+d}			
DBr	15 ± 3	11 ± 3	13 ± 3	12 ± 3	
D_2	0.016 ± 0.03	0.002 ± 0.03	0.015 ± 0.03	0.20 ± 0.03	

 $(D_2, DBr) + DBr^{+2}\Pi_i(v^+)D_2Br^+ + (D, Br)$

^a Units of 10^{-10} cm³ s⁻¹. The error limits represent 2σ values. The Langevin collision limits are 1.5×10^{-9} and 1.1×10^{-9} cm³ s⁻¹ for the HBr⁺ + H₂ and DBr⁺ + D₂ systems, respectively.

^bData from [2].

^c For thermal conditions [11]: k{HBr⁺($i = 3/2, v^+ = 0$) + HBr} = (6.7 ± 1.6) × 10⁻¹⁰ cm³ s⁻¹.

^d Present work.

(3a) are independent of ionic state and much higher than rates of the reactions with H₂ and D₂, which are sensitive to the internal energy of ionic reactants. The differences between rates of reaction (3b) and zero are statistically insignificant for all studied states of the ions $DBr^+({}^{2}\Pi_{i}, v^+)$, excluding $(i = 1/2, v^+ = 1)$, and even the rate coefficient for that highest ionic state is still much lower than the Langevin value for ion-molecule capture.

An energy diagram for reaction (3b) is presented in Fig. 1 for a number of low rotational levels of DBr^+ and D_2 restricted by temperature and photodynamics. The energy of every level is referenced to the lowest spin-orbit, vibrational and rotational state of both reactants. The dashed lines display the boundary of exothermicity with the uncertainty calculated using heats of formation for all the species of reaction (3b) at T = 0 K [12]. The rotational levels of the DBr⁺ ions are restricted in accordance with the results of Xie and Zare [1], who observed a measurable population of only a few levels surrounding J, the rotational level of the intermediate state selected by the laser. According to Fig. 1, only the DBr⁺(${}^{2}\Pi_{1/2}, v^{+} = 1$) and perhaps a small fraction $({}^{2}\Pi_{1/2}, v^{+} = 0)$ collisions are able to surmount the reaction barrier with D_2 .

The rate coefficients k_{1a} and k_{3a} are presented in Fig. 2 as a function of excess energy that is defined as



Fig. 1. Energy diagram for the reaction $DBr^{+}({}^{2}\Pi_{i}, v^{+}, J^{+}) + D_{2}(v = 0, J)D_{2}Br^{+} + D$. The energy E = 0 is referenced to the lowest internal energy level of the reactants. The threshold of exothermicity based on the data from [12] is shown by dashed lines (with error limits).



Fig. 2. Rate coefficients of the reaction $XBr^+({}^{2}\Pi_i, v^+) + X_2(v = 0) \rightarrow X_2Br^+ + X$, (X = H, D) as a function of excess internal energy (see text, Eqs. (8) and (9)). The horizontal error bars are dominated by uncertainty in heats of formation for the H₂Br⁺ and D₂Br⁺ ions.

$$\Delta E_{i,v} = \langle E \rangle_{i,v} - \Delta(\Delta_{\rm f} H_0), \qquad (8)$$

where $\Delta(\Delta_{\rm f} H_0)$ is the difference between the T = 0 K heats of formation of products and reactants;

$$\langle E \rangle_{i,v} = \sum_{J} \sum_{J^+} \varepsilon_{i,v}(J, J^+) N_J N_{J^+}, \qquad (9)$$

where $\varepsilon_{i,v}(J,J^+)$ is the total internal energy of the reactants, $\{\mathbf{XBr}^+({}^{2}\Pi_i, v^+, J^+); X_2(J)\}$ above the lowest level $\{\mathbf{XBr}^+({}^{2}\Pi_{3/2}, v^+ = 0, J^+ = 0); X_2(J = 0)\}$ and N_J and N_{J+} are the relative rotational level populations of the X_2 molecule and \mathbf{XBr}^+ ion,

respectively. Here X = H for reaction (1b) or X = D for reaction (3b). The rotational distribution of the DBr⁺ ions was assumed to be that of the HBr⁺ ions as measured by Wales et al. [13] under the same ionization scheme: $N_{1/2}:N_{3/2}:N_{5/2}$: $N_{7/2} = 0.49$: 0.34:0.14:0.03, neglecting rotational relaxation. The terminal rotational distribution of the H₂ in the free jet under our typical conditions were estimated in [2], based on the data of Latimer [14], as $N_0:N_1:N_2:N_3 = 0.16:0.71:0.09:0.04$ (with an accuracy ~ 0.04 for all numbers). We assume that the rotational relaxation times in H₂ and D₂ are the same. Taking into account the different nuclear statistics of the D₂ molecules, we estimate $N_0:N_1:$ $N_2:N_3 = 0.43:0.30:0.24:0.03$ for D₂ in the jet.

The heats of formation at T = 0 K for H₂, HBr⁺, H, H₂Br⁺, D₂, D were taken from [12] as 0, 262, 51.6, 218, 0, 52.5 kcal/mol, respectively. The heat of formation for DBr⁺ was estimated as 261.9 kcal/mol using the heats of formation for the pairs (D, Br⁺) and (H, Br⁺) along with the known zeropoint energies of DBr⁺ and HBr⁺. The heat of formation for D₂Br⁺ was estimated as

$$\Delta_{\rm f} H_0 \{ D_2 B r^+ \} = \Delta_{\rm f} H_0 \{ H_2 B r^+ \} + \Delta_{\rm f} H_0 \{ D_2 O^+ \}$$
$$- \Delta_{\rm f} \ H_0 \{ H_2 O^+ \}$$
$$= 217 \ \text{kcal/mol.} \tag{10}$$

Accuracy of the values of $\Delta_f H_0 \{HBr^+\}, \Delta_f H_0 \{DBr^+\}, \Delta_f H_0 \{H_2Br^+\}$ and $\Delta_f H_0 \{D_2Br^+\}$ is about $\pm 0.4, \pm 0.4, \pm 0.7$ and ± 1.2 kcal/mol, respectively. These errors dominate the error limits shown in Figs. 1 and 2.

The apparent energy dependent rate coefficients of reactions (1b) and (3b) appear to match to each other surprisingly well. The major point of concern regards the small absolute value of the rate coefficients for the ions in the highest internal states for which the exoergicity is in excess of 0.1 eV. In fact, the values of the rate coefficients measured in the present work should be strictly considered only as lower limits, if relaxation processes (spin–orbit or/ and vibrational) are collisionally competitive, since relaxation has been left out of the current analysis. It should be noted however, that a first order treatment of the kinetics including relaxation suggest that the experimentally determined rate coefficients for both reaction (1b) and (3b) are accurate within the reported error limits, suggesting an inherent dynamic bottleneck to reactivity within the states currently probed. Such bottlenecks may represent restrictions on open product channels, angular momentum barriers, or restrictions not currently recognized.

4. Analysis of possible relaxation processes

Direct data on spin-orbit or vibrational relaxation that may lead to decay of the HBr⁺(${}^{2}\Pi_{1/2}$, $v^{+} = 1$) and DBr⁺(${}^{2}\Pi_{1/2}$, $v^{+} = 1$) states is not present in the literature. Imajo et al. [15] measured the thermal rate of the reaction

$$CO^{+}(A^{2}\Pi_{1/2}, v^{+} = 1) + He$$

$$\approx CO^{+}(A^{2}\Pi_{3/2}, v^{+} = 1) + He$$
(11)

and found the rate coefficient of 1.7×10^{-10} cm³ s⁻¹ for the forward and 1.3×10^{-10} cm³ s⁻¹ for the reverse transition. Sudbo and Loy [16,17] studied the spin–orbit relaxation for neutral NO molecule in specific rotational and vibrational states

$$NO(^{2}\Pi_{3/2}, v, J) + (NO, Ar, He, ...)$$

$$\rightleftharpoons NO(^{2}\Pi_{1/2}, v, J)$$
(12)

and found for $v = 2, J = 21/2, k\{NO\} = 5 \times$ $10^{-11} \text{ cm}^3 \text{ s}^{-1}, k\{\text{Ar}\} = 6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}, k\{\text{He}\}$ $= 3 \times 10^{-12}$ cm³ s⁻¹, which differ significantly. On the other hand, the rate coefficient for the reverse reaction (from the lower $^2\Pi_{1/2}$ to the higher $^2\Pi_{3/2}$ state), $k^*{NO} = 7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, is very close to the value measured by Joswig et al. [18] for the rotationally specific spin-orbit excitation NO $({}^{2}\Pi_{1/2}, J = 1/2 \rightarrow {}^{2}\Pi_{3/2}, J = 5/2)$ in collisions with He $(8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1})$ and Ar $(7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1})$ cm³ s⁻¹). The same order of magnitude ($\sim 10^{-11}$ cm³ s⁻¹) was measured for vibrational relaxation of neutrals: NO(v = 3)/NO [19], CH(v = 1)/(CO, N_2, H_2 [20], while the vibrational quenching of NO^+ (v = 1) by Ar, N₂ and He were found to be much faster under ultra-low temperatures $(9 \times$ $10^{-10}, 1 \times 10^{-9}, 1 \times 10^{-10}$, respectively) [21].

In spite of some inconsistency in the cited experimental data, we must conclude that the rates of spin–orbit relaxation could be high enough to affect our measurements of the rate coefficients for reactions (1a), (1b) and (3a), (3b). However,

possible channels for energy transfer are strictly limited in our low temperature collisions. Translational and rotational degrees of freedom cannot readily absorb these large transition energies according to momentum and angular momentum conservation. If the energy transfer mechanism is to vibration of the ion DBr⁺ (or HBr⁺) $\left[\left(^{2}\Pi_{1/2}, v^{+}\right)\right]$ $(= 1) \rightarrow (^{2}\Pi_{3/2}, v^{+} > 1)]$, it would still be available for driving reactions (1a) and (3a) and should not necessarily lead to a decrease in the rate coefficients observed. So, there is primarily only one channel for collisional quenching of the DBr⁺ (or HBr⁺) (${}^{2}\Pi_{1/2}, v^{+} = 1$) states that can directly influence the interpretation of the results displayed in Fig. 2: ion relaxation via vibrational excitation of the DBr (HBr) or D_2 (H₂) molecules. The rate coefficients for the reactions (1b) and (3b) were measured in the limit of a very low fraction of heavy molecules in the mixture to exclude interference with the reactions (1a) and (3a). Thus, the effect of collisional relaxation between the ions and parent molecules may be significant only if the rate coefficient is more than the rate of the reactions (1a) and (3a), that is 1.5×10^{-9} cm³ s⁻¹. Xie and Zare [1] used REMPI in the mixture of DBr + HBr (2:1) and monitored internal states of ions by laser induced fluorescence (LIF). They observed only one state present for the reactant ion distribution throughout the reaction time (i.e., over many collisions): $[{}^{2}\Pi_{3/2}, v^{+} = 0]$, or $[{}^{2}\Pi_{3/2}, v^{+} = 1]$, or $[{}^{2}\Pi_{1/2}, v^{+} = 0]$, or $[{}^{2}\Pi_{1/2}, v^{+} = 1]$, depending on intermediates chosen in the REMPI scheme. In particular, they observed that > 98% of the DBr⁺ (HBr⁺) ions were in the $({}^{2}\Pi_{1/2}, v^{+} = 1)$ when they used REMPI through the $F^1\Delta_2[^2\Pi_{1/2}]$ Rydberg state. If collisional relaxation of this spin-orbitvibrational state had a rate coefficient \sim 1.5 \times 10^{-9} cm³ s⁻¹ in collisions with the HBr/DBr molecules, relaxation could not have remained undetected in their high HBr/DBr concentrations. Thus, the only possibly significant channel of relaxation left in our experiments is through collision with light molecules.

Consideration of kinetics for the relative concentration of the D_2Br^+ ions, including DBr^+/D_2 relaxation with the rate coefficient k^* , gives the following expression for the point of ion extraction, z_f ,

$$\frac{[\mathbf{D}_{2}\mathbf{B}\mathbf{r}^{+}]}{[\mathbf{D}_{2}\mathbf{B}\mathbf{r}^{+}] + [\mathbf{D}\mathbf{B}\mathbf{r}^{+}]} = \frac{k_{ab}}{k^{**}} \left[1 - \exp(-k^{**}(1/z_{i} - 1/z_{f})n_{0}z_{0}^{2}/u)\right],$$
(13)

where $k^{**} = k_{ab} + k^*(1 - \alpha)$ and all other values are specified in Section 2.

Unfortunately, it is impossible to derive all rate coefficients k_a , k_b , k^* independently from our experimental data. But if we begin with an assumed rate coefficient, k^* for the relaxation process, we can find the rate coefficient, k_b , through best fit of the right side of Eq. (13) to experimental data. This function k_b (k^*) is shown by line 1 in Fig. 3 (the rate coefficients, k_a , are taken as $1.3 \times$ 10^{-9} cm³ s⁻¹). The confidence intervals presented by lines 2 answer to the random experimental error. Finally, line 3 shows the normalized sum of the squared deviations between the left-hand side (experimental data) and right-hand side (model result) of Eq. (13). From this comparison we can conclude that the relaxation processes do not dramatically change the determined rate coeffi-



Fig. 3. Rate coefficient of the reaction, DBr^+ (${}^{2}\Pi_{1/2}, v^+ = 1$) + $D_2 \rightarrow D_2Br^+$ + D, fit to experimental data in the framework of the relaxation model Eq. (13) including decay of the (${}^{2}\Pi_{1/2}, v^+ = 1$) state by collisions with D_2 molecules. Lines 1 and 2 show the value and error limits of the reaction rate coefficient, k_b , at each particular relaxation rate coefficient value, k^* . Deviation of the model from experimental data (in arbitrary units) is shown by line 3.

cients, measured in the present work, and that the low range of the relaxation rates $[k^* = (0 - 1) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}]$ and consequent reaction rate coefficients $k_b = (2 - 4) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ provide the least deviation to our experimental results.

5. Conclusion

Rate coefficients for a variety of internal states of $DBr^+(^2\Pi_i, v^+)$ with DBr were measured to be near collision limited values as seen previously for HBr⁺ with HBr and significantly greater than values observed at 300 K [11]. The rate coefficients for reaction of the same states of DBr^+ with D_2 were found to be insignificant unless the total internal energy was in excess of the reaction barrier. In this case, as with $HBr^+ + H_2$, reaction proceeds at a value of only a few percent of the collision frequency. Simple analysis suggests this is not an artifact of ignoring relaxation in our kinetic analysis while more detailed consideration will be presented in future work. The rate coefficients of the DBr^+/D_2 and HBr^+/H_2 reactions indicate a common dependence on total energy. It is currently suggested that the slow rate for clearly exoergic channels may suggest a dynamic barrier not accounted for in the simple thermodynamic analysis.

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