3 kcal/mole[9]] or the tris-*p*-nitrophenylmethide–tris-*p*-nitrophenylmethyl system ($k \sim 10^9\ M^{-1}\ \text{sec}^{-1}$, $E \sim$ 0.9–2 kcal/mole, depending on metal ion and solvent[10]), we note that k for reaction 1 is considerably smaller, although $E^{\neq}$ remains $\sim$3 kcal/mole. It has been suggested that most simple, unsubstituted radical anions exchange electrons at or near the bimolecular diffusion-controlled limit and significantly lower rates only occur if the anion and its neutral precursor differ substantially in structure.[1b,11] This does not seem to be the case for $[C_6H_6]^{-1}$–$[C_6H_6]$ exchange. We interpret the small k for benzene to be due to an effect significantly different from the larger anion systems and most probably associated with higher specificity in the anion–solvent interactions for the smaller ion. This might be expected due to higher surface charge density on benzenide ion as compared to anthracenide ion or tris-*p*-nitrophenylmethide ion.

The rate data reported here should be of immediate interest for comparison with other information on structurally more complicated anion radicals. Formulation of a detailed theory of electron transfer in aromatic radical systems requires knowledge of substituent effects on k, and the benzene rate constant provides an important reference point for measurements in this field.[12]

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(9) N. Hirota, Ph.D. Thesis, Washington University, St. Louis, Mo., 1963, pp 107–108.

(10) M. T. Jones and S. I. Weissman, *J. Am. Chem. Soc.*, **84**, 4269 (1962).

(11) C. S. Johnson, Jr., "Advances in Magnetic Resonance," Vol. I, Academic Press Inc., New York, N. Y., 1965, p 33.

(12) All esr measurements were made with a JEOLCO 3BSX spectrometer equipped with linear field sweep (Hall element controlled) and operating with 100-kc field modulation.

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Vibrational *vs.* Translational Activation in the H_2,H_2 and H_2,D_2 Exchange Reactions[1]

Sir:

The $H_2 + D_2 \rightleftarrows 2HD$ reaction is of considerable interest because it is the simplest example of an elementary process in which two atoms (or fragments) are exchanged in the collision of a pair of molecules. Moreover, Bauer and his co-workers[2] have recently focused attention on this reaction by the suggestion that the energy needed to cross the activation barrier is provided only by the vibrational energy of the colliding molecules and that the translational energy of relative motion does not contribute.[3] We report here some results of a quasi-classical trajectory study for the H_2,H_2 exchange reaction with particular emphasis on the importance of translational and vibrational energy. The calculation, which is a generalization of previous work on the (H,H_2) exchange reaction,[4] employs an approximate potential surface obtained by a semiempirical valence-bond method of the London–Eyring–Sato type.[5,6] On this surface the saddle-point configuration for the exchange reaction is a square with side 1.970 au, the barrier height being equal to 62.7 kcal/mole.[7] By Monte Carlo averaging over collision trajectories, the total reaction cross section was determined as a function of the initial vibrational states (v, v') of the two molecules and their initial relative kinetic energy. A supplementary study was made of the rectangular (D_{2h}) collisions, which proceed through the lowest energy path of the potential surface.

For D_{2h} reactions, the relative translational energy thresholds $E_R{}^\circ$ are 50.7, 31.4, and 19.8 kcal/mole for both molecules in the zeroth, first, and second vibrational state, respectively. In the three-dimensional calculation the thresholds are slightly above the D_{2h} results (*e.g.*, $v = v' = 0$, $E_R{}^\circ = 52.5$ kcal/mole; $v = v' = 2$, $E_R{}^\circ = 21.8$ kcal/mole). For $v = v' = 0$ in the D_{2h} case, the $E_R{}^\circ$ value corresponds to an energy (translation plus zero-point vibration) of 63.1 kcal/mole. Thus, about 99% of the total energy is available for reaction and both translational and vibrational energy must contribute. For the three-dimensional case, the corresponding figure is 97% of the system energy if rotational energy is excluded.[8] In higher vibrational states there is an increase in the total energy at threshold (*e.g.*, for $v = v' = 2$, the energy is 78.5 kcal/mole in D_{2h} collisions and 80.5 kcal/mole in three-dimensional collisions). It appears that $\sim$98% of the translational energy is available (independent of v and v'), while the percentage of the vibrational energy E_v available varies approximately as $[94 - 246E_v\ (\text{au})]$. This behavior contrasts sharply with models assuming vibrational adiabaticity; *e.g.*, for the D_{2h} collisions, 71% of the vibrational energy would be predicted to be available.[4,9]

The rate constant $k_{st}\ (v, v', T)$ for molecules with vibrational quantum numbers (v, v') was calculated as a function of temperature by integrating the reaction cross section $S_r\ (E_R, v, v', T)$ over a Boltzmann distribution for the translational energy. The contribution $k_B\ (v, v', T)$ of the (v, v') state to the total rate constant $K(T)$ was evaluated by weighting k_{st} with the vibrational Boltzmann distribution. Table I lists some k_{st} and k_B values for 1600°K. By interpolating or extrapolating k_B for the (v, v') states not explicitly calculated and then summing over v and v', the total rate constant $K(T)$ was

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(1) Supported in part by a contract with the U. S. Atomic Energy Commission and by a grant from the Petroleum Research Fund of the American Chemical Society.

(2) S. H. Bauer and E. L. Resler, Jr., *Science*, **146**, 1045 (1964); S. H. Bauer and E. Ossa, *J. Chem. Phys.*, **45**, 434 (1966).

(3) S. H. Bauer, D. Marshall, and J. Baer, *J. Am. Chem. Soc.*, **87**, 5514 (1965).

(4) M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.*, **40**, 2033 (1964); **43**, 3259 (1965).

(5) F. London, *Z. Elektrochem.*, **35**, 552 (1929); H. Eyring and M. Polanyi, *Z. Physik. Chem.* (Leipzig), **B12**, 279 (1931); S. Sato, *J. Chem. Phys.*, **23**, 592, 2465 (1955); F. O. Ellison, N. T. Huff, and J. C. Patel, *J. Am. Chem. Soc.*, **85**, 3544 (1963); R. N. Porter and M. Karplus, *J. Chem. Phys.*, 40, 1105 (1964); J. K. Cashion and D. R. Herschbach, *ibid.*, **40**, 2358 (1964).

(6) A very similar surface has been proposed by R. B. Abrams, J. C. Patel, and F. O. Ellison, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstract N-33.

(7) *Ab initio* configuration–interaction molecular orbital calculations with 1s and 1s′ orbitals on each hydrogen suggest that the saddle-point configuration may be a rhombus or a rhomboid. However, since the resulting barrier height is greater than the energy required for the process $2H_2 \rightarrow H_2 + 2H$, no meaningful conclusions can be drawn. Improved calculations with extended basis sets are in progress. We thank Dr. R. Hoffmann, Dr. J. A. Pople, and Dr. I. Shavitt for suggestions and discussions on this point and Dr. R. M. Stevens for collaboration on these calculations.

(8) For the three-dimensional case, rotational energy is present for many of the collisions, in accord with the Boltzmann weighting used in the Monte Carlo averages. However, this appears to have only a small effect on the threshold.

(9) R. A. Marcus, *J. Chem. Phys.*, **41**, 610 (1964); **45**, 4500 (1966).

Table I. (H_2,H_2) Exchange Rate Constants at 1600°K (cm^3/mole sec)

v	v'	k_{st}	k_B
0	0	3.438×10^4	3.268×10^4
0	1	1.009×10^6	2.397×10^4
1	1	1.634×10^7	9.695×10^3
0	2	1.521×10^7	1.117×10^4
1	2	1.535×10^8	2.816×10^3
0	3	1.530×10^8	4.285×10^3

obtained (*e.g.*, $K(T)$ is 1.332×10^5 cm^3/mole sec at 1600°K and 1.164 cm^3/mole sec at 1000°K). The values of $K(T)$ are well fitted by an Arrhenius plot with an activation energy (E_a) of 61.64 kcal/mole and a preexponential factor (A) of 3.475×10^{13} cm^3/mole sec. Thus, E_a is only slightly less than the classical barrier height. The absolute rate theory values of the rate constants for the same surface are somewhat smaller than those from the trajectory treatment (*e.g.*, $K(T)$ is 0.643×10^5 cm^3/mole sec at 1600°K and 0.296 cm^3/mole sec at 1000°K).

Comparison of our results with the conclusions of Bauer, *et al.*,[2,3] shows agreement in that the rate of H_2,H_2 exchange is greatly enhanced for molecules in excited vibrational states (v and/or $v' > 0$) as compared with molecules in the ground vibrational state ($v = v' = 0$), the translational and rotational degrees of freedom having thermal distributions; *e.g.*, k_{st} ($v = 0$, $v' = 1$) is ~30 times k_{st} ($v = 0$, $v' = 0$) at $T_{tr} = T_{rot} = 1600$°K. However, because of the low population of the excited states, the contribution to $K(T)$ from the ($v = 0$, $v' = 1$) collisions is only 0.74 that from the ($v = v' = 0$) collisions at 1600°K and becomes even less at lower temperatures. By summing over the k_B values at 1600°K, one finds that k_B ($v = v' = 0$) contributes ~25% and all of the excited states 75% of $K(T)$.

Thus, in contrast to the suggestion of Bauer, *et al.*,[2,3] there is no theoretical evidence for a "vibrational threshold." Model calculations show that an increase in the vibrational energy availability is by itself not sufficient to produce such a threshold;[10] the translational energy must be significantly *less* effective as well. Since corresponding results are obtained in calculations on the H_2,D_2 system, further studies are clearly needed to resolve the differences between ref 2 and 3 and the present treatment.

The calculations reported here are only illustrative because they are based on classical mechanics and employ an approximate potential surface. Thus, it is possible that the results do not provide an accurate description of the H_2,H_2 reaction. However, although the absolute value of the rate constant is very sensitive to the potential, particularly to the barrier height, the relative k_{st} and k_B values are much less so. Moreover, it is likely that the calculated efficiency of translational and vibrational energy in overcoming the activation barrier is not atypical for systems in which the reactants and products are similar. For significantly different values, a drastic modification of the potential surface would be required.[11] In more asymmetric reactions (*e.g.*, some endothermic reactions), vibrational energy may have increased importance. An example might be "late-uphill" surface corresponding to $CH_3 + KI \rightarrow K + CH_3I$, the inverse of the reaction for which molecular beam studies[12] indicate that much of the exothermicity appears as internal excitation of products. However, even in this case the available data when combined with microscopic reversibility arguments are not sufficient to show that the excited vibrational states would dominate the reaction for an equilibrium population in the thermal region. For the nonequilibrium case with an excess of excited molecules, there are likely to be measurable effects for reactions involving a significant activation energy and/or endothermicity. It would be of great interest to have more data on exchange reactions with a non-Boltzmann vibrational population produced by the stimulated Raman effect,[13] "chemical activation,"[14] or electron impact.[15]

A more detailed analysis of the H_2,H_2 and H_2,D_2 exchange reactions and related high-energy processes (*i.e.*, dissociation, exchange dissociation, atomization) will be presented.

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[10] A vibrational threshold value v_0 would be defined to exist at a temperature T if

$$\sum_{v'=0}^{v_0} k_B(v_0 - v', v', T) \gg \sum_{v'' \geqslant v'=0}^{v_0-1} k_B(v'' - v', v', T) \approx 0$$

[11] Distortions in the surface such that the reaction trajectory is perpendicular to the initial direction of translational motion while climbing the potential barrier could increase the vibrational–translational efficiency ratio. The distortions discussed in ref 7 are unlikely to be of this type; however, if the barrier were as high as in ref 7, an atomic mechanism would be expected.

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[14] B. S. Rabinovitch and M. C. Flowers, *Quart. Rev.* (London), **18**, 122 (1964).

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[16] Most of the computations were performed while the authors were at Columbia University.

[17] National Science Foundation (1965–1966) and National Institutes of Health (1966–1967) Postdoctoral Fellow.

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Cobalt(III) Complexes of Linear Tetramines. II. Isomerism in the *trans*-Dichloro(1,4,8,11-tetraazaundecane)cobalt(III) Ion

Sir:

Quite recently, Sargeson and co-workers have demonstrated the configurational stability of coordinated asymmetric secondary nitrogen by isolating isomers of cobalt(III) complexes which differ in the configuration about such nitrogen atoms within the complexes.[1] In light of their work, our investigations of cobalt(III) complexes of 1,4,8,11-tetraazaundecane (2,3,2-tet),

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