Intermediate Coupling Probability Matrix Approach to Chemical Reactions. Dependence of the Reaction Cross Section for K + HCl → KCl + H on Initial Translational and Vibrational Energy

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Abstract: A nonstatistical phase space theory is presented which is equivalent to the statistical phase space theory of Light, Pechukas, and Nikitin in one limit. The theory treats channels with low relative orbital angular momentum and low translational energy statistically but uses a partial statistical approximation for large relative orbital angular momenta and high translational energies. It corrects for the properties that the statistical theory generally predicts too large a cross section, never predicts vibrational population inversion, and has the wrong behavior at high energy. The theory may be used in an ab initio way but in the present article it is applied semiempirically to the reaction K + HCl → KCl + H. The calculated reaction cross sections account within experimental error for the behavior of the cross section at high initial translational energy and for the effect of initial vibrational excitation on the cross section. The theory predicts the reaction cross section will decrease if the initial relative translational energy is raised above 12 kcal/mol.

The first exact solution of the quantum mechanical scattering problem associated with internuclear motion in chemical reactions has been carried out recently, although the potential energy surface was inexact.[1] However, except at the lowest energies for the simplest cases, it is not possible to even include all the energetically accessible internal states of the separated reagents and products in the expansion of a trial scattering wave function.[2] For most chemical reactions this is not a limitation which will be removed by the next generation of computers, but is a fundamental problem. Various techniques for approximating and thereby simplifying the quantum mechanical scattering problem have been developed,[3] including quantum mechanical perturbation theories and unitarization procedures and also semiclassical and classical approximations. A second difficulty in performing calculations, either using accurate quantum mechanical scattering theory or using approximate dynamical theories, is that there is at present very little accurate knowledge of the electronic matrix elements which serve as the potential energy surfaces necessary for solution of the scattering problem.[4] Thus not only the quantum mechanical scattering problem but also the electronic problem is difficult to solve. This difficulty necessitates our using even more simplified models and approximations and makes desirable models which do not require accurate potential energy surfaces.

A third consideration also motivates the creation and use of simplified dynamical theories. In most experiments, one does not observe the complete set of state-to-state reaction cross sections but rather a limited number of averaged quantities.[5] In some cases, even these averaged data are unnecessarily detailed and it is desirable to focus attention on an even further reduced set of numbers characterizing the reaction.[6] Dynamical theories which predict correct results for some such averaged properties of reactions, even though they make no predictions or even erroneous predictions for certain details, may be very useful.[6,7] As an example, many experiments yield the dependence of total integral reaction cross sections (where "total" indicates a sum over partial cross sections corresponding to specific final quantum numbers and "integral" indicates an integration over final scattering angles) on initial translational[8-10] and vibrational[11,12] energy. Other experiments yield vibrational or electronic energy distributions of the products without resolving the final quantum state distribution completely.[13] It is desirable to explain these aspects of the dynamics without necessarily calculating all the state-to-state differential cross sections accurately.

Transition-state theory,[14] which does not require knowledge of the whole potential energy surface, has been very useful in correlating data on thermal rate constants and in some cases in predicting them. Transition state theory might also be useful for predicting state-to-state reaction cross sections in the energy region of the reaction threshold,[15-18] but it does not appear to be well suited to treating state-to-state cross sections or higher energy phenomena in general. The statistical phase space theory of chemical reactions[19-26] provides a generalization of transition state theory which may be more useful at higher energies. The statistical phase space theory does not require a detailed knowledge of the potential energy surface. It uses some knowledge of the potential energy surface to define a strong-coupling criterion for the interaction with each other of reagents in specified states with specified energy and angular momentum in each degree of freedom and for interaction of products with each other in the time-reversed reaction. The statistical phase space theory assumes the state-to-state transition probabilities for all strongly coupled states for given values of the conserved quantum numbers are equal. This means that the probability of occurrence of a reaction leading to a set of final states can be calculated directly from a knowledge of only the final states, whether they satisfy the strong coupling criterion, and how much phase space corresponds to them in the classical limit.

The statistical phase space theory is not expected to be valid for weakly inelastic processes which do not require strong coupling.[27] Reactive collisions may sometimes satisfy a strong-coupling criterion and the statistical phase space theory has had some success in treating chemical reactions.[28-39] "Unfortunately the (statistical) phase space model has generally been rather unsuccessful in predicting total cross sections .... Evidently some dynamics is necessary for a reasonable description, since the collisions studied ... are not random processes .... For a range of high l [orbital angular momentum of relative motion] and hence weak coupling, statistical approximations are not valid."[40] In this article we describe a nonstatistical phase space theory which includes the effect of nonstatistical behavior at large l and which may be more useful for correlating data on high-energy chemical reactions and in some cases in predicting new results.

The statistical phase space theory answers the interesting question[41] of what happens in the limiting case that all degrees of freedom of the interacting system are coupled in the most efficient possible way. It has been pointed out[23] that two possible uses of the statistical phase space theory are as a model against which to compare experimental results and as a predictive tool in the absence of much experimental information. Recently Bernstein, Levine, and Ben-Shaul have analyzed the energy requirements and energy disposal in reactive molecular collisions by comparing the actual results to a reference or prior expectation.[42] They have shown[43] that a useful prior expectation is closely related to but different from the predictions of the statistical phase space theory. In some cases the predictions of the present theory, because of its simplicity and incorporation of reasonable physical effects, may also serve as a useful standard against which to compare experiment and against which to measure deviations.

The present nonstatistical phase space theory is a specific example of a class of general partial statistical theories[24,33,44,45] which have been much studied formally but have not been applied in actual calculations on chemical processes. It is also closely related to previous nonstatistical phase space theories of Serauskas and Schlag[46] and the present author.[47] Horie and Kasuga[48] have also developed a phase space theory which favors states of low final velocity.

Theory

The quantum mechanical statistical theory for rearrangement collisions in triatomic systems has been derived elsewhere.[21-23] The spin and electronic orbital angular momentum of the atom and the molecule have been neglected since they are small compared to the rotational angular momentum and the orbital angular momentum of the relative motion of the atom and the molecule.[29c] The (generalized) result for the state-to-state cross section for reactants in state i to produce products in state f is

$$Q_{if} = \frac{\pi\hbar^2}{2\mu_i E_i}\frac{1}{(2J_i+1)}\sum_{L_i}\zeta_{L_i}\sum_{K}(2K+1)\frac{n(f,E,K)}{N_{\mathrm{TOT}}(e,K)}\kappa(i,f) \tag{1}$$

$$= \frac{\pi\hbar^2}{2\mu_i E_i}\frac{1}{(2J_i+1)g_i^{\mathrm{el}}}\sum_{K}(2K+1)\frac{n(i,E,K)n(f,E,K)}{N_{\mathrm{TOT}}(E,K)}\kappa(i,f) \tag{2}$$

where g_f^{el} is the state degeneracy for channel f which is due to electronic and nuclear spin and electronic orbital angular momentum;

$$n(a,E,K) = \sum_{\substack{L_a \\ \Delta(J_aKL_a)}} g_a^{\mathrm{el}}\zeta_{L_a} \tag{3}$$

$$N_{\mathrm{TOT}}(E,K) = \sum_{a} n(a,E,K) \tag{4}$$

$\kappa(i,f)$ is a transmission coefficient to be discussed below; ζ_{L_a} is the "sticking probability",[49,50a] i.e., the probability that a particle incident in channel a with orbital angular momentum of relative motion $L_a\hbar$ will enter the interaction region; i, f, and a are complete sets of quantum numbers including the sets of quantum numbers I, F, and A (which specify both the chemical identity and also all electronic quantum numbers), the vibrational quantum numbers n_i, n_f, and n_a (the lowest vibrational state is numbered 0), and the rotational quantum numbers J_i, J_f, and J_a; and μ_a and E_a are the reduced mass and translational energy for relative motion in the channel a. The total energy and angular momentum are E and K, respectively. The sum over a in eq 4 includes only open (i.e., energetically allowed) channels at total energy E and the sum over L_a in eq 3 includes only states satisfying the angular momentum addition triangle[51] $\Delta(J_aKL_a)$, i.e., $|J_a - K| \leqslant L_a \leqslant J_a + K$. We must take $\kappa(i,f) = \kappa(f,i)$ so that the cross sections predicted by (1) and (2) satisfy the principle of detailed balance[52]

$$g_i p_i^2 Q_{if} = g_f p_f^2 Q_{fi} \tag{5}$$

(where g_f and p_f are the total degeneracy and momentum of relative motion, respectively) at constant E. The above formulas reduce to the usual statistical theory if

$$\kappa(i,f) = 1 \tag{6}$$

and

$$\zeta_{L_a} = \begin{cases} W_a & L_a \leqslant L_{a\,\max}(E_a) \\ 0 & L_a > L_{a\,\max}(E_a) \end{cases} \tag{7}$$

where $L_{a\,\max}(E_a)$ is determined by the strong-coupling criterion and

$$W_a = 1 \tag{8}$$

in the absence of corrections for potential energy barriers and/or steric effects. The statistical theory is valid for completely strong coupling as discussed above.

If the full statistical assumption is not made, eq 1–4 above provide a formally valid approximation if the constraints

$$\zeta_{L_a} \leqslant 1 \tag{9}$$

$$\kappa(i,f) \leqslant 1 \tag{10}$$

are observed. These constraints ensure that the conservation of particle flux theorems[50b] are satisfied; i.e., the conditions 9 and 10 are necessary to prevent the probability of reaction from exceeding the maximum possible probability of collision. The statistical theory of Light, Pechukas, and Nikitin has the advantage that it is actually correct in a limit indicated by the sudden approximation derivation.[20,25] However, by changing eq 6–8 we can obtain nonstatistical (partial statistical) theories which may be more accurate in some practical cases.

Various methods of assigning values to W_a (leaving the rest of the statistical theory unchanged) lead to one class of theories. The assignment in (8) gives the statistical theory of Light, Pechukas, and Nikitin. This choice is implicit in the transition state theory of Wigner and Eyring. For example, the assumption of a loose transition state located at the position of the centrifugal barrier results in a transition state theory rate for the association which is equal to the rate calculated for it by collision theory using eq 1, 3, 7, and 8.[14b,53] This choice is also implicit in the phase space theory of Keck.[23,54] Another possibility is used by Fermi[55] and Eu and Ross;[56] they let W_a depend on the asymptotic velocity in channel a, e.g.,

$$W_a = (v_a/v_0)C_0 \tag{11}$$

where v_0 is the highest possible velocity in any possible exit channel at energy E and total angular momentum $K\hbar$, and $C_0 = C_0(E,K)$ is a constant less than or equal to 1. Serauskas and Schlag[46] have suggested some nonstatistical modifications of the statistical theory formulas for the case of intermolecular vibrational energy transfer in nonrotating systems. They incorporate a factor in the theory to decrease the reaction probability at high velocity because high-velocity collisions are over too rapidly and another factor to decrease the calculated reaction probability at low velocity because low-velocity collisions are too soft. Their theory does not satisfy detailed balance and does not correspond to a special choice of W_a in the formalism above.

To obtain a more satisfactory phase space theory of rearrangements incorporating the first of the Serauskas-Schlag nonstatistical corrections we take

$$\zeta_{L_a} = \begin{cases} W_a(1 - \exp[-(\nu_a \tau_a)^{\beta}]) & L_a \leqslant L_{a\,\max}(E_a) \\ 0 & L_a > L_{a\,\max}(E_a) \end{cases} \tag{12}$$

where τ_a is a measure of the half-collision time in channel a, ν_a is a characteristic frequency of energy transfer, and β is a parameter. The time-for-interaction factor in eq 12 appears with $\beta = 1$ in the Scrauskas-Schlag theory[46] and also in more general discussions[57] of energy transfer, where it is suggested by simple theory. As in the statistical theory, $L_{f\,\max}(E_a)$ is determined by the strong-coupling criterion. In the absence of corrections for potential energy barriers in the a channel or for steric factors associated with tight transition states, the penetration factor W_a is given by eq 8.

The nonstatistical theory in the above form is obviously not applicable to reactions in which there are appreciable effects due to potential energy barriers (above and beyond the centrifugal and endothermicity barriers). However, the statistical theory has three faults even when applied to reactions without these extra barriers: (i) the absolute values of the cross sections are generally too large; (ii) the theory cannot ever predict an inverted vibrational population in the final state;[23] (iii) the reaction cross section does not fall to zero properly at high energies. Fault i may be due to the sticking probability being taken as 1 instead of less than 1. The new sticking probabilities (eq 12) are less than 1 and are thus more realistic. Fault ii is a basic failing of the statistical approach. It is possible for the new theory to predict inverted vibrational populations (an example is given in the present article) but such a prediction is not probable for many cases. Fault iii occurs because at high energy the total collision cross section equals[23,25] the geometrical cross section and strong coupling is still fully allowed for these hard collisions. In the new theory the cross section is reduced at high energy because of the factor in eq 12 which tends to zero as $E \rightarrow \infty$ (and thus τ_i and $\tau_f \rightarrow 0$) since there is not enough time for energy transfer or particle transfer. This correctly mimics the physical reason why the experimental cross section tends toward zero at high energies.

The new theory is not an attempt to provide a fit to every experiment. If ν_f is fixed by some physical argument concerning the speed of molecular motions in the complex (Note: in this article the word "complex" does not necessarily indicate a long-lived one), then the theory provides a framework for a priori calculations of reaction processes which (hopefully) will be accurate and useful for some classes of reactions. The spirit of the phase space theory calculations is to see what information we can obtain without using detailed knowledge about the system in the strong interaction region. The nonstatistical theory requires only simple, approximate average properties of the system in the interaction region: the average frequency of intermolecular energy transfer (ν_a) and the approximate collision duration (τ_a) in any channel. However, the values used for ν_a may also be fixed semiempirically and the theory may be used as a semiempirical one.

A precise definition cannot be given for the characteristic frequency ν_a. A similar quantity appears in Slater's theory of unimolecular reactions, and there it can be shown that ν_a should be the root mean square of the normal frequencies of the complex, weighted with amplitude factors as they affect the crucial coordinate for reactions.[58] Thus a typical value for ν_a might be 4×10^{13} sec^{-1}. A more sophisticated nonstatistical calculation might make ν_a a function of a, E, and K. We will constrain ν_a to be a function of A only, i.e., $\nu_a = \nu_A$.

In the limit that all $\nu_A \rightarrow \infty$, the nonstatistical theory reduces to the statistical theory. Setting the ν_A values equal to constants gives a whole series of theories. In the limit that all $\nu_a \rightarrow 0$, the theory becomes adiabatic and predicts that all collisions are pure elastic. Bunker and Chang[59] have also proposed a series of models in which the degree of adiabaticity or statisticality assumed in the treatment may be parametrically varied. In Bunker and Chang's theory, like the present nonstatistical theory, the reaction is adiabatic in regions of the reaction coordinate $s = -\infty$ to $s = a$ and $s = b$ to $s = \infty$ and semistatistical from $s = a$ to $s = b$. In their theory a and b are not necessarily located at the position of the centrifugal barrier. Their treatment does not satisfy detailed balance. Also unlike the present set of theories their models do not reduce to the statistical theory of Light, Pechukas, and Nikitin in any limit. Both the present set of nonstatistical models and Bunker and Chang's set have the disadvantage that although they span the range of behavior between adiabatic and statistical (or semistatistical) they cannot correctly handle reactions which are not either *and* are not in the range between these limits. For example, some reactions might proceed preferentially into one or a small bundle of states not centered around the adiabatic one. For example, at very high energy it is sometimes likely that the system will follow one diabatic path.

For $\beta = \infty$, the sticking coefficient is reduced to either unity or zero and we again have a statistical theory (but with a different strong-coupling criterion). Such a value for β would save computer time but it appears to be somewhat unreasonable from a theoretical point of view.

Calculations

The system to be considered is

$$\mathrm{K + HCl} \underset{(\mathrm{R2})}{\overset{(\mathrm{R1})}{\rightleftarrows}} \mathrm{KCl + H}$$

The statistical phase space theory has previously been applied[30] to this system but it is apparent[9,11] that the bond energy assumed for KCl in those calculations was too large. The bond energy of KCl is known from thermochemical and spectroscopic measurements only to within an uncertainty of about ±1 kcal/mol.[60] Thus we choose a value for D_e[60a] which makes the (ground state to ground state) endothermicity equal to 1.53 kcal/mol, which is the threshold value obtained[9c] by extrapolation of reaction cross sections determined by molecular beam experiments. The values used for the other properties of K, HCl, KCl, and H are the same as in our previous study[30] except that more recent recommended values[60b] are used for r_e (2.6666 Å) and ω_e (281 cm^{-1}) for KCl.

The strong-coupling criterion used for $L_{a\,\max}(E_a)$ was the same as used in the previous study[30] and is given by eq 9 and 10 of ref 25.

The nonstatistical calculations required estimates of the half-collision times τ_a. In view of the simplicity of the theory a complicated calculation does not seem warranted and we used[61]

$$\tau_a = \Delta R_a / v_a \tag{13}$$

where v_a is the asymptotic velocity in channel a

$$v_a = (2E_a/\mu_a)^{1/2} \tag{14}$$

Table I. Maximum Incident Partial Waves Which Lead to Strongly Coupled Collisions and Which Lead to Reactive Collisions and Maximum $N_{\mathrm{TOT}}(E,K)$ Which Occur in Some Calculations on the Forward and Reverse Reactions

				max N_{TOT}		
n_i	E_i, kcal/mol	$L_i^{\max}$	$L_{iF}^{\max}$	Statistical	Nonstatistical I[a]	Nonstatistical II[a]
		K + HCl → KCl + H				
0	1.8	130	29	163	76	59
	2.15	138	44	243	75	57
	4.14	172	89	1,309	175	141
	4.468	176	92	1,551	173	139
	6.03	195	116	3,048	234	194
	7.95	214	137	5,592	306	260
	12.1	246	176	14,111	587[b]	509
	15.9	270	206	25,415	855	756
1	1.8	130	130	9,359	443	386
	2.15	138	138	10,050	451	390
	4.14	172	172	14,780	607	528
	4.468	176	176	15,589	615	532
		KCl + H → K + HCl				
0	0.5	12	12	221	74	58
	1.5	18	18	628	115	91
	2.5	22	22	1,217	176	141

[a] In these cases the result is rounded to the nearest integer for this table only. [b] In calculation IA, max $N_{\mathrm{TOT}} = 642$.

and ΔR_a is a measure of the interaction length in channel a. For ΔR_a we used

$$\Delta R_a = \begin{cases} \max \begin{cases} (r_a{}^* - R_0) \\ 0.2\ \text{Å} \end{cases} & L_a > 0 \\ R_0 \quad L_a = 0 \end{cases} \tag{15}$$

where $r_a{}^*$ is the position of the maximum in the centrifugal potential which would be computed using the long-range interaction, R_0 is the hard-sphere collision radius, and 0.2 Å is an estimate[62] of the range of the repulsive interaction. Equations 13-15 provide only a qualitative measure of τ_a but they do show the correct dependence on impact parameter and translational energy and they have the advantage of simplicity in that $r_a{}^*$ and R_0 already enter the theory in the formulation of the strong-coupling criterion.

In addition to performing a set of statistical calculations with the new KCl properties we performed two sets of nonstatistical calculations using two different values for the semiempirical parameter β: $\beta = 1$ for set I and $\beta = \frac{1}{2}$ for set II. In each case we assumed

$$\nu_A = \alpha(\omega_e)_A \tag{16}$$

[where $(\omega_e)_A$ is the diatomic vibrational frequency in the group of channels specified by A] and we determined α empirically so that the total cross section

$$Q_i = \sum_f Q_{if} \tag{17}$$

equals the experimental value for $E_i = 4.14$ kcal/mol, $n_i = J_i = 0$. The sum in eq 17 includes all states corresponding to F = (KCl + H). For $\beta = 1$ this procedure yields $\nu_{\mathrm{K+HCl}} = 9.114 \times 10^{12}\ \mathrm{sec}^{-1}$ and $\nu_{\mathrm{KCl+H}} = 8.566 \times 10^{11}\ \mathrm{sec}^{-1}$. For $\beta = \frac{1}{2}$ it yields $\nu_{\mathrm{K+HCl}} = 9.008 \times 10^{11}\ \mathrm{sec}^{-1}$ and $\nu_{\mathrm{KCl+H}} = 8.463 \times 10^{10}\ \mathrm{sec}^{-1}$. To show the effect of using the same β in each channel we performed a few calculations with $\beta = 1$ and $\nu_{\mathrm{K+HCl}} = \nu_{\mathrm{KCl+H}} = 2.794 \times 10^{12}\ \mathrm{sec}^{-1}$ (the geometric mean of the two values used in set I). This will be called calculation IA.

All the calculations reported in this article are for energies below the thresholds for electronic excitation, formation of KH + Cl, and dissociation. All calculations were for initial rotational quantum number $J_i = 0$. Calculations were carried out only for every third incident partial wave ($L_i = 0, 2, 5, 8, \ldots$) and the rest were interpolated.

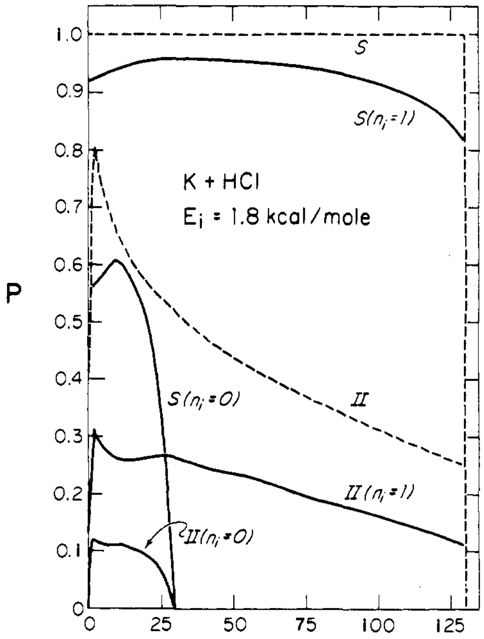

Figure 1. Dashed lines are probabilities of a strong-coupling collision as functions of initial relative orbital angular momentum $L_i\hbar$ for K + HCl collisions at initial relative translational energy 1.8 kcal/mol in the statistical phase space theory (S) and the nonstatistical calculation II. Solid curves are probabilities of reaction for the lowest two initial vibrational states (n_i = 0 and 1) with no initial rotational energy in the two calculational schemes.

Results

The maximum relative orbital angular momentum quantum numbers of the reactants which lead to a strong-coupling collision ($L_i^{\max}$) and to products ($L_{iF}^{\max}$) are given in Table I. Some examples of the dependence of probability for forming a strong-coupling complex and of reaction probability on initial relative orbital angular momentum are given in Figures 1, 2, and 3.

Table I also compares the maximum values of $N_{\mathrm{TOT}}(E,K)$ which occurs in several calculations.

The reaction cross sections are given in Table II where they are compared with the experimental results of Brooks and coworkers.[9,11] The experimental results[11] for a translational energy of 1.8 kcal/mol correspond to a wider velocity distribution than those[9] for higher translational energies and more caution must therefore be used in comparing them with theoretical results at a fixed initial translational energy. Pruett and Brooks estimate[9] relative error bars of 8% and absolute error bars of 50% for the higher translational energies.

Table II also contains the maximum final vibrational and rotational quantum numbers of the products under given conditions and the percentage (PCVE) of vibrationally excited products, i.e., the percentage of product molecules formed with $n_f > 0$.

Examples of final distributions of product vibrational quantum number are shown in Figures 4, 5, and 6.

Discussion

Semiclassically, Figures 1-3 may be interpreted as the probability of strong-coupling collisions and the probability of reaction as functions of initial impact parameter b_i since eq 18 holds in the classical limit.

Table II. Reaction Cross Sections

n_i	E_i, kcal/mol	$n_{f\max}$	$J_{f\max}$	Expt Q_i, Å^2	Statistical Q_i, Å^2	Statistical PCVE	Nonstatistical I Q_i, Å^2	Nonstatistical I PCVE	Nonstatistical II Q_i, Å^2	Nonstatistical II PCVE
					K + HCl → KCl + H					
0	1.8	0	26	0.15	1.72	0	0.53	0	0.32	0
	2.0	0	35		3.16	0	0.78	0	0.56	0
	2.15	0	40	0.50	4.17	0	0.93	0	0.71	0
	2.29	0	44		4.60	0	0.82	0	0.65	0
	2.58	1	52				1.16	23	0.96	15
	2.73	1	56		6.90	10	1.29	27	1.08	20
	2.88	1	60		7.17	13	1.19	32	1.02	25
	3.46	2	71		9.16	24	1.41	46	1.31	37
	4.14	3	83	1.52	10.70	34	1.52	57	1.52	48
	4.468	3	88		11.23	38	1.56	62	1.62	53
	6.03	5	110	1.9	13.40	50	1.64	72	1.89	64
	7.95	8	131	2.03	15.04	59	1.62	79	2.07	72
	12.1	13	169	2.03	16.74	71	1.23[a]	85[a]	1.94	80
	15.9	18	197		17.55	76	1.02	89	1.82	85
1	1.8	10	151	20	70.46	74	10.20	88	13.87	82
	2.15	11	154		65.84	74	9.07	87	12.30	82
	2.29	11	155		64.22	74	8.56	87	11.54	81
	2.88	12	160		58.29	73	7.07	87	9.66	81
	3.46	12	165		53.90	72	6.03	86	8.35	81
	4.14	13	171		49.42	72	5.10	85	7.24	81
	4.468	14	173		47.48	72	4.76	86	6.83	81
					KCl + H → K + HCl					
0	0.5	0	7		16.14	0	2.50	0	2.87	0
	1.5	0	9		6.38	0	0.58	0	1.00	0
	2.5	0	11		4.06	0	0.28	0	0.62	0

[a] Calculation IA yields Q = 1.61 Å^2 and PCVE = 86.

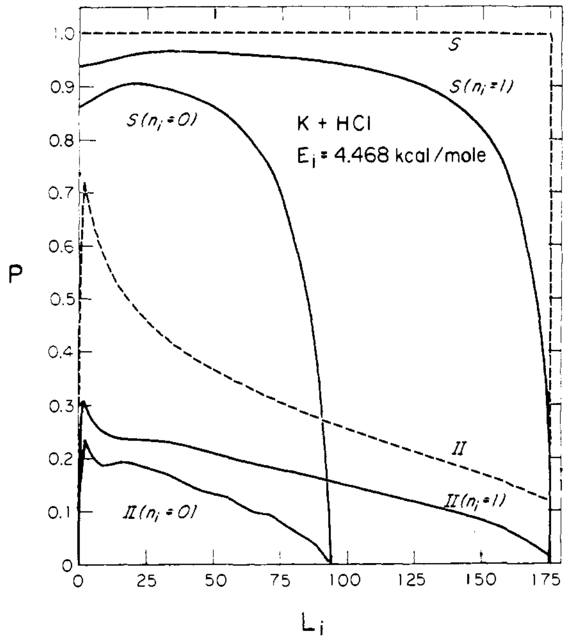

Figure 2. Same as Figure 1 except initial relative translational energy is 4.468 kcal/mol.

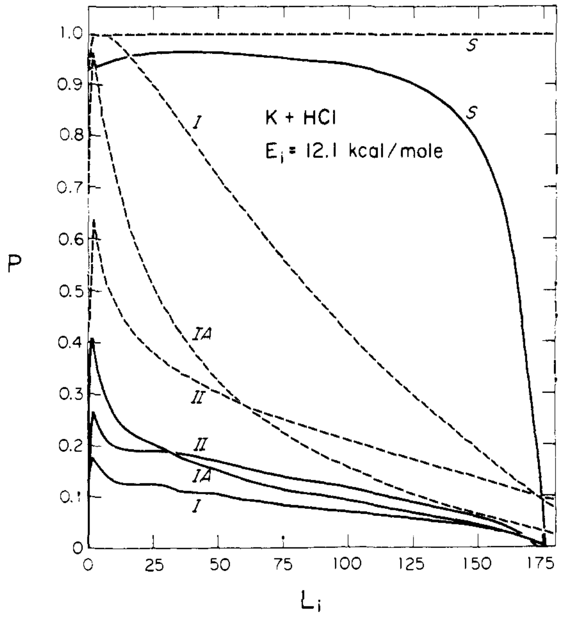

Figure 3. Probabilities of strong-coupling collisions (dashed curves) and probabilities of reaction (solid curves) as functions of initial relative orbital angular momentum $L_i\hbar$ for the reaction K + HCl → KCl + H. The initial relative translational energy is 12.1 kcal/mol and the reagents are in the ground rotational-vibrational state. S: statistical phase space calculation; I, IA, and II: nonstatistical phase space calculations.

$$b_i = \hbar L_i/(\mu_i v_i) \tag{18}$$

We find the dependence of reaction probability of the forward reaction (R1) on initial relative orbital angular momentum $L_i\hbar$ in the statistical calculations is case I[63] for $n_i = 0$ (see Figures 1 and 2) and case II for $n_i = 1$. For the reverse reaction this dependence is case II. These results are in accord with the general expectations[29] for this dependence based on energetics and masses. For case I the maximum relative orbital angular momentum which leads to reaction is less than the maximum relative orbital angular momentum for which a strong-coupling complex may be formed, but for case II these quantities are equal (see Table I). Thus the strong-coupling criterion for the KCl + H channel is very important in these calculations. For the conditions studied here, this strong-coupling criterion often reduces to the constraint that the statistical theory strong-coupling cross section for reaction (R2) not fall below the hard-sphere cross section. It should be emphasized that the present strong-coupling criterion intentionally uses minimal

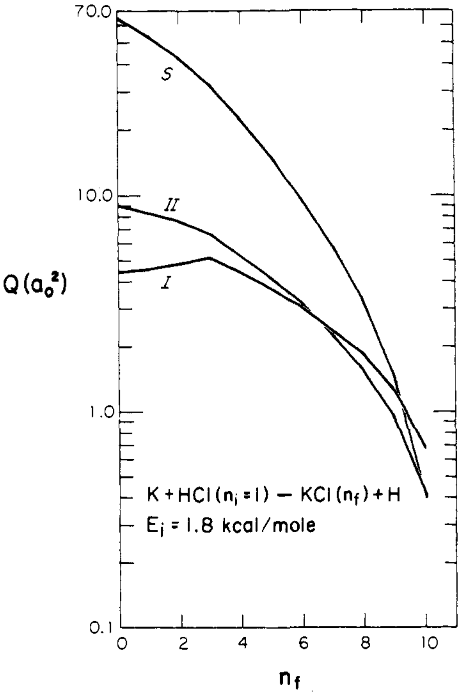

Figure 4. Reaction cross section into specified vibrational states of the product for K + HCl → KCl + H in the statistical phase space theory (S) and the nonstatistical phase space calculations I and II. The initial relative translational energy is 1.8 kcal/mol and the reagents are in the first excited vibrational state with no rotational energy.

knowledge of the potential energy surface and the dynamics and that this is one place where the theory could probably be improved if and when such knowledge is available.

Figures 1 and 2 show that the probability for strong-coupling collisions is appreciably reduced at large impact parameter and high translational energy by the present nonstatistical correction. Further they show that the qualitative features of the dependence of reaction probability on impact parameter are independent of the exact choices made for ν_A and β.

The effect of the nonstatistical correction may be seen by comparing the values of $N_{\mathrm{TOT}}(E,K)$ in the statistical and nonstatistical calculations. Semiclassically, $N_{\mathrm{TOT}}(E,K)$ is the volume (in units of Planck's constant) of phase space which is strongly coupled at total energy E and total angular momentum K for any particular quantized value of the z component of angular momentum. Table I shows that the volume of strongly coupled phase space increases with increasing initial translational or vibrational energy much more slowly in the nonstatistical calculations than in the statistical ones. Because of this, the reaction cross section in the nonstatistical calculations does not increase as rapidly with initial translational or vibrational energy in the nonstatistical calculations and in some cases it even decreases with increasing initial translational energy (see Table II).

The nonstatistical theory correctly predicts that the reaction cross section at low initial translational energy increases when the initial vibrational energy increases (see Table II) and it also correctly predicts that initial vibrational energy is more effective than initial translational energy in increasing the reaction cross section. Figure 1 shows that the increase is due both to increased reaction probability at small L_i and to an increased range of L_i which leads to reaction. It would be interesting to test this and other qualitative features of the present results against trajectory calculations or other dynamical theories.

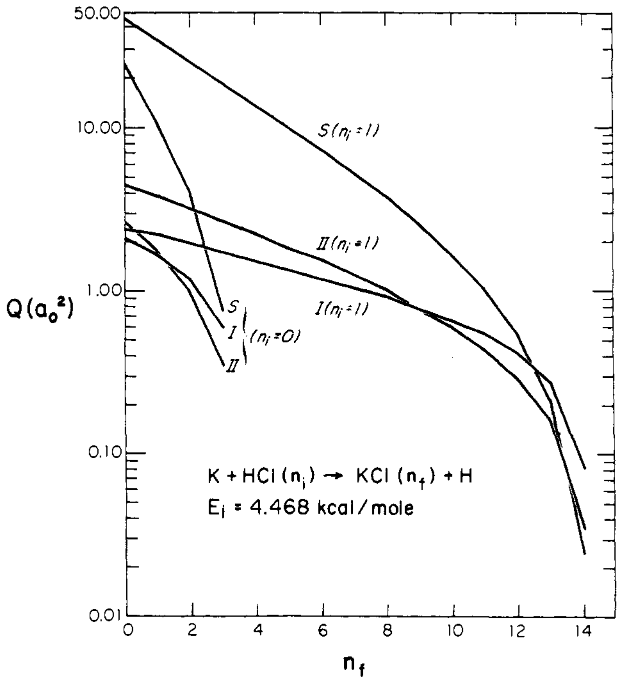

Figure 5. Same as Figure 4 except the initial relative translational energy is 4.468 kcal/mol and the reagents are in the lowest two vibrational states (n_i = 0 and 1) with no rotational energy.

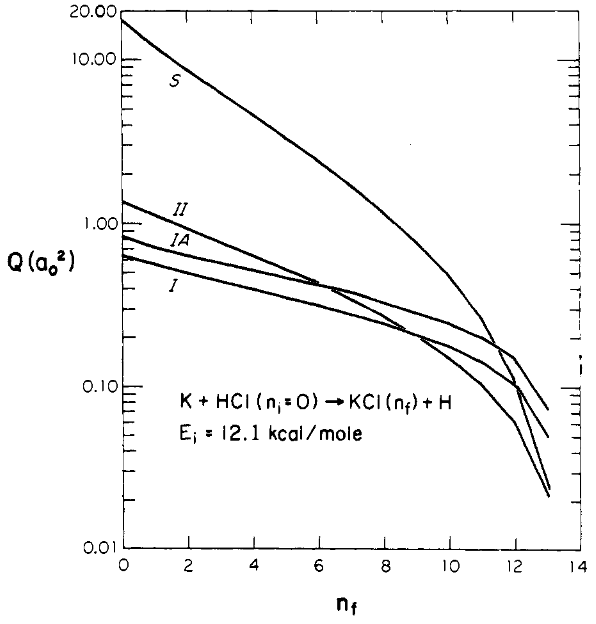

Figure 6. Reaction cross section into specified vibrational states of the product for K + HCl → KCl + H in the statistical phase space theory (S) and the nonstatistical phase space calculations I, IA, and II. The initial relative translational energy is 12.1 kcal/mol and the reagents are in the ground rotational-vibrational state.

The most striking aspect of the comparison of reaction cross sections in Table II is the difference between the rising cross section at high initial relative translational energy in the statistical phase space theory and the near constant or even decreasing experimental reaction cross section at the same energies. The nonstatistical calculations, however, are in qualitative agreement with experiment at these energies and calculation II is even in good quantitative agreement. By dividing the experimental reaction cross section by the statistical phase space theory reaction cross section we obtain an empirical energy dependent correction factor to the statistical phase space theory for K + HCl → KCl +

H. At the six energies where experimental reaction cross sections are available for the ground vibrational state we obtain in this way the correction factors 0.09, 0.12, 0.14, 0.14, 0.13, and 0.12 in order of increasing energy. The present nonstatistical calculations may be considered to provide a realistic physical explanation of the necessity for these correction factors.

A similar example involving the reaction cross section as a function of initial relative translational energy in this energy range is provided by the experimental measurements of Litvak et al.[10] on the reaction cross section for Rb + $CH_3I \rightarrow RbI + CH_3$ at initial relative translational energies of 2.8-36.4 kcal/mol. On the basis of an opacity analysis of the nonreactive scattering, Harris and Wilson[64] concluded the integral cross section rose from about 41 to 44 Å^2 as the initial relative translational energy increased from 3.15 to 3.93 kcal/mol. But Litvak et al.[10] found the reaction cross section decreased by about 15% in this energy range and by about 50% as the initial relative translational energy was further increased to 22.2 kcal/mol. The experimental results can be explained by the present theory by invoking a decreasing probability of strong coupling at larger impact parameters and higher translational energies in both the initial and final states. The inelasticity, if any, associated with weakly coupled flux at these energies and impact parameters would not be reactive scattering and the opacity analysis can overestimate the reaction cross section by relatively larger factors as initial translational energy increases.

In more general terms the results of the experimental studies of these two reactions can be interpreted[6e,9c] in terms of the average state-to-state transition probability[6] associated with reactive transitions being a decreasing function of initial translational energy at initial relative translational energies of about 10 kcal/mol. In other words the number of final states accessible (or classically the accessible phase space) is a rapidly increasing function of energy but the reaction cross section is not increasing in quantitative agreement with an expectation based on a constant state-to-state transition probability. The present theory offers a possible explanation based on the fact that many of the new final states opening up have high enough L_a and E_a that they are not strongly coupled to states of the reagents.

One difficulty with an opacity analysis of the nonreactive scattering of K + HCl is the large rotational inelasticity of the nonreactive scattering in this system.[30] For example, calculation II predicts that the contribution of strongly coupled collisions to rotational excitation of HCl ($n_i = 0$) is 25 Å^2 at E_i = 1.8 kcal/mol and 17 Å^2 at E_i = 2.88 kcal/mol. In addition there are contributions to the rotational excitation from the weak collisions.

It is encouraging that calculation II, which is more accurate than calculation I and than the statistical theory for E_i = 6.03-12.1 kcal/mol and $n_i = 0$, is also more accurate than these other methods for E_i = 1.8-2.15 kcal/mol and $n_i = 0$ and for E_i = 1.8 kcal/mol and $n_i = 1$. Also the largest discrepancies between theory and experiment are for E_i = 1.8 kcal/mol where the experimental errors are largest. The nonstatistical theory provides a clear prediction that the reaction cross section will decrease if the initial relative translational energy is raised higher than 12.1 kcal/mol. It would be interesting to test this experimentally.

The nonstatistical phase space theory is actually capable of very detailed predictions about the results of the reactive collisions and it would be interesting to test as many as possible of these against experiment or other dynamical theories. For example, the nonstatistical phase space theory predicts a final vibrational distribution which is not as steeply peaked at $n_f = 0$ as that predicted by the statistical theory (see Figures 4-6) and in some cases (see, e.g., Figure 4) it is even peaked at $n_f > 0$.

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Determination of Rate Constants for the Electroreduction of Aromatic Compounds and Their Correlation with Homogeneous Electron Transfer Rates

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Abstract: The rate constants for the electroreduction of 16 aromatic compounds, including hydrocarbons, nitriles, nitro compounds, and heterocyclic compounds, at a stationary mercury electrode in *N,N*-dimethylformamide solution were determined. After correction for diffuse double layer effects, the free energies of activation were calculated assuming an adiabatic electron transfer process. They were compared with those for the homogeneous electron exchange reactions which were calculated from reported kinetic data after correction for the diffusional contribution. The results show the existence of the correlation in which the free energies of activation for both the heterogeneous and homogeneous electron transfer reactions are nearly equal, with few exceptions, as predicted by the theories of Marcus and Hush. A correlation was also found between the free energy of activation and the reciprocal of the molecular radius. The absolute values for the free energies of activation, however, differ from those calculated by Marcus theory.

Electron transfer reactions are among the simplest of solution phase reactions and have been the subject of extensive theoretical and experimental studies.[1-19] These reactions involve no breaking or formation of chemical bonds, but rather only changes in the bond lengths and angles and changes in the molecular orientation of the solvent molecules. For the electron exchange reactions of large aromatic molecules, either in homogeneous solution

$$R + R\cdot^- \rightleftarrows R\cdot^- + R$$

or at an electrode

$$R + e \rightarrow R\cdot^-$$

the structural changes in the molecules are small, and the major contribution to the energy of activation is solvent reorganization.

Extensive development of the theory of electron transfer reactions has been accomplished by Marcus,[2] Hush,[3] Levich,[4] Dogonadze,[5] and many others. The theories of Marcus (and Hush) have been applied most frequently, since the consequences of the theoretical treatments are presented in a form which is conducive to experimental evaluation.