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An Approach to the Calculation of High-Energy Displacement Reaction Yields[1]

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Abstract: An attempt is made to calculate the reaction cross section for hot reactions of the type $ZY + X \rightarrow ZX + Y$, where X and Y are isotopes. For this purpose, a model is assumed which permits a simple (classical) treatment of the three interacting particles. The reaction cross section $\sigma(E)$ is obtained by averaging over initial conditions selected in a random manner, by the Monte Carlo method. The results are compared with those obtained by Karplus, *et al.*, for reactions $H_2(D_2) + T \rightarrow H(D)T + H(D)$ and with experiment. In all cases a good fit is obtained.

I. Introduction

Two different models have been used to investigate hot displacement reactions of the kind

$$ZY + X \longrightarrow \begin{cases} ZX + Y \\ YX + Z \end{cases} \tag{I.1}$$

taking place in the gaseous phase. In this reaction X is a hot atom moving with relatively high translational energies (above the threshold energy of the reactions under consideration) and ZY is a molecule which will be assumed to be static. The two parts of the original molecule are atoms or groups of atoms which can be assumed, in a first approximation, to behave as a single particle.

Both models were used to compute the total reaction cross section $\sigma(E)$ as a function of the kinetic energy of the hot atom.

The first model, suggested by Wolfgang and Cross[2a] and somewhat improved by Hsiung,[2b] is based on two principal assumptions: (a) the displacement reaction takes place by a direct billiard-ball-type collision between the projectile and the target atom; (b) the reaction will take place provided the target atom receives kinetic energy exceeding the binding energy between itself and the radical, while the incident hot atom is left with less kinetic energy than its binding energy to the radical.

The second model, which is due to Karplus, Raff, Porter, and Sharma,[3–7] was originally proposed for the analysis of collision reactions in experiments with crossed molecular beams and was lately applied to hot-atom chemistry as well.[8] Karplus and Raff computed differential cross sections for the reaction

$$CH_3I + K \longrightarrow KI + CH_3 \tag{I.2}$$

using a semiempirical potential field which was originally proposed by Blais and Bunker.[9,10] Concerning the reaction

$$H_2(D_2) + T \longrightarrow H(D)T + H(D) \tag{I.3}$$

Karplus, Porter, and Sharma calculated $\sigma(E)$ using a semi-quantum mechanical potential field computed by

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(1) Part of a study to be presented to the Hebrew University, Jerusalem, by M. Baer, in fulfillment of the requirements for a Ph.D. degree.

(2) (a) R. J. Cross and R. Wolfgang, *J. Chem. Phys.*, **35**, 2002 (1961); (b) C. Hsiung, Ph.D. Dissertation, University of Michigan, 1962.

(3) M. Karplus and L. M. Raff, *J. Chem. Phys.*, **41**, 1267 (1964).

(4) L. M. Raff and M. Karplus, *ibid.*, **44**, 1212 (1966).

(5) M. Karplus, R. N. Porter, and R. D. Sharma, *ibid.*, **40**, 2033 (1964).

(6) M. Karplus, R. N. Porter, and R. D. Sharma, *ibid.*, **43**, 3259 (1965).

(7) L. M. Raff, *ibid.*, **44**, 1202 (1966).

(8) M. Karplus, R. N. Porter, and R. D. Sharma, *ibid.*, **45**, 3871 (1966).

(9) H. C. Blais and D. L. Bunker, *ibid.*, **37**, 2713 (1962).

(10) H. C. Blais and D. L. Bunker, *ibid.*, **39**, 315 (1963).

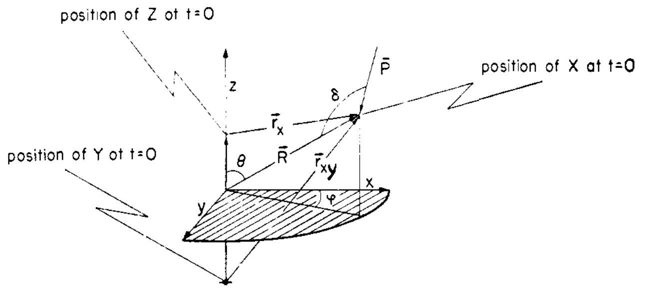

Figure 1. Coordinate space system of the three particles X, Y, and Z at time $t = 0$. The axis of the molecule ZY is along the z axis.

Karplus and Porter.[11] Lately this potential field was modified by Shavitt, Stevens, Minn, and Karplus,[12] and using this potential field Shavitt[13] has computed rate constants for the exchange reactions (I.3). Once given the potential field, the motion of each of the particles in this field is determined by the classical equations of motion and by the initial conditions.

The differences in the above two approaches reflect the different purposes for which they were devised. The first model aimed at examining whether the hot reaction is a simple displacement reaction resulting from a direct billiard-ball-type collision between the atoms X and Y. The criterion according to which this assumption was tested was the existence of an isotope effect in the two reactions

$$CH_4(D_4) + T \longrightarrow CH_3(D_3)T + H(D) \tag{I.4}$$

However, the model turned out to be an oversimplification and the calculations disagreed with the experimental results. It was therefore discarded by the authors themselves.[2a]

The second model had a much broader aim, namely to describe the reaction process fully and to determine a variety of properties found in experiment. The results were in good, and sometimes even excellent, agreement with experiment, but the computations involved were very lengthy and complicated.

The present work attempts to calculate the cross section for exchange reactions by assuming a model which permits a semi-analytic treatment of the behavior of the three particles involved in the reaction.[14] This model is related to the one-dimensional model treated by Mazur and Rubin[15,16] in that the potential field assumed is composed of cutoff potentials; however, the model is three dimensional and this extension obviously complicates the whole treatment. The computations involved are nevertheless comparatively simple and short. Another advantage of this model is that it can be used for a rather large variety of exchange reactions in which the radical is an atom or a group of atoms which can be considered as a single particle, and Y and X are isotopes. The model is tested by comparing the reaction cross section for the reaction (I.3) with those computed by Karplus and Porter,[11] as well as with experiment. The comparison with experiment is through the reaction integral R defined as

$$R = \int_0^\infty \frac{\sigma(E)}{E} \mathrm{d}E \tag{I.5}$$

The reaction integral for these two reactions has been determined experimentally by Seewald, Gersh, and Wolfgang.[17]

In section II, a description of the model is given, including a description of the reaction process. The theoretical and the experimental results are compared in section III and the conclusions summarized in section IV.

II. The Model

1. The Coordinate System and Initial Conditions.

Three particles, Z, Y, and X, take part in the reaction. We shall treat the reaction

$$ZY + X \longrightarrow ZX + Y \tag{II.1}$$

where Z is the radical with a mass M, Y is the target atom with mass m_y, and X is the projectile with mass m_x. The origin is assumed to be at the center of mass of the system ZY and the axis of the molecule to be along the z axis. The distance between Y and Z at time $t =$ 0 is L, and the projectile X is at the point **R**, where R is given, and the two other spherical polar coordinates θ and ψ which determine the direction of **R** are chosen at random (see Figure 1). Thus, at time $t = 0$, the position coordinates of the three particles are

$$\begin{aligned} &Z\left(0, 0, \frac{m_y}{M + m_y}L\right) \\ &Y\left(0, 0, -\frac{M}{M + m_y}L\right) \\ &X\,(R \sin\theta \cos\varphi,\ R \sin\theta \sin\varphi,\ R \cos\theta) \end{aligned} \tag{II.2}$$

The initial momenta of Z and Y are taken as zero. This assumption might influence the results at the very low part of the reaction zone, but its effect is negligible on the whole. As for the projectile, one finds that for a given initial kinetic energy E, the momentum **P** takes the form

$$\begin{aligned} P_x &= P(\cos\theta \cos\varphi \sin\delta \cos\eta - \\ &\qquad \sin\varphi \sin\delta \sin\eta + \\ &\qquad\qquad \sin\theta \cos\varphi \cos\delta) \\ P_y &= P(\cos\theta \sin\varphi \sin\delta \cos\eta + \\ &\qquad \cos\varphi \sin\delta \sin\eta + \\ &\qquad\qquad \sin\theta \sin\varphi \cos\delta) \\ P_z &= P(-\sin\theta \cos\eta \sin\delta + \cos\theta \cos\delta) \end{aligned} \tag{II.3}$$

where

$$P = (2m_xE)^{1/2}$$

and the angles δ and η are spherical angles fixing the direction of the vector **P** in a coordinate system in which **R** is in the direction of the z axis. These two angles are selected at random from their respective distributions as θ and φ.

We note that out of 18 initial conditions, 14 are fixed and 4 are determined at random. Of the latter, the two angles φ and η are chosen from a distribution between 0 and 2π, θ is selected from a distribution between 0 and π weighted by $\sin\theta$, and δ is selected from a distribution between $\pi/2$ and π weighted by $2 \sin\delta \cos$

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[11] R. N. Porter and M. Karplus, *J. Chem. Phys.*, 40, 1105 (1964).

[12] I. Shavitt, R. N. Stevens, F. L. Minn, and M. Karplus, *ibid.*, **48**, 2700 (1968).

[13] I. Shavitt, *ibid.*, **49**, 4048 (1968).

[14] M. Baer and S. Amiel, *Israel J. Chem.*, 7, 341 (1969).

[15] J. Mazur and R. J. Rubin, *J. Chem. Phys.*, **31**, 1395 (1959).

[16] R. J. Rubin, *ibid.*, 40, 1069 (1964).

[17] D. Seewald, M. Gersh, and R. Wolfgang, *ibid.*, **45**, 3870 (1966).

δ. The selection of θ is accomplished by taking cos θ to be uniform -1 and 1 and finding θ from this cosine value, and the selection of δ is performed by taking $\cos^2 \delta$ to be uniform between 0 and 1 and calculating δ from the negative square root of $\cos^2 \delta$.

2. The Potential Energy Field. As far as the coordinate system and the initial conditions are concerned, we have seen that Y and Z, the two components of the original molecule, were treated symmetrically. In order to preserve this symmetry in describing the potential energy field, the coordinate space will be divided into two parts by a plane perpendicular to the molecule axis and intersecting it at the midpoint. Thus, any collision between X and YZ that happens to occur above that plane will lead only, if at all, to the reaction

$$\mathrm{ZY} + \mathrm{X} \longrightarrow \mathrm{ZX} + \mathrm{Y} \qquad \text{(II.4)}$$

whereas if the collision happens beneath that plane, the only resultant reaction will be

$$\mathrm{ZY} + \mathrm{X} \longrightarrow \mathrm{YX} + \mathrm{Z} \qquad \text{(II.5)}$$

Therefore, in the special case where Z and Y are identical atoms, the computations are performed only once, and the results are multiplied by 2.

The potential energy field assumed in this model is

$$V(r_x,r_y,r_{xy}) = V_x(r_x,r_y) + V_y(r_y,r_x) + V_{x,y}(r_x,r_y) + V_{xy}(r_{xy}) \qquad \text{(II.6)}$$

where r_x is the distance between Z and X, r_y is the distance between Z and Y, and r_{xy} is the distance between X and Y.

$V_y(r_y,r_x)$ and $V_x(r_x,r_y)$ are two potential wells which replace the ordinary Morse potential of the target molecule ZY and of the newly formed molecule ZX, respectively; thus

$$V_y(r_y,r_x) = \begin{cases} 0, \ r_y > R_y; \text{ for any } r_x \\ -V_{0y}, \ \rho_y \le r_y \le R_y; \ r_x > R_x \\ \infty, \ r_y < \rho_y; \text{ for any } r_x \end{cases} \qquad \text{(II.7)}$$

and

$$V_x(r_x,r_y) = \begin{cases} 0, \ r_x > R_x; \text{ for any } r_y \\ -V_{0x}, \ \rho_x \le r_x \le R_x; \ r_y > R_y \\ \infty, \ r_x < \rho_x; \text{ for any } r_y \end{cases} \qquad \text{(II.8)}$$

The third term represents the potential when both isotopes X and Y are in close proximity to Z; thus

$$V_{x,y}(r_x,r_y) = \begin{cases} -V_0, \ \rho_x \le r_x \le R_x, \\ \qquad \rho_y \le r_y \le R_y \\ 0, \text{ elsewhere} \end{cases} \qquad \text{(II.9)}$$

The fourth term stands for the repulsion between X and Y and replaces the exponential term appearing in the Blais-Bunker potential

$$V_{xy}(r_{xy}) = \begin{cases} \infty, \ r_{xy} < \rho_{xy} \\ 0, \ r_{xy} > \rho_{xy} \end{cases} \qquad \text{(II.10)}$$

This potential field is assumed to be valid as far as reaction II.4 is concerned, *i.e.*, if the collision takes place above the mentioned plane. In reaction II.5 the index Z replaces the index Y. Part of the parameters are held fixed during the calculations, whereas the others are assumed to be a function of the initial energy E of X. In this sense, it seems that the potential energy field is not conservative. However, as we assume it to be dependent only on the initial energy E, it follows that for a given initial energy the potential $V(r_x, r_y, r_{xy})$ is conservative and the laws of mechanics can be applied.

The distances R_y and R_x stand for the region of attraction between Z and Y and between Z and X, respectively (see Figure 2). Both are estimated from the respective Morse potentials. ρ_y fixes the region of repulsion between Z and Y and is estimated from the Morse potential as well. The depths of the potential wells V_{0x}, V_{0y} are taken to be the depths of the respective Morse potentials

$$V(r_y) = V_{0y}(1 - e^{-\alpha_y(r_y - r_{0y})^2}) - V_{0y} \qquad \text{(II.11)}$$

$$V(r_x) = V_{0x}(1 - e^{-\alpha_x(r_x - r_{0x})^2}) - V_{0x} \qquad \text{(II.11')}$$

We assumed that Y and X are isotopes; therefore the two Morse potentials are identical and yield $R_x = R_y$ and $V_{0x} = V_{0y}$. As for V_0, it is assumed in that special case to be equal to V_{0x}. This choice of V_0 means that as long as the fourth term in the potential field (eq II.6) is ignored, the saddle point region which appears in every potential energy surface is not apparent yet. It therefore turns out that the only term responsible for this saddle point region is the fourth term, *i.e.*, the term that yields the repulsion between X and Y. The distance ρ_{xy} which appears in (II.10) is assumed to be energy dependent and will be determined by the equation

$$V(r_{xy})\big|_{r_{xy}=\rho_{xy}} - \frac{m_y}{m_x + m_y}E = 0 \qquad \text{(II.12)}$$

where $V(r_{xy})$ is chosen to be of the form

$$V(r_{xy}) = E_{ax}e^{-2\alpha(r_{xy} - r_0)} \qquad \text{(II.13)}$$

In this potential α is identical with α_{0x} which appears in the Morse potential (II.11′). The distance r_0 is defined as the closest approach between X and Y in the linear configuration Y–Z–X for which a reaction is still not possible. The reason for considering the linear configuration originates in the fact that the minimum-energy path lies entirely in this configuration. Thus, if X succeeds in approaching Y in the linear geometry up to a distance that is smaller than r_0, then a reaction does occur. This closeness of approach can be achieved only if the reduced particle X–Y has, in the respective center-of-mass system, a kinetic energy equal to or larger than E_{ax}. Since at time $t = 0$ the only particle possessing kinetic energy is the projectile and since the minimum energy required for performing the reaction is E_a (the threshold energy), we can easily derive the connection between E_{ax} and E_a.

$$E_{ax} = E_a\frac{m_y(m_x + m_y + M)}{(m_x + m_y)(m_y + M)} \qquad \text{(II.14)}$$

We notice that whereas α and E_{ax} are well determined, r_0 is not and will be computed by "trial and error."

It remains to deal with ρ_x which determines the region of repulsion between Z and X. This distance is the second energy-dependent parameter and will be extracted from the equation

$$V(r_x)\big|_{r_x=\rho_x} - \frac{M}{M + m_x}E = 0 \qquad \text{(II.15)}$$

where $V(r_x)$ is given by eq II.11′.

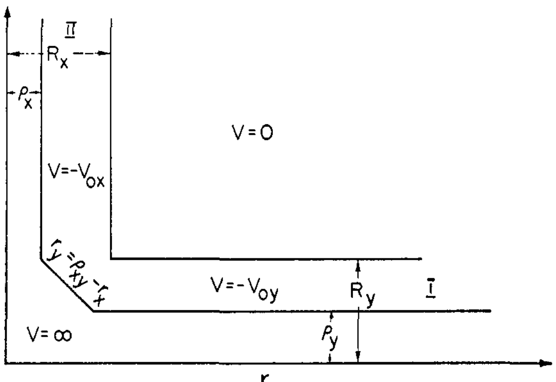

Figure 2. Potential energy surface for the linear configuration.

For a given initial energy E, the potential field in the linear geometry is shown in Figure 2.

We notice that the potential field defined is composed of cutoff potential terms. However, in order to conserve the soft nature of the interaction between the hot particle and the molecule, those components of the potential with which the hot atom may interact while still in possession of its initial kinetic energy E were made energy dependent. This requirement brought into that category the radius of repulsion between X and Y, *i.e.*, ρ_{xy} and the radius of repulsion between X and Z, *viz.* ρ_x.

3. **The Reaction Process.** In order to describe the reaction process we shall refer to the linear configuration. Since the potential energies in the different regions are constant, the relative motion of the three particles can be characterized by a rectilinear motion of the configuration point inside the different regions of the r_x, r_y space.[15,16,18] The transformation from the system of three "linear" particles to the configuration point system is accompanied by transformation from the rectangular coordinates system (r_x,r_y) to another rectangular system (S_x,S_y) where the distances r_x and r_y are skewed. The transformation from (r_x,r_y) to (S_x,S_y) is

$$S_x = r_x + \frac{m_y}{m_x + m_y} r_y$$

$$S_y = \frac{1}{M + m_y}[m_y M(m_x + m_y + M)]^{1/2} r_y \qquad \text{(II.16)}$$

As a result of this transformation, the five lines which define the potential energy surface, $r_x = \rho_x$, $r_x = R_x$, $r_y = \rho_y$, $r_y = R_y$, and $r_y = \rho_{xy} - r_x$ transform into the lines

$$S_y = \left(\frac{M(M + m_x + m_y)}{m_x m_y}\right)^{1/2}(S_x - \rho_x)$$

$$S_y = \left(\frac{M(M + m_x + m_y)}{m_x m_y}\right)^{1/2}(S_x - R_x)$$

$$S_y = \frac{1}{M + m_y}\left(\frac{m_y M(M + m_x + m_y)}{m_x}\right)^{1/2}\rho_y \qquad \text{(II.17)}$$

$$S_y = \frac{1}{M + m_y}\left(\frac{m_y M(M + m_x + m_y)}{m_x}\right)^{1/2} R_y$$

$$S_y = \left(\frac{M(M + m_x + m_y)}{m_x m_y}\right)^{1/2}(\rho_{xy} - S_x)$$

respectively (see Figure 3a and b).

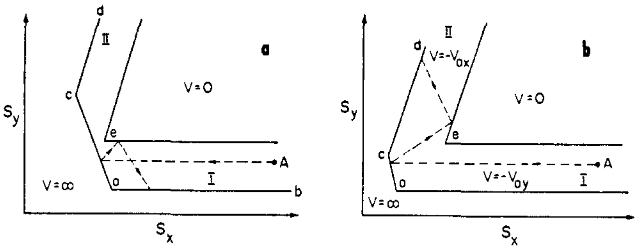

Figure 3. Skewed form of potential energy surface in S_x,S coordinate system (linear configuration).

We recall that since ρ_x and ρ_{xy} are energy dependent, the two lines (ac) and (cd) are energy dependent too and change their positions accordingly.

For low energies, the skewed line (ac) is too close to the corner (e), and the configuration particle (which started at point A) hits this line and is reflected back into region I (see Figure 3a). As the energy increases, the line (ac) moves away from the corner (in such a manner that the angle of inclination is conserved), thus increasing the gap through which the particle is supposed to move into region II. The lowest energy for this is the case is E_a, the activation energy of the reaction (see Figure 3b).

The nonlinear, or the general, case was treated by a computer. To do this, a program was written computing the relative velocities and positions of the three particles following each of the two-body (hard-sphere) collisions. A reaction will occur if Y reaches the boundary of attraction before X does so, and if the translational energy E_{xz} of the reduced particle X–Z fulfills the condition

$$E_{xz} < V_{0x}/\cos^2 \delta$$

where δ is the angle of collision, *i.e.*, the angle between the trajectory of the reduced particle and the radius of the square well at the point of contact. This condition is derived by applying the laws of conservation of energy and momentum for two particles in a square well of depth V_{0x}. This means that for the particle to be able to get out of the square well, not only should its kinetic energy be higher than V_{0x} but the "component" of the kinetic energy along the perpendicular to the potential well should also be higher than V_{0x}.

4. **Computation of the Total Cross Section.** If R is the initial distance between X and the center of mass of the two particles YZ and if $P(E,\theta,\varphi,\delta,\eta)$ is the probability of obtaining a reaction when the initial energy of the projectile is E and the initial angles are θ, δ, and η, then the total reaction cross section is given in the form

$$\sigma(E) = \pi R^2 \int_{\theta_1}^{\theta_2}\int_{\varphi_1}^{\varphi_2}\int_{\delta_1}^{\delta_2}\int_{\eta_1}^{\eta_2} P(E,\theta,\varphi,\delta,\eta) \sin\theta \; d\theta \frac{d\varphi}{2\pi}\, 2 \sin\delta \cos\delta \, d\delta \frac{d\eta}{2\pi} \qquad \text{(II.18)}$$

where θ_i, φ_i, δ_i, and η_i ($i = 1, 2$) are defined through the condition

$$P(E,\theta,\rho,\delta,\eta) = \begin{cases} 1, \; \theta_1 \le \theta \le \theta_2,\; \varphi_1 \le \varphi_2, \\ \quad \delta_1 \le \delta \le \delta_2, \\ \quad \eta_1 \le \eta \le \eta_2 \\ 0, \text{ elsewhere} \end{cases} \qquad \text{(II.19)}$$

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(18) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 102.

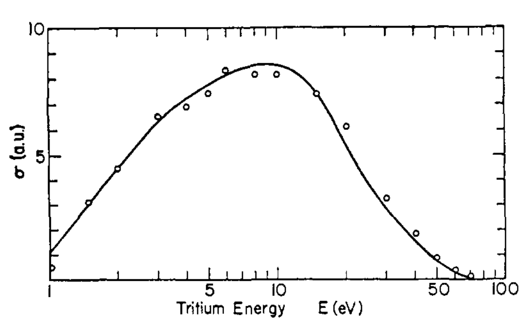

Figure 4. Total reaction cross section as a function of tritium energy in the laboratory system for the reaction $H_2 + T \rightarrow HT + H$: curve, results of Karplus, *et al.*; points, present model.

The limits of the integration are functions of E and of other magnitudes defining the reaction. The integration is, of course, performed numerically, using the Monte Carlo method. If, for a given E and R, one gets from N trajectories, N_r reactions, then $\sigma(E)$ takes the form

$$\sigma(E) = \pi R^2 \frac{N_r(E,R)}{N} \qquad \text{(II.20)}$$

$\sigma(E)$ is, of course, independent of R.

III. Calculation and Results

As concrete examples for testing the model, we chose the various (H_2,H) systems, *viz.* (H_2,T), (D_2,T), and (HD,T). The three systems differ only in the masses of the two atoms of which the hydrogen molecule is composed, whereas the potential field is assumed to be the same.

The total cross section $\sigma(E)$ was computed using the following numerical values: $V_0 = V_{0x} = V_{0y} = 4.4$ eV;[11] $\alpha = 1.89$ Å^{-1};[11] $R = 3$ Å; $L = 0.75$ Å;[11] $R_x = R_y = 1$ Å; $\rho_y = 0.4$ Å; $r_0 = 1.85$ Å; $E_{ax} = 0.21$ eV. The values of r_0 and E_{ax} were determined using the experimental value of the threshold energy E_a for the reaction

$$H_2 + T \longrightarrow HT + H$$

found by Kuppermann and White,[19] *viz.*, $E_a = 0.33$ eV. Since the same values of E_{ax} and r_0 were used for all the systems, it is possible to derive the threshold energy for the other reactions under discussion by the use of eq II.14. Thus, for the reaction

$$D_2 + T \longrightarrow DT + D$$

the value of $E_a = 0.30$ eV is derived; for the reaction

$$HD + T \longrightarrow HT + D$$

the value of $E_a = 0.27$ eV is derived; and for the reaction

$$HD + T \longrightarrow DT + H$$

the value of $E_a = 0.40$ eV is obtained.

Although this model yields the threshold energies of the last three reactions, some caution must be taken since they were obtained neglecting the zero energy of the respective target molecules.

Figures 4 and 5 show the total reaction cross section $\sigma(E)$ as a function of E for reactions I.3. The curves are those computed by Karplus, *et al.*, whereas the points represent the results of the present computations.

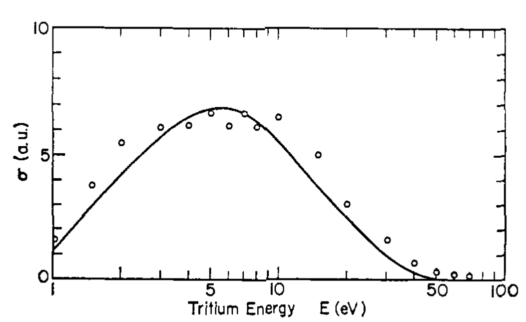

Figure 5. Total reaction cross section as a function of energy for the reaction $D_2 + T \rightarrow DT + D$: curve, results of Karplus, *et al.*; points, present model.

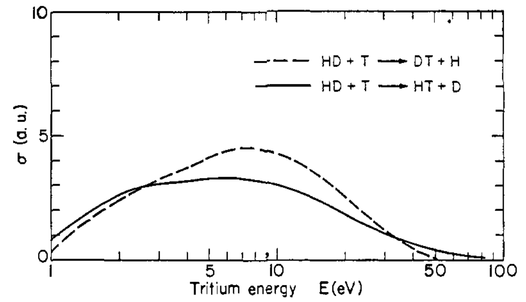

Figure 6. Total reaction cross section as a function of energy: (———) $HD + T \rightarrow HT + D$; (- - -) $HD + T \rightarrow DT + H$.

We notice that the fit for the (H_2T) system is excellent. As for the (D_2,T) system, it seems that the present calculation yields a somewhat larger cross section, but again the fit is good.

Concerning the comparison of the theory with experiment, the only experimental results relevant to these curves involve the concept of the reaction integral R. The ratio of reaction integrals R_{H_2}/R_{D_2} predicted by the present model is 1.15; the theoretical calculation of Karplus, *et al.*, yields the result of 1.37, while the experimental value is 1.15.[20] Another system for which the comparison with experiment is possible is the (HD,T) system. Seewald and Wolfgang[20] found the ratio of the reaction integrals R_{HT}/R_{DT} to be 0.62 ± 0.06. The present model yields the result of 0.89. The total reaction cross section as a function of energy for these reactions is given in Figure 6.

IV. Conclusion

The model discussed in this paper enables the computation of hot displacement reaction cross sections for reactions of the type $ZY + X \rightarrow ZX + Y$, where X and Y are isotopes and Z is an atom or group of atoms which is believed to behave as a single particle. The model follows the general lines of the model assumed by Karplus and Raff, but the different components of the Blais–Bunker potential used by Karplus and Raff are replaced by cutoff potentials, thus permitting a relatively simple treatment of the three atoms X, Y, and Z, during the reaction process. In this sense the model is closely related to the kinematic model of Suplinskas.[21] However, the main difference between the present model and the kinematic model stems from the fact that part

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(19) A. Kuppermann and J. M. White, *J. Chem. Phys.*, **44**, 4352 (1966).

(20) D. Seewald and R. Wolfgang, *ibid.*, **46**, 1207 (1967).

(21) R. J. Suplinskas, *ibid.*, **49**, 5046 (1968).

of the parameters determining the potential field, which governs the motion of the particles is assumed to be dependent on the initial energy of the hot atom X. Doing this we reproduced what the hot particle "sees" from the true surface while possessing its high initial energy. This assumption has fully justified itself, because in contrast to the kinematic model, the present model yields a good fit with the curve for the reaction $D_2 + T \rightarrow DT + D$ computed by Karplus, *et al.*, and also the right isotopic effect for the reactions $HD + T \rightarrow H(D)T + D(H)$. For the respective isotopic ratio R_{HT}/R_{DT} we derived the value of 0.89, the experimental value is 0.62 ± 0.06, and Suplinskas' value is 1.6.

The good fit obtained with the theoretical calculations of Karplus, Porter, and Sharma and with the different experiments indicates that the main repulsive interaction during the reaction process is between the hot atom and the atom to be replaced, *viz.*, atom Y. The nature of this repulsion is not of a pure billiard-ball type; however, it is not of too soft a nature either, since, in contrast to the hard-sphere approximation, the energy-dependent hard-sphere approximation yields the correct results.

The two main features of this model consist (1) in its being easily handled since the calculations involved are short (about 5 to 10 min for each curve) and (2) in its applicability to a large variety of reactions, since the potential field assumed is constructed using the experimental value of the threshold energy for the reactions and other parameters derived from the Morse potential of the molecule ZY.

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The Isoelectronic Principle and the Accuracy of Binding Energies in the Hückel Method

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Abstract: In the Hückel and other methods, binding energies are calculated by subtracting the sum of orbital electronic energies for the molecule from the sum of orbital electronic energies for the separated atoms, and not considering the internuclear repulsion. Since this last may be several orders of magnitude greater than the binding energy, reasonable results could not be obtained without an approximate cancellation with another neglected term. It is shown that such a cancellation is a consequence of the isoelectronic principle (invariance of binding energy to change in atomic number of constituent atom). Numerical examples are given.

In a number of *a priori* and semiempirical methods, of which the extended Hückel method[2] is the best known, one calculates molecular binding energies by subtracting the electronic energy (sum of orbital contributions) of the molecule from the sum of the electronic energies of the atoms, without considering the internuclear repulsion. If we accept the argument that the parameterization in the method effectively simulates a Hartree–Fock calculation, the "electronic energies" are really sums of orbital energies. To get the true electronic energies of atom or molecule, one must subtract off in each case the interelectronic repulsion, which is being counted twice. Thus the above recipe will be valid if

$$V_{NN} \approx V_{ee}^{m} - \sum_{A} V_{ee}^{A} \equiv \Delta V_{ee} \qquad (1)$$

where V_{ee}^{m} and V_{ee}^{A} are the interelectronic repulsions (expectation values) for the molecule and for atom A, and V_{NN} is the internuclear repulsion.[3] The binding energy may be orders of magnitude smaller than V_{NN}. Thus the error in eq 1 must be small (*i.e.*, of the size of the binding energy itself) if reasonable binding energies are to be obtained from a wave function which is reasonable in other respects. Below, we show[4] that this is in fact true in general, being a consequence of the isoelectronic principle.

The proof is closely related to the derivation of a formula[5] for calculating diamagnetic shieldings in molecules, also starting from the isoelectronic principle. According to this principle, two isoelectronic species have the same binding energies if they differ only by a change by unity in a nuclear charge. The example of CO *vs.* N_2[6] is perhaps the best known; one can easily find others.[7] Writing Z_B for the charge of nucleus B, we express this as

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[3] Note that it is the *change* in V_{ee} from atoms to molecule which must be approximately equal to V_{NN}, not V_{ee} itself as has been sometimes stated.

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