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OF BIMOLECULAR EXCHANGE REACTIONS.

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MONTE CARLO CALCULATIONS. III. A GENERAL STUDY
OF BIMOLECULAR EXCHANGE REACTIONS.*

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ABSTRACT

About 10,000 planar trajectories were computed for the reaction
 $A + BC \rightarrow AB + C$. Principal variables were the reactant masses, the type
of interaction potential, and the exothermicity. The activation energy was
assumed negligible. The results consist of distributions of product
emission angle and vibrational and rotational energy.

For the simplified interaction potentials used, the following generali-
zations hold: a normal reaction is one in which AB is most likely to recoil
backwards along the approach line of A; the energy of reaction is predomi-
nantly converted to internal excitation of the product AB; and the final
rotation of AB absorbs as large a fraction of the initial orbital angular
momentum as is consistent with the reaction energy. If the moment of
inertia of AB is too small to allow this fraction to be close to unity,
unusual distributions of emission angle and rotational excitation occur.
Independently, lowered values of the internal energy of AB are observed if
A is much less massive than either B or C, or if the interaction potential

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before the Division of Physical Chemistry, 144th National Meeting, American
Chemical Society, Los Angeles, April 1963.

In part II of this series¹ a computational study was made of the

(1) N. C. Blais and D. L. Bunker, J. Chem. Phys., in press (Dec. 1, 1962).

Mathematical procedures used are partly described in part I: D. L.

Bunker, J. Chem. Phys. 37, 393 (1962).

reactions of alkali metal atoms with methyl iodide. Distributions of vibrational and rotational energy (E_{vib} and E_{rot}) of the diatomic product alkali iodide, and of the angle of emission of methyl in the center-of-mass coordinate system (θ , measured from the initial alkali direction), were obtained for properly weighted random distributions of starting conditions. In these calculations methyl was treated as a single particle.

The results of this investigation were compared with those of molecular beam studies² of the same reactions. Quantities for which comparison was

(2) J. A. Norris, G. H. Kwei, and D. R. Herschbach, J. Chem. Phys., to be published; J. L. Kinsey, G. H. Kwei, and D. R. Herschbach, ibid., to be published.

possible were the most probable values of ($E_{\text{vib}} + E_{\text{rot}}$) and θ . The former were found to be in agreement provided the interaction potential satisfies a criterion recently discussed by Simons³ (hereafter called the Simons

(3) J. Simons, Nature 186, 551 (1960).

criterion): there shall be much attraction between reactants and little repulsion between products. In the language of the analogy of a mass point

sliding on a potential surface, this is a requirement that the "downhill" part of the surface shall occur before the turning point is reached. The most probable values of θ , computed and experimental, were in agreement independently of whether the Simons criterion was met.

The success of these comparisons motivated the extension of the computational technique to the general study of bimolecular exchange reactions, for which the results are reported in this paper. Product energy and angle distributions were computed for a set of hypothetical reactions

for which the assumptions of no activation energy and of planar trajectories were again made. Approximately 10,000 trajectories were computed in groups of about 200. The group variables were: the masses of A, B, and C; the exothermicity of the reaction; whether the interaction potentials were of the Simons or of the opposite type;⁴ whether both ends of BC were reactive

(4) Figs. 2 and 7 of part II, respectively; functional forms given in text.

(not true in part II); whether the reaction was assumed to occur in a molecular beam or bulk gas environment; and various special tests, the usefulness of which will become apparent later. The object of this work was less the search for agreement with individual laboratory experiments than the attempt to understand some of the dynamical features of this general type of reaction.

MATHEMATICAL DETAILS

The mathematical procedures were for the most part identical with those described in parts I and II. Only the variations are tabulated here.

In part II it was a good approximation to regard θ , the angle of emission of species C, as identical with an angle measured from the initial A direction to the line joining B and C when this line had attained a length of at least $10 \text{ \AA}$. When B is not the most massive particle, the line to which θ is measured must be the one joining C with the center of mass of AB. This refinement was accomplished by straightforward geometric calculations which need not be described in detail. In addition, certain reactant configurations which will be identified below give rise to an "exit impact parameter" -- the velocity vector of C is not almost parallel to the line defining θ . Compensation for this effect involved determination of the final derivatives of the variables (using the matrix procedure already present in the program), resolution of the C velocity vector along the line drawn to the AB center of mass, and application of an angular correction whose tangent is given by the vector component ratio. These two corrections were incorporated into the Stretch program midway through the calculations; angular distributions already calculated were corrected, if necessary, with an auxiliary IBM 704 program.

Calculations embodying the possibility that B and C are identical and that the products of the reaction may also be AC + B required the only interaction potential not already described in part II. A highly artificial one was used: as long as the distance relationship $(AB) < (AC)$ was satisfied, the potential was identical with the one used when AC was not a

possible product. When $(AB) > (AC)$, the roles of these two distances in the potential function were simply interchanged. This results in a symmetric potential surface with discontinuities in its derivatives along the locus $(AB) = (AC)$. Such an interaction potential is defined merely as a means of comparing the dynamics of the double-ended potential with those of the single-ended one, by ascertaining the magnitude of the changes arising in the computed results.⁵

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- (5) Whenever this potential was used the quantity assigned a constant value in the starting conditions was x rather than r_1 , and the angle ζ had the initial range $0 - \frac{1}{2} \pi$ (notation of part II). A test showed this was immaterial within the noise level of the results.
-

When the reaction is assumed to occur under bulk gas conditions, the analysis of rotational energy distributions given in part II must be modified. In Eq. 7 of part II v appears before the exponential as a cube rather than a square; the resulting expected distribution of E_{rot} , replacing Eq. 23, is⁶

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- (6) In the notation of part II, the masses of A, B, and C are m_1 , M , and m_2 respectively; b^* is the maximum allowed impact parameter.
-

$$n(E_{\text{rot}}) = \exp[-M(m_1 + m_2 + M)E_{\text{rot}} / (m_1 + M)(m_2 + M)b^{*2}f^2kT]$$

in which T is now the temperature of the gas (replacing the translational temperature of one of the molecular beams). The average fraction of angular momentum appearing as product rotation, f , is now determined from a straightforward plot of $\log n$ vs E .

PRINCIPAL RESULTS

The following cumbersome but mnemonic notation will be adopted to describe combinations of reactant masses. Let L (light) signify a particle whose mass is 2 AMU, M (medium) one whose mass is 16 AMU, and H (heavy) one whose mass is 128 AMU. A parenthetical expression containing the symbolized masses of A, B, and C in order from left to right will be written, thus: (M + LH) means that particle A has mass 16, B has mass 2, and C has mass 128.

Figure 1 shows the complete distribution-type results for ten mass combinations when the interaction potential is exactly the same as in part II (Fig. 2). The exothermicity is about 20 Kcal, and the equilibrium separations are (throughout this paper) 3.23 Å for A-B and 2.139 Å for B-C. The first nine results are for (M + XY) where XY represents all possible combinations of M, L, and H. The tenth is for (L + HH) and was obtained in order better to characterize an anomaly which will be defined in the next paragraph. An additional case, (H + HH), gave results identical with (M + MM) and is not shown. The quantity f is the average fraction of the initial angular momentum which finally appears as rotation of the diatomic product AB.

These results exhibit among them all the principal features elucidated by the investigation. The E_{vib} distributions may be ignored for the time being; the results of part II suggest that the average E_{rot} will vary significantly from case to case, so that if $(E_{vib} + E_{rot})$ shows regularities E_{vib} cannot (and vice versa). The statistically significant deviations from $(E_{vib} + E_{rot})$ peaked at the energy of the reaction occur for (M + HH)

and (L + HH). The θ distributions mostly progress downward from $\theta = 0$ to $\theta = 180^\circ$, at a greater or lesser rate; the exceptions are (M + LH), (M + LM), and perhaps (M + MH). These have θ distributions peaked near the middle of the range and f values substantially less than 1. This phenomenon will hereafter be referred to as anomaly I, and the lowered peak value of $(E_{\text{vib}} + E_{\text{rot}})$ observed when A is less massive than B or C as anomaly II. It will become apparent later that anomalies I and II cannot occur together.

In an effort to determine the detailed differences between the normal results, as exemplified by (M + MM), and those obtained when anomaly I or II is present, calculations designed to facilitate the correlation of initial and final conditions were carried out. Numerous individual trajectories were also examined. The following explanations are indicated.

The Normal Case

The trajectories are primarily simple; the (AB) distance decreases monotonically to a minimum, then oscillates while the (BC) distance increases monotonically (see Fig. 3a of part II). The three particles tend to become collinear when close together; about half the time the A-B-C angle is within 45° of 180° (this is equally true of the anomalous cases). This figure would no doubt be increased if more directional potentials were used. There is no apparent correlation between intermediate A-B-C angles close to 180° and any of the final properties of the trajectory. In fact, the only trajectory parameter which correlates with the results in any way is the impact parameter b .

Figure 2a shows the relation between b and θ for an (M + MM) calculation with the following special features: the starting distributions of BC

rotation and vibration were eliminated (set to 0); the initial relative velocities of A and BC were all equal to the most probable value rather than distributed; the probability of a given value of b is uniform, rather than weighted as b . There is a correlation between small b and small θ ; θ values near 180° tend to come from the largest b 's in the distribution. For other normal cases, related results were obtained. If the θ distribution is more sharply peaked at 0° (e.g., M + HM) the θ values in a plot like Fig. 2a remain small out to larger b values; if the θ distribution is nearly flat (e.g., M + LL) divergence from $\theta \approx 0$ occurs at smaller b . Inspection of individual trajectories shows that near the minimum interatomic distances the aggregate of three particles is rotating most rapidly when the overall θ distribution is flat and least rapidly when it is sharply peaked, and auxiliary calculations confirm that the normal θ distributions have slopes whose magnitude increases in order of increasing minimum average A-B-C moment of inertia and decreasing average initial angular momentum.

The reaction therefore must occur as follows. For small b , A approaches BC and reacts smoothly with it without compressing the B-C bond; AB recoils along the approach line, usually carrying most of the reaction energy as vibration and most of the angular momentum as rotation. For large b , the picture is the same except that the complex A-B-C rotates through a portion of a revolution during its lifetime, giving rise to a trajectory of the type illustrated in Fig. 3a. It should be noted here

that if the maximum allowed b is related to the reaction cross section, so is the shape of the θ distribution.

Anomaly I

Anomaly I occurs whenever the average angular momentum per collision exceeds that calculated for the diatomic product AB with the assumption that all the energy of reaction appears as product rotation. That is,

$$\mu \bar{v} b^* > (2IQ)^{\frac{1}{2}},$$

where μ is the reduced mass of A and B, $\bar{v}$ their average relative velocity, b^* the most probable impact parameter, I the moment of inertia of AB, and Q the energy of reaction. The greater the inequality, the more severe the anomaly. For (M + LH), the ratio of $\mu \bar{v} b^*$ to $(2IQ)^{\frac{1}{2}}$ is about 1.4; for (M + LM), it is slightly greater than 1.

Since the angular momentum cannot be both conserved and largely converted to product rotation, the low f values (and the flat E_{vib} distributions) associated with anomaly I are immediately explained. The most obvious explanation of the θ distributions, viz. that the products must be emitted with an "exit impact parameter" in order to conserve angular momentum, also appears to be the correct one. A correlation between b and θ , obtained under the same conditions as in Fig. 2a, is shown in Fig. 2b. The angle anomaly is present for small values of b . The trajectories show frequent complexities at relatively large interatomic distances (there is an appreciable chance of no reaction), but rotation of the overall complex is slow and the lifetime of the complex small compared to its period of revolution. An inferred typical trajectory, whose features

are approximately independent of b , is illustrated in Fig. 3b. The product AB continues to carry nearly all the internal energy.

Anomaly II

Inspection of the trajectories for $(M + HH)$ and $(L + HH)$ reveals that there are no qualitative differences from the normal case -- the amplitude of vibration of AB is simply smaller in these cases. One has therefore a purely kinematic effect in which the transfer of momentum to C is facilitated by the small mass of A.

Presence of the partial tendency for the atoms to become collinear during reaction allows one to attribute a certain amount of reality to the analogy of a mass point sliding on a potential surface. A partial explanation, or at least isolation of a kinematic feature peculiar to reactions subject to anomaly II, can be attained in this way.⁷

(7) This discussion supersedes one given by D. L. Bunker, *Nature* 194, 1277 (1962).

Three features of the sliding mass point analogy are sensitive to the masses of the reactants.⁸ The potential surface apex angle has been

(8) S. Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes (McGraw-Hill Book Company, Inc., New York, 1941), pp. 100-103.

discussed by F. T. Smith⁹ as a possible factor in the appearance of products

(9) F. T. Smith, *J. Chem. Phys.* 31, 1352 (1959).

with initial energy less than Q . But since the requirements for a small apex angle exactly coincide with those for the appearance of anomaly I (not II), the apex angle cannot be a major factor in the production of anomaly II. (Smith's theory, however, agrees moderately well with the computed E_{vib} distributions, for reasons which will be discussed later.)

The mass of the sliding object representing the system is equal¹⁰ to

(10) The apparent asymmetry of this statement arises from an arbitrary choice of methods of scaling the potential surface. Other equally valid procedures exist; those in which this paragraph becomes untrue will also have different apex angles and scale factors.

the reduced mass of the reactants A and BC. This mass will be smallest (and therefore most easily deflected into a vibrationless path in the exit valley) when either of the reactants is very light; since $(M + LL)$ does not show anomaly II, the representative mass is not the major part of the explanation.

Finally, the potential surface must be scaled in the direction of the exit valley by a factor which approaches extreme values only if the mass of A or C is very small. These extreme values are moreover of opposite character: the surface is compressed along the A-B direction if C is light, extended if A is light. Thus the radius of curvature at the turning point becomes very large (and the mass point might be most easily deflected into a vibrationless trajectory) only under the conditions in which one observes anomaly II.

It seems difficult to make a quantitative theory of this effect, or

even to test the hypothesis further by varying (independently of the particle masses) the radius of curvature of the rather clumsily defined potential surfaces involved in this study. However, one might predict that anomaly II would be comparatively insensitive to the exact form of the interaction potential. The scale factor can vary over more than a factor of ten for laboratory reactions, and it is difficult to imagine a change of this magnitude arising in the curvature of the surface when the potential function is altered.

An illustration of how anomaly II might arise is given, in terms of the potential surface analogy, in Fig. 4.

Other Calculations

Exothermicity

The first nine calculations in Fig. 1 were repeated with the interaction potential altered in such a way as to provide a fivefold increase (to about 100 Kcal) in exothermicity and no other changes. The $E_{\text{vib}} + E_{\text{rot}}$ distributions were unaffected except for minor changes in their width. For all except the anomaly I calculations, the θ distributions were unaffected and the E_{vib} peaks shifted to the right by an amount commensurate with the E_{rot} distributions remaining unchanged. Where anomaly I had appeared in the 20 Kcal calculations, 100 Kcal exothermicity caused an increase in f and a shift of the θ distributions towards those expected for the normal case. All this is exactly in accord with the explanations given above. The 100 Kcal θ distributions for (M + LM) and (M + LH) are shown in Fig. 5.

The Simons Criterion

All the results thus far given were for potential functions which satisfied the Simons criterion, with high reactant attraction and low product repulsion. The opposite type of potential surface, in which most of the kinetic energy is liberated during the departure of particle C, was employed in duplicate calculations for the 20 and 100 Kcal versions of each of the following cases: (M + HH), (M + MH), (M + LM), and (M + LH).

The θ distributions and f values were unchanged -- the former completely, the latter except for increased noise and ill-definition of their corresponding E_{rot} distributions. The $E_{\text{vib}} + E_{\text{rot}}$ distributions, on the other hand, became exothermicity-dependent and wildly unpredictable (see Fig. 6). In no case, however, did an increase in the most probable value of $E_{\text{rot}} + E_{\text{vib}}$ appear.

The conclusion is that conformity with the Simons criterion is a good but not infallible test of the likelihood of product vibrational excitation. In one case it is not necessary (M + LH, 100 Kcal), and in others it is not sufficient (viz., anomaly II).

The Double-Ended Potential

A potential function (described above) in which A and C attracted rather than repelled was used for recalculation of the cases (M + MM), (M + LL), and (M + HH). The possible products were $AB + C$ or $AC + B$. The exothermicity was 100 Kcal and the Simons criterion was satisfied. An additional calculation was done for (M + HH) without the Simons condition.

Some representative results are shown in Fig. 7.

The changes are minor in view of the drastic nature of the potential function alteration. The slopes of the θ distributions are different from those for corresponding mass combinations in Fig. 1; where flattening occurs, small increases are noted in the number of complicated trajectories, the lifetimes of the A-B-C complexes and the amount of spread in b vs θ correlations similar to Fig. 2. There is for some reason a small increase in the tendency for A-B-C to be collinear.

The energy distributions are unchanged except for the appearance of small secondary peaks. These are practically invisible in the $E_{\text{vib}} + E_{\text{rot}}$ distributions, but can be seen at the left in the E_{vib} distributions of Fig. 7. This feature is not related to the "crease" in the potential surface. This is shown by the shaded subdistributions, which contain all those trajectories which passed through the isosceles configuration $(AB) = (AC)$ an odd number of times (usually just once). Unfortunately the number of trajectories leading to E_{vib} in the secondary peaks is so small that it is impossible meaningfully to correlate them with collision parameters. These trajectories do however have a feature in common, which is illustrated in Fig. 8. It is possible that the secondary energy peaks are simply an especially prominent bit of the fine structure all the distributions undoubtedly possess.

Molecular Beam vs Bulk Gas Conditions

Normally the distributions of starting conditions for the trajectories were constructed with the assumptions that the vibrational and rotational

temperatures of BC were 100°K, the temperature involved in the distribution of relative velocities of A and BC was 750°K, and the unnormalized distribution of relative velocities was

$$n(v) = v^2 \exp(-\mu v^2 / 750k) .$$

This corresponds roughly to the molecular beam experiments on alkali + methyl iodide that were simulated in part II. Selected calculations were duplicated with both temperatures set to 300°K and

$$n(v) = v^3 \exp(-\mu v^2 / 300k) ;$$

no significant differences were found. This indicates that should the same reaction be studied under both molecular beam and (for example) spectroscopic conditions, the results may be compared directly within the noise level of the calculations (with attention to the obvious fact that one type of experiment usually measures $E_{\text{vib}} + E_{\text{rot}}$ and the other E_{vib} only).

The Role of the Impact Parameter

Several test calculations were carried out in an effort to correlate b with other features of the trajectories than those involved in the explanations given above. This was done in part because of the results of part II, and in part because of experimental and other computational studies which have meanwhile become available. The results are generally negative.

In part II it was observed that whenever b or the total angular momentum per collision was identically zero, the trajectories were very complicated and the product rotational excitation was extremely small (no significant equal-and-opposite final orbital and rotational angular momenta developed). This was for a set of mass combinations most nearly

equivalent, in this study, to $(M + HM)$. For $(M + HH)$, neither of these statements is true. Since the phenomenon is apparently not subject to generalization, it was not explored further.

Recent molecular beam experiments¹¹ on $K + HBr$ have been interpreted

(11) D. Beck, E. F. Greene, and J. Ross, J. Chem. Phys., to be published.

as evidence that the reaction probability abruptly decreases when b becomes so large that anomaly I would be expected to appear. In anomaly I calculations such as $(M + LH)$ about half the trajectories do not lead to reaction; however, there is no apparent correlation between reaction-no reaction and b . Since the calculated non-reactive trajectories tend to reverse while the separation of A and BC is still large, the properties of the interaction potential at large distances may be a factor here.

Finally, although E_{rot} correlates with b , as would be expected if all the angular momentum appears as product rotation, there is in general no reliable connection between b and E_{vib} even though one may appear if b is the only variable in the starting conditions (with a different potential function).¹² A corresponding lack of correlation occurs for b and

(12) J. C. Polanyi and S. D. Rosner, J. Chem. Phys., to be published.

$(E_{vib} + E_{rot})$, and also for θ and $(E_{vib} + E_{rot})$ since b and θ are uncorrelated.

Conclusions

The computed results, even with their order of presentation determined by hindsight rather than chronology, are not as simple as one might have

hoped; neither are they so hopelessly complicated that useful generalizations cannot be obtained from them. The reliability of these generalizations is affected chiefly by lack of detailed knowledge of the interaction potentials. No highly directional potential functions have been studied; it is possible that these would lead to qualitatively different results, although the tests made here and in part II suggest otherwise. Similarly, the exact details of the potential when all interatomic distances are small certainly affects the shapes of the computed distributions but perhaps not the overall picture. In addition to all this, the effect of allowing 3-dimensional trajectories has yet to be determined, and the possibility of quantum effects should be kept in mind if the predictive rules given below are applied to reactions involving hydrogen.

Subject to these limitations, the generalizations are:

(1) To a good approximation, the observable distributions may be divided into two groups with distinct causative factors. The distributions of θ and E_{rot} (and probably the reaction cross section) are determined largely by masses and molecular geometries, exothermicity, and the details of the potential at large distances; the $(E_{\text{vib}} + E_{\text{rot}})$ distributions are primarily a function of the shape of the potential at small distances. The E_{vib} distribution is the only one affected by all the variables. This generalization is supported by the entire variegated assortment of calculation sets (49 in all). Some of its long-range importance lies in the simplification it may provide of the task of computationally reconstructing actual potential surfaces from the results of molecular beam experiments.

(2) A large class of normal reactions can be identified. These fulfil the following requirements: (a) The interaction potential is such that the energy is converted from potential to kinetic mostly during reactant attraction rather than product repulsion (the Simons criterion); (b) the average angular momentum per collision is not greater than the product diatom can accommodate in its highest possible state of rotational energization (absence of anomaly I); (c) the attacking monatomic species is not much less massive than the other atoms (absence of anomaly II).

(3) The normal θ distributions are approximately trapezoidal in the center-of-mass system; the probability of $\theta = 0^\circ$ (diatomic product recoils along approach line of atom) is at least equal to and often much greater than the probability of $\theta = 180^\circ$ (original atom goes "through" the original diatom and emerges on the other side as part of the diatomic product). This means that in the laboratory coordinate system there is a peak at the angle corresponding to $\theta = 0^\circ$ (a weighting factor, $1/\sin\theta$, is applied in the approximate transformation) and a smaller peak at the angle corresponding to $\theta = 180^\circ$. In the molecular beam experiments² corresponding to the calculations done in part II of this series, the former peak was observed and the latter was not. The results shown in Fig. 1 suggest that the experimenters inadvertently chose the one of the reactant combinations least likely to show the subsidiary peak (in addition to the mass-dependent effect, the secondary peak is at an unfortunate angle with respect to elastic scattering). It is predicted that the double-peaked laboratory θ distribution will eventually make its appearance.

An abnormal θ distribution will be obtained only if condition (b)

in (2) fails; (a) and (c) are immaterial. The center-of-mass distribution, peaked near the middle of its range, will lead to a laboratory distribution either shifted from the position corresponding to $\theta = 0^\circ$ or greatly broadened and distorted (unless, of course, the transformation to laboratory coordinates compresses all θ values into a very narrow angle), depending on whether or not the center of mass distribution approaches 0 at $\theta = 0^\circ$ more rapidly than does $\sin\theta$.

(4) On the average, all the angular momentum is converted to product rotation. This rule fails, for conservation reasons, only under the same conditions given in the preceding paragraph.

(5) The normal distributions of total product internal energy are broadly peaked at a value equal to the total available energy. The shapes (not the peak positions) of the distributions are an exception to rule (1) above; they depend somewhat upon the reactant masses.

For this rule to be true independently of the exothermicity of the reaction, conditions (a) and (c) of (2) are both necessary; failure of an experimental reaction to have large values of $E_{\text{vib}} + E_{\text{rot}}$ can be attributed to failure of one of these. Unfortunately, a high value of $E_{\text{vib}} + E_{\text{rot}}$ does not absolutely guarantee that condition (a) is met. Condition (b) is immaterial for this rule.

(6) The normal E_{vib} distribution peak positions, it follows from the above, may be obtained approximately by subtracting the average rotational energy from the exothermicity of the reaction:

$$(E_{\text{vib}})_{\text{peak}} \approx Q - \frac{3}{4} (\mu b^2 kT/I) ,$$

where, as before, μ is the reduced mass of the reactants, I the moment of

inertia of the diatomic product, and b^* the maximum allowed impact parameter.¹³ The temperature is the translational one characteristic of the approach of the reactants.

(13) This formula is for a bulk gas experiment. For molecular beam conditions, the second term is multiplied by $1/2$ rather than $3/4$.

The factor (μ/I) appearing in the above equation is identical with $1/\sin^2\beta$, with β as defined in the Smith theory⁹ (it is the apex angle of the potential surface; see the discussion of anomaly II above). Thus the equation will rank the predicted E_{vib} of various reactant mass combinations in the same order (everything else being equal) as does the Smith theory, if normal reactions only are considered. However, the exact numerical predictions will be different, and the underlying mechanical assumptions are not closely related.

If condition (a) or (c) in (2) fails, the rightmost term of the equation still gives the difference between $(E_{vib} + E_{rot})_{peak}$ and $(E_{vib})_{peak}$. If condition (b) fails, the entire equation fails and it is only possible to predict that the $(E_{vib})_{peak}$ will occur at a small value of E_{vib} . The broadness of the E_{vib} distribution depends on, among other things, how well condition (b) is fulfilled.

ACKNOWLEDGMENT

The authors are indebted to Mr. Roger Silver, Miss Sue Krainock, and Mr. Ken Thomas for extracting the result distributions from a formidable mass of Stretch output.

Figure Captions

Fig. 1. Values of f and distributions of θ , $(E_{\text{vib}} + E_{\text{rot}})$ and E_{vib} for 10 reactant mass combinations at about 20 Kcal exothermicity. $L = 2$ AMU, $M = 16$ AMU, and $H = 128$ AMU; f is the average fraction of angular momentum converted to product rotation and θ the angle of emission of the monatomic product in the center-of-mass system, measured from the direction of approach of the original monatomic reactant. Distribution categories are 10° wide for θ and 10^{-13} erg wide for product energies.

Fig. 2. Correlations between θ and impact parameter: (a) normal case; (b) anomaly I.

Fig. 3. Stroboscopic representation of illustrative trajectories: (a) normal case; (b) anomaly I.

Fig. 4. Anomaly II shown in analogy of mass point sliding on potential surface: left, normal case; right, anomaly II.

Fig. 5. Distributions of θ at about 100 Kcal exothermicity for mass combinations $(M + LM)$ and $(M + LH)$.

Fig. 6. Distributions of $(E_{\text{vib}} + E_{\text{rot}})$ for interaction potential not satisfying the Simons criterion. Mass combinations $(M + HH)$, $(M + MH)$, and $(M + LH)$ are each shown for exothermicities of 20 and 100 Kcal. For 20 Kcal the distribution categories are 10^{-13} erg wide; for 100 Kcal, 5×10^{-13} erg.

Fig. 7. Distributions of θ and E_{vib} for interaction potential in which diatomic reactant is reactive at both ends. Mass combinations $(M + LL)$,

(M + MM), and (M + HH) are shown; the Simons criterion is satisfied; distribution categories are 10° for θ , 5×10^{-13} erg for E_{vib} . The shaded subdistributions in E_{vib} are trajectories which passed through an isosceles configuration an odd number of times.

Fig. 8. Type of trajectory leading to normal (high energy) E_{vib} peak in Fig. 7 (shown at left), and to subsidiary (low energy) peak (shown at right).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8