

## Energy and Chemical Reaction. II. Intermediate Complexes vs. Direct Mechanisms

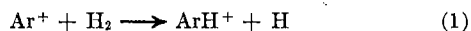
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In the preceding article on "Energy and Chemical Reaction"<sup>2</sup> a number of energy-dependent factors which control elementary chemical reaction were discussed. I reserved for this article consideration of a most fundamental energy-dependent aspect of chemical kinetics. This is the question of whether reaction involves a long-lived intermediate, or whether it proceeds by a direct mechanism. The formation and lifetime of such intermediate complexes are sensitively dependent on the energy of the reaction. With information on this energy dependence now becoming available it seems appropriate to review our understanding of this central aspect of reaction dynamics. As is customary for this journal this is a personal account based largely on my own findings. It concludes with a wider sampling of relevant results on elementary chemical processes, but no comprehensive review is provided.

For several decades many chemists seem to have implicitly assumed that all reactions involved a "long-lived" intermediate, at least at low energies and for strongly interacting reagents. This appears not to have been an objectively reasoned inference, but rather an article of faith. It may have been partly based on a common misinterpretation of transition-state theory, in which it was felt that since the transition-state collision complex is in equilibrium with the reagents, it must be a long-lived species. But as already mentioned in part I of this series<sup>2</sup> many reactions can go directly even at the lowest energies. A good case in point is the process



which has been studied by the chemical accelerator method.<sup>2</sup> This reaction involves the strong ion-induced-dipole interaction and had previously been postulated to go *via* unimolecular decay of an intermediate complex, although the evidence for this was not convincing. Yet, our experiments showed that it can proceed by a direct mechanism even at very low energies ( $\sim 0.1$  eV). Obviously it is necessary to be open-minded on this question of complex formation.

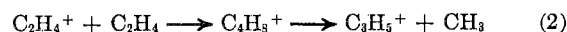
Before proceeding further we should define what we mean by a "long-lived" complex. The units of time that are relevant here are those of molecular motion, typically  $10^{-13}$  sec for a vibration and  $10^{-12}$  sec for a rotation. We may define a reaction involving an intermediate complex as one in which the constituents of the

system are within normal bonding distances of one another for at least a few rotational periods. This will usually correspond to a lifetime  $> 10^{-12}$  sec. By contrast, direct reactions will involve close contact for only one or a few vibrational periods ( $< 10^{-12}$  sec). There will of course be an interesting intermediate range of ambiguity.

A lifetime of  $> 10^{-12}$  sec allows time for internal redistribution of energy, and the eventual decay will then correspond to reasonably normal unimolecular decomposition. Products of the latter process are usually predictable—the most exoergic decay channels tend to be favored. Thus the yield spectrum of the reaction can provide an experimental indication of whether a persistent complex was involved. However, since direct reaction can often give the same products, this is frequently not a reliable indication, particularly for simple systems where there are few possible products.

Obviously the best experimental test for formation of a persistent complex is to detect it directly. This is often not possible unless its lifetime is very long indeed. The spatial symmetry of the product distribution is a more generally applicable test and one which is almost as good. In the center-of-mass system the reagents coming from opposite directions will form a collision complex at the center of mass. If this undergoes several rotations before decomposing it will "forget" which reagent came from which direction. As discussed previously (see part I)<sup>2</sup> the velocity and angular distributions of the products must then be symmetric with respect to a plane passing through the center of mass and normal to the collision axis. This behavior is a necessary but not sufficient indication of a long-lived complex. Though it is not very likely, certain types of direct reaction may yield symmetric distributions. (Thus direct reaction proceeding only through an S wave or hard-sphere collision will give an isotropic distribution. Furthermore at initial kinetic energies which are very low compared to intermolecular potentials some direct reactions which normally display strong forward peaking may show an appreciable degree of forward-backward symmetry.<sup>3</sup>)

Results on the energy dependence of the angular and velocity distributions of products arising *via* complex formation have only recently become available. For reactions such as eq 2 we obtained these using the



crossed-beam chemical accelerator EVA.<sup>4a</sup> At lower

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(2) R. Wolfgang, *Accounts Chem. Res.*, **2**, 248 (1969).

energies the symmetric distribution of products (see part I, Figure 4) indicates the participation of a long-lived  $C_4H_8^+$  complex, but when the energy of the incident  $C_2H_4^+$  exceeds 6 eV, the appearance of significant asymmetry signals the growing dominance of a direct mechanism.<sup>4a</sup> This parallels conclusions on other systems by Henchman,<sup>4b</sup> Durup,<sup>5</sup> Henglein,<sup>6</sup> and collaborators from experiments in which the forward component of product velocity was measured. All data indicate that, if an intermediate complex is formed at all, this happens at lower energies, and that this mechanism tends to be replaced by direct processes at higher energies.

### Criteria for Complex Formation

Formation or nonformation of persistent complexes, and their energy dependence, seem to be consequent on whether two requirements are met. Though simple, these have not always been clearly recognized in the past. There may also be other criteria but, if so, they have not yet manifested themselves, at least in our work. We now examine these requirements to see how they can account for existing data on complex formation.

#### A. Lifetime for Decomposition of the Complex.

The most obvious requirement for formation of a persistent intermediate is that there must be some configuration of the combined reagents which has a lifetime toward unimolecular decomposition which is long compared to  $10^{-12}$  sec.<sup>7</sup> This means qualitatively that the potential surface should contain a potential well, intermediate between the reactant and product valleys. This is indicated in Figure 1 which shows a "reaction coordinate"—a cross section of the potential surface along a reaction path.

What must the depth of the well be to provide a sufficient lifetime? This will depend on the energy of the system and its complexity. The RRKM theory of unimolecular decay<sup>8</sup> provides the most accurate estimate, but sufficient information to apply it is available for

(3) See ref 2, particularly footnote 13a. At energies low compared to the intermolecular attractive potentials there will be an appreciable "pulling-together" effect acting on the reactants. For processes without threshold (e.g., most ion-molecule reactions) this manifests itself as high cross sections. Under these conditions a fraction of events will be consequences of large impact parameter collisions which involve a long spiral path before actual "impact" and reaction occurs. Depending on the angle of such spiraling, products may come off forward, backward, or sideways. Thus with decreasing energy there will then be an increasing appearance of symmetry in the angular distributions. This could readily be mistaken for an increasing contribution by a persistent complex mechanism. (However, with most intermolecular attractive potentials, a finite fraction of impact parameters will always involve little spiraling, and lead to a nonsymmetric component of the angular distributions, even in the limit of zero energy.)

(4) (a) Z. Herman, A. Lee, and R. Wolfgang, *J. Chem. Phys.*, **51**, 452 (1969); (b) L. Matus, *et al.*, *Discussions Faraday Soc.*, **44**, 146 (1957).

(5) M. Durup and J. Durup, Proceedings of the International Mass Spectrometry Conference, Berlin, Sept 1967; *J. Chim. Phys.*, **386** (1967).

(6) A. Ding, A. Henglein, D. Hyatt, and K. Laemann, *Z. Naturforsch.*, **23**, 779, 2090 (1968).

(7) We refer to the lifetime of the complex with respect to all modes of decomposition, not just with respect to any given set of products.

(8) R. A. Marcus, *J. Chem. Phys.*, **20**, 359 (1952).

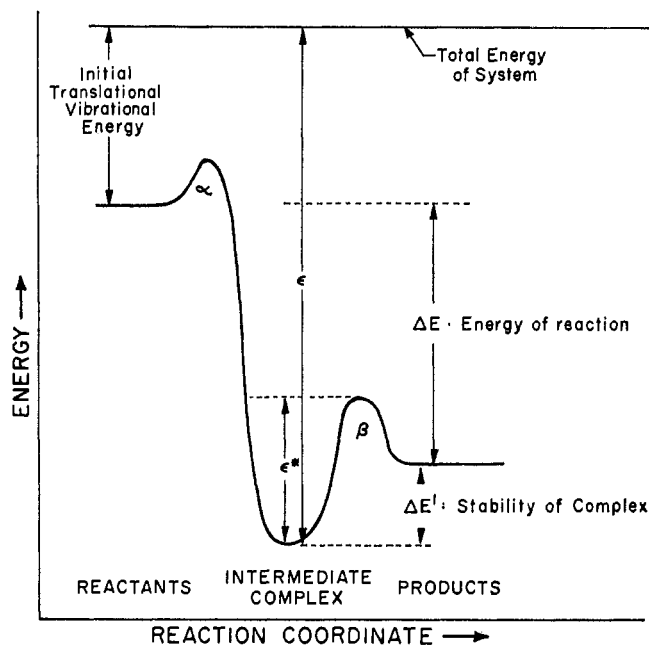


Figure 1. Cross section of a potential energy surface involving an intermediate complex. The heavy line shows the total electronic plus zero-point vibrational energy. The difference between this and the total energy of the system is in the form of vibrational excitation and relative translational energy of reactants (or products). The heights of the barriers  $\alpha$  and  $\beta$  will depend on the exact trajectory across the surface and may well be zero.

only a few systems. However the simple RRR theory<sup>9</sup> gives us a useful, though at best semiquantitative, guide to what this lifetime will be.<sup>10</sup> It also indicates the nature and relationship of three underlying factors which will be important no matter which theory of unimolecular decay is used. According to RRR theory the magnitude of the mean lifetime is

$$\tau \cong 10^{-13} \left( \frac{\epsilon - \epsilon^*}{\epsilon} \right)^{1-s} \text{ sec} \quad (3)$$

where  $\epsilon$  is the total internal<sup>11</sup> energy of the complex. This is the sum of the energy of reaction,  $\Delta E$ , the stability of the complex with respect to products,  $\Delta E'$ , and the translational and vibrational energy of the reactants (see Figure 1). Note that there is no distinction between reactant translational and vibrational energy for the present purpose.<sup>11</sup>  $\epsilon^*$  is the threshold for decomposition of the complex. Whether its magnitude is equal to or greater than  $\Delta E'$  depends on the existence of a barrier to decomposition ( $\beta$ ).  $s$  is the number of

(9) H. S. Johnston, "Gas Phase Reaction Rate Theory," Ronald Press, New York, N. Y., 1966.

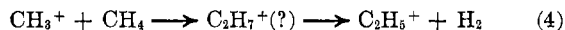
(10) More sophisticated quantum calculations based on RRKM theory indicate that the RRR classical-degenerate estimate of lifetime provides no better than order-of-magnitude accuracy. Lifetimes will generally be much too low if  $s$  is taken as the full number of vibrational modes. The device of taking  $s$  as two-thirds the actual number of vibrational modes is often used to partially compensate for the inherent shortcomings of RRR theory.

(11) Rotational and vibrational energy should, strictly speaking, be distinguished since they have different effects on decomposition and since conservation of angular momentum restricts their interconvertibility.

“active” vibrational modes of the complex between which energy is exchanged. It may be equal to or smaller than the total number of vibrational modes. In studies of unimolecular decay it is often taken to be about two-thirds of the latter.<sup>9,10</sup>

Formation of a complex requires that  $\epsilon^*$  be positive (*i.e.*, it cannot exist if, even when in its ground state, there is no potential well to contain it). The lifetime is maximized and hence intermediate formation is favored if  $\epsilon^*$  and  $s$  are large and  $\epsilon$  is small. Obviously attainment of the necessary lifetime ( $>10^{-12}$  sec) is more likely if the exoergicity of the reaction  $\Delta E$  is small or negative and if the system is complex so that  $s$  is large. Furthermore the life of the complex must become shorter, and the system tends toward direct reaction as the translational and vibrational energy of the reactants increases. This behavior has now been clearly observed.<sup>4a</sup> Products from reaction 2 show a symmetric angular and velocity distribution at low reactant energies, but as the initial energy increases these distributions become increasingly asymmetric and forward peaked, unambiguously indicating that a direct mechanism is becoming dominant.

This condition, that formation of a persistent intermediate requires that it have a lifetime with respect to unimolecular decomposition of  $>10^{-12}$  sec, may be obvious, but it is often not fully appreciated. Consider reaction 4. As with reaction 2 this process involves



many degrees of internal excitation. Furthermore the presumptive intermediate  $\text{C}_2\text{H}_7^+$  was known from other experiments to be a stable species. Hence it was generally assumed that the system involves a long-lived intermediate,  $\text{C}_2\text{H}_7^+$ . Some years ago we started to use EVA to measure angular and velocity distributions of the  $\text{C}_2\text{H}_5^+$ . These experiments stubbornly indicated that, contrary to our expectations, the reaction was largely direct.<sup>12</sup> As shown in Figure 2, the product distribution is not symmetric around the center of mass, but suggests that the  $\text{C}_2\text{H}_5^+$  tends usually to recoil in the direction in which the  $\text{CH}_3^+$  had been going. This implies that the  $\text{CH}_3^+$  “picks up” a  $\text{CH}_2$  from the passing  $\text{CH}_4$  and proceeds on its way before the complex has rotated much. We finally realized that the probable reason for this behavior is that  $\text{C}_2\text{H}_7^+$  is stable with respect to decomposition by only about 0–0.4 eV.  $\epsilon^*$  will therefore be small, possibly as low as 0.1 eV. Given a relative translational energy of 1 eV, an internal energy of the  $\text{CH}_3^+$  of  $\sim 1$  eV, and  $\Delta E \cong 1$  eV, this means that  $\epsilon \cong 3$  eV.  $s$  may be approximated by 14, two-thirds the total number of vibrational modes.<sup>9</sup> Hence it is quite plausible that the lifetime of the complex is less than  $10^{-12}$  sec, its period of rotation.<sup>12a</sup>

(12) Z. Herman, P. Hierl, A. Lee, and R. Wolfgang, *J. Chem. Phys.*, **51**, 454 (1969).

(12a) NOTE ADDED IN PROOF. Even in a direct reaction there may still be ample time for considerable rearrangement. Thus reaction 4 shows evidence for much “scrambling” of H atoms: F. A. Abramson and J. H. Futrell, *ibid.*, **45**, 1925 (1966).

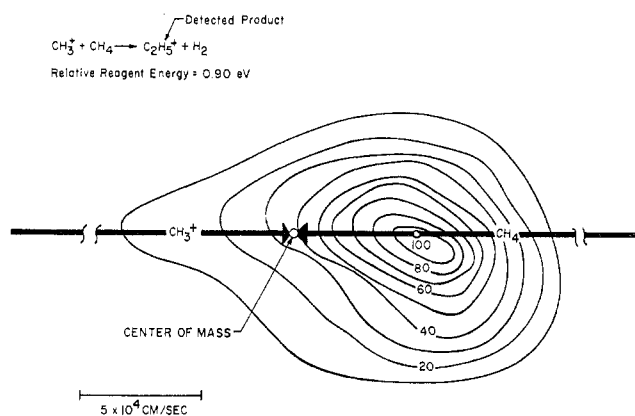


Figure 2. Intensity contour diagram of velocity and angular distributions for the reaction  $\text{CH}_3^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2$ . (See also part I,<sup>2</sup> Figure 4). Note the absence of “forward-backward” symmetry about the center of mass. (The distribution should, however, be symmetric about the collision axis, since the reagents cannot normally distinguish right from left. The deviation from this is an experimental artifact resulting mostly from the fact that there is a distribution of centers of mass, and this gives rise to distortion in the laboratory-to-center-of-mass transformation).

### B. Conversion of Translational to Internal Energy.

Even though a persistent complex having the composition of the combined reagents may be capable of existing, it may not always be formed. A second requirement for formation of a long-lived intermediate is that the relative translational energy of the reagents must be convertible into internal excitation of the complex. There are at least four reasons why this criterion may not be met. If because of these a persistent complex is not formed, reaction may still proceed by a direct channel.

(i) The most obvious reason for reactants not forming a complex is that there is a potential barrier to doing so (“ $\alpha$ ” in Figures 1 and 3) and that there is insufficient energy to overcome it. In the present early state of the study of detailed mechanisms of elementary reaction it is somewhat difficult to find a chemical reaction clearly attributable to this factor. However this situation is well known in nuclear physics. At low kinetic energies a compound nucleus—analogue to a persistent complex in chemical reaction—cannot be formed because of the coulomb repulsion between colliding nuclei. The fact that there is an effective barrier to complex formation does not, however, mean that direct reactions cannot take place; nuclear collisions occurring at energies below the coulomb barrier frequently result in single nucleon transfer.<sup>13</sup> The nature of chemical forces, particularly the absence of an overall coulomb repulsion between most reagents, makes it even less likely that a barrier to complex formation should also be a barrier to all reaction.

(ii) Even if there is sufficient energy to surmount any potential energy barrier, complex formation may not occur if the collision is so off-center that the reactants only make grazing contact (see part I,<sup>2</sup> Figure 9).

(13) R. Kaufmann and R. Wolfgang, *Phys. Rev.*, **121**, 206 (1961).

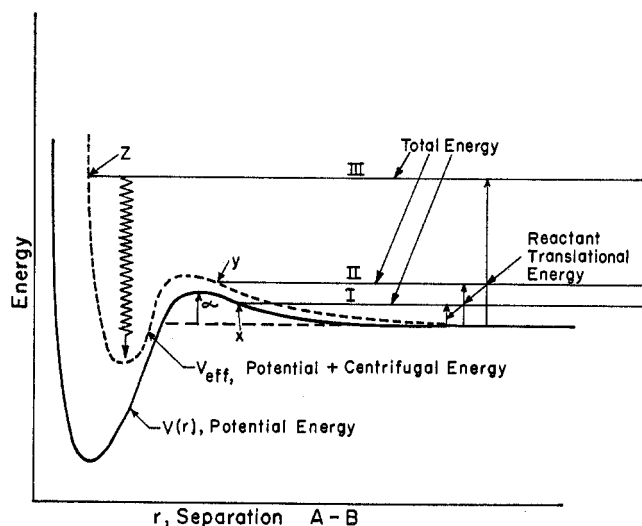


Figure 3. Potential energy of reagents A and B as a function of the separation of their centers of mass,  $r$ , showing why, despite the existence of a potential well, a complex may not form. If there is a potential barrier ( $\alpha$ ), then even in a head-on collision the reagent kinetic energy may be too low; *e.g.*, reagents of relative energy I will come together until their energy is converted into potential energy at point  $x$  and then will rebound. In an off-center collision the centrifugal barrier (dashed line) may prevent formation of complex; *e.g.*, at energy II rebound will occur at distance  $y$ . Although in cases I and II the minimum value of  $r$  attained is too large for a persistent intermediate to be formed, portions of the reagent species may come sufficiently close for direct reaction to occur. Even if the translational energy is sufficient to overcome the potential and centrifugal barriers (III), some of it must still be converted into internal energy of A and B, for the system to "fall" into the potential well (wavy arrow). Otherwise reagents will simply reach point  $z$  and rebound, or alternatively react by a direct mechanism.

This is due to conservation of angular momentum. The effective potential barrier,  $V_{eff}$ , which must be overcome by the translational energy of the reactants,  $E_{tr}$ , is then the sum of the true potential energy  $V(r)$  and the "centrifugal" energy (see Figure 3, case II).

$$V_{eff} = V(r) + E_{tr} \frac{b^2}{r^2} \quad (5)$$

Here  $b$  is the impact parameter, the "off-centeredness" of the collision, and  $r$  is the separation of the center of mass of the reagents. Again the best defined examples of this are found in nuclear systems, such as process 6



studied by us some years ago.<sup>14</sup> In a reasonably on-center high-energy ( $\sim 100$  MeV) collision, oxygen and rhodium can readily form a compound nucleus. However analysis of angular distributions showed that reaction 6 actually occurs in a grazing collision in which several nucleons could be transferred. Both experiment and theory indicate that the importance of such nuclear reactions increases with kinetic energy and that they ultimately become dominant.<sup>14</sup> This is plausible since eq 5 indicates that it becomes more difficult to

convert increasing translational energy into internal modes even for collisions which are only moderately off-center. There is no reason to believe that the same will not also be true for chemical processes.

(iii) There may also be more specifically chemical steric factors which prevent the reagents from forming a persistent complex. The complex may have to have a configuration which cannot be readily attained by the reagents. The required rearrangement of the reagent atoms may be so extensive that, though energetically allowed, it may be very unlikely to happen during the brief time allowed by the collision. In this case translational energy cannot be converted into internal energy of the complex, and the only reactions that can occur will be those proceeding by a direct mechanism.

(iv) This last consideration will probably be most significant with relatively complex reagents. However, with simple species there may be another reason why complete translational to internal energy conversion, to form a persistent complex, might not always be possible. A case in point may be the interaction of  $\text{He}^+$  and  $\text{H}_2$  which Henchman and collaborators<sup>4b</sup> have shown as proceeding without intermediate complex formation. A suggested reason for this finding may be that in such a simple system there are relatively few internally excited levels of the complex. Persistent intermediate formation can occur only if the total energy of the system happens to match one of these levels<sup>15</sup> (see Figure 3, case III). Because polyatomic reagents provide a large density of internal energy states, this restriction on the energy conversion necessary for complex formation is likely to be important only for very simple systems.

## Results and Some Predictions

Having set forth these two criteria for complex formation, let us see how we can use them to systematize data on known reactions and perhaps make some predictions on reactions yet unknown.

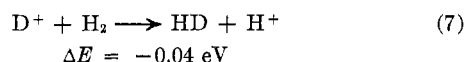
**Simple Systems.** Both criteria indicate that reactions involving only three or four nuclei will be relatively less likely to involve an intermediate complex. The number of vibrational modes for a three-atom system is only three for a nonlinear complex and four for a linear complex. The resultant low density of internal energy (criterion B, iv) levels may make conversion of translational energy and formation of a complex difficult. If a complex is formed, the small number of available vibrational modes,  $s$ , in which energy can be stored means that its lifetime will be short (criterion A). The fact that the energy is being shuffled among so few degrees of freedom requires that

(15) The assumption is frequently encountered that the Langevin cross section for ion-molecule interactions (part I,<sup>2</sup> eq 2) must also be the cross section for complex formation. The basis of this very questionable tenet seems to be the feeling that the system must fall into the well created by the ion-dipole interaction (see Figure 3). This can only occur if the translational energy is converted into radiation or internal vibrations. The probability of the former is negligible and the latter can only happen if an appropriate internal energy level is available.

it will soon be so distributed as to cause decomposition. For such a complex to live for  $>10^{-12}$  sec it is necessary that its inherent stability, as measured by the well depth  $\epsilon^*$ , must be appreciable. Furthermore the total available energy must be small. This in turn means that the energy of reaction,  $\Delta E$ , and the excess energy of the reagents must be near zero.

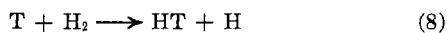
It is indeed plausible that reaction 1 does not involve a persistent complex. There is no reason to believe that  $\text{ArD}_2^+$  even in its ground state has any appreciable barrier to decomposition to form  $\text{ArD}^+$  and  $\text{D}$ .  $\epsilon^*$  is therefore likely to be small and there may even be no well at all.

No study of the analogous reaction 7 has yet been re-



ported. This system is of exceptional interest because its potential energy surface may be accurately calculated. It thus provides an unparalleled opportunity, both to compare experiment with *ab initio* theory and to check on the validity of our simple semiquantitative criteria for complex formation. The stability of  $\text{H}_3^+$  with respect to decomposition to  $\text{H}_2 + \text{H}^+$  is accurately predicted to be  $\sim 5$  eV.<sup>15</sup> There is no barrier to decay apart from this endoergicity,<sup>16</sup> and thus  $\Delta E' = \epsilon^* = 5$  eV (see Figure 1). The complex is triangular, and  $s$  may therefore be taken as 3. The simple formula 4 suggests that for collision energies of the order of 1 eV a persistent complex with a lifetime of ten or more rotational periods is capable of existing. This lifetime decreases rapidly with energy, and it seems probable that a transition from a persistent complex to a direct mechanism will take place in the energy range of a few electron volts. However, if a direct process does dominate down to the lowest energies, this might imply that the density of vibrational energy levels is too low to ensure efficient conversion of translational to the internal energy of a complex<sup>17</sup> (criterion B, iv).

The atomic reaction 8 and its isotopic variants should



show sharp differences from the superficially analogous ionic process 7. A good semiempirical potential energy surface for this system is available.<sup>18</sup> In contrast to the early Eyring-Polanyi surfaces, no well for the  $\text{H}_3$  complex is indicated, *i.e.*,  $\epsilon^* = 0$ . With criterion A not satisfied it is reasonable that calculations of trajectories over this surface therefore show direct reaction at all

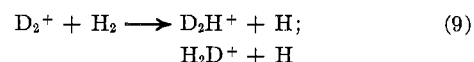
(16) H. Conroy, *J. Chem. Phys.*, **41**, 1341 (1964).

(17) This system also offers the possibility of uncovering a new phenomenon in chemical reactions: resonances corresponding to coincidence of translational energy of reagents with an internal level of the complex. These will only be observed if the density of levels is low and their width, as determined by the lifetimes of the complex, is so small that they do not overlap. Such phenomena are commonly observed in nuclear reactions of thermal neutrons. To find such resonances in chemical reactions very-low-energy beams of precisely controlled velocity will be needed. Their discovery will provide a further close analogy between the phenomenology of compound nuclei and intermediate complexes in chemical reaction.

(18) M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.*, **43**, 3259 (1965); I. Shavitt, R. M. Stevens, F. L. Minn, and M. Karplus, *ibid.*, **48**, 2700 (1968).

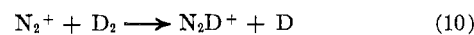
energies. No experimental confirmation of this is available. However, studies of reactions of thermal hydrogen and deuterium atoms in several laboratories<sup>19</sup> and of hot tritium atoms by our group<sup>20</sup> all indicate fair agreement<sup>21</sup> with reaction probabilities predicted by the theory.

Four-center hydrogen-exchange reactions of type 9



have recently been studied by Durup,<sup>5</sup> by Henchman and collaborators,<sup>4b</sup> and by Doverspike and Champion.<sup>22</sup> Velocity distributions of the products show that direct reactions proceeding by deuteron or hydrogen atom transfer are dominant. However, especially at the lowest energies measured ( $\sim 2$  eV), there is a contribution by a process in which the relative translational energy is completely transformed into internal energy. Although "this experiment neither proves nor disproves the existence of a long-lived collision complex,"<sup>22</sup> it is certainly consistent with such. If this does turn out to be the case it implies (criterion A) that  $\text{H}_4^+$  is a bound entity. Because in four-center systems  $s$  can be as large as 6,  $\epsilon^*$  would not have to be as great as it is in the case of  $\text{H}_3^+$ .

On the other hand our results<sup>2</sup> on angular and velocity distributions in the four-center system 10 are very



similar to those for reaction 1. The reaction is dominated by direct processes at all energies. If persistent complex formation occurs at all, it is minor, even at relative energies as low as 0.1 eV. Since this reaction is not very exoergic ( $\Delta E \lesssim 1$  eV),  $\epsilon$  will not be large. As  $s$  may be as great as 6, eq 3 would imply that the  $\epsilon^*$  of the collision complex is small. This could mean that criterion A is not satisfied in that  $\text{N}_2\text{D}_2^+$  has too little stability. The fact that the mass spectrum of hydrazine shows  $\text{N}_2\text{H}_2^+$  as a stable peak suggests, however, that it may instead be criterion B that is not met. This would be reasonable if the stable configuration of the ion were the linear,  $\text{DNND}^+$ , configuration. If that were the case, formation of a persistent complex would be difficult since it would require that the approaching  $\text{D}_2$  stretch practically to the point of dissociation in order to attach to both ends of the  $\text{N}_2^+$ . Our second criterion would thus not be satisfied because of an energetic or steric barrier. Hence translational energy could not be effectively converted into the internal energy of a linear complex (criterion B, i or B, iii).<sup>22a</sup>

A very thoroughly understood class of reactions is of

(19) See, *e.g.*, D. J. LeRoy, B. A. Ridley, and K. A. Quichert, *Discussions Faraday Soc.*, **44**, 92 (1967).

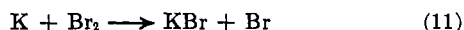
(20) D. Seewald, M. Gersh, and R. Wolfgang, *J. Chem. Phys.*, **45**, 3870 (1966).

(21) M. Karplus, R. Porter, and R. Sharma, *ibid.*, **45**, 3871 (1966).

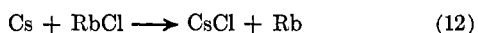
(22) L. D. Doverspike and R. L. Champion, *ibid.*, **46**, 4718 (1967).

(22a) NOTE ADDED IN PROOF. Since submission of this article another particularly interesting and relevant example of complex formation has been detected: E. A. Gislason, B. H. Mahan, C. Tsao, and A. W. Werner, *ibid.*, **50**, 5418 (1969); A. Ding and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **73**, 562 (1969).

course that of alkali atoms with halogens,<sup>23</sup> for instance eq 11. Although studies have only been made at



thermal energies, angular distributions of products as obtained with crossed beams allow a close characterization of the mechanisms involved. In nearly all cases these are direct. This is not surprising since most of these processes are highly exoergic, and it seems unlikely that the intermediates would have the required stability,  $\epsilon^*$ , to compensate for the large available energy,  $\epsilon$ . Some most interesting exceptions were found by Herschbach and associates and provide the basis for the first detailed discussion of the kinematics of the decay of long-lived intermediates in chemistry.<sup>24</sup> The reason that these reactions, for instance eq 12, do in-



volve an intermediate of lifetime  $>5 \times 10^{-12}$  sec was attributed to their near-thermoneutrality and to the probability that the complexes would have reasonable stability ( $\epsilon^* \sim 0.5$  eV) with respect to dissociation. The fact that, with our first criterion (A) thus satisfied, complex formation is indeed observed tends to indicate that criterion B, the possibility of energy conversion, may be readily met for such very simple thermal reactions.

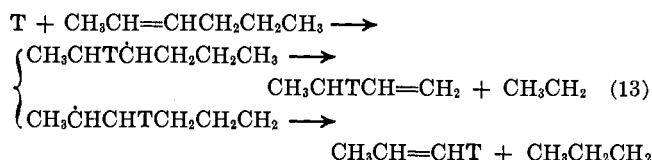
**Polyatomic Systems.** In collisions involving many atoms, the available number of degrees of freedom,  $s$  (eq 3), should be large. This obviously favors intermediate persistent complex formation even if the stability of the complex,  $\epsilon^*$ , is not great. If at a moderate available energy,  $\epsilon$ , no complex is formed, this implies either that there is no configuration which has even a moderate binding energy or that this configuration cannot be attained. The latter would be true for a grazing collision, or because there is an energetic barrier to forming a bound complex, or because so much internal rearrangement is required as not to be feasible in the time of collision.

Very few results on beam or chemical accelerator studies of complex formation between polyatomic reagents are available at this time. The most completely studied systems (reactions 2 and 4) have already been discussed. However hot-atom studies made by us over the last decade provide some interesting illustrations of the operation of our criteria for complex formation in larger systems.

One of our first conclusions on the reactions of hot hydrogen atoms with alkanes and other saturated organic molecules<sup>25</sup> (see, for instance, part I,<sup>2</sup> eq 5-8) was that they proceed by a direct mechanism. This was apparent from the observed product spectra. If a complex is formed, its unimolecular decay tends to favor the more exoergic reaction channels, and no such

tendency was observed. Furthermore we have noted the importance of inertial factors in hot hydrogen reactions (part I).<sup>2</sup> These are due to insufficient time being available for certain relaxation motions within the period of the interaction.<sup>25</sup> Since formation of a persistent complex allows adequate time for all possible nuclear motions, these factors would only be operative in direct interactions. These and other considerations, fully discussed elsewhere,<sup>26</sup> led to rejection of early suggestions that hot hydrogen atom reaction with alkanes involved persistent intermediate complexes. This conclusion is certainly reasonable since it is difficult to visualize how a monovalent neutral atom could be strongly bound by a saturated compound (criterion A).

On the other hand, hot-atom reaction with alkenes can apparently involve a persistent intermediate complex.<sup>27</sup> We know this because certain specific products, unexpected on the basis of the systematics of direct reactions with alkanes, appear in large yield. With 2-hexene, for instance,<sup>27</sup> recoil tritium gives tritiated 1-butene and propylene. These form *via* intermediate hexyl radicals, which preferentially decompose by the most exoergic route, mainly by rupture of the appropriate C-C bond (eq 13). This is most plausible since



the tritium atom can be strongly bonded by 1-hexene to form hexyl radicals. With  $\epsilon^*$  in the region of several electron volts, the large number of available degrees of freedom,  $s$ , then ensures that the radical intermediate has an appreciable lifetime. Indeed, studies of the pressure phase dependence of collisional deactivation indicate that such radicals may have lifetimes of the order of  $10^{-10}$  sec or longer.<sup>28</sup> Analogous thermal systems, studied by Rabinovitch and collaborators, have become some of the best understood examples of unimolecular decay.<sup>29</sup>

It is equally important to note that hot hydrogen reactions with alkenes till have probabilities for direct reactions as large, or larger, than those for complex formation.<sup>26</sup> These reactions are the same abstraction and direct displacement processes observed with alkanes (see part I,<sup>2</sup> eq 5-8). This demonstrates the importance of our second criterion (B): even if a long-lived complex can exist it may not always be formed. Presumably these direct reactions result from grazing collisions (B, ii), and from events in which the position of the impacting atom is such that it is sterically or en-

(26) R. Wolfgang, *Progr. Reaction Kinetics*, **3**, 99 (1965).

(27) D. Urech and R. Wolfgang, *J. Am. Chem. Soc.*, **81**, 2025 (1959); "Chemical Effects of Nuclear Transformations," Vol. II, International Atomic Energy Authority, Vienna, 1961, p 99.

(28) J. K. Lee, B. Musgrave, and F. S. Rowland, *J. Am. Chem. Soc.*, **82**, 2545 (1960).

(29) G. H. Kohlmaier and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 1692, 1709 (1963).

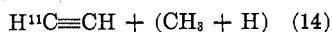
(23) D. R. Herschbach, *Advan. Chem. Phys.*, **10**, 319 (1966).

(24) W. B. Miller, S. A. Saffron, and D. R. Herschbach, *Discussions Faraday Soc.*, **44**, 108 (1967).

(25) R. Wolfgang, *Ann. Rev. Phys. Chem.*, **16**, 15 (1965).

ergetically impossible for it to add to the double bond.

As final examples, results of some of our studies of atomic carbon, both hot and thermal, are cited.<sup>30</sup> We showed that with hydrocarbons reaction proceeds mainly by insertion of C atoms into existing bonds, to form an intermediate adduct which subsequently decomposes (*e.g.*, eq 14). The polyvalent character of  $^{11}\text{C} + \text{C}_2\text{H}_6 \longrightarrow \text{H}^{11}\text{CCH}_2\text{CH}_3 \longrightarrow$



atomic carbon allows it to be bound to alkanes. Because of the increased number of C-C bonds, the complex in its ground state will be stable by several electron volts with respect to both reactants and products.  $\epsilon^*$  will therefore be large, in marked contrast to hydrogen atom-alkane systems, and criterion A may thus be satisfied.

Reactions analogous to (14) might be expected to be possible for perfluorinated systems as well, since in this case also a strongly bound intermediate should be ca-

(30) C. MacKay and R. Wolfgang, *Science*, **148**, 899 (1965).

pable of existing. Very recent studies<sup>31</sup> have, however, uncovered no evidence of this. The only reaction tentatively identified, F abstraction to form CF, probably proceeds directly. Apparently there is a barrier to insertion of C into C-F bonds. This again indicates the importance of our second criterion (B). The fact that a strongly bound complex is capable of existing does not guarantee that it will be formed.

In conclusion we must emphasize again that systematic study of the competition between direct reaction and persistent intermediate complex formation is still at an early stage. Yet it appears that the factors underlying this competition are becoming clear and are starting to provide a basis for making at least tentative predictions.

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(31) D. Blaxell, C. MacKay, and R. Wolfgang, *J. Am. Chem. Soc.*, in press.

## The Chemiluminescence of Organic Hydrazides

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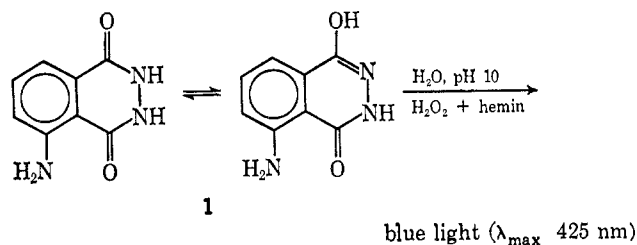
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Chemiluminescence is the production of light in excess of black-body irradiation by a chemical reaction. The definition effectively includes any reaction that yields visible light at room temperature, since emission by "black bodies" at this temperature is negligible in the visible region of the spectrum. A wide variety of compounds are known to be chemiluminescent, but this paper will be concerned only with acyl derivatives of hydrazine. Since several reviews of chemiluminescence have appeared recently,<sup>1</sup> our treatment of the



(1) (a) K. D. Gundermann, "Chemilumineszenz Organischer Verbindungen," 1st ed, Springer-Verlag, New York, N. Y., 1968; (b) K. D. Gundermann, *Angew. Chem. Intern. Ed. Engl.*, **4**, 566 (1965); (c) F. McCapra, *Quart. Rev. (London)*, **20**, 485 (1966); (d) J. W. Haas, *J. Chem. Educ.*, **44**, 396 (1967); (e) E. H. White in "Life and Life," 1st ed, W. D. McElroy and B. Glass, Ed., Johns Hopkins Press, Baltimore, Md., 1961, p 183.

historical aspects of the problem will not be exhaustive. Probably the best known example of chemilumines-

