Energy and Chemical Reaction. I. Dynamics of Simple Ionic and Atomic Processes

RICHARD WOLFGANG

Department of Chemistry, University of Colorado, Boulder, Colorado 80302

Chemists have been concerned about the interplay of transformations of matter and of energy in chemical changes for perhaps a century. It may therefore seem both naive and presumptuous to try to discuss the effect of energy on the course of chemical reaction in a short article. But on looking at the matter more closely, one finds that nearly all of the enormous amount of available information concerns the dependence of thermal reaction rates on the difference in chemical potential between products and reactants and on the magnitude of the barrier. The effect of the actual energy of the reactants on mechanism, as well as on rate, has been systematically studied for only about a decade. Our knowledge of this fundamental aspect of chemical reaction is still at the primitive stage where the most elementary concepts are being developed and tested. This article is thus an early attempt to provide a unified picture of the effect of reactant energy—particularly translational—on chemical reaction.

The most familiar type of energy dependence of reaction is the temperature variation of the rate. As any chemistry freshman knows, an increase in temperature means an increase in energy and a consequent rise in rate as measured by an "activation energy." But let us see how much such thermal measurements tell us about the actual energy dependence.[1] Figure 1 shows an example of an "excitation function"—the probability that a reaction will occur upon a collision at a certain relative translational energy. Also given are the Maxwell–Boltzmann distributions of all collision energies at two temperatures. The kinetic energy distribution of collisions which lead to reaction is determined by the product of these functions. We call it the reaction function. An interesting (but not always familiar) fact is that the Arrhenius activation energy is the mean energy of all collisions subtracted from the mean energy of reactive collisions.[2] But the most significant aspect of the typical situation shown in Figure 1 is that tripling the temperature, though it will increase the rate by many orders of magnitude, changes the average kinetic energy of reaction by only a few kilocalories. Compare this with the yardstick of chemical energy, the chemical bond of perhaps 100 kcal/mol, and the energy range of chemical reaction, now known to extend over many hundreds of kilocalories.[3] It is then obvious that classical measurements on temperature dependence tell us prac-

tically nothing about the effect of reactant energy.

Only relatively recently have we started systematically to investigate the effect of reactant energy on the dynamics of reaction—on what kind of products are formed, on the rate, and on the mechanism. For reaction between atoms and molecules information has been obtained largely by recoil measurements, mostly radiochemical[4] and also photochemical.[5] In the case of ion–molecule processes mass spectrometric methods have been used.[6] For the future, however, experiments with apparatus producing beams of chemicals at controlled and variable energies offer the greatest promise. In order to emphasize the analogy of such devices to cyclotrons and other tools of nuclear physics we have called them "chemical accelerators."[7] The importance of chemical accelerators to chemistry is now being realized, and various modes of acceleration and detection are under intensive development at many laboratories.[7] However, relatively few results are yet available. Furthermore, for technological reasons early chemical accelerators were restricted to the very high energy region ($\gtrsim 25$ eV/molecule). Only recently have we reported results which span the full energy range.[8-10] These have made possible an evaluation of the detailed dynamics of ion–molecule reactions as a function of energy[8,9] and of the behavior of hot atom reactions between 1 and 50 eV.[10]

Surprising though it may seem, it is then clear that we are at an early stage of this field of the energy dependence of reaction—a field frequently called "hot chemistry." With only fragmentary data available it is perhaps premature and certainly dangerous to try to identify and unify the factors which control this fundamental aspect of chemical kinetics. Nevertheless that is what this article attempts. Undoubtedly many of the concepts stated here will be elaborated and

(1) M. Menzinger and R. Wolfgang, *Angew. Chem.*, in press.

(2) R. C. Tolman, *J. Am. Chem. Soc.*, **42**, 2506 (1920).

(3) In this article molecular rather than molar energy units will generally be used; 1 eV/molecule ≡ 23,052 cal/mol.

(4) For recent reviews see: (a) R. Wolfgang, *Ann. Revs. Phys. Chem.*, **16**, 15 (1965); (b) *Progr. Reaction Kinetics*, **3**, 97 (1965); (c) F. Schmidt-Bleek and F. S. Rowland, *Angew. Chem. Intern. Ed. Engl.*, **3**, 769 (1964).

(5) See, for instance: (a) R. M. Martin and J. E. Willard, *J. Chem. Phys.*, **40**, 2999, 3007 (1964); (b) A. Kuppermann and J. M. White, *ibid.*, **44**, 4352 (1966); (c) C. C. Chou and F. S. Rowland, *J. Am. Chem. Soc.*, **88**, 2612 (1966); (d) R. G. Gann and J. Dubrin, *J. Chem. Phys.*, **50**, 535 (1969).

(6) "Ion-Molecule Reactions in the Gas Phase," Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966.

(7) (a) R. Wolfgang, *Sci. Am.*, No. 10, 44 (1968); (b) R. Wolfgang, L. Branscomb, and R. Zare, *Science*, **162**, 318 (1968).

(8) Z. Herman, J. Kerstetter, T. Rose, and R. Wolfgang, *J. Chem. Phys.*, **46**, 2844 (1967).

(9) Z. Herman, J. Kerstetter, T. Rose, and R. Wolfgang, *Discussions Faraday Soc.*, **44**, 123 (1967).

(10) M. Menzinger and R. Wolfgang, *J. Am. Chem. Soc.*, **89**, 5992 (1967).
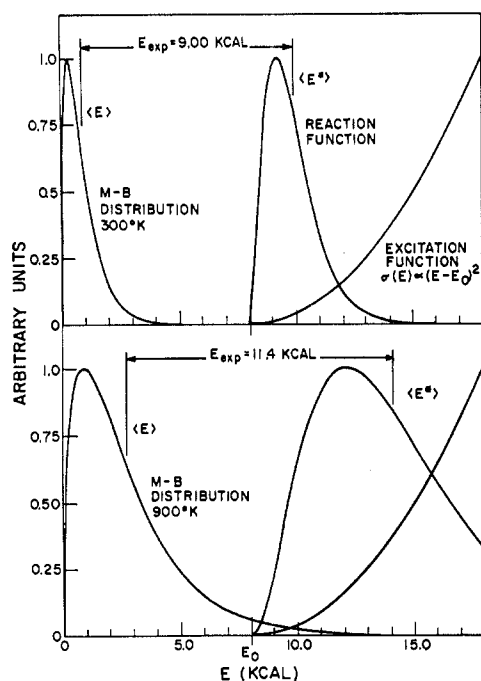
Figure 1. Effect of temperature on the energy of chemical reaction. Shown in each diagram is a hypothetical example of an "excitation function," together with Maxwell–Boltzmann distributions of relative energies of the reactants at 300°K and 900°K. Also given is the reaction function—the energy distribution of reactions as dependent on the products of the former two functions. Note that an enormous change in temperature—threefold—has relatively little effect on the activation energy, E_{exp}, and the mean energy of reaction.

modified in later work. Some may turn out to be wrong. It is hoped, however, that this early attempt to unify the structure of the field will provide some useful directions for future research, if only by providing some working hypotheses to be critically tested.

Types of Reactant Energy

This discussion is concerned primarily with the effect of the translational energy of the reagents on the reaction. To what extent does this limit its generality? We are well justified in not considering electronic energy in this context, because electronically excited reactants are in a very real sense qualitatively different species, with an intrinsic reactivity determined by their electronic structure. Accordingly their reactions must be described using separate potential surfaces.

There is no such clear distinction between translational and vibrational–rotational excitation, and the main reason for not explicitly discussing the latter is that available relevant evidence is still quite sparse. Both of these forms of energy reside in nuclear motion and are readily interconvertible on collisions. This complementarity becomes obvious on regarding the representations of translational and vibrational energy on simple potential energy surface diagrams. Consider a given reaction, which is promoted by kinetic energy, but yields products which are highly vibrationally excited. Microscopic reversibility then tells us that the reverse reaction will be favored by vibrational energy

(although there may also be other channels for this reverse process which preferentially require translational energy). Thus experiments on translational energy dependence which give information on the state of the products can actually provide equivalent information on the vibrational–rotational energy dependence.

Complete "understanding" of a chemical reaction is largely summarized in its potential energy surface. Such a surface can be constructed from data on the behavior of the system with kinetic or vibrational energy, but once constructed it will then represent both translational and internal energy dependences. To the extent that we understand the hot chemistry of translationally excited species, we indirectly gain complementary knowledge of the vibrationally–rotationally hot reactions.

Eight Concepts of Energy Dependence

Our discussion centers around eight qualitative generalizations abstracted from identified quantitative trends of kinetic energy dependence. These concepts, italicized where they first appear, are presented in the framework of accounts of the dynamics of ion–molecule and atom–molecule reactions. Consideration of these collisional processes will be followed by a separate article on the basic question of direct reaction mechanisms vs. intermediate persistent-complex formation. The article is illustrated with examples, largely from our own work, that helped develop these concepts which represent our understanding of the energy dependence of reaction. The eight concepts to be discussed are: (I) the decreasing range of effective interaction with increasing energy; (II) the loss of chemical specificity at the upper end of the chemical energy range (30–100 eV); (III) the energy dependence of the partition of available energy among products; (IV) the increasing number of reaction channels with energy; (V) limitations on energy transfer in high-energy reactive collisions; (VI) the increasing importance of secondary decomposition of products at higher energies; (VII) the role of steric factors; (VIII) the importance of inertial factors at medium and high energies.

Energy Depenence of Dynamics of Ion–Molecule Reactions

Reactions of gaseous ions are distinguished as a class by usually having no apparent barrier to reaction (provided of course that the process in question is exothermic). This fact is generally explained by the charge–induced-dipole interaction which draws the ion and neutral reactant together. Even though they may originally have been at rest, the reagents acquire sufficient kinetic energy to overcome any intrinsic barrier amounting to a few kilocalories/mole or a few tenths of an electron volt/molecule. Furthermore, most ions probably have an intrinsically lower barrier and greater reactivity than corresponding neutral species. Thus Ar^+ is a radical species isoelectronic with Cl or CH_3, but it has a far greater electron de-
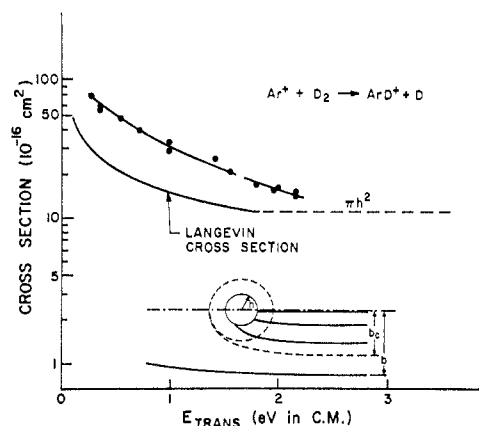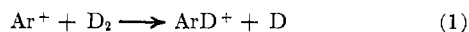
Figure 2. Decreasing range of effective interaction with energy illustrated for the reaction $Ar^+ + D_2 \rightarrow ArD^+ + D$. The "Langevin cross section" gives the cross section for "close collision" at low energies. Ions approaching (see inset) with impact parameter $b < b_c$ are drawn together. At higher energies the interaction radius is better approximated by h, the distance at which attractive and repulsive forces balance ($\approx$ "viscosity" radius). Experimental cross sections are indicated by points.[12]
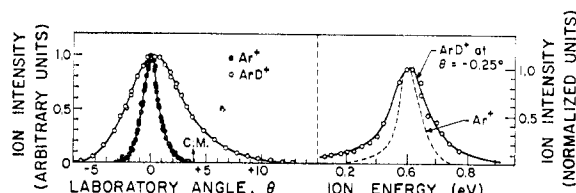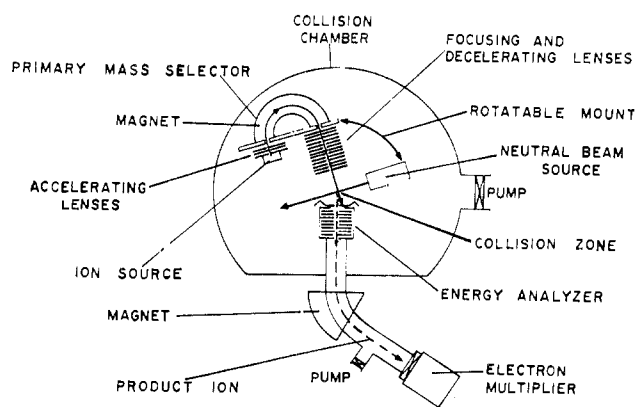

Figure 3. Chemical accelerator EVA. Ions formed by electron bombardment are accelerated, mass analyzed by magnetic deflection, and electrostatically brought to the desired energy. Products formed by collisions with a crossing molecular beam are detected by a mass spectrometer. Energy distributions are measured by passage through a charged grid, and angular distributions by rotating the sources with respect to the detector. Examples of these are shown.

ficiency, as measured by its electron affinity. Accordingly it is an extremely electrophilic reagent, and is correspondingly more reactive. Similarly, most negative ions are highly reactive nucleophiles.

The absence of a barrier means that ion–molecule reactions can provide simple examples of *the decreasing range of effective interaction with increasing collision energy,* a factor that appears important in all of hot chemistry. This is illustrated in Figure 2[11] for the reaction

$$Ar^+ + D_2 \longrightarrow ArD^+ + D \tag{1}$$

An ion attracts a molecule by means of the dipole it induces in it. This potential, amounting to the order of half an electron volt, draws the reagents together. As a result, reactants which would otherwise pass each other at a distance, b (the "impact parameter"), undergo a close-in collision. The cross section for close collision (defined as one in which the centrifugal barrier is overcome) is given by the familiar Langevin formula[6]

$$\sigma(E) = \pi b_c{}^2 = \pi\left(\frac{2\alpha e^2}{E}\right)^{1/2} \tag{2}$$

where α is the molecular polarizability. Obviously the drawing-in effect becomes less important with increasing energy, and both the critical impact parameter, b_c, and the cross section become smaller. (This expression becomes meaningless when at higher energies $b_c < h$, where h is the distance at which in the absence of reaction repulsive forces balance the attraction.) If there is no barrier, close collision will result in reaction. Hence low-energy reaction cross sections[12] are often, though by no means always, crudely approximated by eq 2. (Cross sections tend to continue to diminish at higher

energies, when attractive forces become negligible. Reasons for this are discussed later.) Long-range attractive forces operate between all types of reagents. Hence, were it not for the existence of barriers, all chemical reactions would have total cross sections which decrease with energy.

What are the effects on reaction mechanism of the decrease in the range of effective interaction with increasing energy? Only recently has information become available on the variation of the detailed dynamics of several reactions over what is essentially the full spectrum of chemical energy. We obtained this for several ion–molecule processes using our chemical accelerator EVA.[9] This is a variable-energy crossed-beam apparatus providing for both angular and energy analysis of products, the first such device used for the study of chemical reaction. Figure 3 shows how a mass- and energy-selected ion beam is crossed with a molecular beam. The angular distributions of product ions are measured by a fixed mass spectrometer detector as the sources are rotated about the point of beam intersection. Their energy is determined by a grid system which electrostatically stops all ions below a given potential.

From the angular and velocity measurements (shown in Figure 3 for the reaction $Ar^+ + D_2 \rightarrow ArD^+ + D$) we can compute the corresponding distributions in the center-of-mass (CM) coordinate systems. Some examples of such representations of the data are shown in Figure 4. The ion comes from the left, the molecule from the right, their relative velocities being such that

(11) C. F. Giese and W. B. Maier, *J. Chem. Phys.*, **39**, 739 (1963).
(12) The reaction cross section is the probability for reaction on collision multiplied by the total collision cross section.
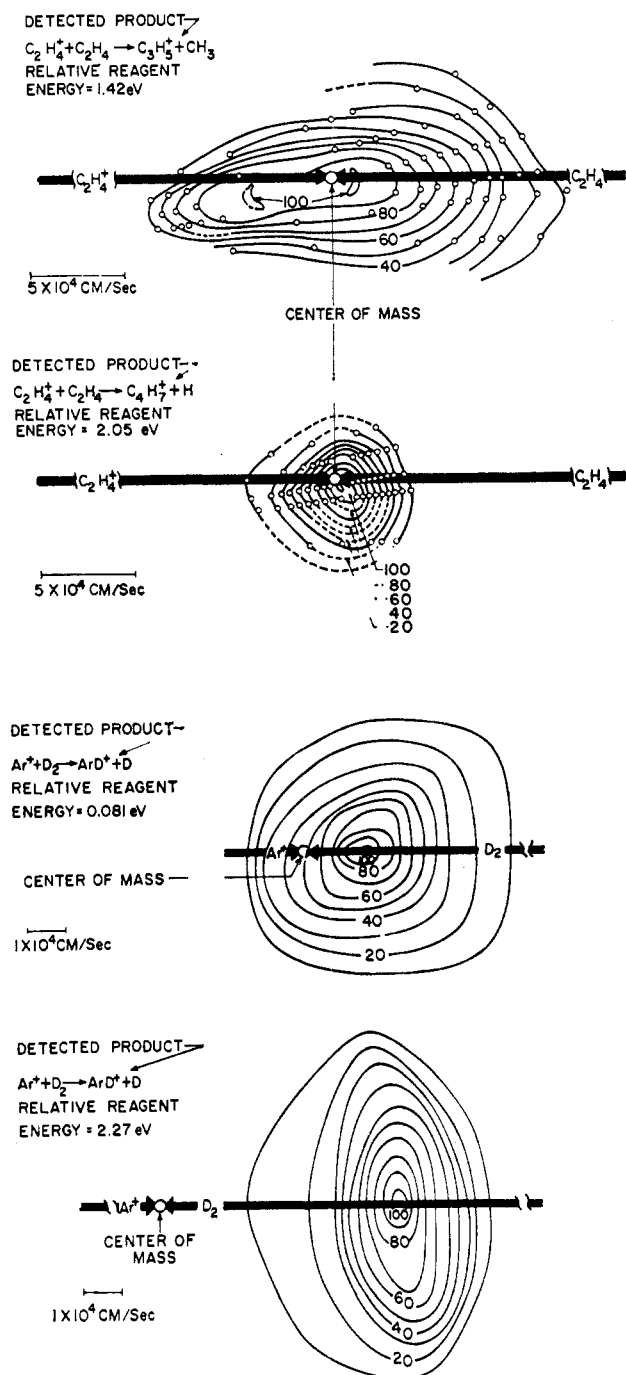
DETECTED PRODUCT—
$C_2H_4^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_3$
RELATIVE REAGENT
ENERGY = 1.42 eV

$|C_2H_4^+|$ $C_2H_4|$

CENTER OF MASS

5×10^4 CM/Sec

DETECTED PRODUCT—
$C_2H_4^+ + C_2H_4 \rightarrow C_4H_7^+ + H$
RELATIVE REAGENT
ENERGY = 2.05 eV

$|C_2H_4^+|$ $|C_2H_4|$

5×10^4 CM/Sec

DETECTED PRODUCT—
$Ar^+ + D_2 \rightarrow ArD^+ + D$
RELATIVE REAGENT
ENERGY = 0.081 eV

CENTER OF MASS —

1×10^4 CM/Sec

DETECTED PRODUCT—
$Ar^+ + D_2 \rightarrow ArD^+ + D$
RELATIVE REAGENT
ENERGY = 2.27 eV

Ar^+ D_2
CENTER OF
MASS

1×10^4 CM/Sec

Figure 4.   Velocity and angular distributions in the center of mass of products of several reactions (as determined by EVA). Arrows show the direction and velocity of reactants in the center-of-mass system.   Contours show the relative intensity of product having a given velocity and angle with respect to the center of mass and collision axis (Cartesian coordinate system: see R. Cross and R. Wolfgang, *J. Phys. Chem.*, **73**, 743 (1969)).

the center of mass is fixed in the middle of the diagram. The amounts of product, emitted from the center of mass with velocity μ and angle θ with respect to the reactant ion velocity vectors, are shown by contours indicating relative intensity.   Such data, obtained as a function of initial collision energy, are the most complete yet obtained about any elementary chemical reaction.
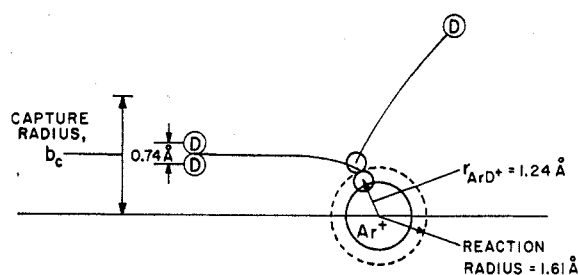
Figure 4 shows two different types of product inten-

CAPTURE
RADIUS,
b_c 0.74 Å $r_{ArD^+} = 1.24$ Å
Ar^+ REACTION
RADIUS = 1.61 Å

Figure 5.   Mechanism of the reaction $Ar^+ + D_2 \rightarrow ArD^+ + D$ as deduced from data exemplified in Figure 4.[9] D_2 approaching Ar^+ with an impact parameter smaller than the Langevin value is accelerated into collision with the ion by a charge–induced-dipole force.   At the reaction radius shown a D atom attaches to the Ar^+; the other is reflected.

sity contours.   For the reaction

$$C_2H_4^+ + C_2H_4 \longrightarrow C_3H_5^+ + CH_3 \tag{3}$$
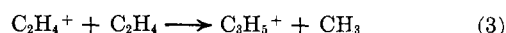
there is a roughly equal probability for $C_3H_5^+$ to be emitted toward the left and the right; in fact within experimental error the distribution of products is symmetrical with respect to a plane passing through the center of mass and normal to the collision axis.   This loss of directionality strongly implies that an intermediate $C_4H_8^+$ is formed which has a sufficiently long lifetime ($>10^{-12}$ sec) to undergo several rotations.   It thus "forgets" the direction from which the reagents come, and on breaking up will emit products equally to the left and to the right.[13]   Figure 4 also shows the distribution of $C_4H_7^+$ formed by a competing mode of reaction between $C_2H_4^+ + C_2H_4$.

On the other hand Figure 4 shows that, for reaction 1, most of the ArD^+ recoils in the same direction in which Ar^+ was going.   This shows definitively that there is little contribution by an ArD_2^+ intermediate sufficiently long-lived to undergo many rotations.   Instead the asymmetry of the product distribution about the center of mass shows the reaction is "direct" in the sense that it is complete in a time comparable to or less than one rotation.

These data have made possible the first detailed consideration of the dynamics of direct ion–molecule reactions such as (1) over the entire energy range.[9]   The resulting model is shown in Figure 5.   As the reactants approach, the ion induces a dipole in the molecule. The resulting attraction between the reactants accelerates them and draws them together.   At some distance of closest approach the deuterium atom is transferred. The remaining, liberated D atom then undergoes a quasi-elastic scattering off the ArD^+.   The ion–induced dipole between the ArD^+ and the D now mutually decelerates these products.   However this deceleration is of lesser magnitude than the acceleration of the

(13) Z. Herman, A. Lee, and R. Wolfgang, *J. Chem. Phys.*, in press. Although the product distribution from a reaction involving a persistent-complex intermediate must have symmetry with respect to a plane normal to the collision axis, it will not normally be isotropic. (This system could also "forget" directions if electron exchange between reactants occurs rapidly compared to the time of collision. Higher energy data, where the distribution becomes strongly forward peaked, indicate this is not a serious factor.)

reactants, because the polarizability of D is smaller than that of D_2 and because, at closest approach, the separation between D and ArD^+ is greater than that of the Ar^+ and D_2. The only adjustable parameter in this model is the distance of closest approach, Ar^+–D. When this is set at *ca.* 1.3 Å, the predicted velocities of the ArD^+ are in excellent agreement with the mean measured velocities at all initial energies.

What does this simple model of direct reaction predict about the dependence on the kinetic energy of collision? If the reactants start at rest the attractive force will pull them straight toward each other, into a head-on collision. The products would then rebound, the ArD^+ going back in the direction from which the Ar^+ came. If the reactants have a relative kinetic energy of a few tenths of an electron volt or less, comparable to or less than the ion–induced-dipole potential, they will tend to spiral into each other. Products will come off forwards, backwards, or sideways depending on the total angle of spiraling.[13a] That in turn will depend on the impact parameter *b*, the "off-centeredness" of their initial trajectories (see Figure 5). As the reactant energy increases and the cross section declines, the range of impact parameters for which reaction can occur becomes smaller. The amount of spiraling then becomes less and the angular distributions of products will tighten up to an increasingly narrow forward cone. This can be seen from the two energies illustrated in Figure 4.

We thus see how the same model of direct reactions predicts angular distributions changing from largely forward with appreciable backward scattering at the lowest collision energy[13a] to strongly forward at greater velocities. At higher energies still, >25 eV in the laboratory and >3 eV in the CM system, the long-range attractive force becomes relatively negligible, and there is little acceleration of the products from this source. Henglein's early work in this energy range[14] had shown that most events can then be regarded as the ion going by the D_2, picking up a D atom, and leaving the remaining D as a "spectator" hardly affected by the reaction. This implies that the force between the ion and the reactant molecule as a whole is relatively insignificant and that the pick-up has the character of a short-range ion–atom interaction. Recent more detailed investigation of this high-energy region has shown that, as might be expected, there is also an important component of rebound reaction, presumably resulting from head-on collision in a linear Ar^+–D–D configuration.[15,16] But this is also describ-

able in terms of short-range ion–atom, atom–atom collisions.

At higher energies still, the cross section for formation of ArD^+ declines further toward zero. This would be expected from the basic model which predicts that only a certain amount of the available energy will, on the average, appear as translation. The rest appears as vibration and rotation of the ionic product. As this exceeds the dissociation limit the reaction is replaced by fragmentation.

$$Ar^+ + D_2 \longrightarrow Ar^+ + 2D \qquad (4)$$

or

$$\longrightarrow Ar + D^+ + D$$
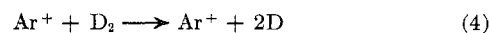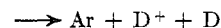
When the available energy is in the region of tens of electron volts, formation of new chemical bonds becomes unlikely and fragmentation dominates. We regard this as being effectively the end of the "chemical" energy range. Chemical specificity is associated with differences in energy of a few electron volts, and these are now relatively negligible. Thus it is not surprising that the chemical action of kilovolt hydrogen, helium, or other ions is very similar. We are now in the energy range of radiation chemistry where it is well known that (apart from secondary "track density" effects) the chemical character of the incident entity is of little significance. It seems likely that this *loss of chemical specificity* already becomes important at energies around 10 eV (center of mass), although the lack of relevant data makes this a prediction rather than an observation. When the dynamics of very high energy reactions between Cl and D_2 are studied, they are likely to look similar to those of Ar^+ and D_2.

Our discussion implies a further generalization. *The partition of available energy among translation and internal modes of the product is itself energy dependent.* Figure 6 compares the prediction of our model with experimental data for reaction 1.[17] If the reactants start at rest some of the energy of reaction appears as translation of the products. But as the collision velocity rises there is an increasing net conversion of kinetic energy of the reactants into vibrational energy of the product, ArD^+. Eventually this is limited by dissociation of the product, preventing its observation, and causing the deviation of high-energy data from the prediction of the simple theory.[15]

Dynamics of Atom–Molecule Reactions

The discussion of the dynamics of ion–molecule processes has illustrated three energy-dependent factors which enter into all chemical change. However one can make a good case for the proposition that study of reactions between neutrals can ultimately provide a better insight into the more subtle factors which control

(13a) Note Added in Proof. At extremely low energies (<0.1 eV), some impact parameters will be very large, resulting in a long spiraling path before actual "impact" occurs. As a result the time of interaction may be quite long and the product distribution may show a degree of forward–backward symmetry. Despite the appearance of a long-lived intermediate thus presented, this does not mean that a persistent complex, defined as an entity in which all atoms are bound at reasonably normal bond distances far greater than 10^{-12} sec, is formed.

(14) A. Henglein, K. Lacmann, and G. Jacobs, *Ber. Bunsenges. Physik. Chem.*, 69, 279 (1965).

(15) L. D. Doverspike, R. L. Champion, and T. L. Bailey, *J. Chem. Phys.*, 45, 4385 (1966).

(16) W. R. Gentry, E. A. Gislason, Y. Lee, B. H. Mahan, and C. Tsao, *Discussions Faraday Soc.*, 44, 137 (1967).

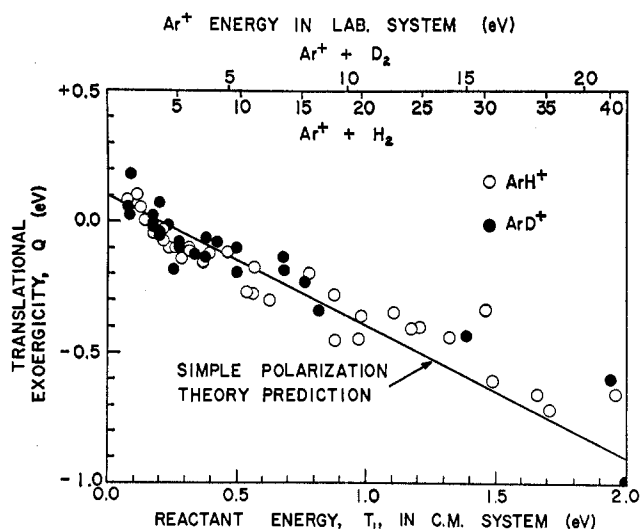(17) P. Hierl, Z. Herman, J. Kerstetter, and R. Wolfgang, *J. Chem. Phys.*, 48, 4319 (1968).

Figure 6. Translational exoergicity, Q, for the reaction $Ar^+ + D_2(H_2) \rightarrow ArD^+(ArH^+) + D(H)$. Q is the relative kinetic energy of products minus that of reactants. Predictions of the simple model are shown. Deviations at higher energies are at least in part apparent, being due to nonobservation of excited products which carry so much internal energy that they decompose.

chemical reaction. Unlike ion–molecule processes, neutral reactions usually do have a barrier, and a central problem of kinetics is determining the nature of barriers and how they are overcome. Then too, there are no long-range ionic forces to mask the shorter range "chemical" forces which govern the intimate aspects of reaction.

While reactions between neutral species are thus perhaps more interesting, they are also harder to study as a function of energy. Most information has come from hot atom studies using recoil methods, and chemical accelerator results are only just starting to come into the picture.

Recoil Methods. Nuclear recoil methods have given us the overview that we have of the nature of atom–molecule reactions above threshold.[4] In this technique, now becoming familiar to most kineticists, a very high kinetic energy radioactive atom is produced by nuclear reaction. In the case of hydrogen, for example, the process $^3He + n \rightarrow p + T$ yields a tritium atom having an energy of the order of 10^5 eV. This is generated in the medium in which it is to react by irradiating with neutrons a mixture containing ^3He. The very fast atoms lose energy in successive collisions until they are reduced to less than 100 eV. They thus enter the chemical range from the top and undergo more collisions.[18] These result either in reaction in which the hot atoms become incorporated in a labeled molecule or become thermalized. In the latter case they are removed by scavengers, such as iodine. Products formed by hot reaction are then identified and assayed

by radio gas chromatography.[4a,b] Typical results are shown in Table I.

Table I
Products of Reaction of Hot Hydrogen Atoms (T from Nuclear Recoil) with Some Hydrocarbons

Reagent[a]	HT	CH_3T	C_2H_5T	C_3H_7T	$CH_2T\cdot$	$C_2H_5T\cdot$	C_2H_3T	Other Products
CH_4	19	25	...	...	5	...	...	<2
C_2H_6	36	2.4	22	...	8.5	0.7	1.1	<2
C_3H_8	39	2.6	1	21	2.6	1.7	2.4	<2

% of T incorporated in product

[a] Scavenged reagents at about 1-atm pressure. Data from: D. Seewald and R. Wolfgang, *J. Chem. Phys.*, **47**, 143 (1967); A. H. Rosenberg and R. Wolfgang, *ibid.*, **41**, 2159 (1964); D. Urch and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2982 (1961); R. T. K. Baker and R. Wolfgang, unpublished.

The extent of hot reaction can be controlled by use of inert moderators, such as neon. Data thus obtained can be quantitatively interpreted using the kinetic theory of hot reactions.[19] This does not yield excitation functions (the functional relationship between cross section and energy), but it does provide several interesting quantities: the "reactivity integral" for a given reaction, which is related to the area under the excitation function; the mean logarithmic energy loss on collision; and the relative mean energy at which products are formed.

Photochemical recoil methods are essentially similar. The hot atom is produced by photolysis of a molecule such as HI.[5] The advantage of this technique is that the initial energy of the hot atom may often be well known. Its major disadvantage is that this energy is relatively low ($\lesssim 3$ eV) and the method is therefore restricted to this energy region. It is also limited as to species which can be cleanly produced, and has in fact been applied only to hydrogen.

Chemical Accelerator Methods. The obvious advantages of chemical accelerators are just starting to be realized for neutral reactions. We have recently made the first beam measurements of atom–molecule reactions in the energy range from 1 eV up using a device called ADAM.[10] In these experiments tritium atoms of controlled and variable energy were allowed to interact with thick hydrocarbon targets. Product yield were measured by radio gas chromatography (see Figure 7). This resulted in the first measurements of the thresholds of the hot-atom reaction. Furthermore, analysis of the results provided a good indication of the low-energy portion of the excitation function. In the nearer future results on yields from single collisions in crossed beams should become available and these will give definitive excitation functions. In the somewhat more distant future angular and velocity analysis of the products offers even more exciting prospects.

Factors Controlling Hot-Atom Reactions. A most striking aspect of hot reactions is the number of reaction modes that are opened at higher energies.

(18) The adiabatic principle of atomic physics indicates that at this point the atoms will normally be in a low-lying electronic state, as in the case of tritium.[4a,b] This is confirmed by experiment.

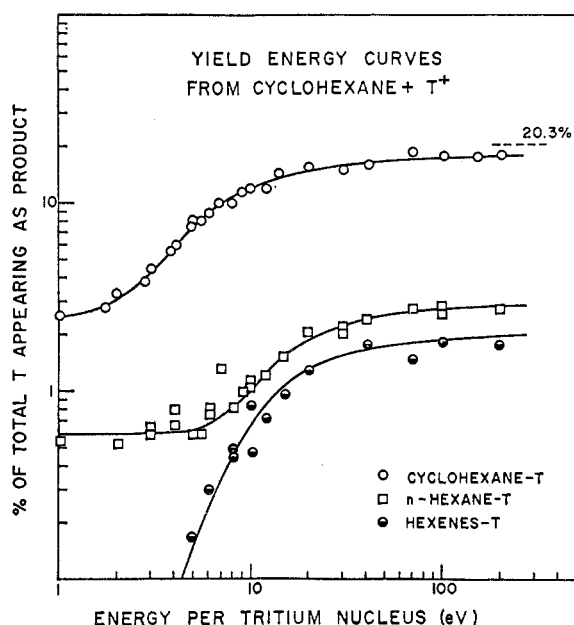(19) R. Wolfgang, *J. Chem. Phys.*, **39**, 2983 (1963).

Figure 7. Product yields obtained on impact of T atoms of given initial energy on solid cyclohexane.

Figure 8. Excitation functions for hot hydrogen reactions. At the top is that calculated[23] for T + H_2 → HT + H. At the bottom is a generalized schematic representation of the reaction T + RH to give labeled products. R'T represents products, formation of which requires rupture of two bonds.

Thus when thermal atomic hydrogen reacts with propane the only process observed is abstraction (eq 5).

$$T + C_3H_8 \longrightarrow C_3H_7 + HT \qquad (5)$$
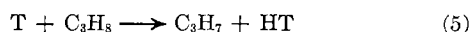
As is seen from Table I this is still a major reaction of hot hydrogen. But in addition, replacement of hydrogen atoms and, to a lesser extent, of alkyl groups becomes important (eq 6 and 7). A more minor process,

$$T + C_3H_8 \longrightarrow C_3H_7T + H \qquad (6)$$

$$T + C_3H_8 \longrightarrow CH_3T, C_2H_5T \qquad (7)$$
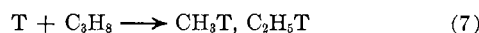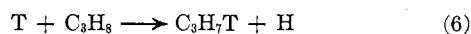
replacement of two atoms or groups, is also observed (eq. 8). Clearly these latter reactions have higher

$$(e.g.)\ T + C_3H_8 \longrightarrow CH_2T + C_2H_5 + H \qquad (8)$$
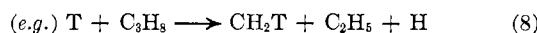
thresholds and are therefore not important in thermal systems. We know from activation energies and photochemical measurements that the threshold for abstraction is below 0.5 eV. Chemical accelerator data, as shown in Figure 7, indicates a threshold near 1 eV for H replacement. For double replacement, involving rupture of a C–H and a C–C bond, the threshold is about 4.5 eV.

Related to this *increasing number of reaction channels with energy* is the much higher collision yield for all reactions. We know this from reactivity integrals obtained from kinetic theory analysis of recoil data.[4a,b] These indicate probabilities of reaction on collision at about 5 eV, which are of the order of 0.1 to 1 magnitude larger than for thermal processes. This is a consequence of the fact that at the higher energies the system is no longer constrained to pass over the narrow saddle-point, minimum-energy channel of the potential-energy surface. At high energies almost any approach to the barrier can cause it to be surmounted.

We thus know that there is increasing probability of reaction from threshold to 5–10 eV: the excitation function rises (see Figure 8). At higher energies there
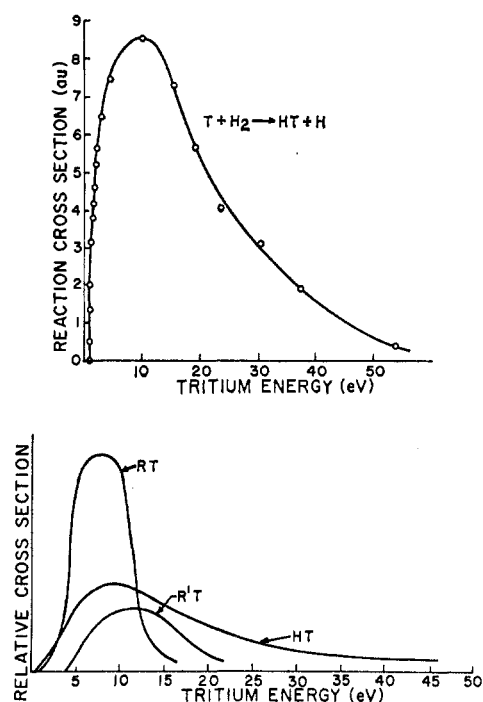
is good reason to suspect that it drops again. This is due to limitations on *energy transfer in high-energy reactive collisions:* the hot atom starts to have difficulty in disposing of enough of its energy so that it can become chemically bound. One possible means of doing so would be by transferring momentum to an ejected atom of reasonably similar mass in a so-called "billiard-ball" collision. However we can calculate that the probability for such substantial momentum transfer is very low.[20] Were this billiard-ball mechanism important one would expect that tritium would preferentially replace an atom of similar mass. But the yield of CD_3T from CD_4 is actually lower than that of CH_3T from CH_4.[4b]

The other generally available energy sink is excitation of the product molecule. That would lead to its secondary decomposition, and this has indeed been observed. But it is extensive only if the product molecule is intrinsically fragile. In the case of tritium there is little indication of the multiple bond rupture which would result from a very high level of internal excitation. Indeed most of the yield derives from rupture of a single bond with only a smaller contribution of two-bond rupture products.[4a,b] In accord with this, extensive studies by Rowland and collaborators indicate that most products of recoil tritium reaction contain on the order of a few electron volts rather than tens of electron volts of excitation energy.[4a,b]

The conclusion, schematically shown in Figure 8, that excitation functions for replacement reactions of hydrogen decline again above 5–10 eV has recently

(20) R. J. Cross and R. Wolfgang, *J. Chem. Phys.*, **35**, 2002 (1961).

been more directly confirmed by analysis of data from the ADAM accelerator. Why cannot a higher energy atom dump enough of its energy into the molecule so that it can be captured? Almost certainly the answer is that the time of collision of a fast hydrogen atom is so short ($\sim 10^{-14}$ sec) that it can transfer energy only into bonds near the area of contact. Since there is no time for energy to flow further into the molecule (the characteristic time for intramolecular energy flow is 10^{-13} sec), only the energy which can be absorbed by these bonds, of the order of 5–10 eV, can be lost. If the hydrogen then still retains substantial energy, it will simply be inelastically scattered and keep moving. This argument suggests that larger and heavier hot atoms should be able to react to somewhat higher energies and that, on the average, a larger number of bonds can be broken. Available data indicate that this is the case.[4a,b,21]

For one type of process—abstraction—there is a further means of energy disposal which can permit reaction at higher energies. If this process occurs by a grazing or stripping mechanism (see Figure 9) much of the energy can go into translation of the product. Recoil studies provide evidence that the mean energy at which abstraction occurs is higher than that for displacement, despite the fact that it has the lowest threshold.[22] Theoretical trajectory calculations also suggest that abstraction can occur at high energies.[23,24] Accordingly, Figure 8 indicates a high energy "tail" for abstraction. This postulated stripping mechanism also rationalizes the fact that abstraction is the only hot reaction which appears to have a marked bond energy dependence.[25] In a grazing collision kinetic energy is obviously not efficiently available to break the bond of the atom being abstracted. Hence the probability of carrying away a bound atom depends in part on the strength of its bond.

Despite the fact that the amount of excitation energy in the product is subject to definite limitations, it will still be substantial. The secondary decomposition of products is of increasing importance in hot reactions. This has been amply demonstrated, particularly by Rowland and collaborators[4a,b] for reactions involving a somewhat unstable product, e.g., eq 9. Somewhat

$$T + \overline{CH_2CH_2CH_2} \longrightarrow H + \overline{CHTCH_2CH_2} \longrightarrow$$
$$CH_2TCH{=}CH_2 \quad (9)$$
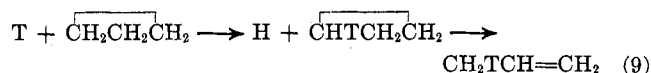
obviously, *the importance of secondary decomposition of the primary product increases with increasing energy.* The clearest demonstration of this factor comes from beam studies of ion–molecule reactions. In studying reaction 3, we found that with increasing energy of the
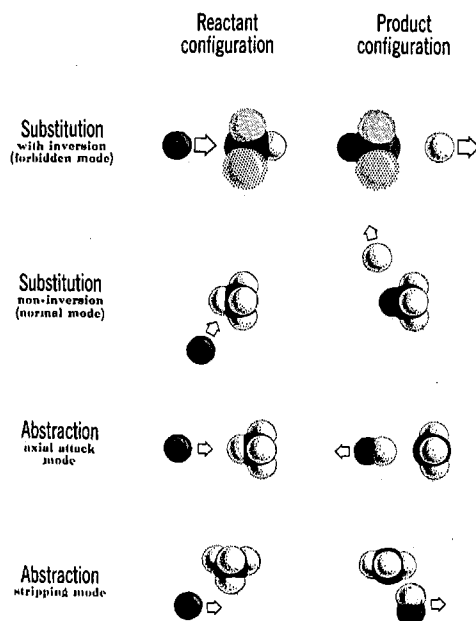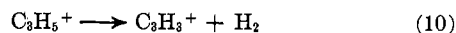

Figure 9. Steric control of reaction modes in hot atom reaction.

incident $C_2H_4^+$ the yield of $C_3H_5^+$ declined sharply. On the other hand that of $C_3H_3^+$ rises.[13] Studies of the velocity and angular distributions of these products indicate that the $C_3H_3^+$ is formed by further decomposition of excited $C_3H_5^+$ as produced in reaction 4

$$C_3H_5^+ \longrightarrow C_3H_3^+ + H_2 \quad (10)$$

The factors so far discussed as controlling the energy dependence of reaction involve primarily the total probability of reaction. What controls the relative yields of the various primary products? One of the early findings in hot-atom chemistry was the highly specific nature of the product spectrum (see Table I). Although energetically allowed, many processes are absent or occur with low efficiency. Clearly, *the role of steric factors is significant.* Which reaction occurs is largely determined by the impact parameters—the "off-centeredness"—and angles of collision.[4a,b] Thus C–C bonds are less frequently broken, despite their greater weakness. Figure 9 shows, in highly schematic form, how the initial trajectories largely determine whether abstraction or displacement occurs. A grazing interaction or an approach approximately coaxial with a C–H bond can cause abstraction. A sideways approach or a Walden inversion are sterically favorable for a replacement process.

Inertial factors are important at medium and high energies. A "golden rule" of hot-atom chemistry states that reactions requiring rotational–vibrational motions having a long relaxation time compared to the time of collision are disfavored. An example is the Walden inversion mechanism of hydrogen replacement by recoil tritium (Figure 9). This has been experimentally shown to be negligible relative to the noninversion mode if the other ligands are heavy.[4a,b] The incoming hot-atom's velocity is such that it spends only $\sim 10^{-14}$ sec near the central atom unless it is captured. But the

(21) R. J. Cross and R. Wolfgang, *Radiochim. Acta*, 2, 115 (1964).
(22) R. T. K. Baker and R. Wolfgang, *J. Am. Chem. Soc.*, 90, 4473 (1968).
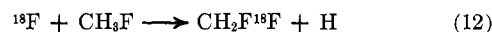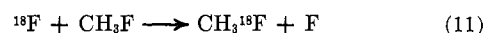(23) M. Karplus, R. Porter, and R. Sharma, *J. Chem. Phys.*, 46, 3871 (1966).
(24) P. J. Kuntz, E. M. Nemeth, J. C. Polanyi, and W. H. Wong, to be published.
(25) J. W. Root, W. Breckenridge, and F. S. Rowland, *J. Chem. Phys.*, 43, 3694 (1965).

motion of heavy substituents dictates a characteristic time of 10^{-13} sec for the vibration which leads to inversion. Until inversion occurs, no strong orbital can become available to bind the incident atom. Thus, although a hydrogen may be ejected in the process, reaction to capture the new atom tends to be forbidden. There is no such restriction on the noninversion mode of replacement. This vibrational–rotational inertial rule explains many apparent quirks in the yields of hot hydrogen reactions; for instance that replacement of a heavy atom is less likely if there is another heavy atom attached to the same central atom, or why reaction of T with CH_3CF_3 yields far more CH_3T than CF_3T. Like all such "negative" rules, this one is proven not so much by any positive evidence, but by the lack of any exceptions.[4a,b]

Collisions of heavy energetic species are slower than those of hot hydrogen and are therefore less constrained by slow vibrational–rotational relaxation times. But they tend to be governed by a complementary "translational inertial hypothesis."[26] This states that, other things being equal, reactions which involve a smaller change in the magnitude of linear momentum tend to be favored. Thus in the collison of hot ^{18}F with CH_3F, the

(26) L. Spicer and R. Wolfgang, *J. Am. Chem. Soc.*, **90**, 2426 (1968).

$$^{18}F + CH_3F \longrightarrow CH_3{}^{18}F + F \qquad (11)$$

$$^{18}F + CH_3F \longrightarrow CH_2F^{18}F + H \qquad (12)$$

former reaction (11) is favored because the momentum of the products can best approximate that of the reactants.

This catalog of factors controlling the energy dependence of chemical reaction is surely incomplete. Effects such as electronegativity and "induction," which are important in thermal processes, must also operate at higher energy, though probably with relatively less consequence. Apart from being incomplete this account is also most certainly imperfect and oversimplified. At the present early stage of the field it could hardly be otherwise.

Finally, it should also be kept in mind that while some of the concepts discussed are completely general, others are applicable to direct reactions only. Indeed we have given no explicit discussion of the very important and closely related question of the competition between direct mechanisms and those involving an intermediate persistent complex. This will be discussed in a subsequent article.