

THE DYNAMICS OF UNIMOLECULAR REACTION¹

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HISTORICAL INTRODUCTION

Six years ago the existence of unimolecular reactions constituted the outstanding scandal of physical chemistry. It seemed impossible to deny that the molecules reacting had, on the average, an excess energy which could be calculated from the temperature coefficient of reaction rate in the well-known way. Yet it seemed equally impossible to discover any mechanism by which such activated molecules could be produced as fast as they were destroyed by the reaction. There were only three ways imaginable by which molecules could be activated; these were absorption of radiation, collision with other ordinary molecules, and collision with reaction products which still retained high energy. The radiation hypothesis floundered in difficulties almost from the day of its birth; it managed to survive only by clothing its naturally simple form in such a maze of complications that for a time no one could be quite sure what it was or what it predicted, but by 1925 it had been virtually abandoned. The energy chain theory, proposed by Christiansen (1) in 1923, never met with much favor, yet has been astonishingly hardy. So far as unimolecular reactions were concerned, it faced two serious difficulties. One difficulty was that the rates were independent of the presence of enormous amounts of inert gas, which might have been

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expected to have a deactivational effect; the high specificity of electronic energy transfers was cited as evidence that this would be possible, but there remained an uncomfortable feeling that decent chemical molecules would never behave so. The other difficulty was that some of the unimolecular reactions were endothermic, and for them an energy chain would appear quite impossible. It is not our purpose to trace the further history of energy chains, although it is a most interesting one. Whenever a difficulty has been encountered in reaction kinetics, energy chains have been proposed; nobody takes them quite seriously, and yet after the difficulty has been resolved in another way, it may be observed that they are again being brought out as the explanation of another reaction. At the moment it seems possible that energy chains may actually play a rôle in certain types of explosions; but in view of their long history, one feels the need of caution in admitting this.

The third imaginable way of obtaining activations was by ordinary collisions; it could not have been as interesting as its more esoteric rivals, since all the early calculations made what must now seem the obvious error of representing such a complex molecule as nitrogen pentoxide by a system with only one degree of freedom. Both Rodebush (2) and Lewis and Smith (3) were very close to the present accepted solution; Lewis and Smith missed it apparently through a somewhat belated confidence in the radiation hypothesis; Rodebush, even earlier, could hardly have failed to calculate the rate of activation correctly, if he had calculated it at all, but his attention was focussed on the actual reaction process. There was thus a period of almost three years during which it was repeatedly shown that collisional activation could not be fast enough to account for the rate of unimolecular reactions; then, quite suddenly, at the end of this period, it was shown by Christiansen (4), Hinshelwood (5), Fowler and Rideal (6), Rice and Ramsperger (7), and Kassel (8) that it could be. Christiansen's work was incompletely developed; Fowler and Rideal's ignored, intentionally, the almost sacred principle of microscopic reversibility. The theories of Hinshelwood, Rice and Ramsperger, and Kassel were all quite similar; in essentials, they were as follows.

THE ACCEPTED THEORY AND ITS WEAKNESSES

An activated molecule is one whose total internal energy exceeds some limit, appropriate to the reaction in question; such molecules decompose spontaneously at rates which may be a function of their total energy. The activated molecules are produced at collisions. To calculate the rate at which they are produced, it is assumed that at every collision the internal energy of the two molecules is redistributed without regard to its former partition; then it can be calculated without uncertainty that only a negligible fraction of activated molecules will survive a collision. It is then assumed that the rate at which collisions produce activated molecules is equal to the rate at which they would destroy them, if the Maxwell-Boltzmann quota were maintained. It is never quite maintained, since some activated molecules are lost through reaction, but the maintenance is better the higher the pressure. It is only necessary to make precise assumptions about the energy states in which the molecule in question can exist and the specific reaction rates of those which are activated, in order to calculate the rate of reaction at any temperature and pressure. It turns out that this can always be done to give agreement with experiment, although for nitrogen pentoxide the margin is uncomfortably close.

It is our present problem to search this theory for weaknesses and omissions which might have been overlooked in its younger days. It has been shown rather well that the assumption in regard to the rate of production of activated molecules is correct within two or three per cent, which is a quite sufficient refinement. The exact energy levels of complex molecules are not yet known experimentally, but there is little reason to think that our guesses on this point introduce serious errors. There remain then the assumption of complete redistribution of energy at every collision and the assumed specific reaction rates of the various activated states. Both of these require careful consideration.

REDISTRIBUTION OF ENERGY AT COLLISIONS

We shall consider first the evidence concerning redistribution of energy at collisions. The assumption which has been made is

that this redistribution is complete; this need not be taken quite literally, however. The rate of destruction of activated molecules will be almost unchanged if it is assumed that an activated molecule loses only about one-fifth of its energy at the average collision, instead of one-half. The question to be answered is whether this fifth will be lost in one collision, one hundred, or one million. Theoretical physics supplies no definite answer. Kallmann and London (9) have shown that such transfers may be highly specific, and have indicated the possibility that they may even occur with somewhat enhanced diameters in cases of very good resonance. It has been demonstrated by O. K. Rice (10), however, that the method used does not give very good results in simpler cases, because of an unsatisfactory treatment of the relative motions of the two particles, and these enhanced diameters are thus doubtful. The more recent work of Zener (11) is not very directly applicable to the problem in question, since it is restricted to diatomic molecules and low quantum numbers; for such cases, it indicates values of about 10^{-5} for the probability of internal energy transfer at collisions. Experimental physics also is of little help. Kneser (12) has found that the velocity of sound in carbon dioxide rises at high frequencies to the theoretical value for a diatomic gas of the same molecular weight. This suggests that at these frequencies vibrational energy cannot come into equilibrium with translational and rotational in a quarter-cycle, during which about 1000 collisions are made. It does not exclude the possibility that vibrational energy transfers as such take place with greater rapidity. Miss Kornfeld and Hilferding (13) have studied the thermal conductivity of gas mixtures; when these mixtures contained hydrogen as one component, the conductivity was less than that calculated on the assumption that energy transfers between the unlike molecules took place as readily as others, but sufficient results are not available to permit any definite conclusions.

The evidence from unimolecular reaction rates is itself somewhat ambiguous. Practically all of the numerical calculations that have been made are based quite explicitly on the assumption of complete redistribution. It is likely that this assumption would

not have been made so frequently had not attention in former times been so sharply focussed on nitrogen pentoxide. The author believes that existent theory does account for the rate of this reaction. This opinion can be maintained, however, only by the most optimistic arguments, and the assumption of redistribution at every collision is an absolute necessity. Still, it should be emphasized that although there must be redistribution at every collision, there need not be complete redistribution, since the loss of about one-fifth of the excess energy will always be an effective deactivation. This was shown long ago by Rice and Ramsperger, although they did not apply it to exactly the present question. Thus, even for nitrogen pentoxide there is room for some persistence of internal energy. This much persistence would actually be very important for such properties as thermal conductivity, since three collisions instead of one would be needed to remove one-half of the excess energy of a molecule.

For all other known reactions, the rate can be accounted for with a much wider margin. Since our knowledge of the internal energy relationships in complex molecules is so extremely scanty, no accurate statements can be made; but it is probably safe to say that the rates of decomposition of azomethane and of nitrous oxide could be reconciled with the assumption that an activated molecule would lose one-fifth of its excess energy only after a series of ten collisions. It is, however, quite possible to assume also that redistribution occurs at every collision. For still other reactions—the decompositions of at least three different ethers, of propionaldehyde, and of dimethyltriazen—the data would be in harmony with a rate of internal energy transfer probably a hundredfold less. In all of these cases we can only say that the rate of transfer need not be high. It seems possible that the extremely interesting work reported by Kistiakowsky and Nelles (25) furnishes the first example of a reaction for which the assumption of a low rate of energy transfer is absolutely required. For this reaction—the isomerization of dimethyl maleate—there seem to be only about 10^{-4} as many activations as the assumption of redistribution at every collision would require, even when the minimum possible number of effective degrees of freedom is assumed.

Thus, of about twenty known unimolecular reactions there is one that seems to demand redistribution at every collision and one that indicates a much slower transfer of internal energy; none of the others provides definite information on this point.

In this connection the behavior of chemically inert gases is of interest. Ever since the phenomenon of pressure-dependent first-order rate constants was discovered by Hinshelwood, it has been known that inert gases had specific effects in maintaining the high pressure rate—that is, in producing activations. It has always been found that the monatomic gases are relatively inefficient; owing to the experimental difficulties of the measurements, it can only be said that, molecule for molecule, they are not more than one-tenth as efficient as are the reactant gases themselves. The diatomic gases, carbon monoxide and hydrogen, are also ineffective, except for the activation of the very small molecule, nitrous oxide. Hydrogen, on the other hand, is about as efficient as the reactant molecules in a considerable number of cases. More complex substances, such as methane and ethane, show a variable, but usually high, efficiency. It has been shown by O. K. Rice (14) that there is no difficulty in interpreting these results; even such a simple molecule as hydrogen would be able to deactivate the most complex organic molecule, if complete redistribution were attained. Furthermore, at least the general character of the results is about what might be expected; monatomic gases, which could deactivate only by acquiring large amounts of kinetic energy, ought to be inefficient, since processes involving large changes in kinetic energy are known to take place with difficulty. Hydrogen should be the most efficient diatomic gas. One reason for this is that suggested by Oldenberg (15), that a light molecule should be best able to remove the vibrational energy of light hydrogen atoms; another is that, because of its small moment of inertia, hydrogen can take up relatively large amounts of rotational energy without much change in moment of momentum, the conservation of which may cause difficulty in other cases. It seems likely that this second reason may be of greater importance than the one suggested by Oldenberg, since the fact that hydrogen should be able to remove energy

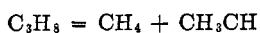
efficiently from a single CH bond does not mean that it would be equally efficient in removing it from the entire molecule.

THE SPECIFIC REACTION RATES FOR ACTIVATED MOLECULES

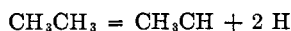
Chemical nature of the reaction process

We come now to a consideration of the second problem, the evaluation of specific reaction rates for the various activated states. The question of the exact nature of the reaction process is absolutely fundamental here. Before the physical mechanism of the elementary process can be discussed, its chemical formulation must first be known. This problem has attracted considerable attention recently, but unfortunately very little progress has been made toward its solution. It is quite likely that different types of chemical processes occur. For the decompositions of the azo compounds studied by Ramsperger the primary process seems to involve the simultaneous splitting of both alkyl groups from nitrogen; the evidence for this comes from the work on the unsymmetrical compound, methylisopropyldiimide. The occurrence of large amounts of ethane and hexane in the reaction products shows that the alkyl groups do not combine at the instant of reaction, since in that case only butane would be formed. The fact that the activation energy for this case is about midway between those for azomethane and for azoisopropane has been interpreted as evidence that both groups come off together, since otherwise the activation energy for the mixed compound would probably be nearly the same as that for azoisopropane, instead of being considerably higher. This argument, however, is admittedly uncertain, and the primary process may be the rupture of a single CN bond. If the other view, that both alkyl groups split off at once, is correct, the reaction process can still be regarded as one in which the breaking of bonds is an important element, although it should not be entirely overlooked that there is an electronic change of the nitrogen atoms corresponding to the transition from —N=N— to $\text{N}\equiv\text{N}$. It is certain that this change is part of the primary process, since part of the energy made available by it is needed for breaking the carbon-nitrogen

bonds. There is no reaction known for which it can be said with assurance that the primary process is the rupture of one bond, without complications. The elementary act in the decomposition of nitril chloride, studied by Schumacher and Sprenger (16), may be of this type, but the structure of that substance is entirely speculative. If the dissociation of nitrogen tetroxide is actually unimolecular, as it is usually supposed to be, it presumably involves nothing more than the breaking of a single bond. The decomposition of metal alkyls may also have the same simple character, but our knowledge of such reactions is very meager. Until recently it was considered probable that the decompositions of the higher hydrocarbons were initiated by the rupture of a carbon-carbon bond, since the activation energy for these reactions is 65,000 calories, a value in agreement with old estimates of the strength of the carbon-carbon bond. More recent estimates of this strength, by Mecke (17) and by Hogness (18), are much larger, and appear to require a different primary process, such as formation of a paraffin (or hydrogen) and an olefin. This problem has been discussed recently by F. O. Rice (19) and by Burk (20); Burk upholds the view that a paraffin is split out in the initial act, while Rice assumes free radical formation. Both attempt to obtain evidence from the composition of the reaction products, but without any very striking successes. Rice and Evering report (see p. 140) the occurrence of free radicals in hydrocarbon vapors after passage through a tube at 1000°C. This result is of course of great interest, but must be interpreted with some caution, since it does not necessarily prove that the main course of the reaction at 600°C. involves free radicals. If the main course at 600°C. did not involve free radicals, but a small amount of side reaction starting from free radical formation did occur, with an activation energy of 90,000 cal., this side reaction would be relatively 100 times as fast at 1000°C. But there is also a second explanation for the results of Rice and Evering. It seems possible that the primary process in these reactions may be of the type



This view has the advantage that the methyl group in splitting off captures a hydrogen atom from the carbon to which it was itself attached, rather than from a more distant atom, as is the case when ethylene is the initial product. The heat of the reaction



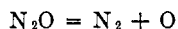
is presumably not much different from that of



which has been estimated by Mecke as 150,000 cal.; on this basis the proposed initial reaction would be about 40,000 cal. endothermic, instead of the 20,000 cal. corresponding to the primary formation of ethylene. It is likely that CH_3CH would behave like a free radical in a Paneth test such as used by Rice and Evering.

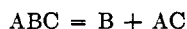
In other cases it is not easy to avoid the assumption of groups splitting off from adjacent atoms rather than from a single atom. Thus methane and formaldehyde are formed from methyl ether, and methane and ketene are formed from acetone; these reactions cannot be interpreted as has been suggested for the case of propane.

The primary process in the nitrous oxide decomposition is certainly



It is not yet established whether the structure of this substance is $\text{N} - \text{O} - \text{N}$ or $\text{N} - \text{N} - \text{O}$, and it is therefore not possible to classify this simplest of all unimolecular reactions.³

It thus appears that at least a large number of the known unimolecular reactions may be considered to be of the type



³ The work of Plyler and Barker (Phys. Rev. **38**, 1827 (1931)), which has appeared since this article was written, seems to prove that nitrous oxide has the linear structure $\text{N}-\text{N}-\text{O}$, so that its decomposition may tentatively be supposed to involve the rupture of only one bond.

as possible, but the model used in developing the theory can be reconstructed. Hinshelwood had made the assumption that all activated molecules, no matter what their total energy, had the same specific reaction rate. This seemed unlikely and also proved to be empirically unsatisfactory. In order to estimate the relative reaction rates of molecules with different energy, let us suppose that there is some characteristic relaxation time, τ , for each chemical species, such that within that time the internal energy distribution will be changed "considerably." The chance that at any instant the degree of freedom involved in the actual reaction process will have sufficient energy for reaction to occur can be calculated in terms of the Hamiltonian function for the molecule and its total energy; there will be, roughly, $1/\tau = A$ different distributions of energy per second, each of which has this calculated chance of being a true reaction distribution. Such a treatment, naturally, made the specific reaction rate increase rapidly with the total energy, and it is only when a rapid increase is assumed that the general theory works out well. The details of the treatment, of course, are approximations without any pretense at physical reality, but the introduction of a rather vaguely defined relaxation time is just the sort of approximation that one might make in treating any macroscopic vibrating system. Polanyi and Wigner (21) stated all this much more explicitly, but they made what turns out to be the rather bad assumption of identifying the constant A with some vibrational frequency of the molecule; there seem to be no good reasons for doing this, and A is actually far more variable from one reaction to another than this identification would permit. It must be kept in mind, however, that the A which occurs in the rate expression,

$$k = Ae^{-E/RT}$$

and which is thus determined experimentally, is not necessarily related in any very simple way to the actual process of energy transfer. The assumption of a relaxation time is a rather severe simplification, and even with this assumption, it is only with the particular form of the theory used by Kassel that the same A falls out for the rate constant as was put in for the relaxation time.

As has been pointed out by O. K. Rice more than once, there must be groups of degrees of freedom within which energy transfer is relatively easy, but between which it is difficult. Complications of this sort muddle the theory to such an extent that neither A nor E of the rate equation have any exactly assignable meaning of a non-statistical character.

Physical nature of the reaction process: the radioactive analogy

In addition to this inherently simple picture of the reaction process, two other theories have been proposed, both based upon quantum mechanics. We shall consider first the view that the reaction process is the non-classical escape through an energy wall that has been so successfully applied to the problem of alpha-particle radioactivity. This possibility was mentioned by Polanyi and Wigner (21) in 1928, but rejected without much consideration. Later it was definitely proposed by Bourgin (22), and it is apparently involved also in the work of Langer (23). The mathematical treatment given by Bourgin, and also that in the recent attempt of Roginsky and Rosenkewitsch (24) at a critical discussion, is far from satisfactory. Although it is clear from the work of Rice and Ramsperger and Kassel that this is a very bad approximation indeed, it is nevertheless assumed that the treatment need consider only the single quantum state that makes the greatest contribution at the temperature in question. But the greatest objections must be made, not against the mathematical methods, but against the idea itself. There are two main criticisms of this character. One is that the degrees of freedom not directly concerned in the process seem to pass out of the picture altogether and the old problem of the source of activations becomes as puzzling as it ever was. The other objection is that if one makes any sort of plausible assumption about the form of the energy hump through which the leak occurs, it turns out that there cannot be any important contribution from this source. The rate of reaction from any quantum state is controlled by two exponential factors, one of which gives the Maxwell-Boltzmann quota for that state, $e^{-W/kT}$, while the other gives

the specific reaction rate which is approximately of the form e^{-2FM} where

$$F^2 = \frac{8\pi^2m}{h^2} \quad M = \int_{x_1}^{x_2} \sqrt{V(x) - W} dx$$

With reasonable numerical values, the decrease in the Boltzmann factor with increase in W will be much more than compensated by the increase in the rate of leak, almost up to the top of the energy hump. It may be advantageous for the molecule to leak through the last few hundred calories instead of climbing all the way, but for all practical purposes the theory collapses upon analysis. This was really shown by Roginsky and Rosenkewitsch, although rather obscurely, and it is possible that they did not themselves realize it. The case of radioactivity is different, largely because the energy wall there, although high, is very thin, and the rate of leak is therefore enormously increased. It must thus be considered very unlikely that there is any resemblance in mechanism between unimolecular reaction and radioactive decomposition.

Physical nature of the reaction process: the Auger effect picture

We come now to consideration of the other proposed quantum mechanical mechanism for unimolecular reaction; this is the generalized Auger effect. The simple Auger effect is the spontaneous ionization of an excited atom. It is naturally necessary for the excitation energy to exceed the ionization energy of the unexcited particle; the electron is then ejected with sufficient velocity to balance the energy account. By the generalized effect, we shall understand any non-radiative transition of a system from a state in the discrete region of its energy spectrum to one in the continuum; the two states must of course have the same energy. The phenomenon of predissociation involves an effect of this character. It has been suggested by O. K. Rice and by Kassel that unimolecular reactions are analogous to predissociation; but since this latter phenomenon involves some features extraneous to the former case, it seems better to speak merely of an Auger effect, as has since been done by Roginsky and Rosenke-

witsch. There is little doubt that unimolecular reaction may be correctly described in this way. However, the question arises whether in so doing we may not be using a more complex apparatus than the problem requires. The situation seems to the writer to be as follows: if the reaction process involves an electron quantum jump, then probably the language of the Auger effect is needed. If, however, the elementary act takes place adiabatically, it would appear that the molecule merely breaks as any mechanical system might, owing to the accumulation of vibrational energy at a weak point; if this is so, then the reaction process has really nothing to do with quantum mechanics.

The situation suggested here is really very similar to that which is developing with bimolecular reactions. The quantum mechanical theory of these processes, which has been given by Eyring and Polanyi and which is discussed by Eyring (see p. 103), is really only a quantum mechanical theory of the interatomic forces; within the force field given by their calculations, the atoms are supposed to move in an essentially classical way, giving an adiabatic reaction process. Such a mechanism may not be unobjectionable, but the method has been applied in a sufficient number of cases to make it very probable that it does represent the most important features of the process. Likewise it may be hoped that unimolecular reactions have an essentially classical mechanism.

It is unfortunate that the electronic structure of molecules is still so little understood; the physicist has been much concerned during the last few years with this problem, but the results obtained so far are of little use to us here. It does seem that very profound changes in binding can occur without anything that is really a quantum jump, and there is thus some support for our idea that the mechanism of unimolecular reaction is essentially classical. But at the present time it cannot be said that none of the known reactions involves an electronic change.

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