

THE MECHANISM OF ENERGY EXCHANGE IN UNIMOLECULAR REACTIONS

OSCAR KNEFLER RICE

Department of Chemistry, Harvard University, Cambridge, Massachusetts

Received December 3, 1931

It is now generally conceded that, in the case of homogeneous unimolecular reactions taking place in the gas phase, activation is the result of an exchange of energy at collisions. It is important in our study of these reactions to find out what we can about the mechanism of this exchange. The aim of the present paper will be to give an account of two methods of attack by which some information on this subject may be obtained. First, we shall show what may be found out by an analysis of the reaction velocity experiments themselves, particularly those in which a large excess of inert gas is present. Second, we shall indicate what may be done in the way of theoretical calculations on the dynamics of the processes involved, taking into account the intermolecular forces, the vibration frequencies, and the other mechanical properties of the molecules which collide.

ANALYSIS OF REACTION RATE EXPERIMENTS

In most unimolecular gas reactions the reaction consists of a decomposition, in which, naturally, only one molecule is primarily involved. Such reactions, in so far as they have been tested, show a characteristic behavior, in that the unimolecular constant, although roughly independent of pressure at higher pressures, decreases at lower pressures as the pressure of the reacting gas decreases. This decrease occurs because activation is by collision, and first becomes marked at pressures where the time it takes an average activated molecule to react is of the same order of magnitude as the time before a collision which will deactivate it may be expected (1).

We may formulate these considerations in a somewhat over-

simplified way, but one good enough for our present purposes, as follows. We suppose the pressure of reacting gas (which is supposed to be pure, i.e., we consider the situation at the beginning of the reaction) to be p and the fraction of all the molecules which are activated to be W . Then the total number of molecules deactivated per unit time will be given by aWp^2 , where a is a constant. The expression is proportional to the number of collisions made by activated molecules per unit time. If very few of the activated molecules react, then this is the rate of activation also. Let the number of molecules which react per unit time be Kp . Now when aWp^2 equals Kp , that is, when

$$p = K/aW \tag{1}$$

we see that for pressures this low the number of activations per unit time is getting to be of the same order of magnitude per unit time as the number of decompositions taking place. At such pressures the rate of activation will not be sufficient to keep the number of activated molecules up to its equilibrium amount, and equation 1 accordingly gives roughly the pressure at which the rate constant begins to fall off.

If we can calculate a and W it is then possible to predict the pressure at which the falling off in the rate constant should begin. If we assume that deactivation takes place at every collision of an activated molecule with another molecule we can calculate a . And if we assume that an activated molecule is simply one which has an energy greater than a certain amount—neglecting, which is all right for this purpose, the fact that the chance of reaction of an activated molecule probably depends strongly on the energy it has in excess of its energy of activation—then for a molecule with any given number of atoms we could calculate W by the aid of statistical mechanics, provided the oscillating particles in the atom behaved classically. Taking into account the fact that they are quantized, and in spite of the fact that we do not know all the frequencies exactly, we can still estimate W . In general the more complex the molecule, i.e., the greater the number of atoms it contains, the greater will be W , and, hence, the smaller the critical value of p calculated by equation 1.

If now we make the calculation outlined in the above paragraph, and compare the value of p so calculated with the value observed, we find a number of cases in which there is good agreement. They are azomethane (2), methylisopropylidimide (3), nitrous oxide (4), and, probably, nitrogen pentoxide (5). This might be taken as evidence in favor of the assumptions we have made. On the other hand, however, there is a whole series of substances—propionaldehyde (6), several ethers (7), propylamine (8), and dimethyltriazene (9)—which fall off at much too high a pressure. In these cases we must conclude that either there is an impedance to transfer of energy among the various degrees of freedom inside the molecule, so that it acts as though it were a smaller molecule than it really is, with correspondingly small value of W , or else it is not true that deactivation takes place at every collision of an activated molecule (10).

To get further evidence, which may help to decide between these alternatives, we turn to the experiments in which hydrogen, an inert gas, is added to the reacting gas, in particular in the cases of propionaldehyde and four ethers of varying complexity (11). If hydrogen is added to these gases at low pressures, it has about the same effect in increasing the rate constant toward its high pressure value as the same additional pressure of the reacting gas itself would have. Thus hydrogen has about the same effect as an activator or deactivator as the organic molecules. This is true in five cases, in which the pressure at which the falling off in rate actually occurs (with no added hydrogen) varies between 150 and 25,000 times that expected. If this variation is due to a variation of the efficiency of activation and deactivation of the reacting molecule by itself, it must be paralleled in a remarkable manner by the efficiency of activation and deactivation by hydrogen. We therefore conclude that this efficiency is the same in all these cases, and are inclined to refer the premature falling off in rate to an impedance of energy transfer inside the molecule, making it act like a smaller molecule, rather than to any poor transfer of energy at collision (12). Of course, such a conclusion must be accepted only tentatively on the basis of the evidence available. Indeed, at least one case is known—that of propy-

lamine (8)—in which hydrogen actually retards the reaction rate. But we also know that this reaction is attended with complications (subsequent reactions, which may be present in other cases also, but which in this case seem to be affected by hydrogen.)

In general it is found that gases other than hydrogen (and the products of the reaction, which always seem to keep up the rate) do not have much effect on the reaction rate, at least in the case of the ethers and propionaldehyde. In the case of azomethane, ethane has a considerable, and nitrogen a much smaller effect in raising the rate at low pressures (13). In the case of propylamine, nitrogen and helium have an effect similar to that of hydrogen.

In the next section an attempt will be made to indicate what is to be expected theoretically for the effects of inert gases.

THEORETICAL CONSIDERATIONS

The theory of the interchange of vibrational and translational energy has been developed on the basis of quantum mechanics by Zener (14), but it has not been applied to the case at hand. We shall give an outline of the essential features of the theory and give the results of its application, confining ourselves to the case of inert gases, as this is much simpler than finding the action of large organic molecules on each other.

Even the case of an organic molecule and an inert gas is much too complicated for a general treatment. We shall, therefore, greatly idealize it. If we are interested in the case of exchange of the translational energy of the inert molecule and the vibrational energy of a hydrogen atom attached to a carbon atom, we may simplify the situation, considering the collision of a free atom and an oscillator fixed in space. We may further simplify the problem by assuming the atom to be moving in the line along which the oscillator vibrates.

We shall consider the vibrator to have the frequency of the transverse vibrations (due to the *bending* of the valence bond) of the hydrogen in the organic molecule, since this frequency is lower than the frequency associated with the longitudinal vibrations, and will on this account be able to transfer energy more readily.

Now the frequency associated with the transverse vibrations of

the hydrogen (15) is about 1400 wave numbers (cm.^{-1}), which corresponds to an energy of about 4000 cal. per mole.¹ An activated molecule contains about 50,000 or 60,000 cal. per mole. This may be distributed among varying numbers of degrees of freedom in the molecule. If it really acts like a much smaller molecule and this energy must all be distributed among a small number of oscillators which do not communicate energy to any great extent with the rest of the molecule, then some of these oscillators may be rather highly excited. If, on the other hand, the energy is distributed over a large number of oscillators, one would rarely expect to find an oscillator in any higher state than its first excited vibrational level. Be that as it may, we shall assume, just to get an idea of orders of magnitude involved, that we have simply a collision between a particle with the normal kinetic energy for one direction ($1/2 kT$) and an oscillator in the first excited state, and find the probability that after the collision the oscillator is in the lowest state and the particle has taken off the energy as translational energy. The loss of one quantum of vibrational energy, 4000 cal., should be, in the opinion of the author, sufficient to bring an average activated molecule down into the energy region where the Maxwell-Boltzmann quota holds under the conditions in the reacting mixture—that is, to effectively deactivate it (16). If the 4000 cal. is an overestimate of the energy of the vibrator in the molecule, the results will nevertheless not be without significance (though the calculations would have, of course, to be modified), since the removal of a lesser amount of energy might have an appreciable effect tending toward the deactivation of the molecule.

The force constant for the transverse vibration of the hydrogen we shall take as 1.2×10^5 dynes per centimeter, instead of 0.6×10^5 as Andrews does in his discussion on the structure of organic molecules (15). This is obtained from the frequency by taking the effective weight of the vibrating particle as 1, in atomic weight units, instead of $\frac{1}{2}$, as is done by Andrews. This is because we assume that only one atom is involved in this vibration, while

¹ We assume the oscillator to be itself quantized, although its vibrations are really but part of a normal vibration of the molecule as a whole.

Andrews assumed that two are involved; this makes the reduced mass half as large. The author feels that the present assumption is fully as reasonable, but the point is not of great importance.

The other factor which enters into the problem, and in fact plays a most important rôle, is the character of the force between the atom in the large molecule and the colliding particle. This may be expressed approximately as an exponential function, constant $\times \exp. (-\alpha r)$, where α is a constant which determines the sharpness of the collision, and r is the distance between the vibrating atom and the particle (14). From the discussion of Lennard-Jones (17) on intermolecular forces, we may estimate α for the collision of two hydrogen molecules to be about $6 \times 10^8 \text{ cm.}^{-1}$, and we may take it to be the same for the case at hand. However, it is of course true that the colliding particle will not always strike the hydrogen atom just in the direction of its transverse vibrations. Often the blow will be a somewhat glancing one, or will come from an angle, giving a smaller or greater effective value of α . The forces which we thus consider are the ordinary forces of repulsion between atoms, and extend to distances comparable with kinetic theory radii.

The calculation is made in the following way. We first treat the system as though it were composed of the two separate parts—the oscillator, and the free particle which is supposed to be acted upon by a force which is that force to be expected if the oscillator were in a sort of average position, defined by its wave function. The motion of the oscillator is then taken into account as a quantum mechanical perturbation. This gives rise to transitions in which the system goes from a state in which the oscillator has a certain amount of energy to another state in which it has given this energy to the free particle, and the calculations of the transition probabilities can be made, following Zener, in the standard manner. Some details have been done more exactly than in his calculations, but essentially there is no great difference. The approximations are rough in any case, and only the order of magnitude of the results is significant.

The results of the calculations which have been made are presented in table 1. The details will appear later elsewhere.

Calculations have been made, not only with the fundamental constants involved to which approximately those values mentioned above have been given, but also with those constants to which other values have been given. This will enable the reader to tell how the results vary when these constants are varied. It is also of importance in connection with the effects of the different kinds of gases. It will be seen, in general, that hydrogen may be expected to have a much greater effect than other gases of greater

TABLE 1
Transition probabilities

$k_0 \times 10^{-6}$	ν	M	W_1	$\alpha \times 10^{-8}$	γ
<i>dynes per centimeter</i>	<i>cm.⁻¹</i>		<i>calories per mole</i>	<i>cm.⁻¹</i>	
1.2	1400	2	800	9.12	.02
1.2	1400	2	800	7.06	.012
1.2	1400	2	800	5.76	.006
1.2	1400	2	800	4.08	.00085
1.2	1400	2	1600	7.06	.02
1.2	1400	2	1600	5.76	.012
1.2	1400	1	800	7.06	.035
1.2	1400	1	800	5.76	.02
1.2	1400	1	1600	5.76	.045
1.2	1400	4	800	7.06	.0016
1.2	1400	4	800	5.76	.0005
0.48	560	20	800	5.76	.000015

k_0 is the force constant of the oscillator in dynes per centimeter.

ν is the frequency of the oscillator in cm.^{-1}

M is the atomic or molecular weight of the colliding particle.

W_1 is the initial energy of the colliding particle in calories per mole.

α is in cm.^{-1}

γ is the probability of energy exchange taking place.

mass, even allowing, in the case of helium, for the possibility that α may have a greater value, i.e., the collision may be sharper.) These results are in general agreement with the experiments, although in the case of azomethane nitrogen appears to have much more effect than we would expect from the results of the calculation.

On the whole, the probability of transition is seen to come out to be rather low—though by no means inappreciable—even for the

most favorable cases. Considering the parallel between the effectiveness of hydrogen as an activator and deactivator and the effectiveness of the organic molecules mentioned above, it may be—though the present calculations hardly can be said to be final—that our estimate of the efficiency of deactivation by collision will have to be revised downward. It should, of course, be noted that the exact relation between the effectiveness of hydrogen and organic molecules is complicated by certain factors which have not been mentioned. Thus hydrogen is about as effective *pressure for pressure*, as the other gases. But it makes more collisions, presumably, for hydrogen molecules move faster. On the other hand, it may have to strike the organic molecule in a certain place or a certain way. This prevents us from being too definite in our comparison. In any event, our conclusion that the efficiency of activation is about the same for a large number of organic molecules remains unaltered.

We have, of course, neglected any interchange of energy between two vibrators, or between a vibrator and a rotator, both of which processes, but—in the case of inert gases of simpler structure—especially the latter, may be of importance. The author has attempted to get some idea of the effect of exchange of rotational energy of hydrogen and the vibrational energy of the oscillator by trying the case where the mass of the colliding particle is assumed to be one atomic weight unit, as it seems likely that the case where rotational energy is involved will be very similar to the case where translational energy is involved, except that the effective mass will tend to approach the reduced mass of the rotator which is, in the case of hydrogen, one-half of an atomic weight unit.

SUMMARY

Summarizing, we may say that the analysis of reaction rate experiments with pure gases and in the presence of inert gases indicates that the efficiency of activation by collision with other molecules of its own kind is the same for a series of gases, and that hydrogen has the same efficiency as an activator as the reacting gas itself. Other inert gases, except, in general, the products of

the reaction, are less efficient in producing activation. Quantum mechanical calculations, dealing with the transfer of vibrational and translational energy only, indicate that hydrogen should be more effective than other inert gases of simple structure. In general, the trends of the experimental results, but not all details, are reproduced. The quantum mechanical considerations indicate that one collision of an activated molecule with hydrogen in something of the order of forty will produce deactivation.

Note added January 11, 1932: Later calculations indicate that the probability that a colliding hydrogen particle will transfer energy with a vibrator whose characteristics are like those of the carbon-carbon vibrators inside the molecule is greater than the probabilities given here; of course, less energy is transferred at each collision. The difference between hydrogen and helium is in the same direction, but is less. These results will be discussed elsewhere.

REFERENCES

- (1) LINDEMANN: *Trans. Faraday Soc.* **17**, 598 (1922).
- (2) RAMSPERGER: *J. Am. Chem. Soc.* **49**, 1495 (1927).
RICE AND RAMSPERGER: *J. Am. Chem. Soc.* **50**, 617 (1928).
RICE: *Proc. Nat. Acad. Sci.* **14**, 113, 118 (1928).
KASSEL: *J. Phys. Chem.* **32**, 225, 1065 (1928).
- (3) RAMSPERGER: *J. Am. Chem. Soc.* **51**, 2134 (1929).
- (4) VOLMER AND KUMMEROW: *Z. physik. Chem.* **9B**, 141 (1930).
NAGASAKO AND VOLMER: *Z. physik. Chem.* **10B**, 414 (1930).
RAMSPERGER AND WADDINGTON: *Proc. Nat. Acad. Sci.* **17**, 103 (1931).
- (5) RAMSPERGER AND TOLMAN: *Proc. Nat. Acad. Sci.* **16**, 6 (1930).
SCHUMACHER AND SPRENGER: *Proc. Nat. Acad. Sci.* **16**, 129 (1930).
HODGES AND LINHORST: Report given at the meeting of the American Chemical Society in Buffalo, September, 1931. See also MCGRAW: *J. Am. Chem. Soc.* **53**, 3683 (1931).
- (6) HINSHELWOOD AND THOMPSON: *Proc. Roy. Soc. London* **113A**, 221 (1926).
HINSHELWOOD: *Proc. Roy. Soc. London*, **113A**, 230 (1926).
- (7) HINSHELWOOD: *Proc. Roy. Soc. London* **114A**, 84 (1927).
HINSHELWOOD AND ASKEY: *Proc. Roy. Soc. London*, **115A**, 215 (1927).
GLASS AND HINSHELWOOD: *J. Chem. Soc.* **1929**, 1804.
- (8) TAYLOR AND ACHILLES: *J. Phys. Chem.* **35**, 2658 (1931).
- (9) RAMSPERGER AND LEERMAKERS: *J. Am. Chem. Soc.* **53**, 2061 (1931).
- (10) RICE AND RAMSPERGER: *J. Am. Chem. Soc.* **50**, 617 (1928).
RICE: Réunion internationale de chimie physique, Paris, October, 1928, p. 305.

- (11) HINSHELWOOD AND ASKEY: Proc. Roy. Soc. London **116A**, 163 (1927). See also references 6 and 7.
- (12) RICE: Z. physik. Chem. **7B**, 226 (1930).
- (13) RAMSPERGER: J. Phys. Chem. **34**, 669 (1930).
- (14) ZENER: Phys. Rev. **37**, 556 (1931). See also OLDENBERG: Phys. Rev. **37**, 194 (1931).
- (15) ANDREWS: Phys. Rev. **36**, 544 (1930).
- (16) RICE AND RAMSPERGER: J. Am. Chem. Soc. **49**, 1617 (1927), especially figure 1.
- (17) LENNARD-JONES: in Fowler's Statistical Mechanics, Chapter 10. Cambridge University Press, Cambridge (1929).