

EXPERIMENTAL TESTS OF UNIMOLECULAR REACTION-RATE THEORIES¹

HERMAN C. RAMSPERGER

*Gates Chemical Laboratory, California Institute of Technology,
Pasadena, California*

Received December 8, 1931

Some six years ago there existed no adequate theoretical interpretation of homogeneous unimolecular reactions. At that time only one genuine reaction of this type was known, namely, the decomposition of nitrogen pentoxide. At present we have a list of some fifteen unimolecular reactions and a theoretical interpretation which is not badly in disagreement with any of these reactions and is strikingly in accord with some of the most thoroughly studied ones. This state of affairs gives strong support to the belief that the kinetic picture provided by the theory is essentially correct, admitting, however, that the detailed nature of the process is not yet clear. The purpose of this paper is (1) to point out certain unique characteristics of the present theory that are capable of experimental test, and (2) to show to what extent these unique characteristics agree with the experimental data now available.

When a single molecule decomposes or undergoes an internal rearrangement the reaction is said to have a unimolecular mechanism. Frequently, however, in decomposition reactions the entire chemical change that is being measured represents more than one reaction step, but when one of these steps is very much slower than all other steps the course of the chemical change will be an accurate description of the course of the slow step. Now we are in some doubt about the complete mechanism of the decomposition reactions described as unimolecular, yet because they fulfill certain

¹ Contribution No. 303 from the Gates Chemical Laboratory, California Institute of Technology.

requirements expected of a unimolecular process we feel quite certain that we are measuring the rate of a slow unimolecular step. Before a reaction can be designated as having a unimolecular mechanism it must be shown to have certain unique characteristics expected on theoretical grounds for such a reaction.

QUALITATIVE THEORETICAL CONSIDERATIONS

It is now generally accepted that a molecule that is capable of reaction must be activated, that is, have an unusually high energy content. This energy is obtained by collisions with other molecules. Such activated molecules may either react spontaneously or be deactivated by the succeeding collisions. We may then consider two extreme cases. At sufficiently high pressures most of the activated molecules will be deactivated by the frequent collisions that occur, and only a small fraction of the activated molecules react. This will be the case if there is a time lag between activation and reaction. The Maxwell-Boltzmann quota of activated molecules will then be maintained. The molecules reacting in unit volume in an interval of time dt will therefore be a small fraction of the total number of molecules in unit volume; or, mathematically,

$$\frac{dN}{N dt} = k$$

where N is the number of molecules per cubic centimeter and k is the first order reaction rate constant (1).

The other extreme case of pressures sufficiently low so that every molecule is given time enough to react spontaneously before deactivation by collision will give a different result. Here the rate of reaction is identical with the rate of activation. The number of molecules activated per unit volume in a time interval dt is proportional to the number of collisions in unit volume and time dt . The number of such collisions is proportional to the square of the concentration and thus we obtain for the rate of the reaction the expression

$$dN/dt = k_2N^2$$

where k_2 is the second order rate constant. There will evidently be an intermediate pressure range over which the reaction is changing continuously from first order to second order. A reaction having a bimolecular mechanism can be shown to be of second order or of higher order, so that we have a unique criterion for a unimolecular mechanism.

OUTLINE OF PRESENT THEORIES

In order to make this qualitative result quantitative it is necessary to specify more exactly the nature of the activation and to make some assumptions concerning the chance of reaction of activated molecules. The simplest assumption to make is that a molecule is activated if the molecule as a whole contains energy greater than some limiting value ϵ_0 , to be known as the critical energy. We may further suppose that the chance that an activated molecule reacts be independent of the location of the energy within the molecule and independent of the amount of energy in excess of ϵ_0 . This theory is known as Theory I (2).

Before deriving an expression for the rate constant for this theory some method of calculating the rate of activation is needed. The simplest procedure is to use the principle of microscopic reversibility and to set the rate of activation equal to the rate of deactivation at equilibrium (3). The assumption is then made that each collision of an activated molecule removes sufficient energy to deactivate it; thus the rate of activation is equal to the number of collisions per unit time made by activated molecules. When the quota of activated molecules is not maintained, their rate of formation may still be set equal to the rate of deactivation under equilibrium conditions, since the fact of reaction does not affect the rate at which they are formed.

Let W be the fraction of activated molecules calculated from the distribution law. The number of collisions of activated molecules at equilibrium, which is also the rate of activation at both high and low pressures, is then aN^2W where a is a kinetic theory constant. This rate of activation is to be balanced by the combined rates of deactivation and reaction. If Z is the actually existing number of activated molecules per unit volume, the rate

of deactivation is aNZ , and since a fraction of the activated molecules react, their rate of reaction is bZ , b being the specific rate constant for activated molecules. Then

$$aN^2W = aNZ + bZ \quad (1)$$

Let k be the fraction of all of the molecules reacting per second. Then

$$k = bZ/N \quad (2)$$

Solving for Z from equation 1 and substituting in equation 2 we obtain

$$k = \frac{bW}{1 + \frac{b}{aN}} \quad (3)$$

At high pressures the actually existing number of activated molecules is $Z = NW$. Then the rate constant is

$$k_\infty = bNW/N = bW$$

and substituting in equation 3 we have

$$k = \frac{k_\infty}{1 + \frac{k_\infty}{aNW}} \quad (4)$$

$a = 4s^2 \sqrt{\pi kT/m}$, where s is the molecular diameter, m is the mass of a molecule, and k is the gas constant per molecule. From classical statistical mechanics

$$W = \int_{\epsilon_0}^{\infty} W_\epsilon d\epsilon = \int_{\epsilon_0}^{\infty} \frac{1}{\Gamma\left(\frac{n}{2}\right)} \left(\frac{\epsilon}{kT}\right)^{\frac{n-2}{2}} e^{-\frac{\epsilon}{kT}} \frac{d\epsilon}{kT} = \frac{1}{\Gamma\left(\frac{n}{2}\right)} \left(\frac{\epsilon_0}{kT}\right)^{\frac{n-2}{2}} e^{-\frac{\epsilon_0}{kT}} \left(1 + \frac{n-2}{2} \frac{kT}{\epsilon_0} \dots\right)$$

where ϵ_0 is the critical energy and n is the number of internal squared terms. The second and higher terms can usually be neglected.

When N becomes sufficiently large, the second term in the denominator of equation 4 becomes negligibly small compared

with unity and $k = k_{\infty}$, the first order high pressure rate constant. When, however, N is sufficiently small the second term becomes large compared with unity and k is proportional to N , that is, the reaction is of the second order.

This theory has mathematical simplicity to commend it but some of the most thoroughly studied reactions are not in agreement with it. The assumptions upon which it is based are probably too simple for at least some of the unimolecular reactions. It is particularly undesirable that the chance of reaction of an activated molecule be independent of the energy it has in excess of some minimum quantity. Furthermore, it might be expected that the molecules that react have the necessary energy localized in that part of the molecule where dissociation or rearrangement is to occur.

Theories II and III require that reaction occur when the energy ϵ_0 becomes localized in a limited region of the molecule. An activated molecule is any molecule whose total internal energy, distributed in any manner among all of the degrees of freedom, is greater than ϵ_0 . It is then assumed that this energy is being continually redistributed within the molecule between collisions, thus making it possible to localize sufficient energy so that reaction results. This also gives a kinetic picture to the time lag between activation and reaction.

We are then interested in the rate at which *activated* molecules of total energy ϵ greater than ϵ_0 change over into *reactive* molecules having a localized energy of ϵ_0 (4). If a condition of equilibrium between reactive and activated molecules were to exist, then the rate at which reactive molecules revert to non-reactive but activated molecules would be identical with the rate at which reactive molecules are formed. It is assumed that the rate at which reactive molecules become non-reactive is proportional to the number of reactive molecules which would exist at equilibrium. This then is also the rate of formation of reactive molecules and, since every reactive molecule reacts, it is the rate of reaction of activated molecules. Now the fraction of activated molecules of energy ϵ which at equilibrium would be reactive (i.e., contain a localized energy ϵ_0) becomes much greater as ϵ is

increased, hence an activated molecule having an energy considerably in excess of ϵ_0 is more likely to react than one with but little excess energy. According to Theory II of Rice and Ramsperger the energy ϵ_0 must be localized in one squared term, and according to Theory III of Kassel (5) (a special case under "Other Theories" b of Rice and Ramsperger) the energy ϵ_0 is localized in two squared terms. Experimental data have not been sufficiently accurate to decide between the two theories. The two squared terms used in Theory III may be identified with a vibrational degree of freedom and the mathematical treatment of this theory is more simple.

An expression for the rate constant as a function of the concentration is similar in form to that of Theory I (6). It is necessary now, however, to specify the energy of activated molecules, for the specific rate constant b of such molecules is now a function of their energy while according to Theory I it was independent of ϵ . One must therefore replace W by $W_\epsilon d\epsilon$ and b by b_ϵ and integrate over all energies from $E = E_0$ to $E = \infty$. We then obtain the equation

$$k = \int_{\epsilon_0}^{\infty} k_\epsilon d\epsilon = \int_{\epsilon_0}^{\infty} \frac{W_\epsilon b_\epsilon d\epsilon}{1 + \frac{b_\epsilon}{aN}} \quad (5)$$

The equations for $W_\epsilon d\epsilon$ and for a have already been given. b_ϵ differs slightly in the two theories. In Theory III it has the value

$$b_\epsilon = A \left(\frac{\epsilon - \epsilon_0}{\epsilon} \right)^{\frac{n-2}{2}}$$

where

$$\left(\frac{\epsilon - \epsilon_0}{\epsilon} \right)^{\frac{n-2}{2}}$$

is the fraction of activated molecules which would at equilibrium have energy ϵ_0 or more in two squared terms and A is the proportionality constant. This constant A may be evaluated in terms of the high pressure rate constant (7) and is found to be

$$A = k_\infty e^{\frac{\epsilon_0}{kT}} \quad (6)$$

In all of these theories classical statistical mechanics has been used. Any actual molecule would be more accurately represented with quantized oscillators. Rice (8) and Kassel (9) have given quantum modifications of Theories II and III. The shape of the curve $\log k$ against $\log p$ obtained with these treatments is not sufficiently different from the classical curve so that the available experimental data enable us to choose between them.

PREDICTIONS OF THE THEORY

Sufficient mathematical theory is now presented so that certain unique characteristics to be expected for a unimolecular reaction are specified. A reaction can be quite definitely designated as unimolecular if it is qualitatively in agreement with the theoretical requirements of a unimolecular reaction and not with those expected for other mechanisms. A quantitative comparison of theory and experiment will allow us to decide which of the several theories most accurately represents the data and will sometimes furnish evidence as to whether the assumptions made were completely justified.

The most important qualitative characteristic of a unimolecular reaction has already been stated, namely, the expectation of a first order rate at sufficiently high pressures, a second order rate at sufficiently low pressures and a continuously changing order at intermediate pressures. However, the form of the pressure-rate constant curve in the region of transition from first to second order is not the same for Theory I as it is for the other theories. The rate equation for Theory I can be put into the form

$$\frac{1}{k} = \frac{1}{k_{\infty}} + \frac{1}{aWN}$$

If then $1/k$ is plotted against $1/N$ (or $1/p$), a straight line of slope $1/aW$ and an intercept at $1/k_{\infty}$ should be obtained (10). Theories II and III will give a curved plot, the curvature being greatest when the number of squared terms is large. Figure 1 shows such a plot applied to the decomposition of azomethane at $T = 603^{\circ}$, and to the decomposition of nitrous oxide at $T = 938^{\circ}$ (upper curve). The straight line is the theoretical curve for Theory I,

while the points are experimental. For azomethane the diameter chosen is 6×10^{-8} cm. and n is 25, while for nitrous oxide the diameter chosen was 3.05×10^{-8} cm. and $n = 2$. It is evident

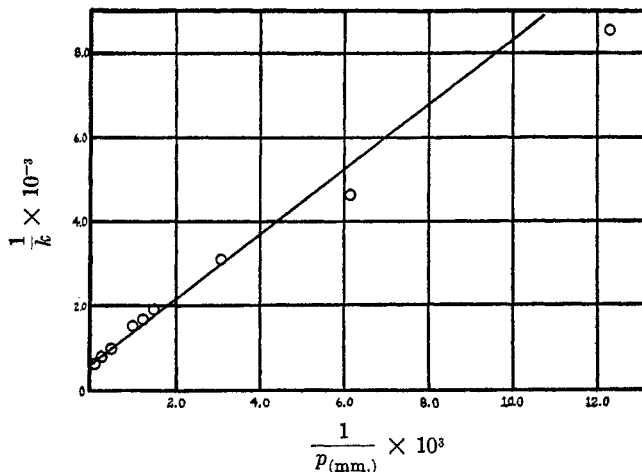


FIG. 1a. NITROUS OXIDE AT 665°C.

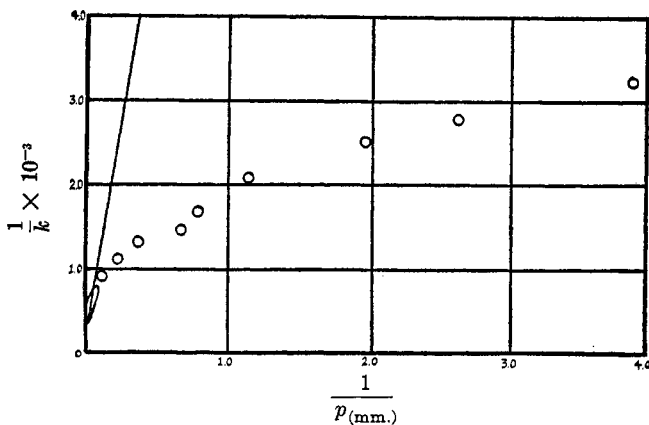


FIG. 1b. AZOMETHANE AT 330°C.

that, in the case of azomethane where the number of squared terms is large, the line representing the experimental points shows a strong curvature, but that the nitrous oxide points fall

very close to the theoretical straight line with the exception of the two lowest pressure points.

The two forms of the theory exhibit another difference which is sometimes capable of experimental test. On the basis of Theory I, as the pressure is lowered the rate falls off to very nearly the same extent at different temperatures, but in the other theories the rate falls off more rapidly at the higher temperature. That is, the temperature coefficient on the basis of Theory I is nearly the same for all pressures extending from those giving a first order rate down to those giving a second order rate, while the other theories have a lower temperature coefficient in the second order region. This may be seen by differentiating the rate expressions for the limiting first and second order regions. At infinitely low pressures both forms of the theory reduce to

$$k = aNW \quad \text{or} \quad k_2 = \frac{k}{N} = aW$$

Then

$$\frac{d \ln k_2}{dT} = \frac{d \ln (aW)}{dT} = \frac{\epsilon_0 - \frac{n-3}{2}kT}{kT^2} = \frac{U_2}{kT^2}$$

For Theory I

$$\frac{d \ln k_\infty}{dT} = \frac{d \ln W}{dT} = \frac{\epsilon_0 - \frac{n-2}{2}kT}{kT^2} = \frac{U_1}{kT^2} \quad (7)$$

where U_2 and U_1 are the Arrhenius heats of activation per molecule. Since the critical energy ϵ_0 is a fixed quantity, we see that in Theory I U_2 is less than U_1 by only $\frac{1}{2}kT$. For Theory III from equation 6

$$\frac{d \ln k_\infty}{dT} = \frac{\epsilon_0}{kT^2} = \frac{U_2}{kT^2}$$

Theory II gives

$$U_1 = \epsilon_0 + \frac{1}{2}kT$$

Thus in Theory III U_2 is smaller than U_1 by $\frac{n-3}{2}kT$. The differences between Theory I and the localized energy theories will

therefore become less if n becomes less, and they of course also become less if the critical energy is localized in more squared terms.

We must now consider another characteristic of a unimolecular reaction which is true of both forms of the theory, namely, the effect of the products of the reaction or of other inert gases on the rate (11). At pressures high enough so that a first order rate constant is obtained the addition of inert gases cannot have an effect, because the rate of activation is already rapid enough to establish the Maxwell-Boltzmann quota of activated molecules. In fact, we should expect that even dissolving the reacting substance in a solvent would not affect the rate, unless the internal nature of the molecules was altered by the very close proximity of other molecules so that the heat of activation or the constant A was changed. When the pressures are such that the reaction is in the region of transition from first to second order, it will be possible for inert gases to increase the rate of activation and thereby increase the number of activated molecules actually present (Z) to a value nearer the equilibrium quota (NW). This they will do if on collision with an activated molecule they remove sufficient energy to deactivate it, for then, by the principle of microscopic reversibility, the rate of activation will be equal to the rate of deactivation. Should the inert gas be as effective in producing activation as the decomposing molecules, we can write for N in equations 4 and 5 the total number of molecules per cubic centimeter and make the appropriate minor changes in the kinetic theory constant a . When the inert products of the reaction are effective in producing activation, the rate constant will not fall off during the run to the extent that would be calculated from the partial pressure of the reacting gas, and, in fact, if the pressure increases during the progress of the run it would even be theoretically possible for the first order constant to increase. If, however, statistical equilibrium is not obtained between the molecules during collision, there may be insufficient energy transferred to the inert gas molecule to deactivate an activated molecule. This may be due to improper orientation of the two molecules or to poor resonance between them, a condition not nearly so likely to exist between two of the reacting molecules. We may there-

fore expect variations in the effect of inert gases from zero to an effect equal to that of the reacting gas itself. When a positive effect is produced we have here a distinguishing characteristic of a unimolecular reaction which will be especially useful in the second order region where it will be necessary to decide between a bimolecular mechanism and a unimolecular mechanism.²

QUALITATIVE COMPARISON OF EXPERIMENT WITH THEORY

The reactions listed in table 1 are those for which the experimental data indicate quite definitely a unimolecular mechanism. The pressure and temperature range over which the reactions have been investigated are given and the constants A and Q in the rate expression

$$k_{\infty} = A e^{-\frac{Q}{RT}}$$

are listed. The values given for n designate the number of classical squared terms required to fit the data with either Theory II or Theory III. In addition to those listed there are several others which are probably also unimolecular but for which the data are less satisfactory or not sufficiently complete for inclusion in the table. These include the decomposition of nitril chloride (26), for which k_{∞} has not been determined, the decomposition of acetone (27), of dipropyl ether (28), and of propylamine (29), which is somewhat similar to ethylamine. The isomerization of maleic ester (30) will be considered later.

We must now examine the evidence for designating these reactions as unimolecular. In each case there is evidence that the reaction is homogeneous. A large increase in the surface to volume ratio has either no effect or only a slight effect on the rate of the reaction. Presumably, also, there are no homogeneous catalysts present, since at least some of these reactions are reproducible with different samples or even with samples prepared by a different method. The amount of an impurity acting as a

² It is desirable to use the terms unimolecular, bimolecular, etc. to apply to the mechanism of the reaction and to distinguish clearly between the mechanism and the order of a reaction. Thus, a unimolecular reaction which is of the second order should no longer be designated as bimolecular.

TABLE I
Data for unimolecular reactions

SUBSTANCE REACTING	P centimeters	T °C.	A	Q calories per mole	n
Nitrogen pentoxide, N_2O_5 (12)	0.00019 to 70.0	0 to 65	4.5×10^{13}	24,700	30
Propionaldehyde, C_2H_5CHO (13)	2.0 to 40.0	450 to 600	$> 1.4 \times 10^{12}$	54,000	11
<i>d</i> -Pinene, $C_{10}H_{16}$ (14)	17.0 to 116.0	184 to 237	5.4×10^{14}	43,700	> 20
Azomethane, $CH_3N=NCH_3$ (15)	0.026 to 70.79	278 to 330	1.07×10^{16}	51,200	25
Diethyl ether, $C_2H_5-O-C_2H_5$ (16)	2.5 to 50.0	426 to 588	$> 3.1 \times 10^{11}$	53,000	6
Dimethyl ether, CH_3-O-CH_3 (17)	3.0 to 90.0	422 to 552	1.9×10^{13}	58,500	11
Azoisopropane, $C_3H_7N=NCH_2CH_3$ (18)	0.025 to 4.60	250 to 290	5.6×10^{13}	40,900	> 40
Ethylene oxide, CH_2CH_2O (19)	2.4 to 90.5	378 to 445	8.4×10^{12}	52,000	> 14
Methylisopropylidimide, $CH_3N=NC_3H_7$ (20)	0.0058 to 13.12	250 to 332	2.8×10^{15}	47,480	33
Methyl ethyl ether, $CH_3-O-C_2H_5$ (21)	2.6 to 54.0	386 to 460	1.2×10^{12}	47,000	8
Methyl propyl ether, $CH_3-O-C_3H_7$ (21)	2.2 to 33.6	400 to 450	4.5×10^{12}	49,000	12
Nitrous oxide, N_2O (22)	8.1 to 800	560 to 667	4.0×10^9	53,000	2
Ethylamine, $C_2H_5NH_2$ (23)	5.0 to 40.0	500 to 540	2.9×10^9	43,400	> 6
Dimethyltriazenne, $CH_3N=N-NHCH_3$ (24)	0.019 to 8.0	200 to 230	4.1×10^{11}	33,800	14
Trichloromethyl chloroformate, $ClCOOCCl_3$ (25)	0.4 to 1.7	260 to 310	1.4×10^{13}	41,500	> 28

catalyst would undoubtedly vary considerably under these circumstances. While not all of these reactions have been shown to be independent of the degree of purification, the similarity in chemical kinetics of the entire group is some justification for classifying them all as uncatalyzed until they should be proved otherwise.

The first qualitative criterion of unimolecularity which we shall examine is that the reaction should be of the first order at sufficiently high pressures. The reaction rates of *d*-pinene, azo-isopropane, ethylene oxide, ethylamine, and trichloromethyl chloroformate have been found to be of the first order over the entire pressure range studied. The decomposition of nitrogen pentoxide is of the first order over the enormous pressure range from 70.0 cm. to 0.006 cm. All of the other reactions have been studied in the region of transition from first to second order and it is often experimentally difficult to include a sufficient pressure range to be certain of the value of the asymptotic high pressure rate constant. The values of A given in the table are therefore somewhat uncertain for all of these transition reactions and are probably a little low in all cases. For propionaldehyde and diethyl ether no very good estimate can be made of k_{∞} , nevertheless for these reactions also the rate constant is approaching a limiting value. In determining whether or not the rate constant has reached its high pressure value, it is found that plotting the rate constant against the pressure is not sufficiently sensitive. An apparently nearly asymptotic curve will prove to be not nearly asymptotic when $\log k$ is plotted against $\log p$. Another method of determining k_{∞} is to plot $1/k$ against $1/p$. If Theory I holds, this should yield a straight line with intercept at $1/k_{\infty}$. It will also be possible to estimate the intercept when the curvature is not great, as would in fact be the case for the localized energy theories if the number of squared terms was small. The values of A for the ethers and nitrous oxide have been found by one or the other of these two methods of extrapolation.³ The values of A for

³ Values of A given in a previous publication by the author (24) were calculated directly from data given in the original papers and therefore differ slightly from the extrapolated values.

azomethane, azoisopropane and dimethyltriazenes are taken directly from the highest pressure data in the original papers, but these values may likewise be a few per cent too low. The criterion of a first order rate at sufficiently high pressures is thus fairly well satisfied by the entire list of reactions.

The second criterion, namely, that at lower pressures the rate constant should decrease with decreasing pressure, has not been experimentally verified in the five reactions already mentioned. However, as we shall see later, a quantitative treatment will show that a sufficiently low pressure has not been reached in these cases to demand a falling off in the rate. The other reactions all show a continuously changing order as the pressure is decreased, but in no case has the asymptotic second order constant been reached. Such an enormous pressure range is required to obtain both the limiting first and second order rate constants that they cannot be readily realized, except possibly when the number of squared terms is small. In this case the transition occurs more rapidly. For this reason the decomposition of nitrous oxide comes nearest to a realization of both orders.

The qualitative effect of inert gases in maintaining the rate at pressures in the transition region has been tested in most of these reactions. That such an effect is present is indicated by the fact that the first order rate constant remains nearly constant during the course of a run even though the partial pressure of the reacting substance decreases to a rather low value. This is clearly so with the two azo compounds and with dimethyltriazenes, and in the low pressure nitrogen pentoxide experiments of Ramsperger and Tolman and also in those of Schumacher and Sprenger (12). However, Hodges and Linhorst (12) find, especially in their lowest pressure experiment, a falling off during the run which is even somewhat greater than it would be without the products present. The reaction products partly maintain the rate of nitrous oxide and propionaldehyde.

When the reaction products were added to the ethers an increase in rate resulted, except in the case of diethyl ether where some unexplained retardation occurred. Hydrogen has the most effect in maintaining the rate of decomposition of all of the ethers, it

being as effective as the ethers themselves. However, large amounts of hydrogen do not increase the rate above the high pressure asymptotic value, which is of course as it should be. Gases such as helium, nitrogen, carbon monoxide, methane, and others have little or no effect in maintaining the rate of ether decomposition. Nitrogen has little effect in maintaining the decomposition rate of azomethane, but ethane is nearly as effective as azomethane itself (31). The effect of nitrogen, oxygen and particularly carbon dioxide in maintaining the rate of decomposition of nitrous oxide gave the first evidence that this reaction was really unimolecular. At the lower pressures studied this reaction is much more nearly of the second order than of the first order with respect to initial pressure. The effects of these inert gases and a later study of the reaction at high pressures have shown quite conclusively that this reaction is unimolecular rather than bimolecular.

On the whole it must be concluded that the effects of inert gases in maintaining the rate are a specific property of both the inert gas and the reacting substance. The best explanation seems to be that a lack of resonance between the inert gas and the reacting molecules hinders the transfer of energy in those cases where the inert gas is without influence.

The decomposition of nitrogen pentoxide (32) and the rearrangement of pinene (14) have been found to react but little faster in solution than in the gas phase. Here the theory indicates that no change should occur unless the solvent alters the internal nature of the molecule. The data on the temperature coefficient of these reactions is not good enough to determine whether the small increase in rate is to be ascribed entirely to a change in the heat of activation.

QUANTITATIVE COMPARISON OF EXPERIMENT AND THEORY

We have now shown that from a qualitative point of view the reactions listed in table 1 have the unique characteristics expected on theoretical grounds for unimolecular reactions. We shall now make a quantitative comparison between experiment and theory.

When $1/k$ is plotted against $1/p$ as in figure 1 the experimental

points will show a curvature in such a direction that the rate is maintained better at the lower pressures if a localized energy theory is being obeyed. Such a curvature is found for all of the ethers and for the two azo compounds which fall off. For dimethyltriazenes the curvature is very slight, and for nitrous oxide a very nearly straight line is obtained. Approximately straight lines are obtained with propionaldehyde and with nitrogen pentoxide, but the data for nitrogen pentoxide are not very

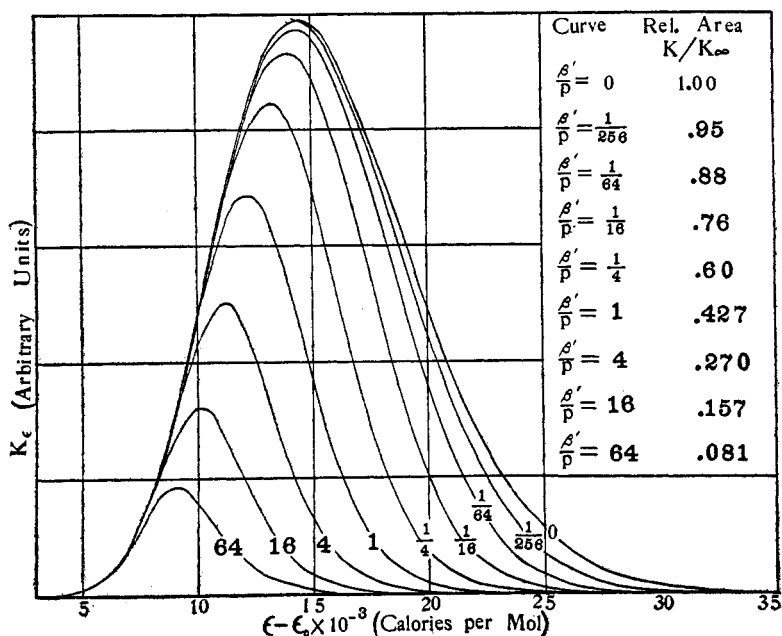


FIG. 2. AZOMETHANE AT 330°C.

accurate over the relatively small pressure range in which the rate is decreasing. From the slope of the straight line one obtains the quantity aW . Three constants appear in aW ; the molecular diameter for which a reasonable kinetic theory value is chosen, ϵ_0 which is obtained from U_1 by equation 7, and n whose value can then be determined from the experimental value of aW . For nitrous oxide, n is found to be about 2; for propionaldehyde, $n = 11$; and for dimethyltriazenes, $n = 14$. For nitrogen

pentoxide an impossibly high value of n would be obtained with this theory.

A localized energy theory must be applied to the other reactions. Equation 5 is put into a form suitable for integration (2, 5) and either a graphical or a numerical integration is performed for each of several pressures. A graphical plot for azomethane at $T = 603^\circ$ and $n = 25$ is shown in figure 2. The outer curve is for infinite pressure while the other curves are for pressures which may be

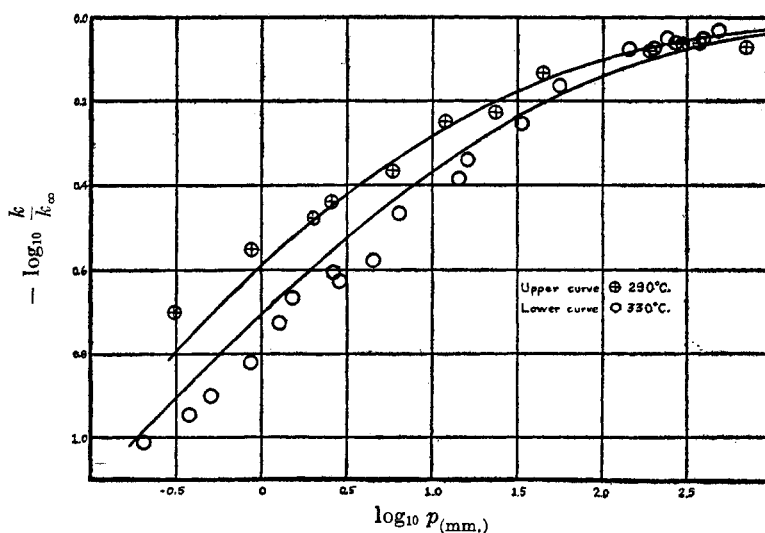


FIG. 3. AZOMETHANE AT 290°C. AND AT 330°C.

calculated from the values of $\frac{\beta'}{p}$, where β' is 13.6 when $s = 6 \times 10^{-8}$ cm., p being in millimeters.

From the relative areas a curve may be plotted of $\log k/k_\infty$ against $\log p$. Figure 3 shows two such theoretical curves for azomethane, the upper one being for $T = 563^\circ$ and the lower one for $T = 603^\circ$. The relative positions of the curves at different temperatures are fixed. In order to fit the data best it will be permissible to move the two curves simultaneously to the right or left; this operation results only in a small change in the molecular diameter. The relative position of the experimental points can

be shifted up or down only by an amount depending on the uncertainty in k_{∞} . The best allowable fit between the experimental points and theoretical curves has been made in figure 3.

The value of n has been determined in similar manner for the other reactions which showed curvature on the $1/k$ against $1/p$ plot. In some cases, however, the uncertainty in the experimental value of k_{∞} allows a considerable latitude in fitting the curve. In all of these cases Theory II or Theory III can be made to fit the data probably within the experimental error. The rates of the azo compounds, azomethane and methylisopropylidimide, at the lowest pressures studied differ from the Theory I curve by a factor of ten. For those reactions for which no falling off was observed, a lower limit for n may be determined by assuming that they would begin to fall off in rate at pressures just below the lowest pressures studied. If a reduction in rate constant of only five to ten per cent is made, Theory I and the localized energy theories will give about the same value of n , and since Theory I is easier to apply it has been used to determine n for these reactions.

The number of squared terms has now been evaluated for all the reactions listed in table 1 except nitrogen pentoxide. The rapid rate of decomposition of this substance has been an outstanding difficulty for rate of reaction theories ever since its discovery. The difficulty was most acute when experiments made a few years ago showed no decrease in the rate down to pressures of 0.03 mm., and in some cases even showed an increase. During the past two years three papers have appeared, all of which show a falling off in rate which appears at pressures of about 0.06 mm. and continues down to the lowest pressure studied, at 0.002 mm., where the rate constant has fallen to less than half its high pressure value (12). To account for such a maintenance of the rate would require thirty squared terms, which, if they were classical oscillators, would correspond to a specific heat due to vibration of about 30 cal. per mole. The application of Kassel's quantum theory would permit nearly the same maintenance of the rate with a vibrational specific heat of 20 to 24 cal. per mole and a diameter of 17×10^{-8} cm. (33). Now the value of n is no greater in all of the other reactions listed than would be permitted, and in fact is much

smaller than specific heat data would allow in some of these reactions. The decomposition of nitrogen pentoxide is therefore somewhat exceptional in that even the choice of the most favorable frequencies for quantum oscillators requires so high a specific heat for a molecule of only seven atoms. However, the quantitative discrepancy between theory and experiment is not now so very serious.

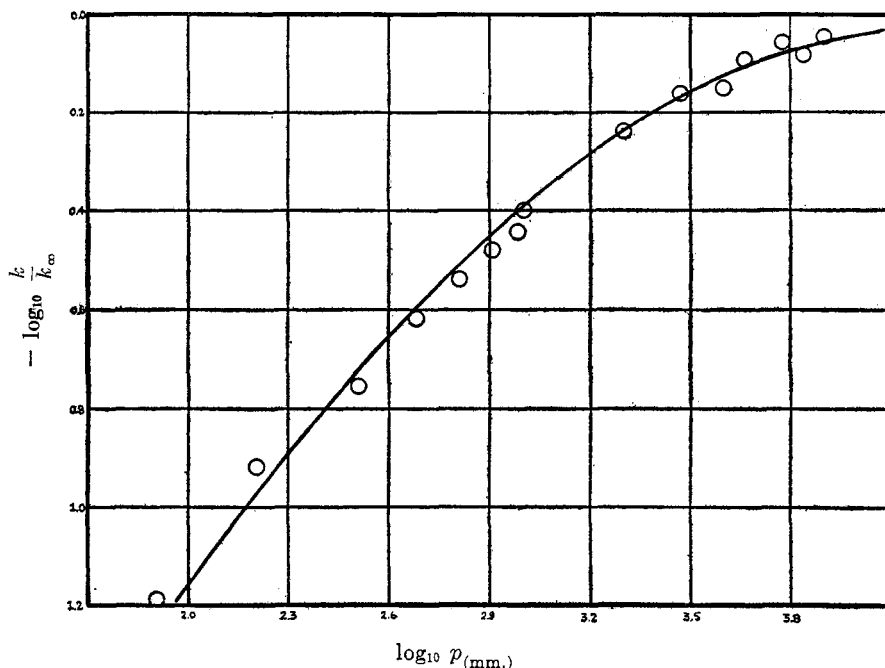


FIG. 4. NITROUS OXIDE

Some discussion of the three reactions which seemed to fit Theory I must be given. On account of the uncertainty in k_{∞} , propionaldehyde can be made to fit Theory II nearly as well as Theory I (2). The decomposition of dimethyltriazenes can be fitted nearly though not quite as well by Theory II. Rate constants at still lower pressures would be necessary to decide definitely between the two forms of the theory. Finally, in the case of nitrous oxide, only two squared terms are necessary to fit the

data (22). The distinction between Theory I and Theory III disappears when $n = 2$, and, in fact, the data could be fitted as well or better with $n = 4$ or with two quantized oscillators, although then the molecular diameter will come out a little smaller than the kinetic theory value. Figure 4 shows a $\log k/k_\infty$ against $\log p$ plot for this reaction using $n = 2$ and $s = 3.05 \times 10^{-8}$ cm.

It seems especially significant that molecules differing as greatly in molecular complexity as nitrous oxide and the azo compounds do should be equally well in agreement with the theory. The theoretical curve of $\log k$ against $\log p$ for a molecule having $n = 2$ is very different in shape from one having $n = 33$, for the former curve falls off very much faster with decreasing pressure. It also seems significant that in those reactions requiring a large number of squared terms, where the difference between Theory I and the localized energy theories is large enough to be capable of experimental proof, the experimental data agree with the localized energy theories in the shape of the curve and in a difference in form at two different temperatures.

We may conclude that we have now available a considerable number of reactions which, because they fulfill the qualitative requirements of unimolecular theories, can safely be designated as unimolecular. The quantitative interpretation supports strongly the belief that reaction occurs when the critical energy becomes more or less localized in a particular part of the molecule.

INTERNAL REARRANGEMENTS

Internal rearrangements of molecules represent an especially simple type of unimolecular change. The only reaction of this type in table 1 is the rearrangement of pinene to dipentene. A still simpler mechanism is the rearrangement of stereoisomers, either of the geometrical type or of the optical type. An example of geometrical rearrangement has recently been published, namely, the conversion of maleic ester into fumaric ester (30). There is fair evidence that the reaction is unimolecular. This reaction, however, is very much slower than that calculated even for only two squared terms. There have been two suggestions

made to account for reactions such as those of the ethers, which are sufficiently slow so that fewer degrees of freedom are required than are available (34). One suggestion is that energy exchange within the molecule occurs only in a limited portion of the molecule, so that the molecule behaves as if it had fewer degrees of freedom. The other suggestion is that the rate of activation is much less than is assumed in the theory owing to the fact that complete redistribution of energy does not occur on collision. The authors have indicated that both of these suggestions are necessary to account for the slow rate of this rearrangement.

REFERENCES

- (1) LINDEMANN: *Trans. Faraday Soc.* **17**, 598 (1922).
- (2) RICE AND RAMSPERGER: *J. Am. Chem. Soc.* **49**, 1617 (1927).
- (3) HINSHELWOOD: *Kinetics of Chemical Change in Gaseous Systems*, p. 127. The Clarendon Press, Oxford (1926).
- (4) RICE AND RAMSPERGER: *J. Am. Chem. Soc.* **49**, 1622 (1927).
- (5) KASSEL: *J. Phys. Chem.* **32**, 225 (1928).
- (6) RICE AND RAMSPERGER: *J. Am. Chem. Soc.* **49**, 1621 (1927).
- (7) KASSEL: *J. Phys. Chem.* **32**, 233 (1928).
- (8) RICE: *Proc. Nat. Acad. Sci.* **14**, 114, 118 (1928).
- (9) KASSEL: *J. Phys. Chem.* **32**, 1065 (1928).
- (10) KASSEL: *J. Phys. Chem.* **32**, 229 (1928).
- (11) RICE, O. K.: Réunion internationale de chimie physique, Paris, October, 1928, p. 314.
- (12) DANIELS AND JOHNSON: *J. Am. Chem. Soc.* **43**, 53 (1921).
RAMSPERGER AND TOLMAN: *Proc. Nat. Acad. Sci.* **16**, 6 (1930).
SCHUMACHER AND SPRENGER: *Proc. Nat. Acad. Sci.* **16**, 129 (1930).
HODGES AND LINHORST: *Proc. Nat. Acad. Sci.* **17**, 28 (1931).
- (13) HINSHELWOOD AND THOMPSON: *Proc. Roy. Soc. London* **113A**, 221 (1926).
- (14) SMITH, D. F.: *J. Am. Chem. Soc.* **49**, 43 (1927).
KASSEL: *J. Am. Chem. Soc.* **52**, 1935 (1930).
- (15) RAMSPERGER: *J. Am. Chem. Soc.* **49**, 912 (1927).
RAMSPERGER: *J. Am. Chem. Soc.* **49**, 1495 (1927).
- (16) HINSHELWOOD: *Proc. Roy. Soc. London* **114A**, 84 (1927).
- (17) HINSHELWOOD AND ASKEY: *Proc. Roy. Soc. London* **115A**, 215 (1927).
- (18) RAMSPERGER: *J. Am. Chem. Soc.* **50**, 714 (1928).
- (19) HECKERT AND MACK: *J. Am. Chem. Soc.* **51**, 2706 (1929).
- (20) RAMSPERGER: *J. Am. Chem. Soc.* **51**, 2134 (1929).
- (21) GLASS AND HINSHELWOOD: *J. Chem. Soc.* **1929**, 1805.
- (22) 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).
- (23) TAYLOR, H. A.: *J. Phys. Chem.* **34**, 2761 (1930).

- (24) RAMSPERGER AND LEERMAKERS: *J. Am. Chem. Soc.* **53**, 2061 (1931).
- (25) RAMSPERGER AND WADDINGTON: Unpublished data of this laboratory.
- (26) SCHUMACHER AND SPRENGER: *Z. Elektrochem.* **35**, 653 (1929).
- (27) HINSELWOOD AND HUTCHINSON: *Proc. Roy. Soc. London* **111A**, 245 (1926).
- (28) GLASS AND HINSELWOOD: *J. Chem. Soc.* **1929**, 1805.
- (29) TAYLOR AND ACHILLES: *J. Phys. Chem.* **35**, 2658 (1931).
- (30) KISTIAKOWSKY AND NELLES: *Z. physik. Chem., Bodenstein Festband*, p. 369 (1931).
- (31) RAMSPERGER: *J. Phys. Chem.* **34**, 669 (1930).
- (32) EYRING AND DANIELS: *J. Am. Chem. Soc.* **52**, 1472 (1930).
- (33) KASSEL: *J. Am. Chem. Soc.* **52**, 3972 (1930).
- (34) RICE: *Z. physik. Chem.* **7B**, 226 (1930).