ARRHENIUS FACTORS (FREQUENCY FACTORS) IN UNIMOLECULAR REACTIONS

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IT is well known that the temperature-dependence of the velocity constant (k) of a reaction can be written in the form

$$k = A \exp(-E/RT) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where E is the energy of activation and A is termed the Arrhenius factor. (A is alternatively termed the frequency factor, temperature-independent factor, non-exponential factor, and pre-exponential factor.) It is obviously desirable to be able to calculate Arrhenius factors from first principles and thereby to understand the precise nature of their dependence, if any, on temperature or pressure.

When the transition-state theory is applied to unimolecular reactions two possible cases can emerge.[1] By this theory

$$k = \kappa \frac{\boldsymbol{kT}}{\boldsymbol{h}} \frac{F_{\ddagger}}{F_{\mathrm{i}}} \exp(-E_0/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where κ is the transmission coefficient and $F_{\ddagger}$ and F_{i} are partition functions for the activated and the initial state respectively. This expression can be shown to equal $\kappa(\boldsymbol{k}T/\boldsymbol{h})\,(1/f_{\mathrm{v}}) \exp(-E_0/\boldsymbol{R}T)$, where f_{v} is the partition function for one vibrational mode; f_{v} is equal to $[1 - \exp(-\boldsymbol{h}\nu_0/\boldsymbol{k}T)]^{-1}$, where ν_0 is the vibrational frequency. We can distinguish two possible cases: on the one hand, the temperature is high and then f_{v} equals $\boldsymbol{k}T/\boldsymbol{h}\nu_0$ and the rate constant is reduced to $\kappa\nu_0 \exp(-E_0/\boldsymbol{R}T)$; at relatively low temperatures f_{v} tends to unity and the rate constant therefore is equal to $\kappa(\boldsymbol{k}T/\boldsymbol{h}) \exp(-E_0/\boldsymbol{R}T)$. In practice the two cases cannot be distinguished because the value of $\boldsymbol{k}T/\boldsymbol{h}$ is approximately 10^{13} sec.$^{-1}$ in the temperature range in which most gas reactions are conducted, and this value is of the same order as a vibrational frequency (ν_0). We can therefore assume a value for the Arrhenius factor of about 10^{13} sec.$^{-1}$. This approach implies that an equilibrium concentration of activated complexes is maintained and that the frequency of decomposition of the activated complex is equal to some normal frequency of the molecule.

In 1928, Polanyi and Wigner[2] called attention to the prevalence of values of 10^{13} sec.$^{-1}$ for the Arrhenius factors of the unimolecular reactions then known. They cited a number of unimolecular decompositions in solution from a previous compilation by Christiansen,[3] and also the values obtained from the gas-phase thermal decomposition of dinitrogen pentoxide,

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[1] Szwarc, *Chem. Rev.*, 1950, **47**, 75.
[2] Polanyi and Wigner, *Z. phys. Chem.*, 1928, *A*, **139**, 439.
[3] Christiansen, *Z. phys. Chem.*, 1923, *A*, **104**, 451.

acetone, azomethane, $Pr^i{\cdot}N{:}N{\cdot}Pr^i$, dimethyl ether, diethyl ether, and propionaldehyde and from the gas-phase racemisation of pinene. We may note that all the gas-phase thermal decompositions cited are now known to involve chain reactions or composite reaction mechanisms, and hence it is fortuitous that the Arrhenius factors are in the region of 10^{13} sec $^{-1}$. These criticisms must not, however, detract from the importance of Polanyi and Wigner's suggestion which focused attention on the possibility of classifying reactions according to the "normality" or "abnormality" of the Arrhenius factors. As we shall observe at the conclusion of this Review it implied a close connection between the experimentally determined Arrhenius factor and the reaction mechanism proposed.

Different treatments of the Arrhenius factor are given by the various theories of unimolecular reactions. In Kassel's theory[4] this parameter is a constant which represents the frequency with which internal transfers carry energy into the critical oscillator; in Hinshelwood's earlier approach,[5] A is a fixed probability of dissociation for molecules where the total energy E exceeds E_0, the activation energy. In the variety of formulations employed by Slater,[6] the Arrhenius factor is a specially weighted average of the vibration frequencies in the molecules which always lies between the least and the greatest of the fundamental frequencies. The transition-state theory also considers the Arrhenius factor as a vibration frequency.

It is possible to use Slater's theory[6] to predict the variation of the Arrhenius factor with pressure from the variation of the activation energy with pressure of reactant. If we define the activation energy derived from the limiting rate constant as E_0, and that from temperature-dependence of the general pressure rate constant as E_a, then we can make use of the relation

$$k = k_{\infty} I_m(\theta)$$

where θ varies as collision frequency [$I_m(\theta) \approx 1$, when θ is large] and we derive on differentiation with respect to temperature

$$E_a = E_0 - mkTA_m(\theta)$$

where $A_m(\theta)$ varies from 0 to 1 as θ varies from ∞ to 0. Thus, as

$$k = A \exp(-E_a/\boldsymbol{k}T)$$

then

$$\begin{aligned} A &= k \exp(E_a/\boldsymbol{k}T) \\ &= A_{\infty} \exp(-E_0/\boldsymbol{k}T) \,.\, I_m(\theta) \exp(E_a/\boldsymbol{k}T) \\ &= A_{\infty} I_m(\theta) \exp[-mA_m(\theta)] \end{aligned}$$

The Arrhenius factor A will therefore fall from the limiting pressure value A_{∞} as the pressure drops both because $I_m(\theta)$ decreases with decrease in θ and because $A_m(\theta)$ increases with decrease in θ.

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[4] Kassel, *J. Phys. Chem.*, 1928, **32**, 225.

[5] Hinshelwood, "Kinetics of Chemical Change," Oxford, 1940.

[6] Slater, "Theory of Unimolecular Reactions," Cornell Univ. Press, 1959.

Essential Experimental Conditions

In any evaluation of the Arrhenius factors of unimolecular gas reactions, it is primarily important to consider the nature of the experimental evidence available. Such evidence may indicate that any one of several possible explanations must be considered before a detailed theoretical assessment of an "abnormal" Arrhenius factor is attempted. The Arrhenius factor is usually determined from extrapolation of the log k–$1/T$ graph to $1/T = 0$. Thus the normal experimental uncertainty in the activation energy will be reflected in the Arrhenius factor. For typical gas-phase thermal decompositions an error limit of $\pm$ 2 kcal.mole^{-1} in the activation energy will result in an error limit of $\pm$ 0·7 in $\log_{10} A$. It is necessary also to emphasise that the reaction studied must be predominantly homogeneous and genuinely of first order before attempting to assess the significance of the Arrhenius factor. The following two examples illustrate the importance of showing that chain reactions are absent and that the limiting pressure has been attained.

(a) *Absence of chain reactions.* We have already stated that the reactions cited by Polanyi and Wigner in favour of the 10^{13} sec.$^{-1}$ Arrhenius factor were in fact decompositions that followed a chain mechanism. It is possible for such reactions to exhibit a "normal" Arrhenius factor. We may illustrate as follows: the Rice–Herzfeld[7] mechanism for the decomposition of ethane can be written:

$$C_2H_6 \rightarrow 2CH_3 \quad \ldots \ldots \quad (1)$$
$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \quad \ldots \ldots \quad (2)$$
$$C_2H_5 \rightarrow C_2H_4 + H \quad \ldots \ldots \quad (3)$$
$$H + C_2H_6 \rightarrow H_2 + C_2H_5 \quad \ldots \ldots \quad (4)$$
$$2H \rightarrow H_2 \quad \ldots \ldots \quad (5)$$
$$H + C_2H_5 \rightarrow C_2H_6 \quad \ldots \ldots \quad (6)$$
$$H + CH_3 \rightarrow CH_4 \quad \ldots \ldots \quad (7)$$
$$CH_3 + C_2H_5 \rightarrow C_3H_8 \quad \ldots \ldots \quad (8)$$
$$2C_2H_5 \rightarrow C_4H_{10} \quad \ldots \ldots \quad (9)$$

If we assume this mechanism to be valid and that reactions (5), (7), (8), and (9) are negligible, then

$$\frac{-\,d\,[C_2H_6]}{dt} = k[C_2H_6] = \left(\frac{k_1k_3k_4}{2k_6}\right)^{\frac{1}{2}}[C_2H_6]$$

Thus the Arrhenius factor will in fact be composite and will equal $(A_1A_3A_4/2A_6)^{\frac{1}{2}}$. If $A_6 \approx A_4$ then the experimentally observed Arrhenius factor will be the geometric mean of A_1 and A_3 and, though approximately 10^{13} sec.$^{-1}$, will have no simple significance and cannot therefore be related to a single reaction step.

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[7] See Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Inc., New York, 1954.

(b) *Freedom from fall-off characteristics.* We have already mentioned that the theory of unimolecular reactions indicates that the velocity constant will reach a limiting value at any one temperature when a limiting pressure of reactant has been attained, and that the activation energy and Arrhenius factor are also pressure-dependent below this limiting pressure. If the reaction is carried out in the pressure-dependent region, it is therefore possible that it will be assigned to a class of reaction possessing a low Arrhenius factor, when, in fact, the true Arrhenius factor is normal.

There is much published work dealing with unimolecular gas-phase decompositions: consequently, our selection is not comprehensive. The examples chosen are those that we consider to be well established. In two cases we use apparently reliable results to indicate the need for further investigation.

"Normal" Arrhenius Factors

We shall consider that Arrhenius factors lying between $10^{11\cdot5}$ and $10^{14\cdot5}$ sec.$^{-1}$ are "normal", and subdivide the available results into two major groups.

(a) *Compounds decomposing by a free-radical mechanism.* We can represent such decompositions by the scheme $A{-}B \rightarrow A\cdot + \cdot B$. Many reactions of this type have been investigated for, when the reverse reaction has zero activation energy, the activation energy of the decomposition reaction can be identified with the bond-dissociation energy D(A–B). Szwarc *et al.*[1] have demonstrated that many such decompositions occur and that the Arrhenius factor is usually "normal". Before we summarise some of these data, it is necessary to make one reservation. On occasion, workers have *assumed* a constant value of the Arrhenius factor for a series of compounds and calculated activation-energy differences from the rate constants obtained at one particular temperature. Butler and Polanyi[8] introduced the use of a 10^{13} factor in their attempts to determine D(R–I) values in alkyl iodides from first-order velocity constants based upon decomposition of the iodides to give iodine. They acknowledged that their procedure was a considerable over-simplification but considered the derived energy value to be better than that obtained from log k–$1/T$ plots. They realised that the activation energy derived from the use of the 10^{13} factor was relatively insensitive to 50% changes in k. In fact, it now seems possible that the good agreement of their D values with modern values is largely fortuitous and that in the pyrolysis of alkyl iodides the first reaction is a dehydrohalogenation step.[9]

Many bond-breaking reactions have been studied and, when the Arrhenius factor is normal, the activation energy has been identified with the bond-dissociation energy. Thus a pattern of bond-dissociation energies

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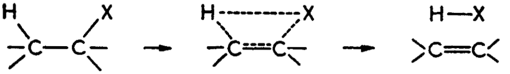
[8] Butler and Polanyi, *Trans. Faraday Soc.*, 1943, **39**, 19.

[9] Holmes and Maccoll, *Proc. Chem. Soc.*, 1957, 175.

in organic molecules has emerged (see Sehon and Szwarc[10] and Cottrell[11] for detailed considerations) and the self-consistency of the results has been shown for the derivation of heats of formation of free radicals and the prediction of bond-dissociation energies.

However, it is necessary to add a word of caution in interpreting these measurements. Kinetic schemes can be oversimplified, and from apparently small assumptions important consequences can arise. A good example is provided by the controversies over $D(C_6H_5{\cdot}CH_2\text{–}H)$. The original value[12] of 77·5 kcal. mole^{-1} has frequently been taken as the basis for a bond-dissociation energy pattern, and the fact that the Arrhenius factor for the toluene pyrolysis was 2×10^{13} sec.$^{-1}$ probably served as additional verification. Blades, Blades, and Steacie[13] obtained, however, an activation energy of 90 kcal.mole^{-1} and an Arrhenius factor of 5×10^{15} sec.$^{-1}$ on repeating Szwarc's work. Although we may accept the argument of Sehon and Szwarc[10] that the discrepancies are due to side reactions consequent upon the greater percentage decompositions employed by Blades *et al.*, yet we must still note that the new revised value[10] of $D(C_6H_5{\cdot}CH_2\text{–}H) = 83$ kcal.mole^{-1} implies that the Arrhenius factor for the decomposition of toluene (and the xylenes?) is greater than 2×10^{13} and probably about 3×10^{14} sec.$^{-1}$. Such a value is within the "normal" range.

(b) *Compounds decomposing by a molecular mechanism.* Many gaseous compounds undergo thermal decomposition without production of free radicals. Such a decomposition mechanism may be considered as established when, over a wide range of experimental conditions, the composition of the products is constant and the reaction rate and products are unaffected by typical free-radical removers (*e.g.*, nitric oxide, toluene, propene). Typical examples of a molecular decomposition are provided by dehydrohalogenation reactions investigated by Maccoll *et al.*[9,14], Howlett,[15] and Barton.[16] Thus, the most probable mechanism is as in scheme (1). The transition state is therefore a four-centre type, associated



.......(1)

with a bending mode in which a hydrogen and a halogen atom come towards one another. The activation energies fall in the 40—60 kcal.mole^{-1} range and the Arrhenius factor is normal ($\log_{10}A$ = 12·6—14·6).

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[10] Sehon and Szwarc, *Ann. Rev. Phys. Chem.*, 1957, **8**, 439.

[11] Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1958.

[12] Szwarc, *J. Chem. Phys.*, 1948, **16**, 128.

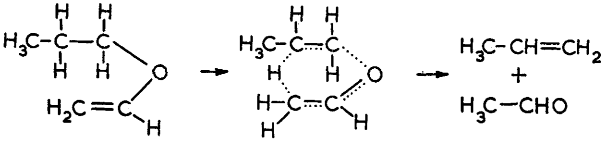
[13] Blades, Blades, and Steacie, *Canad. J. Chem.*, 1954, **32**, 298.

[14] Green, Harden, Maccoll and Thomas, *J. Chem. Phys.*, 1953, **21**, 178.

[15] Howlett, *J.*, 1952, 4487.

[16] Barton *et al.*, *J.*, 1949, 165; 1951, 2039; *Trans. Faraday Soc.*, 1949, **45**, 725; 1950, **46**, 114.

Six-centre transition states are exemplified by the thermal decomposition of propyl vinyl ether ($\log_{10}A = 12{\cdot}6$) (see scheme 2).[17]



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"Abnormal" Arrhenius Factors

We shall consider reactions where the Arrhenius factors are less than $10^{11\cdot5}$ or greater than $10^{14\cdot5}$ to be "abnormal" and we shall subdivide the available results into four major groups.

(a) *Entropy of activation less than —7 e.u.* The transition-state theory of reaction kinetics can be formulated in a thermodynamic fashion. When this is done, the expression for the rate constant for a unimolecular reaction becomes:

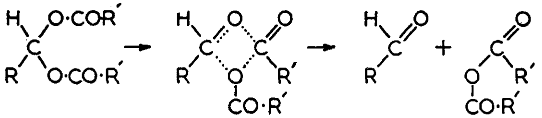
$$k = \text{e.}\,(\boldsymbol{k}T/\boldsymbol{h}) \exp(-E/\boldsymbol{R}T) \exp(\Delta S/\boldsymbol{R})$$

and thus the Arrhenius factor, A, is equivalent to

$$\text{e.}\,(\boldsymbol{k}T/\boldsymbol{h}) \exp(\Delta S/\boldsymbol{R})$$

Thus, if the entropy of activation lies between —7 and +7 e.u. then the Arrhenius factor will be "normal". This implies that the restrictions on motion in the transition state will be only slightly different in these cases from those in the initial state. However, when the entropy of activation is lower than —7 e.u., then we can expect the transition-state configuration to have significantly greater rigidity than the initial state: similarly, when the entropy of activation is greater than +7 e.u. we can expect the transition-state configuration to have much more freedom of vibration than in the initial state. We shall examine some cases for each of these classes where molecular models indicate that such an argument is most plausible.

We shall cite a few examples for a negative entropy of activation. Thus the thermal decompositions of many esters have a large negative entropy of activation and therefore a transition state with restriction on freedom of rotation. Coffin *et al.*,[18] showed that for esters of the type $R{\cdot}CH(O{\cdot}CO{\cdot}R')_2$, whose decomposition mechanism is presumably as scheme (3), the



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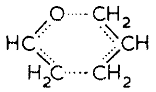
[17] Blades, *Canad. J. Chem.*, 1954, **31**, 418.

[18] Coffin *et al.*, *Canad. J. Res.*, *B*, 1931, **5**, 636; 1932, **6**, 417; 1937, **15**, 229, 247, 254, 260.

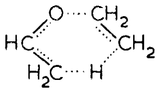
Arrhenius factor lies between $10^{9\cdot2}$ and $10^{11\cdot1}$, corresponding to entropies of activation of -18 to -10 e.u. To form the cyclic transition state a considerable restriction of motion of the reactant is necessary. Reactions with large negative entropies of activation are usually associated with cyclic transition states. Examples are to be found in the work of Murphy, who postulates six-membered-ring transition states for the reactions shown in Table 1.

TABLE 1. *Reactions with 6-centre cyclic transition states.*

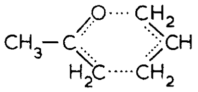
Reaction	Ref.	Transn. state	$\log_{10}A$	Entropy of activn. (e.u.)
$CH_2{:}CH{\cdot}CH_2{\cdot}O{\cdot}CH{:}CH_2 \rightarrow CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$	19	(I)	11·70	−7·7
$CH_2{:}CH{\cdot}O{\cdot}C_2H_5 \rightarrow CH_2{:}CH_2 + CH_3{\cdot}CHO$	20	(II)	11·43	−10·2
$CH_2{:}CH{\cdot}CH_2{\cdot}O{\cdot}C(CH_3){:}CH_2 \rightarrow CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$	21	(III)	11·73	−7·7



(I)



(II)



(III)

One further example will be mentioned, namely, the racemisation of 2,2′-diamino-6,6′-dimethylbiphenyl, for which the Arrhenius factor is $2{\cdot}35\times10^{10}$. This is rather low, for it is difficult to understand how the transition state can have a restriction on rotation that is not present in the initial state. Kistiakowsky and Smith[22] suggested that the Arrhenius factor was low owing to the rotation of the heavy groups that was necessary to achieve the transition state. It seems more likely that this would be reflected in the activation energy than in the Arrhenius factor, and we shall have occasion to refer to this suggestion for relatively low values again in relation to *cis*→*trans*-isomerisation.

(b) *Entropy of activation greater than* $+7$ *e.u.* This group of Arrhenius factors ($>10^{14\cdot5}$) indicates that the transition state is "looser" than the initial state and thus allows, for example, more rotational freedom than is permissible in the ordinary molecule. We can illustrate these statements by considering some decyclisation reactions (which proceed by a molecular mechanism) and by the free-radical decomposition of some compounds

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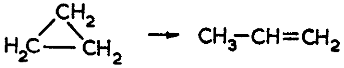
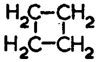
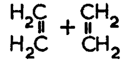
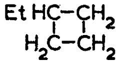
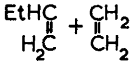
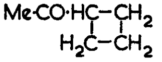
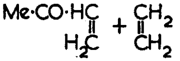
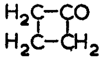
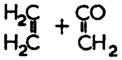
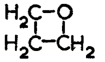
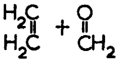
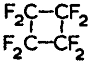
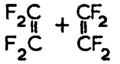
[19] Schuler and Murphy, *J. Amer. Chem. Soc.*, 1950, **72**, 3155.
[20] Blades and Murphy, *J. Amer. Chem. Soc.*, 1952, **74**, 1039.
[21] Stein and Murphy, *J. Amer. Chem. Soc.*, 1952, **74**, 1041.
[22] Kistiakowsky and Smith, *J. Amer. Chem. Soc.*, 1936, **58**, 1043.

which are known to have hindered internal rotation. We shall select one example of the breaking of a three-membered ring:



where the Arrhenius factor is $10^{15.17}$ sec.$^{-1}$.[23] It is plausible to suggest that there is greater freedom of torsional movement in one C–C bond in the activated state. There are many kinetic studies of the breaking of four-membered rings. Those which decompose into two fragments are summarised in Table 2. It is noticeable that, when the molecule contains either a carbonyl or an ether group, the Arrhenius factor is lowered. Possibly the freedom of rotation in the transition state is less when an oxygen atom is present.

TABLE 2. *4-Centre decyclisation reactions.*

Compound	Products	$\log_{10}A$	E (kcal.mole^{-1})	Ref.
	 $H_2C=CH_2 + H_2C=CH_2$	15·6	62·5	24
	 $EtHC=CH_2 + H_2C=CH_2$	15·56	62·0	25
	 $Me{\cdot}CO{\cdot}HC=CH_2 + H_2C=CH_2$	14·53	54·5	26
	 $H_2C=CH_2 + CO=CH_2$	14·56	52·0	27
	 $H_2C=CH_2 + O=CH_2$	14·79	60·0	28
	 $F_2C=CF_2 + CF_2=CF_2$	15·95	74·1	29

Examples of high Arrhenius factors in molecules decomposing by free-radical mechanisms have been found for dialkyl peroxides. It is suggested[30] that this can be accounted for by the entropy increase consequent upon free rotation about the O–O bond in the activated complex, such rotation

[23] Chambers and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 399.
[24] Genaux and Walters, *J. Amer. Chem. Soc.*, 1951, **73**, 4497; 1953, **75**, 6196.
[25] Wellman and Walters, *J. Amer. Chem. Soc.*, 1957, **79**, 1542.
[26] Daignault and Walters, *J. Amer. Chem. Soc.*, 1958, **80**. 541.
[27] Das, Kern, Coyle, and Walters, *J. Amer. Chem. Soc.*, 1954, **76**, 6271.
[28] Bittker and Walters, *J. Amer. Chem. Soc.*, 1955, **77**, 1429.
[29] Atkinson and Trenwith, *J.*, 1953, 2082.
[30] Hoare, Protheroe, and Walsh, *Trans. Faraday Soc.*, 1959, **55**, 548.

being impossible in the ordinary molecule. Similarly, the Arrhenius factors obtained for the following decompositions:

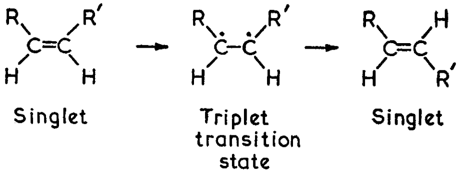
$$CH_3{\cdot}CO{\cdot}CO{\cdot}CH_3 \rightarrow 2CH_3{\cdot}CO$$
$$Ph{\cdot}CH_2{\cdot}CO{\cdot}CH_3 \rightarrow Ph{\cdot}CH_2 + CH_3{\cdot}CO$$
$$Ph{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}Ph \rightarrow Ph{\cdot}CO{\cdot}O + CH_2{\cdot}Ph$$
$$Ph{\cdot}CO{\cdot}COPh \rightarrow 2Ph{\cdot}CO$$

may reflect the freedom of rotation of both radicals in the activated complex.[31] Values have been derived for the Arrhenius factors for the thermal decompositions (unimolecular) of ethane[32] and neopentane:[33]

$$CH_3\text{–}CH_3 \rightarrow CH_3 + CH_3 \qquad \log_{10}A = 14{\cdot}8\text{—}15{\cdot}7$$
$$CH_3\text{–}C(CH_3)_3 \rightarrow CH_3 + C(CH_3)_3 \qquad \log_{10}A = 17$$

Leigh, Szwarc, and Bigeleisen,[32] however, regard their values for ethane as preliminary and subject to some experimental error, and Engel *et al.*[33] have derived their values from a Rice–Herzfeld mechanism, and it may therefore contain errors involved in the determination of the Arrhenius factors of two reactions.

(c) *Low values for the transmission coefficient.* We have already mentioned that the rate constant for a unimolecular reaction can be shown to be $\kappa\nu_0 \exp(-E_0/\boldsymbol{R}T)$. In most cases, κ, the transmission coefficient, is approximately unity but, in cases where there is a change from one type of electronic state to another, the transmission coefficient is low, reflecting the low probability of crossing between energy levels of different multiplicities. When therefore reaction mechanisms of this type occur, it is to be expected that the Arrhenius factor of such reactions will be abnormally low. About 25 years ago a number of gas-phase *cis-* → *trans*-isomerisations were found to possess low Arrhenius factors, and it was consequently suggested that the reaction mechanism was of the following type:



In the transition state the planar R–C–H groups are mutually perpendicular. As this reaction mechanism requires two transitions between states of different multiplicity, it is to be expected that a low Arrhenius factor will be observed. However, as Trotman-Dickenson has pointed out,[34] the experimental evidence for this mechanism is not unambiguous, and in one case (but-2-ene) the early work has now been shown to be

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[31] Szwarc, *Discuss. Faraday Soc.*, 1953, **14**, 125.
[32] Leigh, Szwarc, and Bigeleisen, *J. Amer. Chem. Soc.*, 1955, **77**, 2193.
[33] Engel, Combe, Letort, and Niclause, *Compt. rend.*, 1957, **244**, 453.
[34] Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955.

invalid.[35] If it were necessary to support low values of the transmission coefficient upon the evidence from gas-phase reactions, we should have insufficient grounds for this. However, the recent solution and liquid-phase evidence for the thermal isomerisation of dimethyl maleate and maleic acid[36] suggests that the original singlet → triplet → singlet mechanism is in fact the most likely reaction path, as $\log_{10}A$ varies between 4·2 and 6·1. This would correspond to probabilities of $\sim 10^{-3}$ or 10^{-4} for each of the two transitions. Further evidence for low transmission coefficients in unimolecular reactions is desirable. We may also remark that the majority of *cis*- → *trans*-isomerisations proceed by a mechanism which does not involve multiplicity changes but presumably occurs by a twisting mechanism about the $>C=C<$ bond. It is therefore a little surprising that many of the so-called normal isomerisations possess Arrhenius factors which are surprisingly low for gas reactions where the transition state cannot be claimed to have restrictions on rotation that are absent in the initial state. A few examples are cited in Table 3.

TABLE 3. *Kinetic parameters for* cis → trans-*isomerisation.*

Compound	$\log_{10} A$ (sec.$^{-1}$)	E (kcal.mole^{-1})	Ref.
cis-But-2-ene	13·8	62·8	35
cis-Stilbene	12·8	42·8	37
,, (liquid)	10·4	36·7	38
Me *cis*-cinnamate	10·6	41·6	39
cis-β-Cyanostyrene	11·6	46	40

It has been claimed by Kistiakowsky and Smith[39] that these low Arrhenius factors are due to rotation of the heavy groups from their position in the initial state to the transition state (compare p. 139). If the two possible reaction mechanisms (*i.e.*, "forbidden" and "normal") were operating *together*, then it is quite feasible for the Arrhenius factor to be lower than the expected 10^{13}. The rate constants for the singlet → triplet → singlet mechanism [$k \sim 10^5 \exp(-25{,}000/\boldsymbol{R}T)$] are approximately the same as those given in Table 3, and a slight curvature of the $\log k$–$1/T$ plot will result if the two mechanisms operate together. The available data are insufficient to detect such a curvature.

(d) *Fission into more than two fragments.* Until recently it was assumed that when a compound decomposed by a free-radical mechanism, the primary reaction involved fission of one bond and the subsequent

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[35] Rabinovitch and Michel, *J. Amer. Chem. Soc.*, 1959, **81**, 5065.
[36] Davies and Evans, *Trans. Faraday Soc.*, 1955, **51**, 1506.
[37] Kistiakowsky and Smith, *J. Amer. Chem. Soc.*, 1934, **56**, 638.
[38] Taylor and Murray, *J.*, 1938, 2078.
[39] Kistiakowsky and Smith, *J. Amer. Chem. Soc.*, 1935, **57**, 269.
[40] Kistiakowsky and Smith, *J. Amer. Chem. Soc.*, 1936, **58**, 2428.

production of two free radicals. However, observation of the pyrolysis of di-isopropylmercury[41] furnished evidence that two-bond fission into three fragments was a feasible mechanism. This suggestion was made from comparison with the analogous cases of dimethyl-[42] and diethyl-mercury[43] and from knowledge of the thermochemistry of mercury dialkyls. Table 4 summarises the data. The approximation equivalence of the activation energy with the energy required to break both mercury–carbon bonds for the case of R = Pr^i pointed to this different mechanism. The high value for the Arrhenius factor could not be explained in terms of a chain reaction or in terms of free rotation in the transition state. A suggestion by Hinshelwood and his co-workers[44] that high Arrhenius factors could correspond to spreading of the energy of activation into more than one bond was therefore adopted as the most likely explanation. This suggestion has also been adopted for a number of reactions where the Arrhenius factors are high. The reactions have a common mechanistic feature which can be represented by the two decomposition possibilities:

TABLE 4

R in R_2Hg	$\log_{10}A$	E (kcal.mole^{-1})	D_1+D_2 (kcal.mole^{-1})
Me	13·5	51·5 ± 2	59 ± 4
Et	14·1	42·5 ± 2	50 ± 6
Pr^i	16·7	40·4 ± 1	41 ± 7

$$\left.\begin{array}{lll} & R_2M \rightarrow R\cdot + \cdot MR & \text{(slow)} \\ \text{followed by} & \cdot MR \rightarrow M + \cdot R & \text{(fast)} \end{array}\right\} \quad . \; . \; . \; . \; \text{Mode 1}$$

$$\text{or} \quad R_2M \rightarrow R\cdot + M + \cdot R \quad . \; . \; . \; . \; . \; \text{Mode 2}$$

the functional group M reverting from its bivalent to its zerovalent state. The cases where M = Hg, N_2, and CO have been most extensively investigated. Pritchard[45] has interpreted these reactions on the basis of the Fowler and Guggenheim equation:[46]

$$k = \lambda\,[\exp(-E/\mathbf{R}T)]\sum_{r=0}^{s-1}[(1/r!)\,(E/\mathbf{R}T)^r]$$

which is taken to be the general expression for a unimolecular velocity constant. This rate constant is the product of λ (a molecular constant)

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[41] Chilton and Gowenlock, *Trans. Faraday Soc.*, 1953, **49**, 1451.
[42] Gowenlock, Polanyi, and Warhurst, *Proc. Roy. Soc.*, 1953, *A*, **218**, 269.
[43] Carter, Chappell, and Warhurst, *J.*, 1956, 106.
[44] Peard, Stubbs, and Hinshelwood, *Proc. Roy. Soc.*, 1952, *A*, **214**, 471.
[45] Pritchard, *J. Chem. Phys.*, 1956, **25**, 267; Clark and Pritchard, *J.*, 1956, 2136.
[46] Fowler and Guggenheim, "Statistical Thermodynamics," Cambridge University Press, 1949, p. 521.

and the fraction of activated molecules. The condition for a molecule to be activated is that it should have an energy exceeding E distributed over s internal vibrations (or oscillators). On this basis, by choosing a value for λ of about 10^{13} sec.$^{-1}$ and using derived values for the critical energy of activation [$E = D$(RM–R) for mode 1, $E = D$(RM–R) $+$ D(R–M) for mode 2], it is possible to obtain good agreement between the observed and the calculated value of the rate constant: it must be assumed that the effective number of oscillators, s, contributing to the decomposition by mode 2 increases as the size of the group R increases. Extension to the ketone and peroxide series also resulted in a reasonable agreement between theory and experiment and it was concluded that high Arrhenius factors were therefore explicable in terms of simultaneous decompositions by two or more mechanisms. This initially attractive suggestion has been subjected to severe criticism by Johnston,[47] who pointed out that λ must be much lower than 10^{13} sec.$^{-1}$ as the molecular complexity increased and that therefore the increase due to the summation term would be largely (if not completely) counterbalanced. These criticisms have been incorporated into a more developed form of Pritchard's theory by Steel,[48] who utilises Kassel's and Slater's theories of unimolecular reactions. On the alternative bases of either lightly coupled or orthogonal oscillators, where the critical energy is localised in only z of the s oscillators, both approaches lead to the formula:

$$k_\infty = \lambda' \frac{1}{(z-1)!}\left(\frac{E}{RT}\right)^{s-1} \exp\left(-\frac{E}{RT}\right)\left[1 + (z-1)\left(\frac{E}{RT}\right)^{-1} + \ldots + (z-1)!\left(\frac{E}{RT}\right)^{1-z}\right]$$

where λ' is the frequency of reaction of molecules which contain the critical energy localized with the z "critical" oscillators, and will therefore be of the order of 10^{12}—10^{14} sec.$^{-1}$. This formula clearly leads to high Arrhenius factors, and Steel has further considered the effect on the Arrhenius factors of necessary phase relationships of the critical oscillators, *i.e.*, he has considered how the oscillators must not only have the necessary energy requirements, but must also be undergoing extension at the same time for reaction to occur. We may therefore conclude that a satisfactory theoretical basis for some observed high Arrhenius factors is now emerging and that localisation of the activation energy in more than one mode is the essential feature of such a theoretical basis.

Conclusion

It appears from this Review that there is a necessary relation between the Arrhenius factor of a reaction and the reaction mechanism. In general,

[47] Johnston, *Ann. Rev. Phys. Chem.*, 1957, **8**, 249.

[48] Steel, personal communication; *J. Chem. Phys.*, 1959, **31**, 899.

unimolecular reactions will have Arrhenius factors which fall within the range $10^{11\cdot5}$–$10^{14\cdot5}$ sec.$^{-1}$. When reactions have Arrhenius factors smaller than $10^{11\cdot5}$ sec.$^{-1}$, then an explanation may be forthcoming from either restrictions on motion in the transition state ($\Delta S \leqslant -7$ e.u.) or a low transmission coefficient owing to the rate-determining step incorporating a "forbidden" transition. Reactions that possess large Arrhenius factors (greater than $10^{14\cdot5}$ sec.$^{-1}$) may involve either a "loose" transition state ($\Delta S \geqslant +7$ e.u.) or the participation of a three- or four-fragment decomposition due to the activation energy's "spreading out" into more than one bond. In all these reactions, it is necessary for certain experimental conditions to be fulfilled before any correlation of mechanism with Arrhenius factor can be more than tentative.

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