Decomposition Reactions of Radicals

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1 Introduction

Radical decomposition reactions have long been recognised as playing an important part in the complex mechanisms of pyrolysis, combustion, photo-oxidation, polymer degradation, and other processes. Thus in the radical-chain mechanisms for the decompositions of organic compounds, originally suggested by Rice and Herzfeld,[1] the chain-propagating steps involve radical decomposition reactions. In the pyrolysis of acetaldehyde, for example, the chain-propagating steps are

$$CH_3\cdot + CH_3\cdot CHO \longrightarrow CH_4 + CH_3\cdot\dot{C}O$$
$$CH_3\cdot \dot{C}O \longrightarrow CH_3\cdot + CO$$

The free valence in the radical permits the decomposition to proceed with the formation of a multiple bond in the molecular product, thereby reducing the endothermicity of the reaction. Accordingly bond strengths in free radicals are very much lower than in the corresponding molecules. It is apparent that for a complete understanding of complex processes such as pyrolyses it is necessary to have kinetic and thermodynamic data on the elementary reactions, including radical decompositions.

Quantitative information on these reactions has been slow in appearing in comparison with other radical reactions. A recent compilation of gas-phase unimolecular reactions,[2] together with subsequent data, shows that about 50 rate constants for radical decompositions have been reported. The relative paucity of data is readily appreciated from a consideration of the difficulties involved. The activation energies for radical decompositions usually lie within the range 10—40 kcal. mole^{-1}, whereas those for radical–radical and radical–molecule reactions fall within the ranges 0—2 and 5—15 kcal. mole^{-1} respectively. At temperatures convenient for measuring the rates of the decompositions (400—700°K) it is apparent that these other types of radical reaction will also be occurring and adding to the complexities of the system. It is also clear from the temperature range why most of the work on radical decompositions has been performed in the gas phase, and the bulk of this Review deals with gaseous systems.

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[1] F. O. Rice and K. F. Herzfeld, *J. Amer. Chem. Soc.*, 1934, **56**, 284.

[2] H. E. O'Neal and S. W. Benson, 'Kinetic Data on Gas Phase Unimolecular Reactions', NSRDS-NBS, U.S. Department of Commerce, in the press.

It is only comparatively recently that attention has been focussed on devising specific reaction systems suitable for studying radical decompositions. While useful information has sometimes been derived indirectly from studies initiated for different ends, on the whole this is much less desirable than the direct approach.

The purpose of this Review is to illustrate the kinetic approach to radical decomposition reactions by considering (i) the methods for studying these reactions, (ii) the interpretation of the results in terms of thermodynamics and theories of unimolecular reactions, and (iii) existing data on these processes.

Discussion will be restricted to the decompositions of thermally equilibrated radicals as the decompositions of chemically activated alkyl radicals have already been reviewed.[3]

2 Experimental Methods

The problems involved in a kinetic study of a radical decomposition are best illustrated by reference to a specific example:

$$C_2H_5\cdot \longrightarrow H\cdot + C_2H_4 \qquad (1)$$

The initial requirement is to measure the rate constant, k_1, which is defined by equation

$$\frac{-d[C_2H_5\cdot]}{dt} = +R_H = +R_{C_2H_4} = k_1[C_2H_5\cdot]$$

where square brackets denote concentration (mole ml.$^{-1}$ or mole l.$^{-1}$) and R denotes rate of formation of product (mole ml.$^{-1}$ sec.$^{-1}$ or mole l.$^{-1}$ sec.$^{-1}$). Such a decomposition reaction is of course unimolecular and the rate constant, k_1, is in first-order units, usually sec.$^{-1}$. The rate constants are then measured over as wide a temperature range as possible and the temperature dependence is assumed to obey the Arrhenius equation $k = A \exp(-E/RT)$ from which the Arrhenius parameters, the A-factor and the activation energy, are derived. As for any kinetic study of a radical reaction, there are three problems to be solved: (i) a suitable source of radicals is required, (ii) the rate of the reaction must be measured, and (iii) the concentration of the radicals must be determined, although this is usually done indirectly. These problems are discussed below.

A. Radical Sources.—(i) *Pyrolysis.* In general, pyrolytic sources of radicals are not suitable for studying radical decomposition reactions. A few results on alkyl radicals have been derived from the pyrolyses of hydrocarbons.[4] Since, however, the reactions have to be carried out at very high temperatures, the overall mechanisms are extremely complex and it is usually difficult to decipher unambiguous data on isolated elementary reactions.

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[3] B. S. Rabinovitch and M. C. Flowers, *Quart. Rev.*, 1964, **18**, 122; B. S. Rabinovitch and D. W. Setser, *Adv. Photochem.*, 1964, **3**, 1.

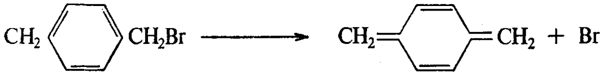
[4] J. H. Purnell and C. P. Quinn, *Proc. Roy. Soc.*, 1962, *A*, **270**, 267; C. P. Quinn, *Trans. Faraday Soc.*, 1963, **59**, 2543.

An exception to this general rule is the formation of alkoxy-radicals from the decomposition of peroxides[5] or nitrites,[6] *e.g.*:

$$[(CH_3)_2CHO]_2 \longrightarrow 2(CH_3)_2CHO\cdot$$
$$(CH_3)_2CHONO \longrightarrow (CH_3)_2CHO\cdot + NO$$

These reactions occur at relatively low temperatures since the O—O and N—O bonds are weak.

Occasionally information on radical decompositions has been obtained from toluene-carrier studies of the pyrolyses of molecules. Thus the rate of the decomposition



has been reported from a study of the pyrolysis of dibromo-*p*-xylene.[7]

(ii) *Photolysis.* The photodecompositions of aldehydes, ketones, and acetates have been extensively used as sources of alkyl,[8] acyl,[9] and alkoxy-radicals:[10]

$$RCHO + h\nu \longrightarrow R\cdot + \cdot CHO$$
$$RCOR^1 + h\nu \longrightarrow RCO\cdot + R\cdot^1$$
$$RCO_2R^1 + h\nu \longrightarrow RCO\cdot + R^1O\cdot$$

Unfortunately these are not the only primary photochemical modes of decomposition,[11] as other radical and molecular elimination reactions can occur, particularly with compounds containing H atoms in the γ-position relative to the carbonyl group, *e.g.*:

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 + h\nu \longrightarrow CH_3{\cdot}CO{\cdot}CH_3 + C_2H_4$$

Another complication arises from 'down-chain' methyl-radical splits:[9]

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHO + h\nu \longrightarrow CH_3\cdot + CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$$

The generation of these additional radicals and molecules leads to complications in studying the reactions of the radicals of primary interest. In the case of aldehyde photolyses, this difficulty is somewhat alleviated since, at higher temperatures, the majority of the alkyl radicals in the system are produced in a thermal chain sequence:

$$R\cdot + R{\cdot}CHO \longrightarrow RH + R\dot{C}O$$
$$R\dot{C}O \longrightarrow R\cdot + CO$$

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[5] M. J. Yee Quee and J. C. J. Thynne, *Trans. Faraday Soc.*, 1967, **63**, 2970.
[6] D. L. Cox, R. A. Livermore, and L. Phillips, *J. Chem. Soc.* (*A*), 1966, 245.
[7] M. Levy, M. Szwarc, and J. Throssell, *J. Chem. Phys.*, 1954, **22**, 1904.
[8] J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, 1961, **1**, 107.
[9] J. G. Calvert, *Chem. Rev.*, 1959, **59**, 569.
[10] M. H. J. Wijnen, *J. Amer. Chem. Soc.*, 1960, **82**, 3034.
[11] R. B. Cundall and A. S. Davies, *Progr. Reaction Kinetics*, 1967, **4**, 149.

Although a lot of work has been done on radical decomposition reactions from direct photolyses of carbonyl compounds the results, on the whole, have not been entirely unambiguous and these compounds have lost favour to the azo-compounds which photodissociate cleanly to give alkyl radicals:[12]

$$\mathrm{RN{=}NR} + h\nu \longrightarrow 2\mathrm{R}\cdot + \mathrm{N_2}$$

With 3660 Å radiation there appears to be only one major primary split and there is no evidence for the formation of activated radicals. One minor disadvantage is that it is not always possible to work at as high a temperature as one would like, owing to the onset of the pyrolysis of the azo-compound, and it is not clear what effect this has on the photolytic system.

(iii) *Photosensitised decompositions.* The mercury-photosensitised decompositions of alkanes was the first method to yield quantitative results on the decompositions of alkyl radicals.[13] Mercury vapour is excited to the triplet state ($^3P_1$) by 2537 Å radiation from a low-pressure mercury arc and sensitises the decompositions of alkanes and other hydrogen-containing compounds:

$$\begin{aligned}\mathrm{C_3H_8} + \mathrm{Hg}(^3P_1) &\longrightarrow \mathrm{Pr^n} + \mathrm{H}\cdot + \mathrm{Hg}(^1S_0)\\ &\longrightarrow \mathrm{Pr^i} + \mathrm{H}\cdot + \mathrm{Hg}(^1S_0)\end{aligned}$$

As this example shows, a mixture of radicals is formed when there is more than one type of C—H bond in the parent molecule. The proportions of radicals are mainly determined by the dissociation energies of the C—H bonds. It is possible to study the decomposition of one of the radicals provided its decomposition product is not formed by other reactions. With the development of gas chromatography there has been a revival in the application of mercury-photosensitisation as a method of generating radicals for studying decomposition reactions.[14] A considerable merit of the method is that it lends itself to extensive variation in the overall pressure of the system, which, as will be shown later, is important in studying the decompositions of smaller radicals.

To overcome the difficulties of multiple radical formation which plague direct photolyses, Calvert[9] introduced the radical-sensitised decomposition of aldehydes for producing acyl and alkyl radicals. Thus azomethane has been selectively photolysed (3660 Å) in the presence of propionaldehyde to yield the propionyl radical:[15]

$$\begin{aligned}\mathrm{C_2H_5{\cdot}N{=}N{\cdot}C_2H_5} + h\nu &\longrightarrow 2\mathrm{C_2H_5}\cdot + \mathrm{N_2}\\ \mathrm{C_2H_5}\cdot + \mathrm{C_2H_5{\cdot}CHO} &\longrightarrow \mathrm{C_2H_6} + \mathrm{C_2H_5{\cdot}CO}\end{aligned}$$

The method is based on two properties of aldehydes: (i) they are transparent to light of 3660 Å and (ii) the acyl-H atom is much more rapidly abstracted than

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[12] D. H. Slater, S. S. Collier, and J. G. Calvert, *J. Amer. Chem. Soc.*, 1968, **90**, 268.
[13] S. Bywater and E. W. R. Steacie, *J. Chem. Phys.*, 1951, **19**, 319; 326.
[14] L. F. Loucks and K. J. Laidler, *Canad. J. Chem.*, 1967, **45**, 2767.
[15] J. A. Kerr and A. C. Lloyd, *Trans. Faraday Soc.*, 1967, **63**, 2480.

the alkyl-H atoms. The decomposition of aldehydes can also be sensitised by the selective photolysis of chlorine or bromine.[16]

Radical- or atom-sensitised decompositions of aldehydes are not particularly suitable for extensive pressure studies but the method has the considerable merit that the radicals are formed in a thermal reaction and are consequently thermally equilibrated.

The decompositions of alkanes, sensitised by methyl radicals, have also been used in studying alkyl-radical decompositions.[17,18] As with mercury photosensitisation there is always the problem of generating mixtures of radicals when the alkane contains different types of C—H bond.

(iv) *Additions to olefins.* Hydrogen-atom addition reactions to olefins, the reverse of radical decomposition, have been widely applied for the production of alkyl radicals:

$$H\cdot + C_2H_4 \longrightarrow C_2H_5\cdot$$

These reactions are highly exothermic (*ca.* 40 kcal. mole^{-1}) and give rise to chemically activated radicals. Rabinovitch and his co-workers[3] have made extensive studies of the decompositions of chemically activated alkyl radicals and have used the results to test the various theories of unimolecular reactions.

Recent studies of the additions of NF_2 radicals to olefins have yielded information on the decompositions of the adduct radicals, *e.g.*, $CH_3\cdot CH(NF_2)\cdot\dot{C}H\cdot CH_3$ radicals from the addition of NF_2 to but-2-ene.[19] Likewise the rates of decomposition of chloro- and bromo-alkyl radicals have been determined from studies of the photochemical chlorination and bromination of olefins.[20] In these systems the information on the radical decompositions has been derived from a detailed kinetic treatment of the overall mechanisms and these studies come within the category of indirect determinations.

B. Measurement of the Decomposition Rate.—Of the three problems to be solved in measuring the rate constant of a radical decomposition, the rate of the reaction is the least difficult to solve. This is achieved by following the rate of formation of the product molecule; for the ethyl decomposition [reaction (1)] the rate of formation of ethylene is measured. Ideally the rate of formation of H atoms should also be determined and there should be agreement between the two rates. Since the atoms and radicals can undergo several reactions to yield products that may also be formed in other ways, it is seldom possible to carry out this check.

It is, of course, extremely important to ascertain that the molecular product

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[16] J. C. Amphlett and E. Whittle, *Trans. Faraday Soc.*, 1967, **63**, 80.
[17] M. C. Lin and K. J. Laidler, *Canad. J. Chem.*, 1966, **44**, 2927.
[18] A. S. Gordon, S. R. Smith, and C. M. Drew, *J. Chem. Phys.*, 1962, **36**, 824.
[19] A. J. Dijkstra, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.* (*A*), 1967, 105, 864.
[20] G. Huybrechts, L. Meyers, and G. Verbeke, *Trans. Faraday Soc.*, 1962, **58**, 1128; H. Schmitz, H. J. Schumacher, and A. Jager, *Chem. Ber.*, 1942, *B*, **51**, 281.

from the radical decomposition is not formed in other reactions, or to make corrections where such reactions are known to occur. For ethyl radicals the rate of formation of ethylene from the decomposition has to be corrected to allow for the disproportionation:

$$2C_2H_5\cdot \longrightarrow C_2H_6 + C_2H_4$$

although this correction is quite small. Ambiguity in product formation is much less of a problem with oxygen-containing radicals than with alkyl radicals. It has frequently been pointed out that secondary radicals, generated by hydrogen-atom abstraction from the parent molecule, could yield the same decomposition product as the principal radicals. This point is illustrated by the photolysis of azo-n-butane for studying n-butyl decomposition:

$$\begin{aligned} C_4H_9{\cdot}N{=}N{\cdot}C_4H_9 + h\nu &\longrightarrow 2C_4H_9\cdot + N_2 \\ C_4H_9\cdot &\longrightarrow C_2H_5\cdot + C_2H_4 \end{aligned}$$

It is conceivable that the radical $\cdot CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}N = N{\cdot}C_4H_9$, from radical attack on the parent azo-compound, could also decompose to give ethylene. It has been argued that since the formation of the latter radical involves abstraction of a primary *C*–H atom it is much less likely to be formed than those from the abstraction of the secondary *C*–H and consequently it should not be an important source of ethylene.[21]

C. Measurement of the Radical Concentration.—Since the steady-state concentrations of radicals in the types of system described above rarely exceed 10^{-10} mole.ml.$^{-1}$, direct determination of the concentration is not possible. Considerable success has recently been achieved in directly determining atom concentrations in gaseous systems by applying electron spin resonance techniques.[22] If the difficulties in interpreting the extremely complex e.s.r. spectra of gaseous radicals can be resolved,[23] direct measurement of radical concentrations would be possible, and absolute rate-constant measurements would assume a different dimension. At present the difficulty of measuring the radical concentration is circumvented by measuring the rate constant for the decomposition relative to the rate constant of some other reaction of the radical. Frequently the reference reaction is the formation of the dimer from radical combination:

$$2C_2H_5\cdot \longrightarrow n\text{-}C_4H_{10} \tag{2}$$

For reactions (1) and (2) we have

$$R_{C_2H_4} = k_1[C_2H_5\cdot] \text{ and } R_{n\text{-}C_4H_{10}} = k_2[C_2H_5\cdot]^2$$

and thus

$$k_1/k_2^{\frac{1}{2}} = R_{C_2H_4}/R_{n\text{-}C_4H_{10}}^{\frac{1}{2}}$$

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[21] W. E. Morganroth and J. G. Calvert, *J. Amer. Chem. Soc.*, 1966, **88**, 5387.

[22] J. A. Kerr, *Ann. Reports*, 1967, **64**, 72; S. W. Benson and W. B. DeMore, *Ann. Rev. Phys. Chem.*, 1965, **16**, 397.

[23] A. Carrington, *Proc. Roy. Soc.*, 1968, *A*, **302**, 291.

To obtain k_1 it is then necessary to know k_2, the rate constant for the combination of the radicals. Comparatively few rate constants for radical combination reactions have been measured. The most commonly used method is the rotating-sector technique which determines the lifetime of the radicals. Although the method does not provide precise values of these rate constants, it seems clear that for small alkyl radicals the rate constants for combination are very high, approaching the collision rates. Rotating-sector measurements of radical combinations cannot be carried out over very wide ranges of temperature, but the few results available indicate small or zero temperature coefficients. There is also some indirect evidence from cross-combination ratios for pairs of different radicals,[8] which supports the contention that $E = ca.\ 0$ kcal. mole^{-1} for radical combinations. For the combination of methyl radicals the rate constant has been determined to be $k = 10^{13\cdot 34}$ (mole^{-1} ml. sec.$^{-1}$) independent of temperature,[24] and this value is often assumed for other radical combinations.

In the photo-initiated chain-decompositions of aldehydes[8] at temperatures above about 600°K the rates of formation of the radical dimers become very slow in comparison with those of other products. Consequently at these temperatures it is not possible to achieve a measurable rate of formation of dimer at low percentage conversions of the aldehyde. The concentrations of the radicals have been measured from their reaction with the parent aldehyde:

$$\mathrm{R\cdot} + \mathrm{R{\cdot}CHO} \longrightarrow \mathrm{RH} + \mathrm{R\dot{C}O} \tag{3}$$

for which we have

$$R_{\mathrm{RH}} = k_3[\mathrm{R\cdot}][\mathrm{R{\cdot}CHO}]$$

The values of k_3 are extrapolated from results at lower temperatures, where radical dimer formation was observed, and hence from the measured rate of formation of alkane, R_{RH}, and the known concentration of aldehyde, [R·CHO], it is possible to calculate [R·]. The calculated values of [R·] are, however, sensitive to the predicted values of k_3, and quite large errors can be introduced in determining the rate constants for the radical decomposition reaction.

3 Thermodynamics of Radical Decompositions

The kinetics and thermodynamics of radical decomposition reactions and the reverse radical- or atom-addition reactions are related *via* the equilibrium constant:

$$\mathrm{R} \underset{(-4)}{\overset{(4)}{\rightleftharpoons}} \mathrm{r} + \mathrm{M} \tag{4}$$

From kinetics, the equilibrium constant is given by the ratio of rate constants:

$$K_{4,-4} = k_4/k_{-4} = (A_4/A_{-4}) \exp[-(E_4 - E_{-4})/RT]$$

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[24] A. Shepp, *J. Chem. Phys.*, 1956, **24**, 939.

and the temperature-dependence of the rate constants has been assumed to obey the Arrhenius equation. From thermodynamics the equilibrium constant is related to the standard free-energy change:

$$-RT \ln K_p = \Delta G^\circ$$

and since

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where ΔH° and ΔS° are the standard enthalpy and entropy changes, it follows that

$$K_{4,-4} = (A_4/A_{-4}) \exp[-(E_4 - E_{-4})/RT] = \exp(\Delta S^\circ/R).\exp(-\Delta H^\circ/RT)$$

By equating coefficients we have

$$\Delta H^\circ = E_4 - E_{-4} \text{ and } \Delta S^\circ = R \ln(A_4/A_{-4})$$

so that activation energies are considered in terms of the enthalpy change and the A-factors in terms of the entropy change.

A. Activation Energies.—When there is an increase in the number of moles during the reaction (Δn) the relation between ΔH° and the activation energy difference (ΔE) is modified owing to the change in standard states:

$$\Delta H^\circ = \Delta E + \Delta nRT$$

and hence for radical decompositions where $\Delta n = +1$

$$\Delta H^\circ{}_4 = \Delta E_4 + RT = E_4 - E_{-4} + RT$$

The RT correction, which is usually *ca.* 1 kcal. mole^{-1}, allows for the fact that enthalpies are measured at constant pressure whereas activation energies are measured at constant volume. It should also be noted that $\Delta H^\circ{}_4$ defines the bond dissociation energy D(r—M) in the radical R (equation 4).

The application of these relations will be illustrated by considering the decompositions of the n-propyl radical:

$$\text{n-}C_3H_7\cdot \longrightarrow CH_3\cdot + C_2H_4 \tag{5}$$

$$\text{n-}C_3H_7\cdot \longrightarrow H\cdot + C_3H_6 \tag{6}$$

The enthalpy changes can be calculated from the thermochemical equation

$$\Delta H^\circ{}_5 = D(CH_3\text{—}CH_2\cdot CH_2\cdot) = \Delta H_f{}^\circ(CH_3\cdot) + \Delta H_f{}^\circ(C_2H_4) - \Delta H_f{}^\circ(\text{n-}C_3H_7\cdot)$$

$$\Delta H^\circ{}_6 = D[CH_3\cdot CH(CH_2)\text{—}H] = \Delta H_f{}^\circ(H\cdot) + \Delta H_f{}^\circ(C_3H_6) - \Delta H_f{}^\circ(\text{n-}C_3H_7\cdot)$$

Bond-dissociation energies in a variety of radicals have been calculated in this way since the enthalpies of formation of many atoms and radicals are known.[25] When this information is not available reasonable estimates of the

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[25] S. W. Benson, *J. Chem. Educ.*, 1965, **42**, 502; J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465.

enthalpy data can be made by the method of additivity of bond or group properties, whereby thermodynamic properties are taken to consist of individual additive contributions of the component parts of the molecules.[26] This method of estimating enthalpies, entropies, and heat capacities has met with considerable success and is now widely accepted as yielding generally reliable estimates of these properties. For the n-propyl decompositions the thermochemical calculations yield $D(CH_3—CH_2{\cdot}CH_2{\cdot}) = 26$ and $D[CH_3{\cdot}CH(CH_2)—H] = 36$ kcal. mole^{-1} with estimated errors of about $\pm$ 2 to $\pm$ 3 kcal. mole^{-1}.

The activation energies from kinetic studies of the radical decompositions can now be compared with these enthalpy changes calculated from thermochemistry, if the activation energies for the reverse radical- and atom-addition reactions [(−5) and (−6)] are known. A growing body of information on these types of addition reaction is available,[22] and when direct measurements have not been made it is often possible to obtain a reasonable estimate of the activation energies from analogous reactions. The relations between the enthalpy changes and activation energies for the n-propyl decompositions are shown in Figure 1.

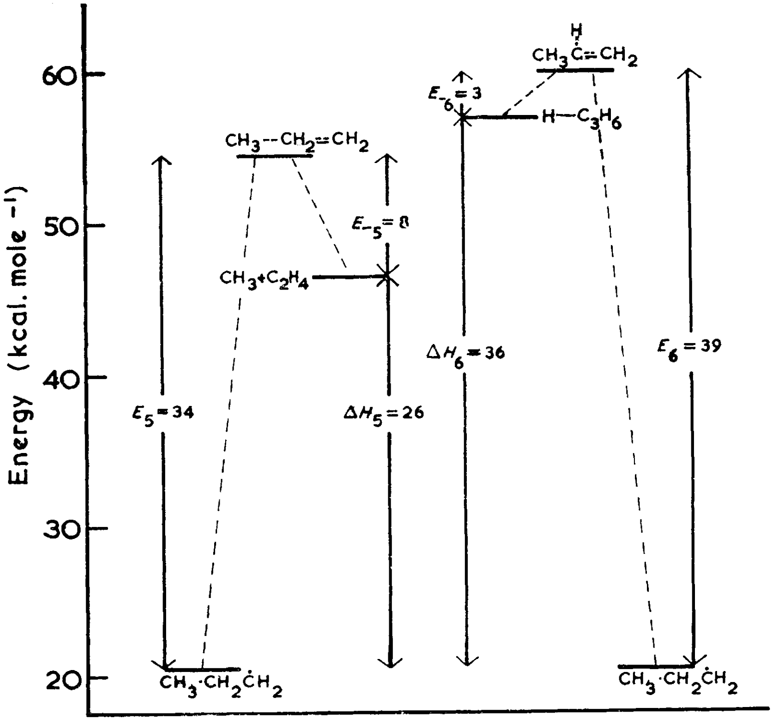

Figure 1 *Energy diagram for the decomposition of the n-propyl radical:*
$n\text{-}C_3H_7{\cdot} \longrightarrow CH_3{\cdot} + C_2H_4$ (5) and $n\text{-}C_3H_7{\cdot} \longrightarrow H{\cdot} + C_3H_6$ (6)

[26] S. W. Benson and J. H. Buss, *J. Chem. Phys.*, 1958, **29**, 546.

A correction should be applied to the activation-energy difference to allow for the fact that thermodynamic enthalpy data refer to 298°K, whereas the activation energies will have been measured at higher temperatures. This correction corresponds to the net enthalpy change in decreasing the temperature of the system from the mid-point of the experimental temperature range in the kinetic experiments to 298°K, and is given by

$$-\int_0^T \Delta C_p \mathrm{d}T,$$

where ΔC_p is the heat-capacity change for the reaction. The complete expression, relating the enthalpy change to the activation energy difference, becomes

$$\Delta H^\circ_3 = E_3 - E_{-3} + RT - \int_0^T \Delta C_p \mathrm{d}T$$

For most radical decompositions the temperature correction is small and is largely offset by the RT correction for the change in the number of molecules. Consequently it is usually adequate to equate the two correction terms and identify ΔH° with the experimentally observed difference in activation energies. In view of the errors involved in the calculated values of ΔH° and in determining the activation energies, the agreement between ΔH° and $(E_f - E_r)$ would not be expected to be much better than ±2 kcal. mole^{-1}.

B. *A*-Factors.—Precise statistical mechanical calculations of entropies of free radicals are usually not possible since the required information on the structures and vibrational and rotational properties is not available. Reasonable estimates can be made, however, since the major contributions to the total entropy are from translational and electronic terms that can be evaluated precisely and the largest uncertainties reside with the minor terms for vibrational and rotational contributions. The entropies of methyl, ethyl, n-propyl and isopropyl radicals have been calculated over the temperature range 200—1000°K by use of consistent vibrational and rotational models.[27] These calculated values were considered to be good to ±0·5 cal. mole^{-1} deg.$^{-1}$ for $CH_3\cdot$ and ±1 cal. mole^{-1} deg.$^{-1}$ for $C_2H_5\cdot$ and $C_3H_7\cdot$.

As previously mentioned an alternative approach for calculating entropies involves the method of additivity of bond or group properties, and entropies of radicals calculated by this method should not be in error by more than ±1 cal. mole^{-1} deg.$^{-1}$. Less precise estimates (±2 cal. mole^{-1} deg.$^{-1}$) can be made by taking the values of entropies of closely related molecules and making corrections for symmetry changes and the electronic entropy of the radical.

The entropies of radicals derived by the above methods are usually tabulated for a standard state of 1 atm.,[2,28] whereas comparisons of ratios of *A*-factors with ΔS° require entropies corresponding to a standard state of 1 mole ml.$^{-1}$ or 1 mole l^{-1}. The entropies in pressure units (S_p) are converted to concentration units (S_c) by the equation

$$S^\circ_p = S^\circ_c + R \ln (p_1/p_2)$$

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[27] J. H. Purnell and C. P. Quinn, *J. Chem. Soc.*, 1964, 4049.
[28] J. G. Calvert and J. N. Pitts, 'Photochemistry', Wiley, New York, 1966, p. 819.

where the last term is the entropy increase in expanding the gas. It follows that $S^\circ_p = (S^\circ_c + 20{\cdot}1)$ or $(S^\circ_c + 8{\cdot}2)$ cal. mole^{-1} deg.$^{-1}$ when the concentration units are mole ml.$^{-1}$ and mole l.$^{-1}$ respectively.

To illustrate a typical comparison between ΔS° calculated from thermodynamic entropy data and from experimental A-factors we shall consider the decomposition and formation reactions of the acetyl radical:

$$CH_3{\cdot}CO \underset{(-7)}{\overset{(7)}{\rightleftharpoons}} CH_3{\cdot} + CO$$

The required entropy data at 298°K is $S^\circ(CH_3{\cdot}) = 46{\cdot}4$, $S^\circ(CO) = 47{\cdot}3$, and $S^\circ(CH_3{\cdot}\dot{C}O) = 64{\cdot}5$ cal. mole^{-1} deg.$^{-1}$, hence $\Delta S^\circ = 29{\cdot}2$ cal. mole^{-1} deg.$^{-1}$ (standard state 1 atm.) or 9·1 cal. mole^{-1} deg.$^{-1}$ (standard state 1 mole ml.$^{-1}$). For the decomposition reaction $A_7 = 10^{10{\cdot}3}$ (sec.$^{-1}$) while for the reverse radical formation reaction $A_{-7} = 10^{8{\cdot}58}$ (mole^{-1} ml. sec.$^{-1}$), leading to a kinetic estimate of $\Delta S^\circ = 7{\cdot}9$ cal. mole^{-1} deg.$^{-1}$ (standard state 1 mole ml.$^{-1}$) which is in reasonable agreement with the thermodynamic data. The results are typical of the agreement to be expected in these comparisons.

C. *A*-Factors and Transition-state Theory.—The A-factor for a unimolecular reaction is given from transition-state theory by the expression

$$A = (ekT/h) \exp (\Delta S^\ddagger/R)$$

where k and h are Boltzmann's and Planck's constants respectively and $\Delta S^\ddagger$ is the entropy of activation. For radical decompositions the assumption is sometimes made that the structures of the initial and transition states are similar and hence $\Delta S^\ddagger = 0$, giving $A = ekT/h = 10^{13{\cdot}5}$ (sec.$^{-1}$) at 600°K. Since the overall entropy change for radical decompositions, ΔS°, is positive it seems likely that $\Delta S^\ddagger \geqslant 0$ and consequently estimates of A-factors based on the assumption $\Delta S^\ddagger = 0$ are lower limits.

The application of transition-state theory to these systems comes down to estimating $\Delta S^\ddagger$, the entropy of activation. O'Neal and Benson[29] have recently developed a method of estimating $\Delta S^\ddagger$ for four- and six-centre unimolecular reactions, based on empirical assignments of bending, stretching, and torsional frequencies. The same principles have been applied to radical decompositions.[2] For the decompositions of the n-propyl radical [reactions (5) and (6)] values of $\Delta S^\ddagger_5 = 0{\cdot}8$ and $\Delta S^\ddagger_6 = 0{\cdot}2$ cal. mole^{-1} deg.$^{-1}$ have been estimated, leading to $A_5 = 10^{13{\cdot}8}$ and $A_6 = 10^{13{\cdot}6}$ sec.$^{-1}$ at 600°K. While such calculations do not give precise values of A-factors they nevertheless form a useful basis for examining the general validity of experimental A-factors.

4 Theories of Unimolecular Reactions

Since radical decompositions are unimolecular reactions they can be treated by the various theories of unimolecular reactions. This section will deal with

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[29] H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 1967, **71**, 2903.

the applications of the theories to these reactions rather than with the detailed developments of the theories.

One of the early successes of unimolecular rate theory was the prediction of the decrease of the apparent unimolecular rate constant, with a corresponding change from first- to second-order kinetics, as the pressure in the system is decreased. As the theories of unimolecular reactions developed it became clear that the pressure region at which this fall-off behaviour could be observed depends on two things: (i) the number of vibrational degrees of freedom of the reacting molecules, and (ii) the term E/RT, where E is the critical energy needed to bring about the reaction which is usually identified with the experimental activation energy. Experiment has confirmed the theoretical deduction that the pressure-sensitive region shifts to lower pressures as the size of the reacting molecules and the activation energy increase. Benson[30] has compiled a useful table based on the Rice–Ramsperger–Kassel (RRK) theory of unimolecular reactions, whereby the pressures at which the unimolecular rate constants fall off markedly from their high-pressure limits can be readily estimated from a knowledge of the activation energy of the reaction and the number of vibrational modes of the reactant species.

It has already been pointed out that bond strengths in radicals are much lower than in the corresponding molecules and consequently the activation energies for radical decompositions are considerably lower than for molecular decompositions. This lowering of the activation energy results in a considerable increase in the pressure at which the rate constants for radical decompositions show pronounced falling-off from their high-pressure values. In a recent study of the thermal decomposition of ethane,[31] information was obtained simultaneously on the reactions (8) and (9) where the activation energies are $E_8 = 86$ and

$$C_2H_6 \longrightarrow 2CH_3\cdot \tag{8}$$

$$C_2H_5\cdot \longrightarrow C_2H_4 + H\cdot \tag{9}$$

$E_9 = 38$ kcal. mole^{-1}. At 958°K the pressures at which the first-order rate constants k_8 and k_9 fell to half their high-pressure values were approximately 20 and 400 mm. respectively. It is clear that pressure-dependent kinetics are much more of a problem with radical decompositions than with molecular decompositions.

Although several instances of pressure-dependence of unimolecular rate constants for radical decompositions had previously been reported, the first attempt to make quantitative measurements on this type of system was by O'Neal and Benson, who studied the effect of pressure on the decomposition of the acetyl radical.[32] The results were treated by the Lindemann–Hinshelwood (LH) theory:

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[30] S. W. Benson, 'Foundations of Chemical Kinetics', McGraw-Hill, New York, 1960, p. 234.

[31] M. C. Lin and M. H. Back, *Canad. J. Chem.*, 1966, **44**, 2357.

[32] H. E. O'Neal and S. W. Benson, *J. Chem. Phys.*, 1962, **36**, 2196.

$$\mathrm{CH_3{\cdot}\dot{C}O + M \underset{(11)}{\overset{(10)}{\rightleftharpoons}} CH_3{\cdot}\dot{C}O^* + M} \tag{10), (11}$$

$$\mathrm{CH_3{\cdot}\dot{C}O^* \xrightarrow{(12)} CH_3{\cdot} + CO} \tag{12}$$

The asterisk denotes an energised molecule, *i.e.*, a molecule containing sufficient vibrational energy to react. Following the LH treatment, first-order kinetic behaviour of the decomposition reaction can be explained by assuming that there is a small stationary concentration of energised molecules, that is, the rate of de-energisation [reaction (11)] is rapid compared with the rate of decomposition [reaction (12)]. From a steady-state treatment of this simple mechanism it can be shown that the rate of the radical decomposition, R_{CO}, is given by (13).

$$R_{\mathrm{CO}} = \frac{k_{10}k_{12}[\mathrm{M}][\mathrm{CH_3{\cdot}\dot{C}O}]}{k_{11}[\mathrm{M}] + k_{12}} \tag{13}$$

In expression (13) it is assumed that M corresponds to the total pressure in the system and there is usually no attempt to allow for the varying efficiencies of different molecules in the deactivation reaction. At high concentrations, *i.e.*, high pressures, $k_{11}[\mathrm{M}] \gg k_{12}$ and the rate becomes

$$R_{\mathrm{CO}} = \frac{k_{10}k_{12}[\mathrm{CH_3{\cdot}\dot{C}O}]}{k_{11}} = k_{\infty}\,[\mathrm{CH_3{\cdot}\dot{C}O}]$$

where k_{∞} is the high-pressure limiting rate constant, and the reaction obeys first-order kinetics. At low pressures the opposite condition applies, $k_{11}[\mathrm{M}] \ll k_{12}$ and the rate is given by

$$R_{\mathrm{CO}} = k_{10}[\mathrm{M}][\mathrm{CH_3{\cdot}\dot{C}O}] = k_0[\mathrm{M}][\mathrm{CH_3{\cdot}\dot{C}O}]$$

where k_0 is the low-pressure limiting rate constant and the reaction now follows second-order kinetics.

The observed first-order rate constant (k') can be defined as

$$R_{\mathrm{CO}} = k'[\mathrm{CH_3{\cdot}\dot{C}O}] \tag{14}$$

and from equations (13) and (14) it can be shown that

$$\begin{aligned} 1/k' &= k_{11}/(k_{10}k_{12}) + 1/(k_{10}[\mathrm{M}]) \\ &= 1/k_{\infty} + 1/(k_0[\mathrm{M}]) \end{aligned}$$

It follows that when $1/k'$ is plotted against $1/[\mathrm{M}]$ for a fixed temperature there should be a linear relation with the intercept equal to $1/k_{\infty}$ and the slope equal to $1/k_0$. A series of such lines is then obtained by making measurements over a range of pressures for different temperatures, and the values of k_{∞} and k_0 at each temperature are found from the intercepts and slopes. A typical set of data are shown in Figure 2. An Arrhenius treatment of the rate constants

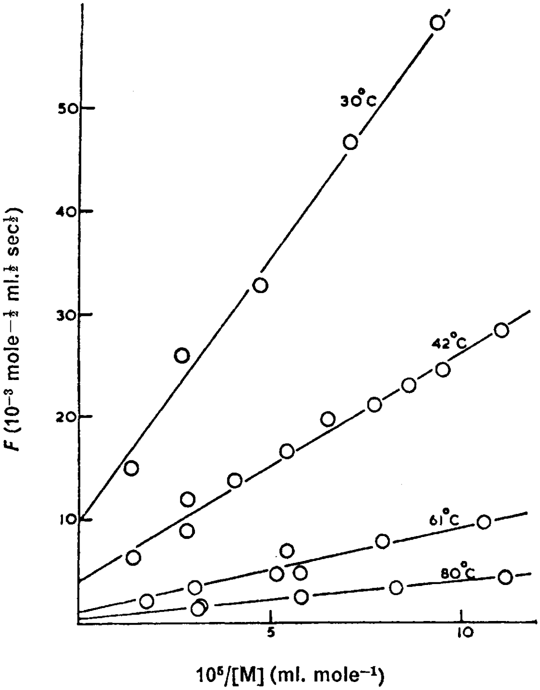

Figure 2 *Lindemann–Hinshelwood plots showing the effect of pressure on the decomposition of the propionyl radical:* $C_2H_5\cdot CO\cdot + M \xrightarrow{k'} C_2H_5\cdot + CO + M$; F = function equivalent to $1/k'$ [From J. A. Kerr and A. C. Lloyd, *Trans. Faraday Soc.*, 1967, **63**, 2480]

yields E_∞ and E_0, the limiting high- and low-pressure activation energies, and A_∞ and A_0, the limiting high- and low-pressure A-factors. Most of the results given in section 5 for the limiting high- and low-pressure Arrhenius parameters of radical decompositions have been derived by the above method.

The shortcomings of the LH theory are well known. Although the LH plots described above are remarkably linear for the radical decomposition reactions so far studied, this is only because the pressure ranges in most of the systems are very limited. For other unimolecular reactions where it has been possible to carry out large pressure variations, the LH plots deviate considerably from linearity at high pressures. This deviation arises from the deficiency of the theory to take account of the effect on the rate constants of differing energy contents of the energised molecules. The effect of this deficiency is worse on the values derived from the slopes of the LH plots (k_0) than those from the intercepts (k_∞). Consequently the derived values of E_0 are not so reliable as those for E_∞. From the thermochemical point of view this is not so serious since it is the high-pressure limiting activation energy which is related to the enthalpy change of the reaction.

An alternative procedure for extrapolating to k_∞ and k_0 involves plotting $1/k'$ against $1/[\mathrm{M}]^{\frac{1}{2}}$ and gives better linear relations over wide pressure ranges for molecular reactions.[33] Such extrapolations have been made for the decomposition of the $C_2H_5\cdot$ radical,[34] where the pressure range was considerably larger than is normally possible for radical decompositions. The $C_2H_5\cdot$ radicals were generated by mercury-photosensitisation which appears to be the most useful source of radicals for studying the effect of pressure variations on the rate constants.

In studying the fall-off behaviour of the rate constant for a thermal unimolecular reaction the normal procedure is to obtain the high-pressure limiting rate constants experimentally and to observe the decrease in the rate constants over a pressure range varying by a factor of several hundreds from the high-pressure limit. So far it has not proved possible actually to measure the high-pressure limiting rate constants for any of the radical decompositions that exhibit fall-off behaviour. Accordingly all the measurements in these pressure-sensitive systems have been made in the fall-off region. The difficulty of reaching the high-pressure limit is a practical one; the pressure range may be limited by the volatility of the radical source or the addition of a large pressure of third-body molecules interferes with the analysis. Clearly, thermal decompositions of radicals are not the most suitable reactions for testing theories of unimolecular reactions, although it should be pointed out that much valuable information has been derived from studies of the decompositions of activated radicals from the additions of H atoms to olefins.[3]

The Rice–Ramsperger–Kassel (RRK) theory and the extension by Marcus (RRKM) have been applied to the results on the decompositions of the $C_2H_5\cdot$ and $CH_2\cdot O\cdot CH_3$ radicals, where the ranges of pressure were sufficient to warrant the application of the more elaborate theories.[4,14,31,34,35] These theories have been extensively treated elsewhere[3,30,36] and only a brief outline of their relevance to the present reactions will be given here.

The simple LH mechanism is modified as follows:

$$\mathrm{A} + \mathrm{A} \underset{(16)}{\overset{(15)}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{A} \qquad (15, 16)$$

$$\mathrm{A}^* \xrightarrow{(17)} \mathrm{A}^\ddagger \qquad (17)$$

$$\mathrm{A}^\ddagger \xrightarrow{k^\ddagger} \text{product}$$

where a distinction is made between energised molecules A* and activated complex molecules $\mathrm{A}^\ddagger$ that have attained the transition-state configuration.

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[33] E. W. Schlag and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, 1960, **82**, 5996.
[34] L. F. Loucks and K. J. Laidler, *Canad. J. Chem.*, 1967, **45**, 2795.
[35] M. C. Lin and K. J. Laidler, *Trans. Faraday Soc.*, 1968, **64**, 79.
[36] K. J. Laidler, 'Chemical Kinetics', McGraw-Hill, New York, 1965, p. 150.

From a molecular model consisting of a system of loosely-coupled harmonic oscillators the RRK theory gives for the apparent unimolecular rate constant:

$$k' = \frac{k^{\ddagger}\,e^{-\epsilon^{*}/kT}}{(s-1)!}\int_{0}^{\infty}\frac{x^{s-1}\,e^{-x}\,dx}{1+\dfrac{k^{\ddagger}}{k_6[A]}\left(\dfrac{x}{b+x}\right)^{s-1}}$$

where $x = (\epsilon - \epsilon^{*})/kT$, $b = \epsilon^{*}/kT$ and the terms are defined as follows: the rate constants refer to the above general mechanism, k = Boltzmann's constant, ϵ = total energy content of the reacting molecule, ϵ^{*} = critical energy for the reaction, s the number of effective oscillators is related to the total number of vibrational modes ($3n - 6$ where n is the number of atoms) and the remaining terms have their usual meaning. For a given value of s the integral corresponds to a particular variation with the concentration [A]. The normal procedure is to determine empirically which value of s predicts the observed variation of k' with pressure. The integrals can now be evaluated readily with the aid of computer programmes. A typical RRK plot is shown in Figure 3. The least satisfactory feature of the RRK theory is the arbitrary nature of the parameter s, which, although usually corresponding to half to two-thirds of the total vibrational modes, cannot be found *a priori*.

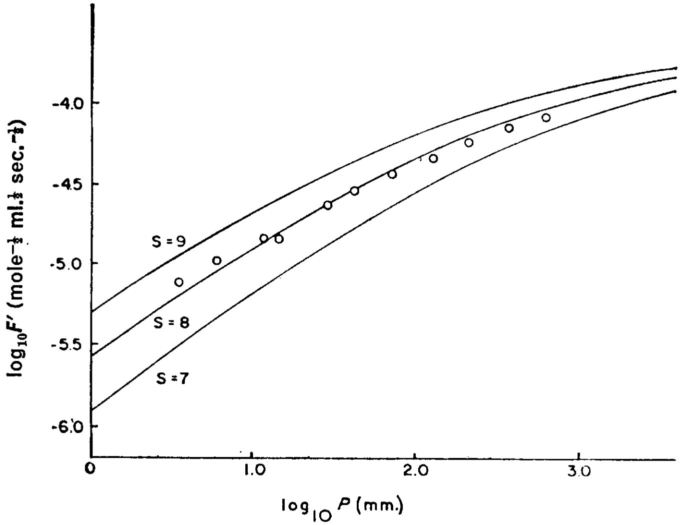


Figure 3 *Rice–Ramsperger–Kassel plot of* $\log_{10}$ *(function equivalent to* k'*) against* $\log_{10} P$ *for*
k'
decomposition of ethyl radical: $C_2H_5\cdot + M \longrightarrow H\cdot + C_2H_4 + M$; circles are experimental results, curves are calculated with S = 7, 8, and 9 [From L. F. Loucks and K. J. Laidler, *Canad. J. Chem.*, 1967, **45**, 2795]

The results of the decompositions of the $C_2H_5\cdot$ and $\cdot CH_2{\cdot}O{\cdot}CH_3$ radicals, generated by mercury-photosensitisation, have recently been treated by the

RRKM theory.[35] This theory is undoubtedly the most satisfactory approach to unimolecular reactions. The RRK model consisting of a system of classical oscillators is replaced by a model which takes into account the individual molecular vibrations and internal rotations and also the zero-point energy levels. In the high-pressure limit the RRKM theory incorporates the transition-state description of the unimolecular decomposition but discards the assumption inherent in the RRK theory that the partition function of the activated complex is unaffected by the distortions of the bonds. For thermal reactions the procedure in applying RRKM theory is analogous to that for RRK theory; the fall-off behaviour of the rate constants is compared with the theoretical curves based on different molecular models, but this time without the adjustable parameter *s*. As seen from Figure 4 the fall-off curves calculated for the $C_2H_5\cdot$ decomposition by the RRKM theory give excellent fits with the experimental data, on the basis of a model involving active rotations in the energised radical and the activated complex.

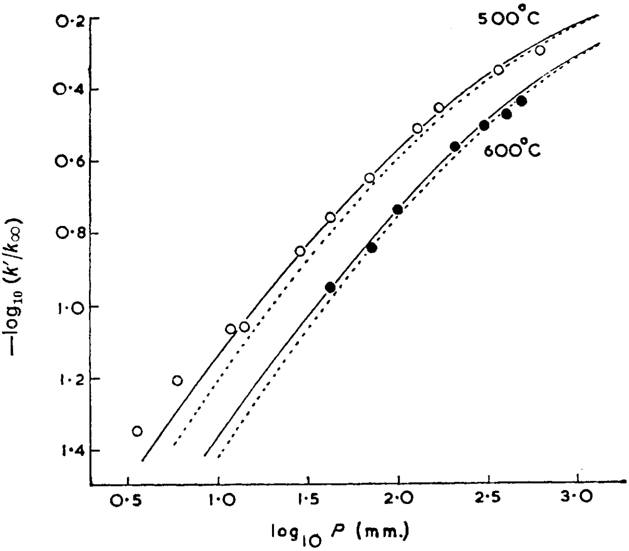


Figure 4 *Rice–Ramsperger–Kassel–Marcus plots of* $\log_{10}(k'/k_\infty)$ *against* $\log_{10} P$ *for the decomposition of ethyl radical:* $C_2H_5\cdot + M \xrightarrow{k'} H\cdot + C_2H_4 + M$; circles are experimental results, curves are theoretical based on two models [From M. C. Lin and K. J. Laidler, *Trans. Faraday Soc.*, 1968, **64**, 79]

It is clear that the RRKM theory will be more widely applied as data on radical decompositions becomes more extensive.

5 Results on Radical Decompositions

Quantitative data are listed in the Table, which is intended to summarise existing information rather than give all available results. Where more than one study

Table *Kinetic and thermodynamic data on radical decompositions*

Reaction	Radical source	Temp. (°K)	E (kcal. mole^{-1})	log A (sec.$^{-1}$ and mole^{-1} ml. sec.$^{-1}$)	Ref.	ΔH°_{298} (kcal. mole^{-1})	ΔS° (cal. mole^{-1} deg.$^{-1}$)^a	ΔH°_{298} (kcal. mole^{-1})	ΔS° (cal. mole^{-1} deg.$^{-1}$)^a
						Kinetic data		Thermodynamic data^b	
		Alkyl Radicals							
$C_2H_5\cdot \rightarrow H\cdot + C_2H_4$	$Hg(^3P_1) + C_2H_6$	673—773	40·9 (E_∞)	14·4 (A_∞)	*c*	37·9	3·7	38·9	0·2
			31·8 (E_0)	17·8 (A_0)					
$H\cdot + C_2H_4 \rightarrow C_2H_5\cdot$			3·0	13·6	*b*				
n-$C_3H_7\cdot \rightarrow H\cdot + C_3H_6$	$CD_3\cdot + CH_3\cdot CD_2\cdot CH_3$	569—693	37·0	14·1	*d*	34·0	2·3	36·3	3·9
$H\cdot + C_3H_6 \rightarrow$ n-C_3H_7			3·0	13·6	*e*				
n-$C_3H_7\cdot \rightarrow CH_3\cdot + C_2H_4$	$CH_3\cdot + C_3H_8$	533—573	31·4	13·5	*f*	23·5	7·3	25·8	11·6
$CH_3\cdot + C_2H_4 \rightarrow$ n-$C_3H_7\cdot$			7·9	11·9	*g*				
iso-$C_3H_7\cdot \rightarrow H\cdot + C_3H_6$	Photolysis	673—773	36·9	13·8	*h*	34·5	1·4	39·3	3·7
$H\cdot + C_3H_6 \rightarrow$ iso-$C_3H_7\cdot$	$C_3H_7\cdot CHO$		2·6	13·5	*b*				
iso-$C_3H_7\cdot \rightarrow CH_3\cdot + C_2H_4$^{i}	Pyrolysis	713—814	34·5	12·0	*j*	—	—	28·9	13·4
$CH_3\cdot + C_2H_4 \rightarrow$ iso-$C_3H_7\cdot$^{i}	$(CH_3)_3CH$		—	—	-				
n-$C_4H_9\cdot \rightarrow C_2H_5\cdot + C_2H_4$	Photolysis	432—520	28·7	13·6	*k*	20·1	7·1	22·5	13·6
$C_2H_5\cdot + C_2H_4 \rightarrow$ n-$C_2H_9\cdot$	(n-$C_4H_9N)_2$		8·6	12·1	*l*				
n-$C_4H_9\cdot \rightarrow CH_3\cdot + C_3H_6$^{i}	Photolysis	571—689	27·1	12·1	*m*	—	—	23·1	13·4
$CH_3\cdot + C_3H_6 \rightarrow$ n-$C_4H_9\cdot$^{i}	n-$C_4H_9\cdot CHO$		—	—	-				
n-$C_4H_9\cdot \rightarrow H_2 + CH_3\cdot \dot{C}H\cdot CH{=}CH_2$	$CD_3\cdot$ + alkanes	523—773	~30	—	*n*	—	—	14·8	5·3
sec-$C_4H_9 \rightarrow CH_3\cdot + C_3H_6$	$CH_3\cdot$ + n-C_4H_{10}	533—613	32·6	14·8	*o*	25·2	15·1	26·2	13·8
$CH_3\cdot + C_3H_6 \rightarrow$ sec-$C_4H_9\cdot$			7·4	11·5	*g*				
iso-$C_4H_9\cdot \rightarrow H\cdot$ + iso-C_4H_8	Photolysis	602—691	31·0	13·0	*p*	29·6	−2·8	34·4	3·8
$H\cdot$ + iso-$C_4H_8 \rightarrow$ iso-$C_4H_9\cdot$	iso-$C_4H_9\cdot CHO$		1·4	13·6	*q*				

Table—*continued*

Reaction	Radical source	Temp. (°K)	E (kcal. mole^{-1})	log A (sec.$^{-1}$ and mole^{-1} ml. sec.$^{-1}$)	Ref.	ΔH°_{298} (kcal. mole^{-1})	ΔS° (cal. mole^{-1} deg.$^{-1}$)^a	ΔH°_{298} (kcal. mole^{-1})	ΔS° (cal. mole^{-1} deg.$^{-1}$)^a
						Kinetic data		Thermodynamic data^b	
Alkyl radicals									
$\text{iso-C}_4H_9\cdot \rightarrow CH_3\cdot + C_3H_6$	Photolysis	543—598	31·0	12·4	*r*	22·2	4·6	25·1	16·1
$CH_3\cdot + C_3H_6 \rightarrow \text{iso-C}_4H_9\cdot$	$(\text{iso-C}_4H_9N)_2$		8·8	11·4	*b*				
$\text{t-C}_4H_9\cdot \rightarrow H\cdot + \text{iso-C}_4H_8$	Photolysis	666—797	43·6	15·5	*s*	42·2	9·1	41·3	7·4
$H\cdot + \text{iso-C}_4H_8 \rightarrow \text{t-C}_4H_9\cdot$	$\text{t-C}_4H_9\cdot CHO$		1·4	13·6	*q*				
$\text{t-C}_4H_9\cdot \rightarrow CH_3\cdot + C_3H_6{}^i$	Photolysis	742—797	46·3	15·2	*s*	—	—	32·0	19·7
$CH_3\cdot + C_3H_6 \rightarrow \text{t-C}_4H_9\cdot{}^i$	$\text{t-C}_4H_9\cdot CHO$		—	—	–				
$\text{neo-C}_5H_{11}\cdot \rightarrow CH_3\cdot + \text{iso-C}_4H_8$	HCl catalysed	762	34	13	*t*	25·7	7·4	24·0	17·3
$CH_3\cdot + \text{iso-C}_4H_8 \rightarrow \text{neo-C}_5H_{11}\cdot$	decompn. neo-C_5H_{12}		~8·3	~11·4	*b*				
$\text{cyclo-C}_5H_9\cdot \rightarrow C_3H_5 + C_2H_4$	$CD_3\cdot + \text{cyclo-C}_5H_{10}$	573—718	37·7	14·5	*u*	27·4	18·3	28·7	21·8
$C_3H_5\cdot + C_2H_4 \rightarrow \text{cyclo-C}_5H_9\cdot$			~10·3	~10·5	*b*				
$\text{sec-C}_6H_{13} \rightarrow \text{n-C}_3H_7\cdot + C_3H_6$	Decompn. C_2H_6, addition $C_2H_5\cdot$ to C_2H_4, and isomerization $\text{n-C}_6H_{13}\cdot \rightarrow$ sec-C_6H_{13}	822	22·4	13·5	*v*	13·8	6·3	22·9	15·9
$\text{n-C}_3H_7\cdot + C_3H_6 \rightarrow \text{n-C}_6H_{13}\cdot$			~8·6	~12·1	*b*				
Halogeno-radicals									
$C_2H_4Cl \rightarrow Cl\cdot + C_2H_4$	Photochlorination	298—327	23·9	13	*w*	22·4	−1·4	21·3	3·7
$Cl\cdot + C_2H_4 \rightarrow C_2H_4Cl$	of C_2H_4		1·5	13·3	*x*				
$CH_2\cdot Cl\cdot \dot{C}HCl \rightarrow Cl\cdot + C_2H_3Cl$	Photochlorination	298—327	23·8	13	*w*	22·9	2·7	22·7	5·5
$Cl\cdot + C_2H_3Cl \rightarrow CH_2Cl\cdot \dot{C}HCl$	of C_2H_3Cl		0·9	12·4	*x*				

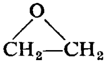
Table—*continued*

Reaction	Radical source	Temp. (°K)	E (kcal. mole^{-1})	log A (sec.$^{-1}$ and mole^{-1} ml. sec.$^{-1}$)	Ref.	ΔH°_{298} (kcal. mole^{-1})	ΔS° (cal. mole^{-1} deg.$^{-1}$)^a	ΔH°_{298} (kcal. mole^{-1})	ΔS° (cal. mole^{-1} deg.$^{-1}$)^a
						Kinetic data		Thermodynamic data^b	
		Halogeno-radicals							
$CHCl_2{\cdot}\dot{C}HCl \rightarrow Cl{\cdot} + CHCl{=}CHCl$	Photochlorination of CHCl = CHCl	313—335	20·3	13	*w*	19·3	2·3	20·1	4·9
$Cl{\cdot} + CHCl{=}CHCl \rightarrow CHCl_2{\cdot}\dot{C}HCl$			1·0	12·5	*x*				
$CHCl_2{\cdot}\dot{C}Cl_2 \rightarrow Cl{\cdot} + CHCl{=}CCl_2$	Photochlorination of C_2HCl_3	433—497	20·4	13·7	*y*	19·7	5·0	19·8	7·6
$Cl{\cdot} + CHCl{=}CCl_2 \rightarrow CHCl_2{\cdot}\dot{C}Cl_2$			0·7	12·6	*x*				
$C_2Cl_5{\cdot} \rightarrow Cl{\cdot} + C_2Cl_4$	Photochlorination of C_2Cl_4	300—388	16·8	12·8	*b*	16·8	1·8	17·5	6·3
$Cl{\cdot} + C_2Cl_4 \rightarrow {\cdot}C_2Cl_5$			~0	12·4	*z*				
${\cdot}C_2H_4Br \rightarrow Br{\cdot} + C_2H_4$	Addition of HBr to C_2H_4	298—327	11·1	12·9	*aa, b*	8·2	1·8	8·8	4·0
$Br{\cdot} + C_2H_4 \rightarrow {\cdot}C_2H_4Br$			2·9	12·5	*bb, b*				
${\cdot}CH_2{\cdot}C_6H_4{\cdot}CH_2Br \rightarrow Br{\cdot}CH_2Br{\cdot} + CH_2{:}C_6H_4{:}CH_2$	Toluene-carrier pyrolysis $BrCH_2{\cdot}C_6H_4{\cdot}CH_2Br$	748—814	40	13	*cc*	—	—	—	—
${\cdot}C_2H_4NF_2 \rightarrow {\cdot}NF_2 + C_2H_4$	Addition NF_2 (N_2F_4) to olefin	373—428	13·7	12·9	*dd*	−1·8	10·5	−0·2*	—
${\cdot}NF_2 + C_2H_4 \rightarrow {\cdot}C_2H_4NF_2$			15·5	10·6	*dd*				
${\cdot}C_3H_6NF_2 \rightarrow {\cdot}NF_2 + C_3H_6$	,, ,,	334—391	13·5	13·4	*dd*	−0·2	14·6	0·9*	—
${\cdot}NF_2 + C_3H_6 \rightarrow {\cdot}C_3H_6NF_2$			13·7	10·2	*dd*				

Table—*continued*

Reaction	Radical source	Temp. (°K)	E (kcal. mole^{-1})	log A (sec.$^{-1}$ and mole^{-1} ml. sec.$^{-1}$)	Ref.	ΔH°_{298} (kcal. mole^{-1})	ΔS° (cal. mole^{-1} deg.$^{-1}$)^a	ΔH°_{298} (kcal. mole^{-1})	ΔS° (cal. mole^{-1} deg.$^{-1}$)^a
						Kinetic data		Thermodynamic data^b	
		Halogeno-radicals							
$\cdot C_4H_8NF_2 \rightarrow \cdot NF_2 + CH_2{=}CH{\cdot}CH_2{\cdot}CH_3$	Addition $NF_2(N_2F_4)$ to olefin	334—391	10·3	12·5	*dd*	−3·3	11·0	0·9*	—
$\cdot NF_2 + CH_2{=}CH{\cdot}CH_2{\cdot}CH_3 \rightarrow C_4H_8NF_2$			13·6	10·1	*dd*				
$\cdot C_4H_8NF_2 \rightarrow \cdot NF_2 + CH_3{\cdot}CH{=}CH{\cdot}CH_3$ (*trans*)	,, ,,	334—391	13·6	14·0	*dd*	1·7	20·6	1·6*	—
$CH_3CH{=}CHCH_3$ (*trans*) $+ NF_2 \rightarrow \cdot C_4H_8NF_2$			11·9	9·5	*dd*				
$\cdot C_4H_8NF_2 \rightarrow \cdot NF_2 + CH_3{\cdot}CH{=}CH{\cdot}CH_3$ (*cis*)	,, ,,	334—391	13·6	14·0	*dd*	1·7	20·6	2·8*	—
$CH_3CH{=}CHCH_3$ (*cis*) $+ \cdot NF_2 \rightarrow \cdot C_4H_8NF_2$			11·9	9·5	*dd*				
$\cdot C_5H_{10}NF_2 \rightarrow \cdot NF_2 + (CH_3)_2C{=}CH{\cdot}CH_3$	,, ,,	314—373	9·7	13·3	*dd*	−0·4	19·7	4·0*	—
$(CH_3)_2C{=}CH{\cdot}CH_3 + \cdot NF_2 \rightarrow \cdot C_5H_{10}NF_2$			10·1	9·0	*dd*				
$\cdot C_6H_{12}NF_2 \rightarrow \cdot NF_2 + (CH_3)_2C{=}C(CH_3)_2$	,, ,,	314—373	8·3	12·1	*dd*	0	17·4	6·3*	—
$\cdot NF_2 + (CH_3)_2C{=}C(CH_3)_2 \rightarrow \cdot C_6H_{12}NF_2$			8·3	8·3	*dd*				
cyclo-$\cdot C_5H_8NF_2 \rightarrow$ cyclo-$C_5H_8 + \cdot NF_2$	,, ,,	334—391	9·8	11·4	*dd*	−1·2	11·4	7·1*	—
$\cdot NF_2 +$ cyclo-$C_5H_8 \rightarrow$ cyclo-$\cdot C_5H_8NF_2$			11·0	8·9	*dd*				

Table—*continued*

Reaction	Radical source	Temp. (°K)	E (kcal. mole^{-1})	log A (sec.$^{-1}$ and mole^{-1} ml. sec.$^{-1}$)	Ref.	ΔH°_{298} (kcal. mole^{-1})	ΔS° (cal. mole^{-1} deg.$^{-1}$)[a]	ΔH°_{298} (kcal. mole^{-1})	ΔS° (cal. mole^{-1} deg.$^{-1}$)[a]
						Kinetic data		Thermodynamic data[b]	
	Oxygen-containing radicals								
$H\dot{C}O \rightarrow H\cdot + CO$ $H\cdot + CO \rightarrow H\dot{C}O$	Hg($^3P_1$) + 	298	14·4 1·0	13·0 13·8	*ee* *b*	13·4	−3·7	18·5	1·1
$CH_3\cdot\dot{C}O \rightarrow CH_3\cdot + CO$ $CH_3\cdot + CO \rightarrow CH_3\cdot\dot{C}O$	Photolysis $CH_3\cdot CO\cdot CH_3$ in presence of HI	473—568	15·0 (E_∞) 12·0 (E_0) 3·9	10·3 (A_∞) 14·5 (A_0) 8·6	*ff* *gg*	11·1	7·9	13·0	9·1
$CF_3\cdot\dot{C}O \rightarrow CF_3\cdot + CO$ $CF_3\cdot + CO \rightarrow CF_3\cdot\dot{C}O$	Photolysis Cl_2 or Br_2 in presence of $CF_3\cdot CHO$	298—521	10 4	10·4 9	*gg* *hh*	6	6·4	14*	15*
$C_2H_5\cdot\dot{C}O \rightarrow \dot{C}_2H_5\cdot + CO$ $C_2H_5\cdot + CO \rightarrow C_2H_5\cdot\dot{C}O$	Photolysis $(C_2H_5N)_2$ in presence of $C_2H_5\cdot CHO$	303—353	14·7 (E_∞) 10·5 (E_0) 5	13·3 (A_∞) 15·6 (A_0) 11	*ii* *ii*	9·7	10·5	10·3	11·0
$\cdot CH_2OH \rightarrow H\cdot + H\cdot CHO$ $\cdot H + H\cdot CHO \rightarrow \cdot CH_2OH$	Hg($^3P_1$) + CH_3OH	673—773	29 3	13·1 13·6	*jj* *b*	26·0	−2·5	28·5	1·0
$CH_3\cdot O\cdot CH_2\cdot \rightarrow CH_3\cdot + HCHO$	Hg($^3P_1$) + $CH_3\cdot O\cdot CH_3$	473—573	25·5 (E_∞) 18·1 (E_0)	13·2 (A_∞) 16·4 (A_0)	*kk*	—	—	11·3	12·3
$CH_3\cdot + H\cdot CHO \rightarrow CH_3\cdot OCH_2\cdot$			—	—	—				
$CH_3\cdot O\cdot O\cdot CH_2\cdot$ **P** $CH_3O\cdot + H\cdot CHO$ $CH_3O\cdot + H\cdot CHO \rightarrow CH_3\cdot OO\cdot CH_2\cdot$	Photolysis $(CH_3O)_2$	394—453	5·8 —	— —	*ll* -	—	—	−37·3	9·5
$CH_3\cdot CO\cdot CH_2\cdot \rightarrow CH_3\cdot + CH_2CO$ $CH_3\cdot + CH_2CO \rightarrow CH_3\cdot COCH_2$	Photolysis $CH_3\cdot CO\cdot CH_3$	365—435	41 —	— —	*mm* -	—	—	35·2	10·9

Table—*continued*

Reaction	Radical source	Temp. (°K)	E (kcal. mole^{-1})	log A (sec.$^{-1}$ and mole^{-1} ml. sec.$^{-1}$)	Ref.	Kinetic data ΔH°_{298} (kcal. mole^{-1})	Kinetic data ΔS° (cal. mole^{-1} deg.$^{-1}$)^a	Thermodynamic data^b ΔH°_{298} (kcal. mole^{-1})	Thermodynamic data^b ΔS° (cal. mole^{-1} deg.$^{-1}$)^a
Oxygen-containing radicals									
$C_2H_5\cdot O\cdot \rightarrow CH_3\cdot + H\cdot CHO$	Photolysis $C_2H_5\cdot CO_2\cdot C_2H_5$	288—468	13·0	10·5	*nn*	—	—	11·2	12·4
$CH_3\cdot + H\cdot CHO \rightarrow C_2H_5\cdot O\cdot$			—	—	–				
$(CH_3)_2CHO\cdot \rightarrow CH_3\cdot + CH_3\cdot CHO$	Pyrolysis Pr^i ONO in presence of NO	433—473	17·3 (E_∞) 8·3 (E_0)	11·8 (A_∞) 13·1 (A_0)	*oo*	—	—	6·6	17·3
$CH_3\cdot + CH_3\cdot CHO \rightarrow (CH_3)_2CHO\cdot$			—	—	–				
sec-$C_4H_9O\cdot \rightarrow C_2H_5\cdot + CH_3\cdot CHO$	Pyrolysis sec-$C_4H_9\cdot ONO$	423—463	17·5 (E_∞) 10·6 (E_0)	13·4 (A_∞) 14·5 (A_0)	*pp*	—	—	4·2	19·1
$C_2H_5\cdot + CH_3\cdot CHO \rightarrow$ sec-$C_4H_9O\cdot$			—	—	–				
t-$C_4H_9O\cdot \rightarrow CH_3\cdot + CH_3\cdot CO\cdot CH_3$	Pyrolysis $[Bu^tO]_2$ in presence of NO	398—436	22·8 (E_∞) 13·4 (E_0)	14·7 (A_∞) 15·7 (A_0)	*qq*	17·8	25·3	3·8	20·3
$CH_3\cdot + CH_3\cdot CO\cdot CH_3 \rightarrow$ t-$C_4H_9O\cdot$			5·0	9·2	*b*				
$CH_3\cdot\dot{C}HO\cdot C_2H_5 \rightarrow CH_3\cdot CHO + C_2H_5\cdot$	$CH_3 + (C_2H_5)_2O$	418—453	23·5	10·9	*rr*	2·9	10·5	3·7	14·8
$C_2H_5\cdot + CH_3\cdot CHO \rightarrow CH_3\cdot\dot{C}HO\cdot C_2H_5$			20·6	8·6	*b*				
$C_6H_5\cdot OCH_2\cdot \rightarrow C_6H_5\cdot CHO + \cdot H^i$	$CH_3\cdot + C_6H_5\cdot O\cdot CH_3$	453—539	21	12·5	*ss*	—	—	22	—
$H\cdot + C_6H_5\cdot CHO \rightarrow C_6H_5\cdot OCH_2\cdot$			—	—	–				
$CH_3\cdot SO_2\cdot \rightarrow CH_3\cdot + SO_2$	$CH_3\cdot + SO_2$	298—437	22·4	13·0	*tt*	20·9	10·1	21	15·0*
$CH_3\cdot + SO_2 \rightarrow CH_3\cdot SO_2\cdot$			1·5	10·8	*tt*				
$C_2H_5\cdot SO_2\cdot \rightarrow C_2H_5\cdot + SO_2$	$C_2H_5\cdot + SO_2$	301—348	19·9	14·4	*uu*	16·8	15·6	—	19·0*
$C_2H_5\cdot + SO_2 \rightarrow C_2H_5SO_2\cdot$			3·1	11·0	*uu*				

References for Table

[a]Standard state 1 mole ml.$^{-1}$; [b]ref. 2; [c]ref. 34; [d]W. M. Jackson and J. R. McNesby, *J. Amer. Chem. Soc.*, 1961, **83**, 4891; [e]K. Yang, *J. Amer. Chem. Soc.*, 1962, **84**, 3795; [f]ref. 17; [g]R. J. Cvetanović and R. S. Irwin, *J. Chem. Phys.*, 1967, **46**, 1964; [h]ref. 45; [i]reaction involves isomerisation, see section 6; [j]ref. 47, ref. 48; [k]ref. 21; [l]J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1960, 1611; [m]J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1960, 1602; [n]A. S. Gordon, *J. Chem. Phys.*, 1961, **34**, 331; [o]M. C. Lin and K. J. Laidler, *Canad. J. Chem.*, 1967, **45**, 1315; [p]E. L. Metcalfe and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1960, 5072, J. R. McNesby and W. M. Jackson, *J. Chem. Phys.*, 1963, **38**, 692; [q]D. G. Dalgleish and J. H. Knox, *Chem. Comm.*, 1966, 917; [r]ref. 12; [s]R. N. Birrell and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1960, 4218; J. R. McNesby and W. M. Jackson, *J. Chem. Phys.*, 1963, **38**, 692; [t]K. H. Anderson and S. W. Benson, *J. Chem. Phys.*, 1964, **40**, 3747; [u]A. S. Gordon, *Canad. J. Chem.*, 1965, **43**, 570; [v]C. P. Quinn, *Trans. Faraday Soc.*, 1963, **59**, 2543; [w]R. Eckling, P. Goldfinger, G. Huybrechts, G. Martens, L. Meyers, and S. Smoes, *Chem. Ber.*, 1960, **93**, 3014; [x]P. B. Ayscough, A. J. Cocker, F. S. Dainton, S. Hurst, and M. Weston, *Proc. Chem. Soc.*, 1961, 244; [y]G. Huybrechts, L. Meyers, and G. Verbeke, *Trans. Faraday Soc.*, 1962, **58**, 1128; [z]P. Goldfinger, G. Huybrechts, and G. Martens, *Trans. Faraday Soc.*, 1961, **57**, 2210; [aa]D. A. Armstrong and J. W. T. Spinkes, *Canad. J. Chem.*, 1959, **37**, 1210; [bb]R. J. Cvetanović, *Adv. Photochem.*, 1963, **1**, 173; [cc]ref. 7; [dd]ref. 19; [ee]R. J. Cvetanović, *Canad. J. Chem.*, 1955, **33**, 1684; [ff]ref. 32; [gg]ref. 16; [hh]estimated from $CH_3\cdot + CO \rightarrow CH_3\cdot\dot{C}O$; [ii]ref. 15; [jj]M. K. Phibbs and B. de B. Darwent, *J. Chem. Phys.*, 1950, **18**, 495; [kk]L. F. Loucks and K. J. Laidler, *Canad. J. Chem.*, 1967, **45**, 2767; [ll]Y. Takezaki, T. Mizazaki, and N. Nakohara, *J. Chem. Phys.*, 1956, **25**, 536; [mm]R. K. Brinton, *J. Amer. Chem. Soc.*, 1961, **83**, 1541; [nn]M. H. J. Wijnen, *J. Amer. Chem. Soc.*, 1960, **82**, 3034; [oo]ref. 6; [pp]R. L. East and L. Phillips, *J. Chem. Soc.* (*A*), 1967, 1939; [qq]ref. 5; [rr]J. Long and G. Skirrow, *Trans. Faraday Soc.*, 1962, **58**, 1403; [ss]M. F. R. Mulcahy, B. G. Tucker, D. J. Williams, and J. R. Wilmshurst, *Austral. J. Chem.*, 1967, **20**, 1155; [tt]A. Good and J. C. J. Thynne, *Trans. Faraday Soc.*, 1967, **63**, 2708; [uu]A. Good and J. C. J. Thynne, *Trans. Faraday Soc.*, 1967, **63**, 2721.

* Estimates based on group-additivity rules.

has been carried out, the latest result is usually quoted. While many of the data have appeared in the comprehensive compilation of O'Neal and Benson,[2] to which the reader is referred for greater detail, a significant number of subsequent results are also included. Comparisons between the kinetic and thermodynamic estimates of ΔH° and ΔS° as detailed in the previous sections are given wherever possible. Discussion of the results will be limited to reactions where discrepancies exist in these comparisons.

There is reasonably good agreement between the kinetic and thermodynamic data for the decompositions of the alkyl radicals, notable exceptions being some of the decompositions yielding hydrogen atoms and the decomposition of the 1-methylpentyl radical. It seems likely in the latter cases that the kinetic data for the decomposition reactions are in error.

The kinetic data for chloro- and bromo-alkyl radicals are remarkably consistent with the thermochemical estimates and this lends considerable support to the kinetic results. Unfortunately there is still little thermodynamic information on difluoroamino-radicals to compare with the reasonably extensive kinetic results for the radical decompositions; approximate enthalpy changes have been obtained from group-additivity calculations and these show satisfactory agreement with kinetic estimates.

The largest anomalies between the kinetic and thermodynamic determinations of ΔH° and ΔS° for radical decompositions arise with oxygenated radicals. Reliable kinetic information on the decomposition of the formyl radical is lacking. There are considerable practical difficulties in studying the reaction, particularly in determining the concentrations of the radicals, and the best estimate of the rate constant for the decomposition is derived from the thermodynamic data.[2] Amphlett and Whittle[16] were unable to detect any pressure-dependence in the decomposition of the $CF_3\cdot\dot{C}O$ radical in the pressure range 10—60 mm., generating the radicals from the selective photolysis of chlorine or bromine in the presence of the aldehyde. This result is difficult to reconcile with the observed pressure-dependence of the $CH_3\cdot\dot{C}O$ and $C_2H_5\cdot\dot{C}O$ radical decompositions. Subsequent work on the azomethane–trifluoroacetaldehyde system [37] has revealed pressure-dependence in the $CF_3\cdot\dot{C}O$ decomposition and accordingly the Arrhenius parameters reported by Amphlett and Whittle[16] appear to have been measured in the fall-off region.

The reactions of alkoxy-radicals, including decompositions, have been reviewed recently.[38] Although the rates of decomposition of several alkoxy-radicals have been measured and thermodynamic estimates of ΔH° and ΔS° are available, there have been few kinetic studies of the reverse radical addition reactions to the carbonyl compounds. These reactions are difficult to study since they compete unfavourably with hydrogen-abstraction reactions. Only for the t-butoxy-radical is all the information available and, as seen from the Table, a major discrepancy exists between the kinetic and thermodynamic

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[37] J. A. Kerr and A. C. Lloyd, unpublished results.

[38] P. Gray, R. Shaw, and J. C. J. Thynne, *Progr. Reaction Kinetics*, 1967, **4**, 63.

data. The thermochemical estimate of ΔH° is least likely to be in error, so this implies that the kinetic data for the decomposition and/or addition reactions are seriously at fault. Several studies of the decomposition have been made, but only the most recent has attempted a quantitative treatment of the pressure-dependence.[5]

6 Radical Isomerisation Reactions

Rearrangements of radicals in gas-phase oxidation and related processes have been discussed,[39] and there is ample evidence for the structural isomerisations of aryl radicals in solution,[40] although kinetic information is lacking. Of considerable kinetic interest are the structural isomerisations of small radicals in the gas phase on which several studies have recently been reported.

It was first suggested by Kossiakoff and Rice[41] that n-alkyl radicals can isomerise by intramolecular hydrogen abstraction, the so-called 'tail biting' reaction:

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}\dot{C}H_2 \longrightarrow CH_3{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \qquad (18)$$

Qualitative support for such reactions has been obtained mainly from studies of alkyl radical additions to simple olefins.[42] Quantitative data are even more difficult to obtain than for radical decompositions since the product of the reaction is another radical. Endrenyi and LeRoy[43] have reported the first Arrhenius parameters for this type of reaction, the isomerisation of n-pentyl to 1-methylbutyl [reaction (18)]. The radicals were generated by the addition of methyl radicals to ethylene and the subsequent addition of the n-propyl radicals to another molecule of ethylene. The occurrence of reaction (18) was inferred from the presence of 2-methylpentane in the products:

$$CH_3{\cdot} + CH_3{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \longrightarrow (CH_3)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \qquad (19)$$

In the presence of a high concentration of methyl radicals, it was assumed that reaction (19) was the major fate of the 1-methylbutyl radicals. The rate constant for reaction (18) is thus given by:

$$R_{1\text{-methylbutyl}} = R_{\text{iso}-C_6H_{14}} = k_{18}[\text{n-}C_5H_{11}{\cdot}] \qquad (20)$$

and the concentration of n-pentyl radicals can be monitored by the reactions:

$$\text{n-}C_5H_{11}{\cdot} + CH_3{\cdot} = \text{n-}C_6H_{14} \qquad (21)$$

$$CH_3{\cdot} + CH_3{\cdot} = C_2H_6 \qquad (22)$$

[39] A. Fish, *Quart. Rev.*, 1964, **18**, 243.

[40] A. F. Trotman-Dickenson, 'Free Radicals', Methuen, London, 1959, p. 113; W. A. Pyror, 'Free Radicals', McGraw-Hill, New York, 1966, p. 266.

[41] H. Kossiakoff and F. O. Rice, *J. Amer. Chem. Soc.*, 1943, **65**, 590.

[42] V. B. Sefton and D. J. LeRoy, *Canad. J. Chem.*, 1956, **34**, 41; A. S. Gordon and J. R. McNesby, *J. Chem. Phys.*, 1959, **31**, 853; M. H. J. Wijnen, *J. Amer. Chem. Soc.*, 1961, **83**, 3752.

[43] L. Endrenyi and D. J. LeRoy, *J. Phys. Chem.*, 1966, **70**, 4081.

from which it can be shown that

$$[\text{n-}C_5H_{11}] = (k_{22}^{\frac{1}{2}}/k_{21})(R_{\text{n-}C_6H_{14}}/R_{C_2H_6}^{\frac{1}{2}}) \qquad (23)$$

From equations (20) and (23) it follows that

$$k_{18}k_{22}^{\frac{1}{2}}/k_{21} = R_{\text{iso-}C_6H_{14}}\, R_{C_2H_6}^{\frac{1}{2}}/R_{\text{n-}C_6H_{14}}$$

and the temperature coefficient of the rate-constant ratio $k_{18}k_{22}^{\frac{1}{2}}/k_{21}$ can be determined by analysis of the ethane and n- and iso-hexane products. The above scheme is somewhat simpler than that of Endrenyi and LeRoy[43] since they had to take account of the fact that hexane is also formed by the combination of n-propyl radicals. From the known value of k_{22} and an assumed value of k_{21} it was deduced that:

$$\log k_{18} = 7{\cdot}15 - 10{,}800/2{\cdot}3\boldsymbol{RT}\,(\text{sec.}^{-1})$$

An activation energy of about 10 kcal. mole^{-1} seems reasonable for this type of process, on the basis of its analogy with a radical hydrogen-abstraction reaction. On the other hand an *A*-factor of $10^{7\cdot2}$ sec.$^{-1}$ is incompatible with transition-state theory calculations on related systems. An estimate based on the method of O'Neal and Benson[29] (see section 3) indicates an *A*-factor in the range 10^{11-12} sec.$^{-1}$ for this type of process.

In the same study Endrenyi and LeRoy[43] were able to estimate a rate constant for the analogous isomerisation of the radical $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}\dot{C}H_2$, although they could not determine the Arrhenius parameters. More work is needed on this type of process before the rate constants can be assigned with confidence.

Although it is reasonable to postulate isomerisation involving intramolecular hydrogen transfer with C_5 and larger radicals, the idea seems less attractive for C_4 and C_3 radicals. Considerable discussion has taken place on the feasibility of reactions such as:

$$\text{iso-}C_3H_7{\cdot} \longrightarrow \text{n-}C_3H_7{\cdot} \longrightarrow CH_3{\cdot} + C_2H_4 \qquad (24)$$
$$\text{t-}C_4H_9{\cdot} \longrightarrow \text{iso-}C_4H_9{\cdot} \longrightarrow CH_3{\cdot} + C_3H_6 \qquad (25)$$

Two types of experiment bearing on this topic have been carried out. In the first, the occurrence of isomerisation–decomposition reactions has been inferred from product analysis of rather complex systems, known to involve the initial radical. For instance, in the photolyses of di-isopropyl ketone[44] and isobutyl-aldehyde[45] and in the pyrolyses of di-isopropylmercury[46] and isobutane,[47] where it has been established that isopropyl radicals are produced, reaction (24) has been suggested as the source of ethylene that is observed in the products at high temperatures. In all of the experiments of this type it has been necessary to postulate simultaneous isomerisation and decomposition of the initial radical, as other products of the isomerised radical, such as radical dimers,

[44] C. A. Heller and A. S. Gordon, *J. Phys. Chem.*, 1958, **62**, 709.

[45] J. A. Kerr and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 921.

[46] B. H. M. Billinge and B. G. Gowenlock, *J. Chem. Soc.*, 1962, 3252.

[47] R. S. Konar, R. M. Marshall, and J. H. Purnell, *Trans. Faraday Soc.*, 1968, **63**, 405.

have not been observed in significant quantities. It should also be pointed out that, in some instances, it is not inconceivable that the products assumed to arise from radical isomerisation could be produced in secondary reactions.[2] Thus ethylene in the isopropyl systems might arise from the reactions:[48]

$$\begin{aligned}&\mathrm{H\cdot + C_3H_6 \longrightarrow n\text{-}C_3H_7\cdot}\\ &\quad\mathrm{n\text{-}C_3H_7\cdot \longrightarrow CH_3\cdot + C_2H_4}\end{aligned}$$

In the second type of experiment concerning C_3 and C_4 alkyl isomerisations, isotopically labelled radicals have been generated either by pyrolysis of a suitably labelled alkane or by decomposition of the alkane sensitised by methyl radicals. Thus reaction (24) has been investigated with $\mathrm{CD_3{\cdot}CH_2{\cdot}\dot{C}H_2}$ radicals produced in the pyrolysis of $\mathrm{CD_3{\cdot}CH_2{\cdot}CH_3}$:[48]

$$\begin{array}{rl} & \longrightarrow \mathrm{CD_3{\cdot}\dot{C}H{\cdot}CH_2 + RH}\\ \mathrm{R\cdot + CD_3{\cdot}CH_2{\cdot}CH_3} & \longrightarrow \mathrm{\dot{C}D_2{\cdot}CH_2{\cdot}CH_3 + RD}\\ & \longrightarrow \mathrm{CD_3{\cdot}CH_2{\cdot}\dot{C}H_2 + RH}\end{array}$$

Mass-spectrometric analysis was carried out for the isotopically labelled ethylenes and it was justifiably argued that the product $\mathrm{CH_2{=}CDH}$ could only arise from the isomerisation–decomposition sequence:

$$\mathrm{CD_3{\cdot}\dot{C}H{\cdot}CH_3 \longrightarrow [\dot{C}D_2{\cdot}CHD{\cdot}CH_3] \longrightarrow CD_2{=}CHD + CH_3\cdot} \tag{24a}$$

In this way the rate of reaction (24*a*) was measured relative to the rate of the alternative decomposition:

$$\mathrm{CH_3{\cdot}\dot{C}H{\cdot}CH_3 \longrightarrow CH_2{=}CH{\cdot}CH_3 + H\cdot} \tag{25}$$

Jackson and McNesby[48] determined $k_{24a}/k_{25} \leqslant 0{\cdot}06$ below 826°K, whereas other determinations without isotopic labelling[44,47] have indicated much higher values of this ratio.

In similar experiments with isotopically labelled alkyl radicals, McNesby and his co-workers have shown that up to 773°K the isomerisations of isobutyl[49,50] and sec-butyl[50] radicals are negligible.

In conclusion it may be said that while the simultaneous isomerisation and decomposition of isopropyl and n- and t-butyl radicals (see Table) may occur at high temperatures, these reactions are by no means established and there is no general agreement regarding their rate constants. It may be further stated that present evidence is wholly against simple isomerisation of C_3 and C_4 alkyl radicals at lower temperatures.

Substantial evidence, based on product analyses, has been obtained for the isomerisations of cyclopropyl[51] and cyclobutyl radicals:[18]

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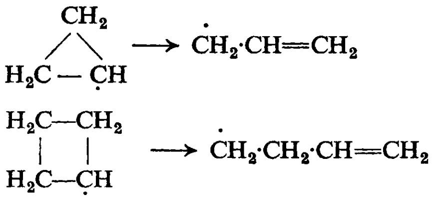
[48] W. M. Jackson and J. R. McNesby, *J. Chem. Phys.*, 1962, **36,** 2272.

[49] J. R. McNesby, C. M. Drew, and A. S. Gordon, *J. Chem. Phys.*, 1956, **24,** 1260; W. M. Jackson, J. R. McNesby, and B. de B. Darwent, *ibid.*, 1962, **37,** 2256.

[50] A. S. Gordon and J. R. McNesby, *J. Chem. Phys.*, 1960, **33,** 1882.

[51] J. R. McNesby and A. S. Gordon, *J. Amer. Chem. Soc.*, 1957, **79,** 825; G. Greig and J. C. J. Thynne, *Trans. Faraday Soc.*, 1966, **62,** 3338; 1967, **63,** 1369.

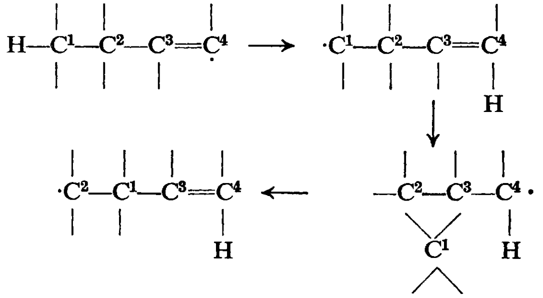


Activation energies of *ca.* 20 kcal. mole^{-1} have been estimated for these reactions but there was insufficient information to obtain the *A*-factors as well.

An interesting type of isomerisation has been reported for alkenyl radicals, produced from the additions of propyl and butyl radicals to alkynes in the gas phase:[52]

$$(CH_3)_2\dot{C}H + CH{\equiv}CH \longrightarrow (CH_3)_2CH{\cdot}CH{=}\dot{C}H$$
$$(CH_3)_2CH{\cdot}CH{=}\dot{C}H \longrightarrow CH_3{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CH{=}CH_2 \qquad (26)$$

Benson and DeMore[53] have suggested the following general mechanism to explain the isomerisation:



and all the systems so far studied can be explained on this basis. Arrhenius parameters corresponding to *E ca.* 10 kcal. mole^{-1} and A *ca.* 10^{11-12} sec.$^{-1}$ have been estimated for the isomerization process (26) by an approximate RRK treatment of the data on the additions of isopropyl and t-butyl radicals to acetylene and propyne.[52] Similar isomerizations have been shown to occur in the liquid-phase reactions between iodine and olefins,[53] and between carbon tetrachloride and hept-1-yne.[54]

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