THE THERMAL UNIMOLECULAR REACTIONS OF HYDROCARBONS

H. M. FREY AND R. WALSH

Chemistry Department, Reading University, Reading, England

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Contents

I. Introduction

As little as 10 years ago it would have been relatively easy to review virtually the whole field covered by the title (and to include compounds other than hydrocarbons) if one merely restricted the contents to examples for which the evidence for their unimolecular nature was strong. The remarkable increase in the number of studies and the wealth of data that have been reported in the past decade has resulted from a number of diverse factors which do not concern us directly, but have forced us to limit the scope of this article. We have therefore restricted our attention, in the main, to a consideration of studies in the gas phase where precise quantitative data have been reported. Examples of reactions involving compounds other than hydrocarbons are only mentioned where they throw light on the hydrocarbon decompositions being discussed. Details of unimolecular reaction theory and its application to experimental results have not been considered as this topic will be discussed elsewhere.

Even with these restrictions the field of review is extensive and diverse. It is therefore necessary to find a method for dividing this topic into various sections. We have been unable to devise a logically consistent scheme which would make such a division simple and not at the same time produce numerous subsections and hence destroy many of the unifying features of this field of work. The arrangement of this article is a compromise which focuses attention on the relationship between the reactants and the transition states involved in the reaction. Four subdivisions then follow naturally though unfortunately, as will become apparent, in some cases the choice in which particular section a specific reaction is placed cannot be made in a completely objective way. The reason for this choice is not merely one of convenience. We wish to emphasize the way in which a consideration of the transition state often allows a unification of many of the kinetic data. It is of course true that in some cases evidence for the nature of the activated complex is largely or entirely based on the kinetics of the reaction, and under such circumstances it is inevitable that good agreement is obtained between, for example, calculated and experimental entropies of activation. However, kinetic evidence is not always the only, or indeed the best, evidence for the detailed nature of the activated complex, and in such situations the transition state theory viewpoint places severe limitations upon the possible kinetic parameters.

The ratio of A factors for the forward and reverse reactions of any particular decomposition (or isomerization) is related to the entropy difference between reactant and product, and such entropies are either available or may be estimated with high precision for hydrocarbons (or hydrocarbon radicals). Thus if the A factor or entropy of activation (to which it is directly relatable by the application of absolute rate theory) for the reaction in one direction is known, the reverse is immediately calculable. For relatively few cases is this information available from experimental results obtained in one study, but not infrequently the entropies of activation for each process have been determined (often under very different experimental conditions) in separate studies. Under such circumstances the consistency of the data can be checked easily, and indeed this procedure does allow one to reject some experimental data immediately. One may go further than this; in some cases the structure of the activated complex can be inferred simply from the nature of the reactant and product and its entropy estimated comparatively precisely. This allows a direct prediction of A factors or, at worst, allows limits to be set on them, which again enables quite searching tests on experimental data.

When several experimental determinations relating to the same reaction are available, we have attempted to assess their relative reliability and where necessary to indicate which set of data we believe to be the "best."

Finally our searches of the literature and reading of the large number of references that this has involved leads us to make several recommendations to authors of experimental work. Arrhenius equations alone should not be quoted, but the rate constants on which these are based should be reported. Entropies and enthalpies of activation should likewise be supported by the rate data and also the Arrhenius parameters. (A significant number of entropies of activation that have been reported in the literature are based on an incorrect formulation of the absolute rate relationships. A correct treatment of the thermodynamic formulation of absolute rate theory for unimolecular reactions leads to the relationships

$$A = (ekT_m/h)e^{+\Delta S^{\ddagger}/R}$$

$$E_a = \Delta H^{\ddagger} + RT_m$$

where A and E_a are the Arrhenius parameters, $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are the entropy and enthalpy of activation, respectively, and T_m is the mean absolute temperature for the range over which rate measurements are made.) A reduction in the number of different units in which rates are reported would obviously also be helpful; the impending change to SI units, however distasteful to workers in reaction kinetics, would be an excellent opportunity for a preferred set of concentration units to be agreed upon.

II. Acyclic Reactants with Acyclic Transition States

This class comprises all the processes which involve the elementary step of bond breaking. There are two subgroups: (i) molecular dissociation to give two radicals, and (ii) radical dissociation to give an olefin and a radical (or atom).

Because of the size of the literature, this review is strictly limited to consideration of hydrocarbons (and alkyl radicals). Moreover, since the reactions of alkyl radicals[1] as well as the chemical activated decompositions of alkanes and alkyl radicals[2] have both been reviewed earlier, the emphasis will be on recent work and much of the older literature will be ignored. One feature of this class of reactions, which is absent for those considered in the other sections, is that their reverse reactions can be, and indeed often have been, studied, albeit usually under different conditions. We felt it would be wrong to consider these decomposition processes without also considering their reverses since microscopic reversibility demands a common transition state, and the rate constants k_{forward} and k_{reverse} must satisfy

$$k_{\text{forward}} = K_{\text{eq}}k_{\text{reverse}} \quad (1)$$

where K_{eq} is the equilibrium constant. If this relationship is to be examined critically, it is necessary to have a fairly precise knowledge of K_{eq}. For the radical reactions involved here, K_{eq} has never been directly measured because of the difficulty of determining radical concentrations experimentally. Fortunately, computations of K_{eq} are now quite reliable, since the thermodynamic parameters required are either well enough known, or capable of sufficiently accurate estimation. However, where estimates are concerned, there are assumptions involved, and we have found that different workers in this field have often made different assumptions either when estimating K_{eq} or when using eq 1.

Our procedure has been as follows: to present the data in the form of a comparison between directly observed first-order rate constants and computed first-order rate constants. The thermodynamic data required to estimate K_{eq} are listed in the Appendix. The values adopted for k_{reverse} are listed and discussed under the appropriate section.

Since our comparison procedure can be, and indeed often has been, reversed, and the rate data reviewed here used to derive thermodynamic data for free radicals, it was necessary for us to use only results from independent studies. Fortunately a good deal of reliable data, particularly on bond dissociation energies, has been obtained by kinetic studies[3,4] of thermal bromination and iodination reactions of hydrocarbons. With one or two simple assumptions about their structures,[5,6] radical entropies can be estimated to good accuracy. For the reactions under review, in almost all cases it is safe to assume that $\Delta H°$ and $\Delta S°$ are known to within ±2 kcal mole^{-1} and ±2 eu, respectively.

One difficulty which has often arisen concerns the temperature at which comparisons are made. Rate constants for forward and reverse reactions are rarely if ever measured over over the same temperature range. Moreover, since $\Delta H°$ and $\Delta S°$ vary somewhat with temperature (*i.e.*, $\Delta C_p°$ is not zero), the Arrhenius equation cannot be strictly obeyed for both forward and reverse reactions. However, experimental techniques are not yet sufficiently sensitive (except perhaps where isotope effects are concerned) to detect curvature in Arrhenius plots over a limited temperature range. Nevertheless, the possibility of such curvature should be borne in mind where extrapolation between widely differing temperature ranges is concerned. The temperatures at which we list computed rate constants are 1000 and 500°K for the molecular and radical bond-breaking processes, respectively. These temperatures fall within or close to the ranges within which such processes are observed.

A. MOLECULAR DISSOCIATION

1. Experimental Methods

The first rate constants for processes of this kind were obtained by the toluene-carrier technique developed by Szwarc.[7] The method has been described recently by Kerr[4] who has discussed its application to the determination of bond dissociation energies and listed the conditions necessary for its satisfactory use. Benson and Buss[8] have criticized the method

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[1] J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, 1, 105 (1961).

[2] B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, 3, 1 (1964).

[3] S. W. Benson, *J. Chem. Educ.*, 42, 502 (1965).

[4] J. A. Kerr, *Chem. Rev.*, 66, 465 (1966).

[5] J. H. Purnell and C. P. Quinn, *J. Chem. Soc.*, 4049, (1964).

[6] S. W. Benson, "Theormochemical Kinetics. Methods for the Estimation of Thermochemical Data and Rate Parameters," John Wiley and Sons, Inc., New York, N. Y., 1968.

[7] M. Szwarc, *Chem. Rev.*, 47, 75 (1950).

[8] S. W. Benson and J. H. Buss, *J. Phys. Chem.*, 61, 104 (1957).

as applied to toluene itself on mechanistic grounds and have shown that many of the early results were mutually inconsistent. It is now known that several of them were wrong,[9] although, interestingly, Price[10] has recently repeated the pyrolysis of toluene itself and demonstrated that earlier work was vitiated by surface effects rather than mechanistic complications. In view of these doubts, Swarc's work is not considered here, but only more recent results, where in some cases aniline[4,11] has replaced toluene as the carrier. It is perhaps worth stressing that these are low-pressure techniques, not very adaptable to the verification of reaction order over a wide pressure range.

Another method, which may now perhaps be generalized, has arisen out of analytical studies of hydrocarbon pyrolyses.[12] It is well established[12] that these are entirely free radical in character and are initiated, in the case of paraffins, by a molecular bond-breaking process, *viz.*

$$AB \longrightarrow A\cdot + B\cdot \qquad (2)$$

If one of the radicals A· or B· is not the chain-propagating radical, a chain-transfer step will follow in which either A· or B· is converted into the chain-propagating radical. If this step produces a unique product, a study of the kinetics of its formation amounts to a direct study of process 2 itself. Of course, if both A· and B· are chain-propagating radicals, as, for example, in the case of n-C_4H_{10} pyrolysis,[13] the method is not applicable.

Another technique, which has been widely applied, is the shock tube.[14] Tsang[15] has developed a competitive technique, in which mixtures of two compounds are simultaneously subjected to a single pulse shock. If the Arrhenius parameters for the decomposition of one compound are known, it acts as an internal standard for the other. Tsang[16] claims that under his conditions secondary reactions cannot occur within the time of the shock, and consequently the kinetics of the initial step of an otherwise complex decomposition can be directly studied.

Apart from these general methods, it is sometimes possible to obtain Arrhenius parameters for these processes by interpretation of the mechanism of a paraffin pyrolysis.[12] Rate expressions for such reactions are often complex and usually yield only a composite rate constant. Thus assumptions about elementary rate constants often have to be made before those of one isolated step can be obtained. This gives an added uncertainty to rate constants deduced from such studies and has led many previous reviewers to ignore them altogether. We feel that, where such data are based upon analytical studies, it should be considered and rate constants judged by their general consistency with values obtained by other methods.

2. *Results*

The observed data for a variety of paraffins, olefins, and aromatic hydrocarbons are listed in Tables I and II,[17-32] together with our computed estimates. Information on the reverse reaction, radical recombination, is very sparse indeed, and we were forced to make several arbitrary (and possibly erroneous) assumptions. (i) For recombination of like radicals, $\log k$ (l. mole^{-1} sec^{-1}) = 10.34 ($2CH_3\cdot$); 10.4 (2Et·, 2n-Pr·, 2n-Bu·, . . .); 9.9 (2i-Pr·, *sec*-Bu·, . . .); 9.5 (2t-Bu·); 9.0 ($2C_3H_5\cdot$). These are in accordance with the literature[32-35] except that a slight temperature dependence for ethyl recombination[35] is ignored, and the quoted value for isopropyl recombination[36] is adjusted to make it more consistent with the other values. There is no known value for allyl recombination. (ii) For recombination of unlike radicals, the geometric mean rule holds, *viz.*

$$k_{AB} = 2(k_{AA}k_{BB})^{1/2}$$

where these rate constants refer respectively to the processes

$$A + B \longrightarrow AB$$
$$2A \longrightarrow A_2$$
$$2B \longrightarrow B_2$$

The implication of this assumption, in the case of methyl and benzyl recombination,[34] for which a rate constant $\log k$ (l. mole^{-1} sec^{-1}) = 8.2 has been obtained, is that for recombination of two benzyl radicals, $\log k$ (l. mole^{-1} sec^{-1}) = 5.5, which seems unreasonably low.

No data exist for recombination of radicals with hydrogen atoms.

From inspection of Tables I and II, it is clear that high A factors are both expected and found, although on the whole calculated A factors are slightly greater than observed. Activation energies are in some cases in good agreement, although in other cases not so.

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(9) R. Walsh, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, 88, 650 (1966).

(10) S. J. Price, *Can. J. Chem.*, 40, 1310 (1962).

(11) G. L. Esteban, J. A. Kerr, and A. F. T. Trotman-Dickenson, *J. Chem. Soc.*, 3873 (1963).

(12) J. H. Purnell and C. P. Quinn, "Photochemistry and Reaction Kinetics," P. G. Ashmore, F. S. Dainton, and T. M. Sugden, Ed., Cambridge University Press, London, 1967, p 330.

(13) J. H. Purnell and C. P. Quinn, *Proc. Roy. Soc.*, A270, 267 (1962).

(14) W. Tsang, *J. Chem. Phys.*, 40, 1498 (1964).

(15) W. Tsang, *ibid.*, 40, 1171 (1964).

(16) W. Tsang, *ibid.*, 43, 352 (1965).

(17) H. B. Palmer, J. Lahaye, and K. C. Hou, *J. Phys. Chem.*, 72, 348 (1968).

(18) H. G. Davis and K. D. Williamson, *World Petrol. Congr., Proc. 5th, N. Y., 1959*, 4, 37 (1960).

(19) C. P. Quinn, *Proc. Roy. Soc.*, A275, 190 (1963).

(20) M. C. Lin and M. H. Back, *Can. J. Chem.*, 44, 2357 (1966).

(21) A. B. Trenwith, *Trans. Faraday Soc.*, 62, 1538 (1966).

(22) G. L. Pratt, *Proc. Roy. Soc.*, A293, 235 (1966).

(23) C. T. Brooks, *Trans. Faraday Soc.*, 62, 935 (1966).

(24) R. S. Konar, R. M. Marshall, and J. H. Purnell, *ibid.*, 64, 405 (1968).

(25) J. Engel, A. Combe, M. Letort, and M. Niclause, *C. R. Acad. Sci. Paris*, 244, 453 (1957).

(26) W. Tsang, *J. Chem. Phys.*, 44, 4283 (1965).

(27) J. A. Kerr, R. Spencer, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 6652 (1965).

(28) M. P. Halstead and C. P. Quinn, *Trans. Faraday Soc.*, 64, 103 (1968).

(29) W. Tsang, *J. Chem. Phys.*, 46, 2817 (1967).

(30) R. J. Akers and J. J. Throssel, *Trans. Faraday Soc.*, 63, 124 (1967).

(31) J. B. Homer and F. P. Lossing, *Can. J. Chem.*, 44, 2211 (1966).

(32) A. Shepp, *J. Chem. Phys.*, 24, 939 (1956).

(33) E. L. Metcalfe and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3560 (1963).

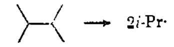
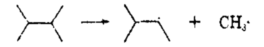
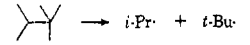
(34) R. J. Kominar, M. G. Jacko, and S. J. Price, *Can. J. Chem.*, 45, 575 (1967).

(35) A. Shepp and K. O. Kutschke, *J. Chem. Phys.*, 26, 1020 (1957).

(36) E. L. Metcalfe and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4620 (1962).

Table I

Molecular Dissociation in Paraffins

Reaction	Observed[a] Log A	Observed[a] E_a	Ref	Log A_r[b]	Ref	Calculated[a,c,e] Log A	Calculated[a,c,e] E_a
$CH_4 \rightarrow CH_3\cdot + H\cdot$	14.6	103	17				105.2
$C_2H_6 \rightarrow 2CH_3\cdot$	16.3	86.0	18	10.34	32	17.0	88.5
	17.45	91.7	19				
	16.0	86.0	20				
	16.3	88.0	21				
	16.1	87.0	22				
$i\text{-}C_4H_{10} \rightarrow CH_3\cdot + i\text{-}Pr\cdot$	18.9	80.0	23	10.4	*d*	17.7	82.2
	17.8	82.5	24				
$neo\text{-}C_5H_{12} \rightarrow CH_3\cdot + t\text{-}Bu\cdot$	17.4	83.0	25	10.2	*d*	17.7	78.2
	16.1	78.2	26				
	16.1	76.0	16	9.9	*d*	17.6	74.7
	16.6	81.1	16	10.4	*d*	17.9	80.6
	16.2	73.0	26	10.0	*d*	17.6	69.3
	16.3	68.5	26	9.5	33	17.3	61.6

[a] A in sec^{-1}; E_a in kcal mole^{-1}. [b] A_r in l. mole^{-1} sec^{-1}. [c] Arrhenius parameters calculated for a mean temperature of 1000°K. [d] See text. [e] Error limits: log A, ±0.4; E_a, ±2 kcal mole^{-1} (not including uncertainties in assumed values for log A_r).

For the reaction most studied

$$C_2H_6 \longrightarrow 2CH_3\cdot$$

the agreement on Arrhenius parameters between various workers is not particularly good, and there is still considerable disagreement[19–21, 37] as to the pressure at which it achieves strictly first-order behavior. Thus Lin and Back[20] and Trenwith[21] use an extrapolation technique to obtain their high-pressure rate constants while Quinn[19] does not. Since, in the temperature ranges at which these studies were carried out, the rate constants are all within a factor of 2 of one another, it seems likely that experimental uncertainties have led to the divergence in Arrhenius parameters.

However, the calculated rate constants are approximately a factor of 3 greater than the mean of the observed at 1000°K. This is within the uncertainty of the calculation, but, if it were real, it would imply either a negative activation energy of about 1 kcal mole^{-1} or curved non-Arrhenius behavior for methyl radical recombination. A direct investigation of the latter at high temperatures would be highly desirable.

Apart from Brook's A factor for i-C_4H_{10} fragmentation,[23] which is clearly too high, all the other A factors are less than calculated. Once again this points in the direction of a negative energy of activation for radical recombination. However, the discrepancies between observed and calculated energies of activation for Tsang's shock-tube results[16, 26] are disturbingly large in some cases. Moreover, the differences in A factors and activation energies occur in a noncompensatory manner, so that the calculated rate constants are between factors of 4 and 300 too fast at 1000°K. Tsang[16, 26] attributed these discrepancies to errors in radical entropy and heat of formation data. We are more inclined to suspect the shock tube.

Where stabilized radicals such as allyl and benzyl are produced, A factors are generally lower, as can be seen from Table II.

Because of the lack of data on recombination, it is impossible to say much about these A factors. Allyl radicals appear to recombine less efficiently than methyls. The calculated A factor for butene-1 dissociation is much higher than the most recently observed value.[28] Measurements of the decomposition rates of chemically activated 1-olefins[38] suggest A factors of $\simeq 10^{14}$ sec^{-1}, in agreement with observed rather than the calculated values. This indicates that one of our assumptions on recombination may be in error. To reduce the methyl allyl cross combination rate constant sufficiently, and retain the geometric mean rule, would require an allyl recombination rate constant of $10^{6.6}$ l. mole^{-1} sec^{-1} which would be far too low to be consistent with the latest results on biallyl dissociation.[30] Thus it may be that the geometric mean rule fails to hold for cross combination of allyl (or benzyl) with alkyl radicals. An investigation of this point would be well worthwhile.

Apart from two of the values[27, 31] in Table II, observed activation energies are in tolerable agreement with computed values. The allyl and benzyl resonance energies have been sources of much uncertainty in the past, but the most recent values[9, 39] are probably reliable to within ±2 kcal mole^{-1}. Thus the very low activation energies observed earlier in the case of butene-1[27] and biallyl pyrolyses[31] are almost certainly in error. Both were measured in fast low-pressure flow systems, and the decompositions were not in their first-order region of pressure dependence.

A recent suggestion that termination reactions involving allyl radicals might require considerable positive energy of activation[40] is not borne out here, except possibly in the case of t-butyl with allyl,[29] a shock-tube derived result. If anything,

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(37) A. B. Trenwith, *Trans. Faraday Soc.*, 63, 2452 (1967).

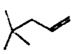
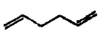
(38) (a) F. H. Dorer and B. S. Rabinovitch, *J. Phys. Chem.*, 69, 1952 (1965); (b) J. W. Simons, B. S. Rabinovitch, and F. H. Dorer, *ibid.*, 70, 1076 (1966).

(39) D. M. Golden, A. S. Rodgers, and S. W. Benson, *J. Amer. Chem. Soc.*, 88, 3196 (1966).

(40) A. S. Kallend, J. H. Purnell, and B. C. Shurlock, *Proc. Roy. Soc.*, A300, 120 (1967).

Table II

Molecular Dissociation in Olefins and Aromatics

Reaction	Observed[a] Log A	Observed[a] E_a	Ref	Log A_r[b]	Ref	Calculated[a,c,e] Log A	Calculated[a,c,e] E_a
 → $CH_3\cdot$ + $C_3H_5\cdot$	12.7	59.1	27	10.0	*d*	15.6	73.6 ± 3.0
	13.9	69.5	28				
 → *t*-Bu· + $C_3H_5\cdot$	15.8	65.5	29	9.6	*d*	15.4	62.2 ± 3.0
 → $2C_3H_5\cdot$	13.4	56.0	30	9.0	*d*	14.1	59.0 ± 4.0
	13.3	45.6	31				
$C_6H_5CH_3 \rightarrow Bz\cdot + H\cdot$	14.8	85.0	10				85.9 ± 1.5
$C_6H_5C_2H_5 \rightarrow Bz\cdot + CH_3\cdot$	14.6	70.1	11	8.2	34	14.0	71.0 ± 2.5
C_6H_5-*n*-$C_3H_7 \rightarrow Bz\cdot + Et\cdot$	14.9	68.6	11	8.2	34	14.1	66.4 ± 2.5
C_6H_5-*n*-$C_4H_9 \rightarrow Bz\cdot$ + *n*-Pr·	14.5	67.1	11	8.2	34	14.3	67.2 ± 2.5

[a] A in sec^{-1}; E_a in kcal mole^{-1}. [b] A_r in l. mole^{-1} sec^{-1}. [c] Arrhenius parameters caculated for mean temperature of 1000°K. [d] See text. [e] Error imits: log A, ± 0.4; E_a, as quoted (not including uncertainties in assumed values for log A_r).

small negative activation energies would produce a more satisfactory agreement, although they may still be zero within the limits of the existing information.

It is clear that agreement within this field of bond breaking and radical recombination is far from satisfactory, and there is considerable scope for further experimentation, particularly in the difficult area of absolute radical recombination measurements.

3. *Nature of Transition States*

The high *A* factors for bond breaking in paraffins and high collision efficiencies for alkyl radical recombination have been widely discussed,[41-47] with the particular case of $C_2H_6 \rightarrow 2CH_3\cdot$ receiving most attention. However, most of what has been said about this reaction applies equally well to other cases. The data are not sufficiently precise to make a discussion of structural effects for particular cases profitable. Most of the high entropy of activation ($\Delta S^{\ddagger} = 17 \pm 2$ eu) may be achieved by a drastic reduction of the restoring force constants for the rocking modes of the two alkyl groups against one another[42,45,46] in the transition state. There are four of these modes, and, if their frequencies are lowered from about 950 to 170 cm^{-1} at 1000°K, about 13 eu is obtained. The remaining 4 eu can be accounted for by an increased moment of inertia and the development of a free internal rotation of the alkyl groups about the stretched C–C bond.

An alternative description of the transition state for ethane with completely developed tumbling of both methyl groups[2,47] is also able to account for the large entropy of activation, and Benson[45] has argued that partial ionic bonding forces offer the best explanation for such freedom of motion. While such forces may well be involved, completely developed tumbling of larger alkyl groups seems unreasonable and is furthermore not supported by the facts.[45]

When stabilized radicals are formed, it seems reasonable to expect some stiffening in the transition state for dissociation.[38a] This offers a qualitative explanation for the lower *A* factors for the dissociations which produce allyl and benzyl radicals. However, the real difficulty with these processes is to explain the lower efficiencies of recombination. On present evidence the transition state must be tighter than for alkyl recombination, yet in the previous section it was seen that no activation energy is involved. There must be a high orientational requirement which leads to a stiffening of the rocking modes of the complex, when compared with the alkyl recombination complex. It appears paradoxical that alkyl radicals with their free electrons occupying localized atomic p orbitals should require less orientation for recombination than allyl radicals, whose free electron occupies a delocalized π molecular orbital. Of course, if present experimental indications prove incorrect this difficulty will be removed; it is interesting to note that for cyclohexadienyl radicals, also resonance stabilized, a recombination efficiency of greater than one in ten collisions has been found.[47a]

In a recent paper, Hay[48] has sought to apply Hückel theory to the problems of radical reactivity, and in particular to the magnitudes of *A* factors. A distinction is drawn between σ and π radicals, which are not very precisely defined, and correlation is drawn between *A* factors and "delocalisation energy" of the products. Some of the correlations presented are exceedingly scattered, and the data quoted are often none too reliable. This approach does not seem to us to shed much light upon the problem.

B. RADICAL DECOMPOSITION

1. *Experimental Methods*

This field has been reviewed by Kerr and Trotman-Dickenson,[1] who have discussed the experimental methods in some detail. The main problem has been to find clean reliable sources of the radical in question. Direct photolyses of aldehydes,[49,50]

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(41) O. K. Rice, *J. Phys. Chem.*, 65, 1588 (1961).

(42) C. Steel and K. J. Laidler, *J. Chem. Phys.*, 34, 1827 (1961).

(43) T. S. Ree, T. Ree, H. Eyring, and T. Fueno, *ibid.*, 36, 281 (1962).

(44) H. S. Johnston and P. Goldfinger, *ibid.*, 37, 700 (1962).

(45) S. W. Benson, *Advan. Photochem.*, 2, 1 (1964).

(46) B. S. Rabinovitch and D. W. Setser, *ibid.*, 3, 1 (1964).

(47) D. W. Setser and B. S. Rabinovitch, *J. Chem. Phys.*, 40, 2427 (1964).

(47a) M. C. Sauer and B. Ward, *J. Phys. Chem.*, 71, 3971 (1967).

(48) J. M. Hay, *J. Chem. Soc.*, *B*, 1175 (1967).

(49) J. A. Kerr and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, 55, 572, 921 (1959).

(50) J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1602, 1611 (1960).

Table III

Decomposition of Alkyl Radicals

	Observed[a]			Reverse[b,e]			Calculated[a,c,e]	
Reaction	*Log A*	E_a	*Ref*	*Log A*	E^a	*Ref*	*Log A*	E_a
$C_2H_5\cdot \rightarrow C_2H_4 + H\cdot$	10.9	31.0	50	10.5	3.2	*d*	13.3	41.7
				±0.6	(±1.5)		±0.8	±2.5
	12.6	40.4	13					
	13.6	38.0	20					
	14.4	40.9	56					
n-Pr· → $C_2H_4 + CH_3\cdot$	15.0	34.5	52	8.9	7.9	*d*	13.5	32.8
				±0.8	±1.1		±1.2	±3.1
	9.3	22.0	73					
	13.5	31.4	58					
i-Pr· → $C_3H_6 + H\cdot$	13.0	35.0	51	10.4	2.8	*d*	13.8	41.7
				±0.6	±1.5		+0.8	±2.5
	13.3	36.9	49					
	13.5	37.0	73					
	16.2	47.2	24					
n-Bu· → C_2H_4 + Et·	10.9	22.0	50	7.9	7.0	*d*	12.8	28.2
				±0.9	±1.6		±1.3	±3.6
	13.6	28.7	53					
sec-Bu· → $C_3H_6 + CH_3\cdot$	15.1	30.6	74	8.5	7.4	*d*	13.4	33.2
				±0.5	±1.4		±0.9	±3.4
	14.6	32.6	59					
i-Bu· → $C_3H_6 + CH_3\cdot$	12.5	26.2	75	(7.5)	(7.4)	*d*	13.0	31.7
				(±1.0)	(±2.0)		±1.4	±4.0
	12.4	31.0	54					
t-Bu· → *i*-$C_4H_8 + H\cdot$	15.6	43.6	76	10.3	1.4	*d*	14.0	42.4
				±0.6	±1.5		±1.0	±3.5
	16.0	44.0	62					

[a] A in sec^{-1}; E_a in kcal mole. [b] A in l. $mole^{-1}$ sec^{-1}. [c] Arrhenius parameters calculated for a mean temperature of 500°K. [d] See text. [e] Estimated error limits quoted beneath each value.

ketones,[51] and azo compounds,[52-54] mercury-photosensitized decompositions of paraffins,[55,56] and some radical-sensitized aldehyde[57] and paraffin decompositions[58-59] have all been used. Recently ethane[20,60,61] and other paraffin[13,62] pyrolyses have been added to this arsenal. The difficulties, as with most free-radical reactions, have been in establishing mechanisms for these systems and in monitoring free-radical concentrations. On the whole, differences between the results of different workers reflect these two particular problems. There is insufficient space in this review to discuss the details of particular reaction schemes, but we do feel that data are not well founded unless based upon complete analytical studies (and not merely pressure changes) and the establishment of mass balances.

The reverse reactions to most of these dissociations involve either hydrogen atom or methyl or ethyl radical additions to olefins. These reactions have also been reviewed.[1,63,64] The problems of studying them are even more severe. Reliable atom or radical sources are hard to come by, and the reaction products, being radicals, are difficult to monitor and often react by further addition to the olefin concerned or combination with the original atom or radical. Hydrogen atoms have been generated by the mercury-photosensitized decomposition of paraffins[65] and H_2,[63] the photolysis of H_2S,[66] radiolysis of C_3H_8,[67] and the application of a microwave discharge to H_2.[68,69] Methods for the production of methyl and ethyl radicals are well known[70,71] and will not be repeated here, except to add that a new source of methyl, the photolysis of biacetyl, has recently been developed.[72]

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(51) C. A. Heller and A. S. Gordon, *J. Phys. Chem.*, 62, 709 (1958).

(52) J. A. Kerr and J. G. Calvert, *J. Amer. Chem. Soc.*, 83, 3391 (1961).

(53) W. E. Morganroth and J. G. Calvert, *ibid.*, 88, 5387 (1966).

(54) D. H. Slater, S. S. Collier, and J. G. Calvert, *ibid.*, 90, 268 (1968).

(55) S. Bywater and E. W. R. Steacie, *J. Chem. Phys.*, 19, 172, 319, 326 (1951).

(56) L. F. Loucks and K. J. Laidler, *Can. J. Chem.*, 45, 2795 (1967).

(57) J. G. Calvert and W. C. Sleppy, *J. Amer. Chem. Soc.*, 81, 1544 (1959).

(58) M. C. Lin and K. J. Laidler, *Can. J. Chem.*, 44, 2927 (1966).

(59) M. C. Lin and K. J. Laidler, *ibid.*, 45, 1315 (1967).

(60) C. P. Quinn, *Trans. Faraday Soc.*, 59, 2543 (1963).

(61) M. C. Lin and M. H. Back, *Can. J. Chem.*, 44, 2369 (1966).

(62) R. S. Konar, J. H. Purnell, and C. P. Quinn, *Trans. Faraday Soc.*, 64, 1319 (1968).

(63) R. J. Cvetanović, *Advan. Photochem.*, 1, 115 (1963).

(64) B. A. Thrush, *Progr. Reaction Kinetics*, 3, 63 (1965).

(65) R. J. Cvetanović and K. R. Jennings, *J. Chem. Phys.*, 35, 1233 (1961).

(66) B. de B. Darwent and R. Roberts, *Discussions Faraday Soc.*, 14, 55 (1953).

(67) K. Yang, *J. Amer. Chem. Soc.*, 84, 719, 3795 (1962).

(68) J. M. Brown and B. A. Thrush, *Trans. Faraday Soc.*, 63, 630 (1967).

(69) J. V. Michael and R. V. Weston, *J. Chem. Phys.*, 45, 3632 (1966).

(70) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworth & Co., Ltd., London, 1955, p 196.

(71) A. F. Trotman-Dickenson, *Chem. Ind.* (London), 379 (1965).

(72) R. J. Cvetanović and R. S. Irwin, *J. Chem. Phys.*, 46, 1964 (1967).

2. *Results*

The data for the bond-breaking processes are listed in Table III,[73–76] together with our computed estimates and the best available data on the reverse reactions. It was necessary, in some cases, to correct literature values, since many of them were based upon assumed values for recombination rate constants, different from those listed in the previous section; this applies to both decomposition and reverse addition. The pioneering work of Bywater and Steacie[55] on radical decompositions, while indicating the trends to be expected in activation energies, did not provide accurate Arrhenius parameters. It has not therefore been included in Table III. Likewise, where a piece of work has been repeated in the same laboratory, only the most recent value is listed. The elegant experiments of McNesby, *et al.*,[77–80] have shown that radicals decompose by β-C–C and β-C–H bond fission to the virtual (and probable) exclusion of all other processes and that, where both modes are possible, β-C–C bond fission is by far the most preferred. Such a conclusion is well supported by the thermochemistry (see Appendix) and makes the claims[24,49–51,75,76] of having observed decomposition modes other than those listed in Table III rather dubious. A possible exception to this conclusion is considered later, but the Arrhenius parameters which have been proposed for such processes are not included in Table III.

The error limits quoted in Table III have been estimated conservatively and take into account possible variations of $\Delta H°$ and $\Delta S°$ with temperature for these reactions, as well as uncertainties in both quoted rate constants and thermochemistry.

a. $C_2H_5\cdot \rightleftharpoons C_2H_4 + H\cdot$

Under the experimental conditions of temperature and pressure, the decomposition is not in its first-order limiting region of pressure dependence. Thus extrapolations are required to obtain the high-pressure Arrhenius parameters. Nevertheless, the most recent values[13,20,56] are in tolerable agreement with that calculated. For the reverse reaction, the Arrhenius parameters quoted are those recommended by Baldwin, Simmons, and Walker,[81] who have recently reviewed the literature on this reaction. These parameters predict a value for the rate constant at 298°K, lying between more recent absolute determinations by Brown and Thrush[68] ($k = 10^{8.08}$ l. mole^{-1} sec^{-1} at 298°K) and Michael and Weston[69] ($k = 10^{8.29}$ l. mole^{-1} sec^{-1} at 298°K).

b. $n\text{-}C_3H_7 \rightleftharpoons C_2H_4 + CH_3$

The most recent decomposition data[58] seem to agree best with that calculated. The results of Back and Takamaku[73] seem to be grossly in error, while the *A* factor obtained by Kerr and Calvert[52] seems too high. The addition of methyl to ethylene has been studied by several workers;[72,82–85] the most recent result[72] is the one quoted, but the error limits cover all the others.

c. $i\text{-}C_3H_7 \rightleftharpoons C_3H_6 + H\cdot$

There is good agreement here among three laboratories[49,51,73] but not with a fourth[24] on the decomposition reaction. Unfortunately, the calculated activation energy is in disagreement with all of this work. It is hard to see what is wrong. The activation energy for the reverse reaction can hardly be less than zero, even though its Arrhenius parameters may be unreliable. These latter were obtained by combining the quoted parameters[81] for $H\cdot + C_2H_4 \rightarrow C_2H_5\cdot$ with relative rate parameters of Yang.[67] Since virtually all the rate data on H· atom additions have been relative to other reactions, this is the only reasonable way to obtain such parameters. An independent check is only possible at 298°K, by combining the relative rate data of Cvetanović and Jennings[65] with either of the absolute measurements[68,69] for $H\cdot + C_2H_4 \rightarrow C_2H_5\cdot$ already mentioned. We performed this check and found that the Arrhenius parameters were able to predict the "absolute" result at 298°K (for either standard[68,69]) to within a factor 4 for all of the olefins for which a comparison was possible. This is not particularly satisfactory, and further work is obviously needed to improve the situation. Some results from studies of solid-phase matrix reactions[86] indicate an activation energy of ~1.5 kcal mole^{-1} for $H\cdot + C_3H_6$.

A further problem is that of the position of attack (orientation) of the hydrogen atom. Terminal addition is known to be favored,[63] and in particular Falconer and Cvetanović[87] have estimated that only about 6% of addition to propylene occurs nonterminally. Thus to a good approximation rate data for hydrogen atom addition to propylene may be taken as rate data for isopropyl formation.

d. $n\text{-}C_4H_9\cdot \rightleftharpoons C_2H_4 + C_2H_5\cdot$

Calvert and Morganroth's recent investigation[53] of this decomposition is in excellent agreement with the calculated result, whereas an earlier value[50] is not. The data for the reverse reaction[50,88,89] are a little scattered, and the calculated value is a weighted mean, whose error limits nevertheless encompass all three values.

e. $sec\text{-}C_4H_9\cdot \rightleftharpoons C_3H_6 + CH_3\cdot$

For the decomposition reaction Calvert[74] has reviewed earlier data, and his quoted value is a recalculated one. It is not in

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(73) R. A. Back and S. Takamaku, *J. Amer. Chem. Soc.*, 86, 2558 (1964).

(74) J. G. Calvert, *Chem. Rev.*, 59, 569 (1959).

(75) E. L. Metcalfe and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 5072 (1960).

(76) R. N. Birrell and A. F. Trotman-Dickenson, *ibid.*, 4218 (1960).

(77) J. R. McNesby, C. M. Drew, and A. S. Gordon, *ibid.*, 24, 1260 (1956).

(78) W. M. Jackson and J. R. McNesby, *J. Amer. Chem. Soc.*, 83, 4891 (1961).

(79) W. M. Jackson and J. R. McNesby, *J. Chem. Phys.*, 36, 2272 (1962).

(80) W. M. Jackson, J. R. McNesby, and B. de B. Darwent, *ibid.*, 37, 2256 (1962).

(81) R. R. Baldwin, R. F. Simmons, and R. W. Walker, *Trans. Faraday Soc.*, 62, 2486 (1966).

(82) R. K. Brinton, *J. Chem. Phys.*, 29, 781 (1958).

(83) A. M. Hogg and P. Kebarle, *J. Amer. Chem. Soc.*, 86, 4558 (1964).

(84) L. Endrenyi and D. J. LeRoy, *J. Phys. Chem.*, 71, 1334 (1967).

(85) L. Mandelcorn and E. W. R. Steacie, *Can. J. Chem.*, 32, 474 (1954).

(86) M. D. Sheer and R. Klein, *J. Phys. Chem.*, 65, 375 (1961).

(87) W. E. Falconer and R. J. Cvetanović, unpublished results quoted in ref 63.

(88) J. A. Pinder and D. J. LeRoy, *Can. J. Chem.*, 35, 588 (1957).

(89) F. W. Lampe and F. H. Field, *ibid.*, 37, 995 (1959).

good agreement with our calculated result or indeed a more recent study.[59] Both observed A factors look too high. For the reverse reaction, the Arrhenius parameters are the most recent,[72] and once again the error limits span previous results.[85,90] The question of orientation of addition to propylene again arises here. Miyoshi and Brinton[90] estimate about 90% addition to the termination position, in which case the observed rate data apply closely to the formation of *sec*-butyl.

f. $i\text{-}C_4H_9\cdot \rightleftarrows C_3H_6 + CH_3\cdot$

There are only two results for the decomposition here.[54,75] The latest of these[54] agrees very well with calculation. There are no data on the reverse reaction apart from Miyoshi and Brinton's estimate[90] that under their conditions (~400°K) only about 10% of the methyls add nonterminally to form isobutyl. We have therefore arbitrarily assumed a tenfold lower A factor than for terminal addition, the activation energy being unchanged. In this case, therefore, our calculated decomposition parameters have rather larger errors limits than usual.

g. $t\text{-}C_4H_9\cdot \rightleftarrows i\text{-}C_4H_8 + H\cdot$

The two observed sets of decomposition parameters[62,76] are in good agreement with one another, but the A factors are again much higher than calculated. In the case of the reverse reaction, the quoted estimate obtained by combining the data of Yang[67] with those of Baldwin, *et al.*,[81] is in quite close agreement with a more recent determination of

$$\log k\ (\text{l. mole}^{-1}\ \text{sec}^{-1}) = 10.56 - (1.42/2.303RT)$$

by Dalgleish and Knox.[91]

h. $n\text{-}C_4H_9\cdot \rightleftarrows 1\text{-}C_4H_8 + H\cdot$

This reaction is not the preferred mode of decomposition of n-butyl,[77] but claims to have observed it[28,61] are based upon the suggestion that equilibrium can be established for $n\text{-}C_4H_9\cdot \rightleftarrows C_2H_4 + C_2H_5\cdot$ under particular experimental circumstances. This is an interesting idea and may open the way to investigation of other nonpreferred radical decomposition routes. The observed Arrhenius parameters are $\log k\ (\text{sec}^{-1}) = 14 - (40/2.303RT)$[61] and $13.7 - (35.8/2.303 \cdot RT)$.[28] These are to be compared with a computed rate constant of $\log k\ (\text{sec}^{-1}) = (12.2 \pm 1.4) - [(38.5 \pm 3.4)/2.303RT]$ based upon a reverse rate constant of $\log k\ (\text{l. mole}^{-1}\ \text{sec}^{-1}) = (9.4 \pm 1.0) - (2.8 \pm 1.4)/2.303RT]$. This latter was an estimate, assumed to be identical with that for H-atom addition to propylene apart from an A factor one power of ten lower, for nonterminal addition. Thus the observed rate constants are tolerably consistent with the calculated.

i. $i\text{-}C_3H_7 \rightleftarrows C_2H_4 + CH_3\cdot$

This decomposition cannot proceed without a simultaneous 1,2-hydrogen shift; it is likely, therefore, to involve a prior isomerization to n-propyl followed by a rapid decomposition of the latter by its usual route. Isomerization will be rate determining. There are persistent claims to have observed this reaction[24,49,51] despite the fact that Jackson and McNesby[79] using isotopic labeling techniques have estimated that, *as an upper limit*, it can only occur at about 6% of the rate of decomposition to propylene and hydrogen atom (in the range 745–823°K). The isomerization reaction would be expected to have a fairly tight transition state (see next section) involving a slight loss of entropy; a path degeneracy of 6 would offset this to some extent. An A factor of $10^{13\pm1}$ would appear reasonable. This leads to a calculated lower limit for the activation energy of 43 ± 3.5 kcal/mole. The quoted activation energies[24,49,41] are all much lower than this, which casts considerable doubt on their validity.

C. MISCELLANEOUS RADICAL DECOMPOSITIONS

A number of isolated rate constants exist in the literature for the decompositions of neopentyl,[92] *sec*-hexyl,[61,93] cyclohexadienyl,[94,95] and oct-1-en-5-yl[96] radicals. In most cases the mechanisms are either less well founded than those already discussed or numerous assumptions are required to obtain values for the rate constants. We therefore do not propose to discuss them further.

D. NATURE OF TRANSITION STATES

There is a good consistency between forward and reverse reactions listed in Table III. We therefore use our calculated Arrhenius parameters as the basis for this discussion, particularly since they are in encouraging agreement with the most recently observed data. The picture that emerges is rather uniform. The A factors are all encompassed within $10^{13.5\pm1}$ sec^{-1}, and activation energies are 42 ± 3 and 32.5 ± 4 kcal mole^{-1} for hydrogen atom and alkyl radical formation, respectively.

Fairly refined experimental work will be necessary if any trends in A factors are to be revealed. Structural effects cannot be very important in differentiating individual cases, and at this stage a fairly crude model will readily explain the magnitude of these A factors and associated activation entropies ($\Delta S^{\ddagger} = 0 \pm 4$ eu).

For the hydrogen-atom split, the reaction coordinate is the C–H bond stretch, and since the reverse activation energy is small the C–H bond must be considerably elongated in the transition state. The only other significant difference between reactant and transition state is likely to be a loss in internal rotational freedom around the C–C bond which will be stiffened in anticipation of the product double bond. Complete stiffening would result in a loss of ~5 eu. Whatever fraction of this is actually lost must be almost precisely offset by gains resulting from lowering of the two bending frequencies associated with the stretched C–H bond, as well as 2.2 eu arising from the path degeneracy of 3.

For the alkyl radical split the reaction coordinate is a C–C bond stretching mode. The reverse reaction in this case has a more substantial activation energy, and it is doubtful if the bond is as elongated in the transition state as in the case of bond breaking in paraffins. But as with the hydrogen split

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(90) M. Miyoshi and R. K. Brinton, *J. Chem. Phys.*, 36, 3019 (1962).

(91) D. G. Dalgleish and J. H. Knox, *Chem. Commun.*, 917 (1966).

(92) K. H. Anderson and S. W. Benson, *J. Chem. Phys.*, 40, 3747 (1964).

(93) C. P. Quinn, *Trans. Faraday Soc.*, 59, 2543 (1963).

(94) R. D. Suart, *Dissertation Abstr.*, 27, B4355 (1967).

(95) S. W. Benson and R. Shaw, *J. Amer. Chem. Soc.*, 89, 5351 (1967).

(96) D. G. L. Jame and G. E. Troughton, *Trans. Faraday Soc.*, 62 145 (1966).

one free internal rotation will become stiffened in going from reactant to transition state. The entropy loss resulting from this (again a maximum of ~5 eu) must be offset by gains from lowered vibrational frequencies. Since the path degeneracy is only one in this case, more vibrational entropy must be gained. Without lowering frequencies of the two alkyl rocking modes nearly as much as for the molecular bond-breaking complex, 5 eu can easily be recovered. Further refinements are hardly justifiable at this stage, but more detailed models of these transition states have been specified[2] for the purposes of calculation of chemically activated decomposition rates.

III. Acyclic Reactants with Cyclic Transition States

This type of reaction includes both isomerizations and decompositions. The latter are dealt with in an accompanying article in this journal and so left out of consideration in this review. Isomerizations may be broken down into several classes: (i) Cope and nonaromatic Claisen rearrangements; (ii) dienyl and so-called "homodienyl," 1,5-hydrogen shifts; (iii) cyclizations of linear conjugated polyenes, so-called "electrocyclic" reactions; and (iv) radical isomerizations.

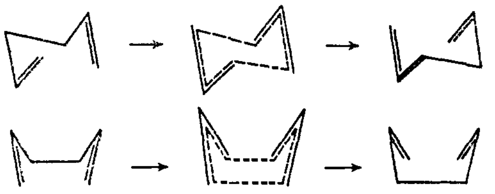
Examples of all these reactions are well known in the liquid phase but only recently have Arrhenius parameters become available for a limited number in the gas phase.

A. COPE AND NONAROMATIC CLAISEN REARRANGEMENTS

An enormous volume of work has been devoted to documenting the Claisen rearrangement[97] and elucidating the details of its steric course and transition state geometry. Only the nonaromatic case, the vinyl allyl ether isomerization, will be considered here. The related Cope rearrangement[97,98] has received marginally less attention but is, if anything, better understood.

The basic requirement for both these rearrangements is a 1,5-diene structure; a linear six-carbon chain for the Cope; and a vinyl allyl ether structure for the nonaromatic Claisen. Both rearrangements[97] are characterized by first-order kinetics, a low energy of activation, and a negative entropy of activation. They are unaffected by radical sensitisors and inhibitors.[97] They plainly proceed by a unimolecular concerted mechanism (in the sense that bonds are broken and formed simultaneously).

Structural determinations for the products for a variety of compounds provide a wealth of evidence pointing to a cyclic transition state involving six atoms.[99–105] Two configurations are possible for the transition state, quasi-chair and quasi-boat, analogous to the conformations of cyclohexane; these are shown below.



In a number of cases, additional geometrical requirements lead to the quasi-boat form for the transition state. The rearrangements of the Diels–Alder dimers of cyclopentadiene[106] and of the *cis*-divinylcycloalkanes[98,107] are examples where this occurs. Where geometric constraints do not exist, however, the transition state prefers to take up the quasi-chair configuration. This has been unambiguously demonstrated in the case of the Cope rearrangement by the elegant experiments of Doering and Roth[108] with *meso*- and *dl*-3,4-dimethyl-1,5-hexadiene. Their argument has been widely discussed[97,98] and will not be repeated here, but their results showed that the quasi-chain transition state is at least 5.7 kcal mole^{-1} more stable (in terms of free energy) than the quasi-boat form, for their system at 225°.[108] Other data, though less conclusive, point to the same conclusion for similar systems.[109] This quasi-chair conformational preference has been enshrined with theoretical respectibility by recent Hückel calculations.[110]

Another question which arises in connection with transition state conformation is that of the axial or equatorial preference of substituents. Once again cyclohexane and its conformational behavior provide the clue. Equatorial positions are favored over axial,[108] the more so the bulkier the substituent group.[109] All these results have been obtained by subtle choice of reactant species and careful analyses of the reaction products, and without resort to particularly careful kinetic studies. Recent kinetic work in the gas phase brings the additional tool of transition state theory to bear upon the problem of transition state structure, and by converse, because of the information already available, the kinetic data are subjected to a fairly stringent test.

The Arrhenius parameters for a number of Cope rearrangements and nonaromatic Claisen rearrangements in the gas phase are listed in Tables IV and V.[111–118] The data for 3-methylhexa-1,5-diene isomerization obtained by Frey and Solly[112] are more reliable than the earlier, and considerably differing, results of Amano and Uchiyama,[119] which are not

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(97) S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 655.

(98) W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, 2, 115 (1963).

(99) A. C. Cope and E. M. Hardy, *J. Amer. Chem. Soc.*, 62, 441 (1940).

(100) A. C. Cope, K. E. Hoyle, and D. Heyl, *ibid.*, 63, 1843 (1941).

(101) A. C. Cope, C. M. Hofmann, and E. M. Hardy, *ibid.*, 63, 1852 (1941).

(102) A. C. Cope and P. H. Towle, *ibid.*, 71, 3423 (1949).

(103) A. C. Cope, D. E. Morrison, and L. Field, *ibid.*, 72, 59 (1950).

(104) A. W. Burgstahler, *ibid.*, 82, 4681 (1960).

105) P. Cresson, *Bull. Soc. Chim. Fr.*, 2629 (1964).

(106) R. B. Woodward and T. J. Katz, *Tetrahedron*, 5, 70 (1959).

(107) E. Vogel, *Angew., Chem. Intern. Ed. Engl.*, 2, 1 (1963).

(108) W. von E. Doering and W. R. Roth, *Tetrahedron*, 18, 67 (1962).

(109) R. K. Hill and N. W. Gilman, *Chem. Commun.*, 619 (1967).

(110) K. Fukui and H. Fujimoto, *Tetrahedron Lett.*, 251 (1966).

(111) V. Toscano and W. von E. Doering, unpublished results quoted by W. von E. Doering and J. Gilbert, *Tetrahedron, Suppl.*, 7, 397 (1966).

(112) H. M. Frey and R. K. Solly, *Trans. Faraday Soc.*, 64, 1858 (1968).

(113) H. M. Frey and R. K. Solly, to be submitted for publication.

(114) H. M. Frey and D. H. Lister, *J. Chem. Soc., A*, 26 (1967).

(115) F. W. Shuler and G. W. Murphy, *J. Amer. Chem. Soc.*, 72, 3155 (1950).

(116) L. Stein and G. W. Murphy, *ibid.*, 74, 1041 (1952).

(117) H. M. Frey and B. M. Pope, *J. Chem. Soc., B*, 209 (1966).

(118) H. M. Frey and D. C. Montague, *Trans. Faraday Soc.*, 64, 2369 (1968).

(119) A. Amano and M. Uchiyama, *J. Phys. Chem.*, 69, 1278 (1965).

Table IV

Cope Rearrangements

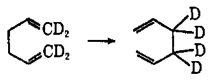
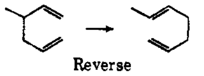
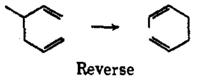
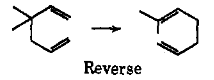
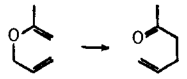
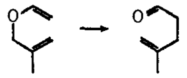
Reaction	*Log A, sec⁻¹*	*E_a, kcal mole⁻¹*	*Ref*
	11.1	35.5	111
	10.55	34.20	112
Reverse	10.39	35.36	112
	10.54	35.72	112
Reverse	10.66	36.72	112
	11.13	34.62	113
Reverse	10.39	36.94	113
	9.97	28.5	114

Table V

Vinyl Allyl Ether Rearrangements

Reaction	*Log A, sec⁻¹*	*E_a, kcal mole⁻¹*	*Ref*
	11.70	30.6	115
	11.73	29.3	116
	11.15	29.1	117
	11.32	27.9	118

listed. Both studies employed gas chromatographic analysis, but Amano and Uchiyama failed adequately to resolve the *cis*- and *trans*-hepta-1,5-diene products under their analytical conditions. If, for this case, the quasi-chair form for the transition state is assumed, the reaction pathways to *cis* and *trans* products must pass through its axial and equatorial forms, respectively. The observed activation energy difference of 1.5 ± 0.3 kcal mole^{-1} thus reflects the greater stability of the equatorial conformation of the transition state. It is interesting to note that in methylcyclohexane the free-energy difference (and probably the energy difference) is 1.71 kcal mole^{-1} in favor of equatorial methyl,[120] a strikingly similar value.

In the analogous 1-methylallyl ether isomerization,[118] a far greater preference in favor of formation of *trans*- rather than *cis*-hex-4-enal is observed. The *cis* product comprises only about 5% of the total. (Arrhenius parameters for its formation were not obtained.) This figure corresponds to a conformational preference in favor of equatorial methyl of ~2.4 kcal mole^{-1} in the transition state. We are not aware, unfortunately, of any conformational data for the corresponding cyclic ether.

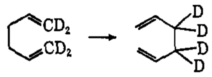
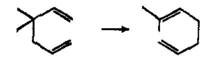
It is clear from the tables that within each class the Arrhenius parameters are very similar. For both rearrangements *A* factors fall within the range 10^{10}–10^{12} while activation energies for the approximately thermoneutral Cope exceed those of the exothermic ($\Delta H^\circ \sim -15$ kcal mole^{-1}) nonaromatic Claisen by about 6 kcal mole^{-1}. Only the case of hepta-1,2,6-triene isomerization offers an exception to the above, and the considerable relief of strain involved in converting an allene structure to a 1,3-diene one readily accounts for the lower activation energy here.

Although the trends are small, methyl substituents, particularly in the 3 position, appear to lower the activation energy slightly, more so for the isomerization of the vinyl allyl ethers than the 1,5-hexadienes, suggesting some degree of charge separation in the transition state of the former.

Detailed *A* factor calculations for these isomerizations have been carried out by Benson and O'Neal.[121] The method, based upon transition state theory, envisages a loose cyclic structure for the transition state. This structure differs from reactant in having a significant "end interaction" which converts the internal rotations of the reactant into partial order bond torsions. This description of some of the vibrational modes of the transition state is adopted for convenience; it avoids the difficulties of estimation of the frequencies of out-of-plane vibrations of the ring. This problem is acknowledged by the authors who claim their calculations, if anything, will tend to overestimate ring entropies, and therefore should provide an upper limit to these *A* factors.

Table VI

Comparison of Observed and Calculated Activation Entropies for Some Cope Rearrangements

Reactions	$\Delta S^{\ddagger}$ (*obsd*)^{a,b}	$\Delta S^{\ddagger}$(*calcd*)^{a,b} *Upper limit*	*Lower limit*^{c}
	−10.8	−9.7	−14.8
	−13.3	−9.6	−15.0
	−10.6	−9.6	−14.2

^{a} In cal mole^{-1} deg^{-1}; standard state, 1 atm. ^{b} Calculated at 500°K. ^{c} Reference 122.

A lower limit is more simply obtained by assuming a transition state which resembles the appropriately substituted cyclohexane. We have carried out this calculation in three cases[122] and the results, in terms of entropies of activation, are listed in Table VI. The upper and lower limits successfully bracket the observed entropies of activation.

The quasi-chair geometry of the transition state is known, but it is doubtful if a precise description of its vibrations is worthwhile since relatively crude calculations are able to put fairly close limits on $\Delta S^{\ddagger}$. To this extent the Benson and O'Neal prescription is rather more complicated than it need be. Some of the minor vibrational frequency adjustments seem scarcely warranted.

All of the *A* factors listed in Tables I and II lie within the expected limits as also do those for some unlisted cases in-

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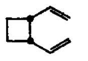
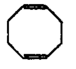
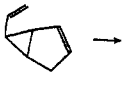
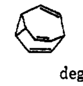
(120) J. C. Celotti, J. Reisse, and G. Chiurdoglu, *Tetrahedron*, **22**, 2249 (1966).

(121) S. W. Benson and H. E. O'Neal, *J. Phys. Chem.*, **71**, 2903 (1967).

(122) R. Walsh, unpublished calculations.

Table VII

Some Multicyclic Cope Rearrangements

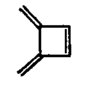
Reactant		*Product*	*Log A, sec^{-1}*	*$\Delta S^{\ddagger}$, eu*	*E_a, kcal $mole^{-1}$*	*Ref*
	→		10.7	−11.7	22.4	127
	→		11.7	−7.2	22.9	128
	→		12.3	−5.0	11.8	129
degenerate			12.9^{a}	−2.3	12.8	130

[a] This value is more recent and covers a wider temperature range. The authors claim their analytical technique is more reliable.

vestigated by Cope.[123] These latter investigations involving highly substituted 1,5-hexadienes were carried out in sealed ampoules and the phase, although unspecified, was probably liquid. A number of Cope rearrangements have been investigated in which ring systems have been added to the basic 1,5-diene structure.[97,98,107,124] Investigations of the isomerizations of the divinylcycloalkanes[107,125] have indicated that the *cis* isomers rearrange at far lower temperatures than the *trans;* indeed *cis*-divinylcyclopropane rearranges so fast that it cannot be isolated even at −40°.[126] The *trans* compounds are believed to rearrange by a different mechanism and are discussed in the last section. The structure of the *cis* compounds is such as to force the transition state into a quasi-chair structure. It is unfortunate that little or no gas-phase kinetic data have been (or indeed can be) obtained for such rearrangements, since their *A* factors ought to be illuminating. The reactant no longer has a free rotation about the 3,4 C–C bond, and the consequence of this ought to be a reduction in the negative entropy of activation, compared with the normal Cope. Very naively one might anticipate that for Cope rearrangements involving cyclic reactants $\Delta S^{\ddagger} = 0, -4, -8$, or −12 eu, depending on whether the reactant has zero, one, two, or three internal rotations. Some liquid and solution results are listed in Table VII.[127–130] The *A* factors and $\Delta S^{\ddagger}$ values are all a little high for the naive model, suggesting perhaps that the transition states are tighter than in the normal Cope. More data are clearly needed in this area before firm conclusions can be drawn.

An attempt[131] to calculate the activation energies for Cope rearrangements of hexa-1,5-diene, *cis*-divinylcyclopropane, and *cis*-1,2-divinylcyclobutane, using a modification of Westheimer's approach,[132] produced E_a's (at 0°K) of 22.8, 17.2, and 18.5 or 16.7 kcal/mole, respectively. The first and third (pair of) values are too low (Tables IV and VII) while the second (for *cis*-divinylcyclopropane) is almost certainly too high for a molecule unstable at −40°. The results do not look particularly promising.

An isomerization reaction which is related to the Cope is

$HC{\equiv}CCH_2CH_2C{\equiv}CH \longrightarrow$ 

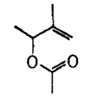
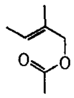
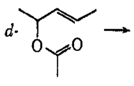
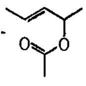
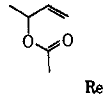
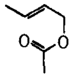
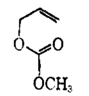
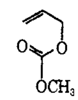
Using both flow and static systems, Huntsman and Wristers[133] obtained

$$\log k\ (\mathrm{sec}^{-1}) = 11.4 - (34.4/2.303RT)$$

The authors suggest that the transition state is so tight that the reaction is essentially single step and the intermediacy of the compound $CH_2{=}C{=}CHCH{=}C{=}CH_2$ is precluded. This may well be the case as the entropy of activation (−9.4 eu) corresponds almost precisely to the complete loss of rotational freedom about the central C–C bond, the other C–C bonds having no internal rotational entropy to lose.

Table VIII

Allyl Ester Rearrangements

Reactant		*Product*	*Log A, sec^{-1}*	*E_a, kcal $mole^{-1}$*	*Ref*
	→		13.5	45.4	134
Reverse			13.2	44.0	134
d- 	→ l-		12.4	38.8	134
			11.3	40	135
Reverse			10.3	37	135
	→		13.7	43	135
Reverse			11.8	38	135

A rearrangement which is closely similar to the vinyl allyl ether isomerization is that of the allyl esters recently studied by Lewis, Hill, and Newman.[134] The evidence from labeling experiments strongly supports a six-membered-ring transition state. A large number of examples was reported and only a selection are given in Table VIII.[134,135] The range of *A* factors is unreasonably large, $10^{10.3}$–$10^{13.7}$ sec^{-1}. Using Benson and O'Neal's tables we estimate $\Delta S^{\ddagger}$ (500°K) $\simeq -11 \pm 3$ eu

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(123) G. Foster, A. Cope, and F. Daniels, *J. Amer. Chem. Soc.*, 69, 1893 (1947).

(124) H. M. Frey, *Advan. Phys. Org. Chem.*, 4, 147 (1965).

(125) E. Vogel, W. Grimme, and E. Dinné, *Angew. Chem. Intern. Ed. Engl.*, 3, 739 (1963).

(126) W. von E. Doering and W. R. Roth, *Tetrahedron*, 729 (1963).

(127) G. S. Hammond and C. D. DeBoer, *J. Amer. Chem. Soc.*, 86, 899 (1964).

(128) J. M. Brown, *Chem. Commun.*, 266 (1965).

(129) M. Saunders, *Tetrahedron Lett.*, 1699 (1963).

(130) A. Allerhand and H. S. Gutowsky, *J. Amer. Chem. Soc.*, 87, 4042 (1965).

(131) M. Simonetta, G. Favini, C. Mariani and P. Gramaccioni, *ibid.*, 90, 1280 (1968).

(132) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 12.

(133) W. D. Huntsman and H. J. Wristers, *J. Amer. Chem. Soc.*, 89, 342 (1967).

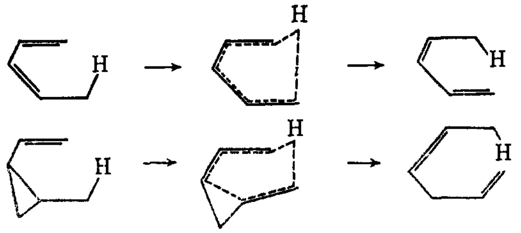
(134) E. S. Lewis, J. T. Hill, and E. R. Newman, *ibid.*, 90, 662 (1968).

(135) E. S. Lewis and J. M. Macdonald, quoted in ref 28.

for these reactions. Thus $10^{11.7}$ sec^{-1} represents an upper limit for their A factors. It appears that some, at least, of the Arrhenius parameters are in error. The reason for this is not apparent. The data were obtained in a stirred flow reactor whose reliability was checked against a known reaction. One test which was not reported was that for heterogeneity. These reactions probably involve a somewhat polarized transition state and may, in consequence, be susceptible to catalysis on glass surfaces.

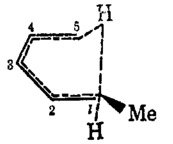
B. DIENYL AND HOMODIENYL 1,5-HYDROGEN SHIFTS

These rearrangements have been reviewed fairly recently.[136,137] They are readily observed in certain *cis*-1,3-dienes and *cis*-1-alkyl-2-vinylcyclopropanes. The structural requirements and probable transition state geometry are pictured below.

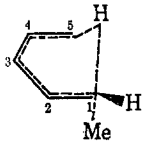


The *cis* configuration of the reactant is a requirement for both isomerizations.[138,139] *trans*-1,3-Dienes[140] and *trans*-1-alkyl-2-vinylcyclopropanes[141] (see last section) only rearrange at much higher temperatures and then by a different mechanism. The reason for this is evident from an examination of models. The *trans* compounds would require enormous distortions to achieve a transition state where hydrogen transfer might become possible.

As with the Cope reactions these isomerizations also show steric preferences which throw some light on transition state conformations. An example of this is the isomerization of *cis*-1,3-hexadiene[142] to give predominantly *cis,trans*-hexa-2,4-diene with less than 3% of *cis,cis*-hexa-2,4-diene. The probable transition states are shown as **1** and **2**. As the hydrogen migrates across the ring from C_1 to C_5 (the suprafacial character of this transfer is assumed for the moment; it is discussed later), the two nonparticipating groups on C_1 adopt conformations approximately in the plane of the ring and axial to (or even further under) it. The equatorial group becomes *trans* to C_2–C_3 and the axial group *cis* to C_2–C_3 in the product. Clearly the large methyl group in the case under discussion prefers the less crowded equatorial conformation **1** leading to the *trans* product.



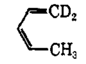
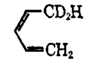
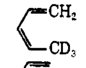
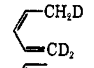
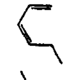
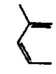
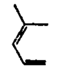
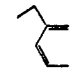
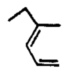
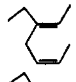
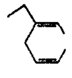
1



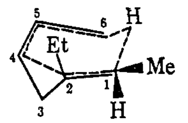
2

Table IX

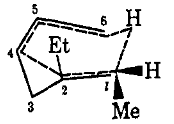
1,5-Hydrogen Shifts in Acylic Compounds

Reactant	*Product*	*Log A, sec⁻¹*	*E_a, kcal mole⁻¹*	*Ref*
		11.93	36.3	144
		11.86	37.7	144
		11.80	32.5	142
		11.24	32.76	140
Reverse		11.72	36.19	140
		10.77	31.64	147
Reverse		11.03	34.53	147
		11.03	31.24	139, 145
		10.95	31.1	146
		11.41	33.54	147
		11.32	33.7	147
		11.27	33.6	147

By contrast with the above case, the pyrolysis of 1,1-diethyl-2-vinylcyclopropane gives approximately 50% of each of *cis,cis*- and *cis,trans*-3-ethyl-2,5-heptadiene.[49] The probable transition states for these isomerizations are **3** and **4**. As the hydrogen migrates from C_1 to C_6, the C_6 carbon drops below the plane of the ring defined by $C_1C_2C_4C_5$ in anticipation of the *cis* configuration of C_3 and C_6 in the product. The two nonparticipating groups on C_1 have conformations which are almost intermediate between axial or equatorial with respect to the plane containing $C_1C_2C_4C_5$. Moreover they are also virtually intermediate between axial and equatorial with respect to the plane containing $C_1C_2C_3$. Thus for a methyl substituent on C_1 there is no particular reason to favor either **3** or **4** and the *trans* or *cis* products to which they respectively lead.



3



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These isomerizations have received substantial documentation[137,143] in the liquid phase with relatively few gas-phase kinetic studies. The Arrhenius parameters for the latter are

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(136) D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Lett.*, 999 (1966).

(137) W. R. Roth, *Chimia*, 8, 229 (1966).

(138) J. Wolinsky, B. Chollar, and M. D. Baird, *J. Amer. Chem. Soc.*, 84, 2775 (1962).

(139) R. J. Ellis and H. M. Frey, *Proc. Chem. Soc.*, 221 (1964).

(140) R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 4770 (1964).

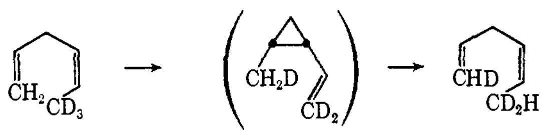
(141) R. J. Ellis and H. M. Frey, *ibid.*, 4184 (1964).

(142) H. M. Frey and B. M. Pope, *ibid.*, *A*, 1701 (1966).

(143) W. R. Roth, *Tetrahedron Lett.*, 17, 1009 (1964).

shown in Table IX.[144–147] Activation energies are characteristically low and fall in the range 31–37 kcal mole^{-1} for both classes of reaction. Such low values essentially preclude any mechanism other than a concerted intramolecular shift.

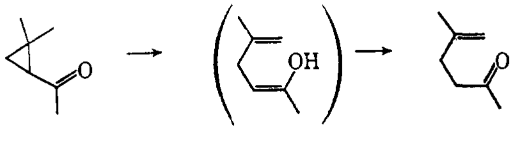
The labeling experiments of Roth and König prove this,[144, 146] and for the *cis*-1,3-pentadiene case the large isotope effects ($k_4/k_9 \simeq 5$ at 470°K) argues in favor of the transfer of a hydrogen. The interesting possibility of the reverse of the homodienyl shift was also indicated by Roth and König.[146] By following the nmr spectrum of *cis*-hexa-1,4-diene-d_3, they obtained evidence for



However, the activation energy[137] of about 42 kcal mole^{-1} is in poor agreement with the reverse activation energy and the enthalpy difference.

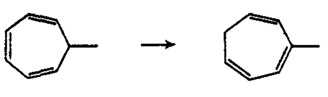
A factors for 1,5-hydrogen shifts are low and similar in magnitude to those for Cope rearrangements. This can be attributed primarily to the loss of two internal rotations in going from reactant to transition state. Prediction of the values of these *A* factors is possible by the Benson and O'Neal method[121] and has been performed for the case of *cis*-2-methylpenta-1,3-diene isomerization. A rather higher *A* factor ($10^{12.3}$ sec^{-1}) than that observed was obtained in this case.[121] However, the consistency of the *A* factors in Table IX lends some weight to their reliability and suggests that the calculation is an overestimate. Thus Benson and O'Neal's transition state is probably too loose. A structure which is considerably tighter and yet still bears some resemblance to the transition state of these isomerizations is one based upon the cyclopentadiene ring. This structure if anything should be too tight. Using such a model we estimate[122] a minimum entropy of activation, $\Delta S^{\ddagger} = -12.0$ eu (at 500°K), or an *A* factor of $10^{10.8}$ sec^{-1}. This figure is lower than most of observed values, but some are disturbing close to it.

This rearrangement has been extended to *cis*-1-alkyl-2-carbonylcyclopropanes[148] and a more recent kinetic study of the isomerization of 2-acetyl-1,1-dimethylcyclopropane[149] in the liquid phase in the temperature range 425–436°K led



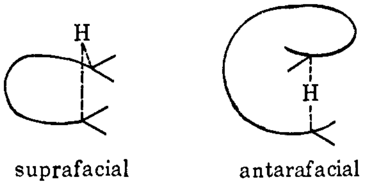
to the rate parameters $\log k\,(\text{sec}^{-1}) = 11.15 - (29.0/2.303RT)$.

Transannular 1,5-hydrogen shift processes have been observed in a number of ring systems.[136] Transition states are usually well defined and controlled primarily by the structure of the ring reactant. They differ from the acyclic cases in that no internal rotations are lost in going to the transition state. Higher *A* factors and smaller negative entropies of activation are therefore to be expected. Confirmation of this has been obtained by Egger[150] in the case



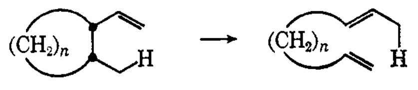
for which $\log k\,(\text{sec}^{-1}) = 12.60 - (33.25/2.303RT)$ and $\Delta S^{\ddagger}$ (500°K) $= -3.9$ eu. Some earlier Arrhenius parameters based on liquid-phase studies[136, 143] which failed to show these differences were probably erroneous.

The problem of why 1,5-hydrogen shifts are relatively commonly observed, whereas 1,3 shifts have not yet been observed and 1,7 shifts are exceedingly rare,[137] has been rationalized by Woodward and Hoffmann.[151] They distinguish between the two kinds of hydrogen shifts in acyclic polyenes shown below.

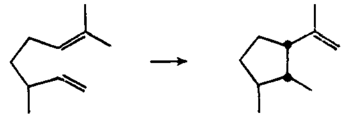


On the basis of symmetry of the highest occupied orbital in the polyenyl radical (the species without the hydrogen atom being transferred), the thermal rearrangements are determined to be antarafacial for 1,3 and 1,7 shifts and suprafacial for 1,5 shifts. The steric difficulty of the antarafacial shift in the 1,3 case rules it out and in the 1,7 case usually makes it a poor competitor with more favorable 1,5 shifts, where, as in polyenes, both are possible.

The 1,5-hydrogen shift reaction may be generalized as follows.



The reaction is exothermic for the cases $n = 0$, 1, and 2 but becomes endothermic when $n = 3$. An example of this last case, the reverse "ene reaction," has been studied by Huntsman and Curry in the gas phase.[152] They obtained log



$k\,(\text{sec}^{-1}) = 9.55 - (35.2/2.303RT)$ for this isomerization. The *A* factor is one of the lowest known for a unimolecular reaction. This is hardly surprising since five internal rotations are lost. The value has been rationalized by transition state

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(144) W. R. Roth and J. König, *Ann.*, 699, 24 (1966).

(145) R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 5578 (1964).

(146) W. R. Roth and J. König, *Ann.*, 688, 28 (1965).

(147) H. M. Frey and R. K. Solly, to be submitted for publication.

(148) D. E. McGreer, N. W. K. Chiu, and R. S. McDaniel, *Proc. Chem. Soc.*, 415 (1964).

(149) R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, 89, 1404 (1967).

(150) K. W. Egger, *ibid.*, 89, 3688 (1967).

(151) R. B. Woodward and R. Hoffmann, *ibid.*, 87, 2511 (1965).

(152) W. D. Huntsman and T. H. Curry, *ibid.*, 80, 2252 (1958).

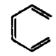
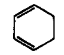
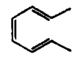
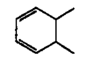
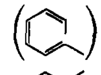
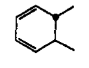
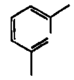
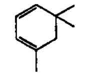
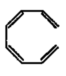
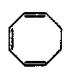
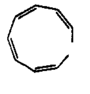
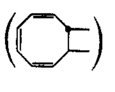
theory,[121] but more examples are required before such calculations can be relied upon. The scope of this reaction in α-carbonyl-ω-olefins and related compounds has recently been investigated, but no Arrhenius parameters were reported.[149,153]

C. CYCLIZATIONS OF LINEAR CONJUGATED POLYENES

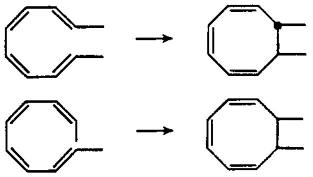
In common with the cyclobutene rearrangements (see next section), the cyclization reactions of *cis*-hexa-1,3,5-triene and higher polyenes are highly stereospecific.[154–157] The explanation for this is based upon orbital symmetry arguments[158,159] which have been extensively discussed elsewhere and are not repeated here.

Table X

Cyclization Reactions of Hexatrienes and Octatetraenes

Reactant	*Product*	*Log A, sec^{-1}*	*E$_a$, kcal mole^{-1}*	*Ref*
		11.85	29.9	160
		11.4	29.4	161
		10.8	33	161
		10.5	31.8	162
		11.0	17.0	163
		10.7	22.4	157

The Arrhenius parameters for such reactions are shown in Table X.[160–163] There are very few gas-phase data, and some liquid- and solution-phase results have been included. Of the gas-phase studies, Egger's data[162] on *cis*-2,6-dimethyl-3,5-heptatriene isomerization is probably the most reliable. It was carried out over a much wider temperature range than the other studies. Schatz[161] attempted to study the isomerizations of the three 2,4,6-octatrienes (*trans,cis,trans*, *cis,cis,cis*, and *trans,cis,cis*). Unfortunately only the first of these gave a clean reaction. The all-*cis* compound isomerized to the *trans,cis,cis*, and the equilibrium mixture (about 84% of the latter) isomerized to *trans*-5,6-dimethylcyclohexa-1,3-diene. In Table X we have assumed that the Arrhenius parameters for the mixture were identical with those of the *trans,cis,cis* isomer. Despite the crudity of the data, it is plain that in the hexatriene isomerizations terminal methyl substituents increase the activation energy by about 3–4 kcal mole^{-1} if they are *cis* and scarcely, if at all, when they are *trans*. This is to be expected since the *cis*-methyl groups will hinder overlap between the ends of the triene system, whereas the *trans* will not. A similar effect can be seen for the two octatetraene isomerizations listed. In fact Huisgen, Dahmen, and Huber[157] also observed the following isomerizations, but did not report kinetic parameters.



If the same A factor ($10^{10.7}$ sec^{-1}) is assumed for these reactions, activation energies of ~18 and 20 kcal mole^{-1} may be estimated. Thus a *cis*-methyl group in these systems seems to raise the activation energy quite consistently by 2 kcal mole^{-1}, although it is less easy to see why from an examination of the models. It should be pointed out that these octatetraene isomerizations are complicated by subsequent fairly rapid isomerization of the product cyclooctatrienes to bicyclo[4.2.0]octa-2,4-dienes.

The A factors for all these reactions seem to center on 10^{11} sec^{-1}, indicating a fairly tight transition state. Either two or three reactant internal rotations are lost in going to the transition state which probably resembles the product quite closely. A crude estimate[122] of $\Delta S^{\ddagger}$ (500°K) > -8.8 eu for *cis*-hexa-3,5-triene itself based upon this assumption is only slightly less than the observed value ($\Delta S^{\ddagger} = -7.3$ eu), which is identical with that of Benson and O'Neal.[121] The observed A factors in this case may be a little high. As with the 1,5-hydrogen shifts, these A factors on the whole are as low as transition state calculations will permit.

D. RADICAL ISOMERIZATIONS

There is almost no reliable kinetic data on radical isomerizations, and yet such reations are certainly believed to occur in a number of systems. The problem of isomerization of the simple alkyl radicals has been partially discussed in the section on radical decompositions. The isotopic labeling experiments of McNesby, *et al.*,[77–80] indicate that for all kinds of propyl and butyl radicals isomerizations compete unfavorably with decomposition reactions. This is not difficult to rationalize since 1,2- or 1,3-hydrogen-shift processes would be involved, and these would require three- or four-membered ring transition states. Undoubtedly they would involve large strain energies and probably negative entropies of activation. The lower limit of 43 ± 3.5 kcal mole^{-1} for the activation energy for $i\text{-C}_3\text{H}_7 \rightarrow n\text{-C}_3\text{H}_7\cdot$, estimated in the previous section, comes as no surprise.

Where 1,4-, 1,5-, or 1,6-hydrogen shifts are involved, however, the much less strained five-, six-, or seven-membered ring transition states are required. Thus claims to have observed normal to secondary radical isomerizations for

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(153) J. M. Conia, F. Leyendecker, and C. Dubois-Faget, *Tetrahedron Lett.*, 129 (1966).

(154) E. Vogel, W. Grimme, and E. Dinné, *ibid.*, 391 (1965).

(155) E. N. Marvell, G. Caple, and B. Schatz, *ibid.*, 385 (1965).

(156) E. N. Marvell and J. Seubert, *J. Amer. Chem. Soc.*, 89, 3377 (1967).

(157) R. Huisgen, A. Dahmen, and H. Huber, *ibid.*, 89, 7130 (1967).

(158) R. B. Woodward and R. Hoffman, *ibid.*, 87, 395 (1965).

(159) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, 87, 2045 (1965).

(160) K. E. Lewis and H. Steiner, *J. Chem. Soc.*, 3080 (1964).

(161) B. S. Schatz, *Dissertation Abstr.*, B27, 3870 (1967).

(162) K. W. Egger, *Helv. Chem. Acta*, 51, 422 (1968).

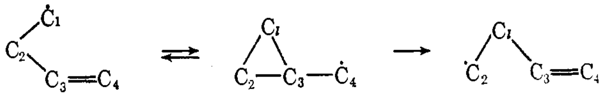
(163) T. D. Goldfarb and L. Lindqvist, *J. Amer. Chem. Soc.*, 89, 4588 (1967).

pentyl,[164,165] hexyl,[60,61,164] and heptyl[164] radicals are much more reasonable. These systems are nonetheless complex, and it is not usually possible to obtain Arrhenius parameters for the isomerizations. Endrenyi and LeRoy[165] have, however, found log k (sec^{-1}) = 7.15 − (10.8/2.303RT) for

$$n\text{-}C_5H_{11}\cdot \longrightarrow sec\text{-}C_5H_{11}\cdot$$

A low A factor is to be expected since three internal rotations are lost in going to the transition state. However, minimum values of $\Delta S^{\ddagger} = -13.3$ eu or $A = 10^{10.5}$ sec^{-1} are obtained if it is assumed that the transition state is as tight at methylcyclobutane,[122] which is almost certainly too tight. The authors propose a transmission coefficient ≪1 to explain the very low A factor. In the absence of other evidence to support this contention, we feel it is more probable that the Arrhenius parameters are in error.

Internal addition processes have been suggested in a number of radicals. The so-called homoallylic rearrangement[166] is a 1,3-addition reaction.



This rearrangement has been proposed[167] to explain the product distribution in the alkyl radical addition to acetylenes.[168,169] No Arrhenius parameters for the internal additions appear to have been determined. The internal cyclization of the pentadienyl radical has also been observed,[170] but Arrhenius parameters for the process were not measured.

IV. Cyclic Reactants with Cyclic Transition States

In this section we consider the isomerizations (and decompositions) of cyclic molecules which are believed to proceed *via* the formation of a cyclic transition complex. *A priori* such reactions should have relatively small entropies of activation and hence so-called "normal" frequency factors. It should, however, be noted that in some cases the fact that $\Delta S^{\ddagger} \sim 0$ is the main evidence for postulating the cyclic nature of the complex.

A. CYCLOBUTENES

The thermal isomerization of cyclobutene to butadiene has been investigated by Walters and his coworkers.[171,172] The reaction is unimolecular and the high-pressure rate constants yield the Arrhenius equation

$$\log k_\infty\ (\text{sec}^{-1}) = 13.26 - (32{,}700/2.303RT)$$

Below about 10 torr the rate constant varies with pressure and has fallen to 13% of its high-pressure value at 0.15 torr. Studies have also been reported for 1-methylcyclobutene[173] and 3-methylcyclobutene[174] at both the high-pressure limit and in the falloff region. In these cases both the shape and position of the experimental curves are in reasonable agreement with theoretical calculations.[175] 3-Methylcyclobutene yields only *trans*-penta-1,3-diene, and in this and all other cases investigated the reaction is found to proceed in a stereospecific fashion. Some of the data so far obtained for cyclobutene isomerizations is shown in Table XI.[176–182]

The small values for the entropy of activation for these isomerizations suggest that the reaction proceeds *via* a twisting of the cyclobutene ring with a simultaneous stretching of the 3,4-carbon bond. This process if it occurs in a concerted fashion also explains the relatively low energies of activation compared with, for example, those found for cyclobutane decompositions. The stereochemistry of the products indicates that the isomerization proceeds with rotation of the groups on carbon atoms 3 and 4 occurring in the same sense, *i.e.*, in a conrotatory manner. Explanations of why this should be so are based on orbital symmetry arguments.[158,159] In the case of a number of bicyclic cyclobutenes and tricyclic cyclobutenes, such a conrotatory process is prevented since the resulting product would be too highly strained, and indeed in one case the reverse process starting from a cyclic diene occurs yielding a cyclobutene.[183] While numerous compounds of this type have been investigated semiquantitatively by Criegee and his coworkers,[184] relatively few have been followed with high precision in the gas phase. Some of those for which Arrhenius parameters are available are shown in Table XII[185–187] (*vide infra*).

Since the formation of the products shown in Table XII cannot occur *via* a conrotatory process, we are faced with the problem of whether the reaction occurs by a concerted disrotatory process or whether it is not concerted at all in this

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(164) A. S. Gordon and J. R. McNesby, *J. Chem. Phys.*, 31, 853 (1959).

(165) L. Endrenyi and D. J. LeRoy, *J. Phys. Chem.*, 70, 4081 (1966).

(166) L. K. Montgomery, J. W. Matt, and J. R. Webster, *J. Amer. Chem. Soc.*, 89, 923 (1967).

(167) S. W. Benson and W. B. DeMore, *Ann. Rev. Phys. Chem.*, 16, 397 (1965).

(168) J. A. G. Dominguez and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 940 (1962).

(169) R. R. Getty, J. A. Kerr, and A. F. Trotman-Dickenson, *ibid.*, *A*, 1360 (1967).

(170) K. W. Egger and S. W. Benson, *J. Amer. Chem. Soc.*, 88, 241 (1966).

(171) W. Cooper and W. D. Walters, *ibid.*, 80, 4220 (1958).

(172) W. P. Hauser and W. D. Walters, *J. Phys. Chem.*, 67, 1328 (1963).

(173) H. M. Frey, *Trans. Faraday Soc.*, 58, 957 (1962); M. A. Karlsson, Ph.D. Thesis, University of Rochester, 1967.

(174) H. M. Frey, *Trans. Faraday Soc.*, 60, 83 (1964); H. M. Frey and D. C. Marshall, *ibid.*, 61, 1715 (1965).

(175) C. S. Elliott and H. M. Frey, *ibid.*, 62, 895 (1966).

(176) H. M. Frey and R. F. Skinner, *ibid.*, 61, 1918 (1965).

(177) D. C. Dickens, H. M. Frey, and R. F. Skinner, *ibid.*, in press.

(178) H. M. Frey, *ibid.*, 59, 1619 (1963).

(179) H. M. Frey, D. C. Marshall, and R. F. Skinner, *ibid.*, **61**, **861** (1965).

(180) R. Srinivasan, personal communication.

(181) H. M. Frey, B. M. Pope, and R. F. Skinner, *Trans. Faraday Soc.*, 63, 1166 (1967).

(182) G. R. Branton, H. M. Frey, and R. F. Skinner, *ibid.*, **62**, 1546 (1966).

(183) K. M. Shumate, P. N. Neuman, and F. J. Fonken, *J. Amer. Chem Soc.*, 87, 3996 (1965).

(184) R. Criegee and H. Furrer, *Chem. Ber.*, 97, 2949 (1964); R. Criegee and H. G. Reihart, *ibid.*, 101, 102 (1968).

(185) J. I. Brauman and D. M. Golden, *J. Amer. Chem. Soc.*, **90**, 1920 (1968).

(186) G. R. Branton, H. M. Frey, D. C. Montagne, and I. D. R. Stevens, *Trans. Faraday Soc.*, 62, 659 (1966).

(187) M. R. Willcott and E. Goerland, *Tetrahedron Lett.*, 6341 (1966).

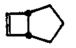
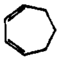
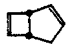
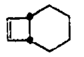
Table XI

Cyclobutene Isomerizations

Reactant	*Product*	*Log A, sec^{-1}*	*E, kcal mole^{-1}*	*Ref*
1-Methylcyclobutene	Isoprene	13.79	35.10	173
3-Methylcyclobutene	*trans*-Penta-1,3-diene	13.53	31.55	174
1-Ethylcyclobutene	2-Ethylbutadiene	13.76	34.83	176
3-Ethylcyclobutene	*trans*-Hexa-1,3-diene	13.49	31.63	177
1-Chlorocyclobutene	2-Chlorobutadiene	13.26	33.64	177
1,2-Dimethylcyclobutene	2,3-Dimethylbutadiene	13.84	36.04	178
1,3-Dimethylcyclobutene	*trans*-2-Methylpenta-1,3-diene	13.65	33.00	179
1,4-Dimethylcyclobutene	*trans*-3-Methylpenta-1,3-diene	13.52	33.39	179
cis-3,4-Dimethylcyclobutene	*cis,trans*-Hexa-2,4-diene	13.88	34.30	180
3,3-Dimethylcyclobutene	4-Methylpenta-1,3-diene	13.93	36.09	181
1,3,3-Trimethylcyclobutene	2,4-Dimethylpenta-1,3-diene	13.90	37.03	181
trans-1,2,3,4-Tetramethylcyclobutene	3,4-Dimethyl-*trans,trans*-hexa-2,4-diene	13.85	33.59	182
cis-1,2,3,4-Tetramethylcyclobutene	3,4-Dimethyl-*cis,trans*-hexa-2,4-diene	14.20	37.7	182

Table XII

Bicyclic Cyclobutene Isomerizations

Reactant	*Product*	*Log A, sec^{-1}*	*E, kcal mole^{-1}*	*Ref*
 →		14.22	26.88	185
 →		14.31	45.51	186
 →		14.0	39.5	187
 →		14.13	43.18	182

sense and in fact involves the formation of a biradical. Certainly it is possible to produce a consistent set of values for the energetics of the isomerizations if a particular stabilization energy is chosen for the biradical. However, for full stabilization of the biradical, the configuration of the transition complex would already have the geometry of the product and would be an electronically excited form of it. Alternatively the distrotatory process becomes allowed if an excited state of the reactant is reached. We believe that as the molecule proceeds along the reaction coordinate these two processes become indistinguishable, but that neither complete excitation of the reactant nor formation of a free biradical occurs. A full discussion of this interesting topic is, however, beyond the scope of this review. We note that additivity relationships have been suggested for the effect of various substituents on the free energy of activation of these isomerizations.[181]

A very interesting case of the thermal cyclization of an acyclic diene to a cyclobutene has recently been reported.[188] This concerns the sterically highly hindered *trans*-1-bromo-*cis*-1,2,3,4-tetraphenylcyclobutene. The cyclization is reversible. Rate data between 34 and 55° (by nmr) yield the parameters $\Delta H^{\ddagger} = 19.0 \pm 0.6$ kcal mole^{-1} and $\Delta S^{\ddagger} = -15.6 \pm 1.7$ eu. A large negative entropy of activation is of course consistent with the very small values of $\Delta S^{\ddagger}$ for the reverse type of isomerization. Unfortunately, owing to the very complex steric interactions in the reactant (and even in the product), it is not possible to estimate quantitatively with any degree of precision the expected value of $\Delta S^{\ddagger}$.

The thermal isomerization of Dewar benzene to benzene may be considered as a special case of the cyclobutene isomerization reaction. Arrhenius parameters have been reported for the thermal isomerization of hexamethyl-Dewar benzene[190] (hexamethylbicyclo[2.2.0]hexa-2,5-diene) to hexamethylbenzene, *viz.*, log A (sec^{-1}) = 12 and E = 31.1 kcal mole^{-1}. Perfluoro-Dewar benzene has also been studied as have a number of monosubstituted pentafluoro-Dewar benzenes. In all cases[189] the entropy of activation is close to zero, and the energies of activation lie between 25 and 30 kcal mole^{-1}. At first sight these energies of activation appear to be remarkably high. They are little less than those for the isomerization of simple alkylcyclobutenes to dienes, yet the reactions are very considerably more exothermic owing to the strain energy of the reactant and the resonance energy of the product. It must, however, be realized that, like other cyclobutenes, orbital symmetry requirements can only be satisfied if the isomerization proceeds in a conrotatory manner. For Dewar benzenes this is clearly impossible, and hence an essentially nonconcerted process of a higher energy path is followed. It is interesting to note that in the presence of a rhodium–olefin complex the energy of activation for the isomerization of hexamethyl-Dewar benzene[190] falls to 19.4 kcal mole^{-1}. As a result of complex formation between the reactant and the rhodium ion, the symmetries of the highest occupied orbitals are changed and the isomerization as a disrotatory process is now allowed.

B. ISOMERIZATION OF CYCLIC RADICALS

There are few precise data available on the ring opening of cyclic radicals. From studies on the mercury-sensitized photolysis of cyclopentane, Gunning and Stock[191] obtained a

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[188] G. A. Doorakian and H. M. Freedman, *J. Amer. Chem. Soc.*, **90**, 582 (1968).

[189] P. Cadman, E. Ratajczak, and A. F. Trotman-Dickenson, Abstracts of the Autumn Meeting of the Chemical Society, Keele, 1968.

[190] H. C. Volger and H. Hogeveen, *Recueil*, 86, 830 (1967).

[191] H. E. Gunning and R. L. Stock, *Can. J. Chem.*, 42, 357 (1964).

value of 37 kcal mole^{-1} for the energy of activation for ring opening of the cyclopentyl radical. From a study of the photolysis of perdeuterioacetone in the presence of cyclopentane, Gordon[192] found no evidence for the formation of a linear C_5 radical but only for its breakdown products, ethylene and an allyl radical. The Arrhenius parameters deduced for this reaction are $10^{14.5}$ sec^{-1} and 37.7 kcal mole^{-1}. There is also evidence for the radical losing a hydrogen atom to yield cyclopentene and for losing a hydrogen molecule to yield the cyclopentadienyl radical.

From similar studies with cyclobutane,[193] a value of 18 kcal mole^{-1} may be deduced for the energy of activation for the isomerization of the cyclobutyl to the butenyl radical. A similar value for the preexponential factor to that found for cyclopentyl may also be obtained. The appreciably lower energy of activation suggests the release of much of the strain of the cyclic radical in the transition complex, and this would be constant with the positive entropy of activation. The methyl radical sensitized decomposition of cyclopropanecarboxaldehyde yields a value of ~20 kcal mole^{-1} for the isomerization of cyclopropyl to allyl.[194] This is, however, based on an assumed A factor of 10^{13}. If a more reasonable value for the A factor of 10^{15} is used, then the activation energy is increased to about 25 kcal mole^{-1}. The energies of activation for these three cyclic radicals do not appear to fit any simple model, and they are not felt to warrant further discussion at this stage since the values are all subject to considerable uncertainties.

C. H_2 ELIMINATION FROM CYCLIC MOLECULES

1. *Cyclopentene*

The decomposition of cyclopentene to cyclopentadiene plus hydrogen has been shown to be a unimolecular process[195] for which $\log k\ (\text{sec}^{-1}) = 12.04 - (58{,}800/2.303RT)$. Similarly 2,5-dihydrofuran yields furan plus hydrogen[196] for which $\log k\ (\text{sec}^{-1}) = 12.72 - (48{,}500/2.303RT)$. In this latter case the elimination must be from the 2 and 5 positions and cannot proceed *via* a rearrangement to 2,3-dihydrofuran since this compound is stable in the temperature range in which the 2,5 compound decomposes. It thus appeared likely that in the cyclopentene decomposition elimination was from the 3 and 5 positions. Recent work with deuterated cyclopentene[197] has shown that indeed the majority of the hydrogen produced does in fact come from a 3,5 elimination (we note this is termed 1,4 elimination). Arguments based on the conservation of orbital symmetry show that these eliminations unlike the 1,2 eliminations are allowed processes and unlike the latter can occur in a concerted fashion. For such concerted processes only a relatively small decrease in entropy in going from reactant to complex is to be expected.

2. *Cyclohexa-1,4-diene*

This compound eliminates hydrogen molecularly to yield benzene. Two separate studies[198,199] have yielded the Arrhenius equations

$$\log k\ (\text{sec}^{-1}) = 12.02 - (42{,}700/2.303RT)$$

$$\log k\ (\text{sec}^{-1}) = 12.36 - (43{,}800/2.303RT)$$

Once again this is a symmetry-allowed process. The molecular elimination of hydrogen from cyclohexa-1,3-diene does not occur, since to conserve orbital symmetry a concerted *trans* elimination would be necessary. As a result this molecule decomposes (at much higher temperatures) by a complex chain process.[95]

1-Methylcyclohexa-1,4-diene decomposes to yield toluene and hydrogen[200] as does the 3-methyl compound;[201] the Arrhenius equations are respectively

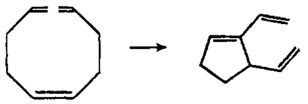
$$\log k\ (\text{sec}^{-1}) = 12.69 - (44{,}690/2.303RT)$$

$$\log k\ (\text{sec}^{-1}) = 12.47 - (42{,}950/2.303RT)$$

It is interesting to note that in the second case elimination of methane does not occur, even though such a process would be more exothermic than the hydrogen elimination actually observed. The formation of ethane and *p*-xylene from 3,3,6,6-tetramethylcyclohexa-1,4-diene has been suggested to occur as a symmetry-allowed concerted molecular elimination.[202] More recent experimental evidence, however, proves that the ethane results from the recombination of methyl radicals formed by an initial carbon–carbon bond rupture.[203] In agreement with these results it has been found that, whereas *cis*-3,6-dimethylhexa-1,4-diene eliminates hydrogen molecularly, the corresponding *trans* compound decomposes (at appreciably higher temperatures) to yield methane and toluene by a radical-chain process.[203]

D. COPE REARRANGEMENT IN CYCLIC SYSTEMS

We have discussed the normal Cope rearrangement in another section. Here we mention only the isomerization of cyclonona-1,2-6-triene to 1,4-divinylcyclopentene noted by Skatteb⌀l and Solomon.[204]



Unlike a normal Cope reaction no free rotations will be lost in forming the transition complex. There will be a small loss of entropy due to some partial bonding between C_1 and C_7

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[192] A. S. Gordon, *Can. J. Chem.*, 43, 570 (1965).

[193] A. S. Gordon, S. R. Smith, and C. Drew, *J. Chem. Phys.*, 36, 824 (1962).

[194] G. Greig and J. C. J. Thynne, *Trans. Faraday Soc.*, 62, 3338 (1966).

[195] D. W. Vanus and W. D. Walters, *J. Amer. Chem. Soc.*, 70, 4035 (1948).

[196] C. A. Wellington and W. D. Walters, *ibid.*, 83, 4888 (1961).

[197] J. E. Baldwin, *Tetrahedron Lett.*, 2953 (1966).

[198] R. J. Ellis and H. M. Frey, *J. Chem. Soc., A*, 553 (1966).

[199] S. W. Benson and R. Shaw, *Trans. Faraday Soc.*, 63, 985 (1967).

[200] H. M. Frey and D. H. Lister, *J. Chem. Soc., A*, 509 (1967).

[201] H. M. Frey and D. H. Lister, *ibid.*, 1800 (1967).

[202] W. Reusch, M. Russell, and C. Dzwella, *J. Org. Chem.*, 29, 2446 (1964).

[203] H. M. Frey, A. Krantz, and I. D. R. Stevens, to be submitted for publication.

[204] L. Skatteb⌀l and S. Solomon, *J. Amer. Chem. Soc.*, 87, 4506 (1965).

which will result in raising the frequency of some of the ring deformation vibrations. Recent experiments[205] confirm this in yielding a value for the A factor for this isomerization of $\sim 10^{12.5}$ sec^{-1}.

V. *Cyclic Reactants with Acyclic Transition States*

In this section we restrict our attention to the reactions of cyclic molecules which have acyclic transition states. In cases where free or partially hindered internal rotations are generated by such a reaction pathway, $\Delta S^{\ddagger} > 0$. There are situations where, while some new rotations are produced, others present in the reactant disappear and under such circumstances $\Delta S^{\ddagger}$ may be close to zero.

A. CYCLOPROPANE

The thermal isomerization of cyclopropane to propylene has been investigated experimentally by several workers.[206] It is one of the best authenticated examples of a unimolecular isomerization. The high-pressure rate constants fit the Arrhenius equation $\log k_{\infty}$ (sec^{-1}) = 15.45 − (65,600/2.303RT). Falloff studies to low pressures have been reported,[207] and theoretical calculations based on various theories of unimolecular reactions have been carried out for this reaction.[208] Controversy about the nature of the transition complex has largely centered about the occurrence or nonoccurrence of a trimethylene biradical intermediate.[208–211] We believe the bulk of the evidence available based on studies of cyclopropane, alkylcyclopropanes, and vinylcyclopropanes is consistent with and supports the intermediate formation of a biradical. The biradical hypothesis is also supported by the results of isotope (perdeuteration) studies.[212] The reaction pathway is thus envisaged as

$$\text{cyclopropane} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{trimethylene} \xrightarrow{k_2} \text{propylene}$$

Perhaps the strongest support for this mechanism comes from the original observation of Rabinovitch, *et al.*,[213] that *cis*- and *trans*-1,2-dideuteriocyclopropanes undergo reversible geometric isomerizations with Arrhenius parameters which suggest that both the structural and geometric isomerizations proceed *via* closely similar pathways. On the basis of the then available data, Benson's[209] analysis yielded the values

$$\log k_1\ (\text{sec}^{-1}) = 16.0 - (64{,}200/2.303RT)$$

$$\log k_{-1}\ (\text{sec}^{-1}) = 13.0 - (8200/2.303RT)$$

$$\log k_2\ (\text{sec}^{-1}) = 12.2 - (9500/2.303RT)$$

Using the more recent values of Falconer, *et al.*,[206] for the Arrhenius parameters for the isomerization of cyclopropane to propylene, Lin and Laidler[206] find

$$\log k_{-1}\ (\text{sec}^{-1}) = 13.35 - (9100/2.303RT)$$

$$\log k_2\ (\text{sec}^{-1}) = 12.42 - (9600/2.303RT)$$

Alkylcyclopropanes also undergo unimolecular isomerizations to yield olefins, and suitably substituted ones in addition undergo geometric isomerizations. In all cases studied the latter processes are faster than the former. Some of the results that have been reported are shown in Table XIII.[214–222] These reactions all have quite large positive entropies of activation which must be largely the result of the new internal rotations present in the trimethylene intermediate.

For several alkylcyclopropanes, studies have been carried out in the pressure region where the rate constant has been observed to be below the high-pressure limit. The more highly substituted the cyclopropane the lower the pressure at which this decrease in the rate constant occurs. This variation with the complexity of the molecule is of course to be expected from both RRK and RRKM theory.

On the basis of the biradical mechanism, the rate of *cis–trans* isomerization should increase with increasing substitution owing to stabilization of the intermediate by alkyl groups, but there are insufficient data to test this. It is also probable that lowering the energy of the biradical also lowers the energy of activation for its structural isomerization. Owing to experimental errors it is preferable to look at the actual rates of isomerization at a particular temperature. The rates do in fact increase as expected, but the effect is remarkably small, *e.g.*, the 1-methyl and 1-ethyl compounds isomerize approximately twice as fast as cyclopropane itself at 730°K.

The use of other substituents on the cyclopropane ring might be expected to produce evidence for or against the biradical mechanism. Such evidence is often difficult to interpret owing to the simultaneous variation of several parameters. Thus a study of 1,1-dichlorocyclopropane indicates that for this compound no intermediate biradical is involved.[223] On the other hand, the pyrolysis of cyclopropylamine does suggest a biradical intermediate.[224] It is also worth noting that the studies of Crawford and Lynch[225] on optically active *trans*-1,2-diphenylcyclopropane lend support to the biradical mecha-

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(205) H. M. Frey and A. M. Lamont, unpublished experiments.

(206) T. S. Chambers and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 56, 399 (1934); W. E. Falconer, T. F. Hunter, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 609 (1961).

(207) H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc.*, A217, 563 (1953).

(208) N. B. Slater, *ibid.*, 218, 224 (1953); G. M. Wieder and R. A. Marcus, *J. Chem. Phys.*, 37, 1835 (1962); M. C. Lin and K. J. Laidler, *Trans. Faraday Soc.*, 64, 927 (1968); R. C. Golike and E. W. Schlag, *J. Chem. Phys.*, 38, 1886 (1963).

(209) S. W. Benson, *ibid.*, 34, 521 (1961).

(210) F. T. Smith, *ibid.*, 29, 235 (1958).

(211) E. W. Schlag and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, 82, 5996 (1960).

(212) S. W. Benson and P. S. Nangia, *J. Chem. Phys.*, 38, 18 (1963).

(213) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *ibid.*, 28, 504 (1958).

(214) J. P. Chesick, *J. Amer. Chem. Soc.*, 82, 3277 (1960).

(215) D. W. Setser and B. S. Rabinovitch, *ibid.*, 86, 564 (1964).

(216) M. L. Halberstadt and J. P. Chesick, *J. Phys. Chem.*, 69, 429 (1965).

(217) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3953 (1959); 1157 (1962).

(218) H. M. Frey and D. C. Marshall, *ibid.*, 191 (1965).

(219) H. M. Frey and D. C. Marshall, *ibid.*, 3052 (1962).

(220) M. C. Flowers and H. M. Frey, *Proc. Roy. Soc.*, A257, 122 (1960).

(221) H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 5717 (1963).

(222) C. S. Elliott and H. M. Frey, *ibid.*, 900 (1964).

(223) K. A. W. Parry and P. J. Robinson, *Chem. Commun.*, 1083 (1967).

(224) P. J. Robinson, personal communication.

(225) R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, 46, 1457 (1968).

Table XIII

Isomerization of Alkylcyclopropanes

Reactant	*Product*	*Log A, sec*$^{-1}$	*E, kcal mole*$^{-1}$	*Ref*
Methylcyclopropane	But-1-ene But-2-ene(*cis*+*trans*) Isobutylene	15.45	65.0	214
1,2-Dideuterio-3-methylcyclopropane	But-1-ene But-2-ene(*cis* + *trans*) Isobutylene	14.43	62.3	215
Ethylcyclopropane	Pent-1-ene Pent-2-ene(*cis*+*trans*) 2-Methylbut-1-ene	14.40	61.6	216
1,1-Dimethylcyclopropane	2-Methylbut-2-ene 3-Methylbut-1-ene	15.05	62.6	217
1,1-Diethylcyclopropane	3-Ethylpent-2-ene	14.84	63.4	218
	3-Ethylpent-1-ene	14.95	63.8	
1,1,2,2-Tetramethylcyclopropane	2,4-Dimethylpent-2-ene	15.54	64.7	219[a]
cis-1,2-Dideuteriocyclopropane	*trans* compound	16.11	65.1	211
cis-1,2-Dimethylcyclopropane	*trans* compound	15.25	59.42	220
cis-1,2,3-Trimethylcyclopropane	*trans* compound	15.78	60.95	221
cis-1-Ethyl-2-methylcyclopropane	*trans* compound	15.08	58.87	222

[a] Recalculated value.

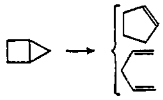
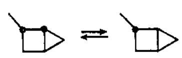
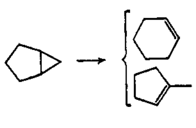
nism, the rate of racemization of the reactant being greater than the rate of *trans–cis* isomerization.

Some saturated bicyclo compounds containing a cyclopropane ring have been studied. The results are presented in Table XIV.[226–231] These isomerizations have smaller entropies of activation than the corresponding monocyclic systems. A biradical intermediate is probably involved once again, but evidence for such a postulate is not as strong in these cases and largely rests on analogy with the latter systems. Since the biradicals which would be formed would not result in any new internal rotations being generated, the decrease in $\Delta S^{\ddagger}$ is to be expected.

The isomerizations of the bicyclo[1.1.0]butanes are perhaps worthy of special note. The Arrhenius parameters shown in Table XIV are consistent with a biradical mechanism but would not rule out completely a concerted formation of the dienes. Recent work[232] with other methyl-substituted bicyclobutanes, *viz.*, *exo,exo*- and *exo,endo*-2,4-dimethylbicyclo[1.1.0]butane and *exo*- and *endo*-2-methylbicyclo[1.1.0]butane, has indicated that either the isomerization proceeds *via* a biradical whose lifetime is too short to allow rotamer equilibration, or it proceeds in a concerted fashion with one ring opening in a conrotatory and the other a disrotatory manner. However, to encompass the experimental results it is necessary to assume that the energies of the breaking bonds are different at any point of the reaction coordinate. The difference between these two mechanisms is almost one of semantics.

Table XIV

Rearrangements of Saturated Bicyclic Systems Containing Cyclopropane Ring

Reactant	*Product*	*Log A, sec*$^{-1}$	*E, kcal mole*$^{-1}$	*Ref*
		14.52	41.40	226
		14.02	40.58	227
		14.45	43.30	228
		14.10	45.60	229
		14.35	52.30	229
		14.45	38.90	230
		(Arrhenius parameters refer to $k_{cis} + k_{trans}$)		
		13.29	57.40	231
		13.89	61.17	231

By analogy with the cyclopropane isomerization, the thermal decomposition of ethylene oxide would be expected to be simple and yield acetaldehyde. However, even at temperatures considerably lower than those used for cyclopropane decomposition, ethylene oxide undergoes complex reactions by a mechanism involving methyl radicals.[233] A careful consideration of the energetics of the transformation of ethylene oxide

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(226) R. Srinivasan, A. A. Levi, and I. Haller, *J. Phys. Chem.*, 69, 1775 (1965).

(227) H. M. Frey and I. D. R. Stevens, *Trans. Faraday Soc.*, 61, 90 (1965).

(228) J. P. Chesick, *J. Phys. Chem.*, 68, 2033 (1964).

(229) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Amer. Chem. Soc.*, 86, 679 (1964).

(230) J. P. Chesick, *ibid.*, 84, 3250 (1962).

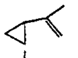
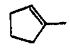
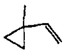
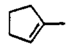
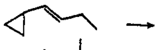
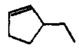
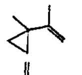
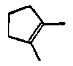
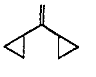
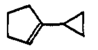
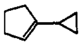
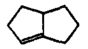
(231) H. M. Frey and R. C. Smith, *Trans. Faraday Soc.*, 58, 697 (1962).

(232) G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.*, 90, 2452 (1968).

(233) K. H. Mueller and W. D. Walters, *ibid.*, 76, 330 (1954); H. W. Thompson and M. Meissner, *Trans. Faraday Soc.*, 32, 1451 (1936).

Table XV

Isomerization of Vinylcyclopropanes

Reactant		*Product*	*Log A, sec^{-1}*	*E, kcal mole^{-1}*	*Ref*
	→		13.61	49.70	235
	→		13.89	50.90	236
	→		14.11	49.35	237
	→		13.79	49.98	238
	→		14.14	50.5	239
	→		14.29	51.06	240
	→		14.01	51.29	240

to acetaldehyde indicates that the aldehyde is formed initially with sufficient energy to undergo carbon–carbon bond fission, and this occurs unless the excited molecule is collisionally stabilized. By carrying out reactions under appropriate conditions, acetaldehyde is in fact found to be the primary product.[234] Thus the apparent difference between cyclopropane and ethylene oxide is not due to a different mechanism in the primary process, but arises because the latter isomerization is more exothermic and the primary product contains a weaker bond.

B. VINYLCYCLOPROPANE

This compound undergoes a thermal unimolecular isomerization to yield predominantly cyclopentene. A number of alkyl-substituted vinylcyclopropanes have also been studied and the results are given in Table XV.[235–240] An inspection of the data shows that, compared with the geometrical isomerization of alkylcyclopropanes, the vinylcyclopropanes isomerize with energies of activation some 13 kcal mole^{-1} lower and with much smaller entropies of activation. If we extend the biradical mechanism already discussed to these isomerizations, then an allylically stabilized biradical will be formed. Since the internal rotation of the vinyl group will be lost in going to the activated complex if such a biradical is formed, there is a corresponding reduction in entropy of activation compared with saturated cyclopropanes. If we assume that the ring closure to the cyclopentene does not have an appreciably higher energy of activation than that for the ring opening of the cyclopropane, then we may equate the value of 13 kcal mole^{-1} quoted above to the stabilization energy of the allyl radical. This value is in good agreement with a value of 12.6 kcal mole^{-1} obtained by other workers.[241] However, this agreement may be fortuitous. Thus a concerted formation of cyclopentene would also yield a value of $\Delta S^{\ddagger} \approx 0$ and a lowering in the energy of activation. A more direct comparison is in principle possible from the rate of *cis–trans* isomerization of *cis*-1-deuterio-2-vinylcyclopropane. Accurate values for the Arrhenius parameters are not yet available, but it is already clear that this geometric isomerization is faster than the isomerization to cyclopentene.[242] It is probable that the difference in energies of activation is ~1 kcal mole^{-1}, which would only alter the calculated value for the allylic stabilization energy by a small amount.[243]

On both a biradical or a concerted mechanism, *cis* substituents on the vinyl group are expected to increase the energy of activation of the structural isomerization.[238] This has been observed in a number of cases.

C. CYCLOBUTANE

The thermal unimolecular decomposition of cyclobutane to ethylene which occurs at around 450° has been very thoroughly studied both in the high pressure and in the falloff region. Various alkylcyclobutanes have also been investigated, and the results reported are shown in Table XVI.[244–253] The decomposition may involve the formation of a tetramethylene or substituted tetramethylene biradical or the simultaneous stretching of two carbon–carbon bonds. If the latter is the case, then in order to account for the high entropy of activation it is necessary to assume that the olefins being formed are already free to rotate in the complex. Again, as in the case of the cyclopropane isomerizations, a consistent picture does emerge in terms of a biradical mechanism.[209] Thus isopropenylcyclobutane decomposes with a lower energy and a smaller entropy of activation than isopropylcyclobutane in agreement with a resonance-stabilized biradical. We note also that the decomposition of acetylcyclobutane (and other similarly substituted compounds) fits this picture. *cis*-1,2-Dimethylcyclopropane also undergoes a geometric isomerization, but unlike the corresponding cyclopropane the geometric isomerization is slower than the structural isomerization. On the biradical hypothesis it might be expected that alkyl substitution would lead to an increase in rate. In most cases this is observed, but the effect is small. Reasons why a small effect is to be expected have been presented.[254]

Bicyclic and tricyclic systems containing cyclobutane rings have received some attention and in a few cases rate studies

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(234) M. L. Neufeld and A. T. Blades, *Can. J. Chem.*, 41, 2956 (1963); S. W. Benson, *J. Chem. Phys.*, 40, 105 (1964).

(235) C. A. Wellington, *J. Phys. Chem.*, 66, 1671 (1962).

(236) H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 3981 (1962).

(237) R. J. Ellis and H. M. Frey, *ibid.*, 959 (1964).

(238) R. J. Ellis and H. M. Frey, *ibid.*, 4188 (1964).

(239) C. S. Elliott and H. M. Frey, *ibid.*, 4289 (1965).

(240) G. R. Branton and H. M. Frey, *ibid.*, 1342 (1966).

(241) K. W. Egger, A. S. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, 86, 5421 (1964).

(242) M. R. Willcott and V. M. Cargle, *ibid.*, 89, 723 (1967).

(243) M. R. Willcott, personal communication.

(244) C. T. Genaux and W. D. Walters, *J. Amer. Chem. Soc.*, 73, 4497 (1951); R. W. Carr and W. D. Walters, *J. Phys. Chem.*, 67, 1370 (1963).

(245) N. N. Das and W. D. Walters, *Z. Phys. Chem.* (Frankfurt on Main), 15, 22 (1958).

(246) P. C. Rotoli, M.S. Thesis, University of Rochester, 1963.

(247) H. R. Gerberich and W. D. Walters, *J. Amer. Chem. Soc.*, 83, 3935 (1961).

(248) H. R. Gerberich and W. D. Walters, *ibid.*, 83, 4884 (1961).

(249) R. E. Wellman and W. D. Walters, *ibid.*, 79, 1542 (1957).

(250) S. M. E. Kellner and W. D. Walters, *J. Phys. Chem.*, 65, 466 (1961).

(251) M. Zupan and W. D. Walters, *J. Amer. Chem. Soc.*, 86, 173 (1964).

(252) R. J. Ellis and H. M. Frey, *Trans. Faraday Soc.*, 59, 2076 (1963).

(253) L. G. Daignault and W. D. Walters, *J. Amer. Chem. Soc.*, 80 541 (1958).

(254) A. C. Cocks and H. M. Frey, *J. Chem. Soc.*, in press.

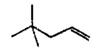
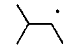
Table XVI

Thermal Decomposition of Cyclobutanes

Reactant	*Product*	*Log A, sec*$^{-1}$	*E, kcal mole*$^{-1}$	*Ref*
Cyclobutane	Ethylene	15.62	62.5	244
Methylcyclobutane	Ethylene + propylene	15.38	61.2	245
1,1-Dimethylcyclobutane	Isobutylene + ethylene	15.68	61.0	246
cis-1,2-Dimethylcyclobutane	Butene-2 + ethylene	15.57	63.0	247
	Propylene	15.48	60.4	247
trans-1,2-Dimethylcyclobutane	Butene-2 + ethylene	15.46	63.4	248
	Propylene	15.45	61.6	248
Ethylcyclobutane	Butene-1 + ethylene	15.56	62.0	249
n-Propylcyclobutane	Pentene-1 + ethylene	15.53	61.6	250
Isopropylcyclobutane	3-Methylbutene-1 + ethylene	15.63	62.6	251
Isopropenylcyclobutane	Isoprene + ethylene	14.61	51.0	252
	1-Methylcyclohexane	14.53	51.0	252
Acetylcyclobutane	Methyl vinyl ketone + ethylene	14.53	54.5	253

Table XVII

Entropy Data for Some Hydrocarbons and Hydrocarbon Radicals

Molecular	*S° (eu)*[a] *300°*	*500°*	*1000°*	*Ref*
	88.3	...	144.0	258
	95.0	...	167.5	258
H·	27.4	30.0	33.4	259
CH_3·	46.5	51.7	60.5	5
C_2H_5·	59.3	66.7	81.6	5
n-C_3H_7·	69.4	80.2	102.3	5
i-C_3H_7·	67.7	78.6	100.3	5
n-C_4H_9·	79.4	93.7	122.9	*b*
sec-C_4H_9·	78.7	93.1	122.1	*b*
i-C_4H_9·	76.5	90.9	120.3	*b*
t-C_4H_9·	73.2	87.3	115.8	*b*
	85.3	103.2	139.5	*b*
Allyl·	61.3	70.5	89.0	*b*
Benzyl·	75.0	91.4	126.5	*b*

[a] Standard state: 1 atm. [b] See text.

have been reported. They do not present any new features and will not be discussed here (see ref 124).

The pyrolysis of oxetane (trimethylene oxide) is very similar to that of cyclobutane. It is necessary to add a free-radical inhibitor (unlike for cyclobutane) in this case; otherwise there does appear to be a chain component of the reaction. The inhibited decomposition (added NO) yields ethylene and formaldehyde.[255] The Arrhenius equation is similar to that for cyclobutane, *viz.*

$$\log k\ (\text{sec}^{-1}) = 14.79 - (60{,}000/2.303RT)$$

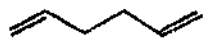
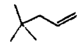
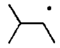
The somewhat smaller A factor is compensated by the lower energy of activation and at ~400° both molecules decompose at almost identical rates. This similarity extends to the 3,3-dimethyloxetane[256] which yields isobutylene and formaldehyde (apparently no inhibitor is required in this case) with rate constants fitting the Arrhenius equation

$$\log k\ (\text{sec}^{-1}) = 15.59 - (60{,}700/2.303RT)$$

These parameters are the same as those for 1,1-dimethylcyclobutane within experimental error as are the rates at ~400°. It seems likely that the Arrhenius parameters for oxetane may both be a little low. The implication of these comparisons is that in the oxetanes the initial rupture is of the carbon–carbon rather than the carbon–oxygen bond.

Table XVIII

Heats of Formation of Some Hydrocarbons and Hydrocarbon Radicals

Molecule	$\Delta H_f°$,[b] *kcal mole*$^{-1}$	*Ref*	*Molecule*	$\Delta H_f°$,[b] *kcal mole*$^{-1}$	*Ref*
neo-C_5H_{12}	−40.27	260	*n*-C_4H_9·	15.8	*a*
	20.0	258	sec-C_4H_9·	12.3	*a*
	−18.1	258	*i*-C_4H_9·	13.8	*a*
H·	52.1	259	*t*-C_4H_9·	6.8	4
CH_3·	34.0	4		5.5	*a*
C_2H_5·	25.7	4	Allyl·	40.6	39
n-C_3H_7·	21.1	*a*	Benzyl·	45.0	9
i-C_3H_7·	17.6	4			

[a] See text. [b]At 298°*K*.

VI. Appendix

The thermodynamic data used in this article were taken, where possible, from the API Tables.[257] Those derived from other sources are listed in Tables XVII and XVIII.[258–260]

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(255) D. A. Bittker and W. D. Walters. *J. Amer. Chem. Soc.*, 77, 1429 (1955).

(256) G. F. Cohoe, Ph.D. Thesis, University of Rochester, 1965.

(257) American Petroleum Institute Research Project No. 44, Thermodynamics Research Centre, Texas A&M University, College Station, Texas, 1953–1968.

(258) S. W. Benson, D. M. Golden, H. E. O'Neal, *et al.*, *Chem. Rev.*, in press.

(259) JANAF Thermochemical Tables, D. R. Stull, Ed., Dow Chemical Co., Midland, Mich., 1960–1967.

(260) G. Pilcher and J. D. M. Chadwick, *Trans. Faraday Soc.*, 63, 2357 (1967).

The entropies of simple alkyl radicals have been calculated by Purnell and Quinn.[5] For other radicals, entropies had to be estimated. The method involved comparison with structurally similar molecules,[5,6] and corrections were made to allow for changes of spin state, changes of symmetry, loss or gain of vibrational modes, and changes in low frequency modes (particularly hindered internal rotors). In most cases at least two different compounds were used for reference. In this way errors were kept to a minimum. The entropies are probably reliable to ±1 eu.

The heat of formation of biallyl calculated by group additivity[258] is probably more reliable than that quoted by Akers and Throssel.[30] The heats of formation of the alkyl radicals $CH_3\cdot$, $C_2H_5\cdot$, i-$C_3H_7\cdot$, and t-$C_4H_9\cdot$ are those recommended by Kerr.[4] They have been determined independently by kinetic studies of both bromination and iodination reactions.[4] The remaining alkyl radical heats of formation are based on the assumption that primary, secondary, and tertiary bond dissociation energies are 98.0, 94.5, and 91.0 kcal mole^{-1}, respectively.[4]

In using these data to estimate $\Delta S°$ and $\Delta H°$ at the required temperatures, allowance was made for temperature variations by use of the formulas

$$\Delta H°_T = \Delta H°_{300} + \overline{\Delta C_p}°(T - 300)$$

$$\Delta S°_T = \Delta S°_{300} + \overline{\Delta C_p}° \ln \frac{T}{300}$$

These are approximate relationships but should be reliable when $\overline{\Delta C_p}°$ is small, which was the case for all the reactions considered. A further simplification to avoid estimations of unknown $C_p°$ values was to eliminate $\overline{\Delta C_p}°$ between these two equations. Temperature corrections for $\Delta H°$ are then simply calculated from those for $\Delta S°$.

To relate forward and reverse rate constants in the quoted units (section 1), these $\Delta S°$ and $\Delta H°$ values have to be converted to the standard state of 1. mole^{-1}. The formulas, which are not always correctly quoted, for doing this are

$$\Delta S° \text{ (1 l. mole}^{-1}) = \Delta S° \text{ (1 atm)} - R\,(1 + \ln [0.0821T])$$

$$\Delta H° \text{ (1 l. mole}^{-1}) = \Delta H° \text{ (1 atm)} - RT$$

where $R = 1.987$ cal mole^{-1} deg^{-1}.