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Some Aspects of the Kinetics of Molecular Reactions

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Experimental data on the kinetics of elementary gas-phase reactions undergone by molecules are reviewed. The classification of reactions is discussed on the basis of the structure of activated complexes. Reaction mechanisms of various types are analysed in detail. The activation energy is shown to be determined additively mainly by activated bonds: the presence of substituents, which play no direct part in the reaction, has little effect on the activation energy. An analysis is made of the effect of conjugated and cumulative π-bonds in the activated complex on the activation energy. Conjugation and cumulation substantially lower the potential barrier to reaction. A list of 206 references is included.

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I. INTRODUCTION

In the present paper the term "molecular reactions" will imply those elementary reactions where the initial systems and products contain only *molecules*—not atoms, radicals, or biradicals.

Investigations of molecular reactions occupy an important place among the numerous papers on the kinetics of elementary reactions which have been published to date. Nevertheless, these results have not been summarised and systematised to the same extent as has been done for the reactions of atoms and radicals. The reasons for this are the considerably greater qualitative diversity of elementary molecular reactions and the far less complete theoretical study that has been made of them because of their greater complexity.

Actually, in the commonest and most thoroughly studied radical substitutions of the type $R + R'X \rightarrow RX + R'$ only one chemical bond is broken, and the transition state has an extremely simple structure. In thermal decompositions of molecules into two atoms or radicals, of the type $R-R' \rightarrow R + R'$, too, only one chemical bond is broken, while the potential barrier to reaction is given by the energy of rupture of the bond R–R'. Radical reactions of this type have been the subject of quite full theoretical study.

A characteristic feature of molecular reactions is that they involve the cleavage of more than one chemical bond, while the activated complex has a more complicated structure. Nevertheless, kinetic investigations of molecular reactions are usually made on a particular restricted class of reactions, and very little attempt has been made to establish an interrelationship between and general laws for the kinetics of molecular reactions belonging to different classes.

The present Review represents an attempt to summarise, analyse, and systematise published information on the kinetics of molecular reactions, the starting point being the additive method for calculating the activation energies of chemical reactions which I have developed[1].

II. CLASSIFICATION OF REACTIONS

A rational classification of elementary reactions is of paramount importance for the analysis and generalisation of kinetic data. It is advisable to base such a classification on the structure of the activated complexes, which reflects most profoundly all the fundamental kinetic features of the reactions.

Szabó[2] worked out a possible classification based on the structure of the activated complexes. It contains a total of 23 different types of reactions and the same number of empirical coefficients for calculating the activation energy. A fundamental defect of this classification is that in many cases forward and reverse reactions are of different types, in spite of the obvious identity of the corresponding activated complexes. As a consequence, the difference between the activation energies of forward and reverse reactions, calculated by Szabó's method, is not in general equal to the heat of reaction, as it should be in reality.

The classification of chemical reactions which I have proposed is also based on the most fundamental features of the structure of the corresponding activated complexes. As before[1] an activated complex is regarded as a molecule whose atoms are combined with one another not by chemical but by weaker, "activated" bonds. Since each activated bond corresponds to a definite chemical bond in the initial system or in the reaction products, the number of activated bonds is given by the sum of the numbers of chemical bonds cleaved N_{cl} and formed N_f:

$$N^{\neq} = N_{cl} + N_f.$$

Table 1 lists the main types of activated complexes. An activated complex of any type is the same for forward and reverse reactions. The only difference between the latter is that formed and cleaved bonds interchange roles. Other activated complexes are also possible, e.g. seven-membered, eight-membered, etc. complexes. However, these are encountered considerably more rarely in the reactions under investigation. This classification covers not only molecular but also radical and biradical reactions.

Analysis of numerous experimental data on the mechanisms of reactions whose molecular character has been established shows that they nearly all involve the formation of either four-membered or six-membered activated complexes†.

† Except for *cis–trans* isomerisations involving an activated complex having $N^{\neq} = 1$. For the mechanism of these reactions see Section IV, 1.

In cases in which the reaction mechanism cannot be represented by the above complexes, there are usually sound reasons for supposing that the reaction is not elementary, but passes through several stages (not excluding the intermediate formation of radicals, for example).

Table 1. Classification of activated complexes.

$N^{\neq}$	N_{cl}	N_f	Structure of activated complex
1	1 0	0 1	A...B
2	1	1	A...B...C
3	2	1	A···B...C...D
	1	2	A...B ·C·
4	2	2	A...B D...C
5	3	2	A...B E·C ·D·
	2	3	
6	3	3	A...B F C E...D

Table 2. Mean energies of bonds in molecules (Q) and in activated complexes ($Q^{\neq}$) at 0°K (kcal)*.

Bond	Q, kcal	$Q^{\neq}$, kcal
H—H	103	48
C—H	99	45
σ-C—C (in alkanes)	79	28
π-C—C (in alkenes)	61	17
π-C—C (in acetylene)	56	9
σ-C—O	80	27
π-C—O (in aldehydes and ketones)	88	18
π-C—O (in acids)	124	45
O—H	105	55
σ-C—N	66	11
N—H	92	25
C_{prim}—Cl	76	18
C_{sec}—Cl	76	25
C_{tert}—Cl	76	32
C_{prim}—Br	63	16
C_{sec}—Br	63	21
C_{tert}—Br	63	26
C_{prim}—I	47	8
C_{sec}—I	47	16
C_{tert}—I	47	24
H—Cl	102	40
H—Br	87	33
H—I	70	23

* Here and subsequently we shall for brevity write "kcal" instead of "kcal mole^{-1}".

Note. Correction for conjugation $\Delta Q^{\neq}_{conj} = 12$ kcal; correction for cumulation $\Delta Q^{\neq}_{cum} = 8$ kcal.

An important characteristic of activated bonds is that their mean energy is about the same in different activated complexes. Table 2 gives values of mean bond energies in molecules and activated complexes, from which it is easy to calculate the activation energy of a chemical reaction by means of the additive principle

$$E = \Sigma Q - \Sigma Q^{\neq} \qquad (1)$$

where Q and $Q^{\neq}$ are the mean energies of a bond in a molecule and in an activated complex respectively.

A more detailed account of the method of calculation will be found in the previous review[1]. Table 2 has been somewhat expanded and refined in comparison with the corresponding previous table[1]; in particular, the bond energies for nitrogen have been added, and also a correction $\Delta Q^{\neq}_{cum}$ for the effect of the cumulation of three or more π-bonds in a chain.

If a reaction involves cleavage of cyclic bonds, one energy of rupture of a carbon–carbon bond in the ring (50, 60, and 72 kcal respectively for cyclopropane, cyclobutane, and cyclopentane) is substituted in Eqn. (1) and also the corresponding energy of an activated bond (4, 12, and 22 kcal for the same rings).[1]

Before surveying published information, we must comment on experimental methods for studying the kinetics of molecular reactions.

III. METHODS OF STUDYING THE KINETICS OF MOLECULAR REACTIONS

In principle the determination of the rate constants of molecular reactions is considerably simpler than of radical or ionic reactions, since the concentrations of all the species involved can easily be measured. Nevertheless, methods for the study of molecular reactions have several peculiarities, associated not so much with determining the rate constants as with proving that the measured constants do relate to the given elementary processes. The reaction under investigation is sometimes complicated by several side-reactions, and this makes an unambiguous interpretation of the results considerably more difficult. The complications met most frequently are due to the occurrence of heterogeneous and radical-chain processes.

Heterogeneous Reactions

Many molecular decompositions and isomerisations are extraordinarily sensitive to the condition of the walls of the reaction vessel. The effect of the walls on reaction velocity may have several causes. The first possibility to be borne in mind is heterogeneous catalysis of the reaction by the walls. Such reactions as hydrogenation and dehydrogenation, for example, can easily be catalysed by various surfaces, especially metallic surfaces. Apparently the wall also catalyses the decomposition of certain alkyl halides (e.g. ethyl chloride[3,5]). In several cases the rates of the homogeneous reaction and of the catalytic reaction on the wall are comparable. In other cases the reaction takes place almost solely on the wall (e.g. the decomposition of ammonia[4]).

The relative rates of homogeneous and heterogeneous (catalytic) reactions is determined by several factors, including the nature and the state of the surface, the ratio of the surface area of the vessel to its volume S/V, and the experimental conditions (temperature and pressure). Heterogeneous catalytic decompositions usually have lower activation energies than the homogeneous reactions, so that the relative contribution of the heterogeneous reaction diminishes with rise in temperature.

In the kinetic study of molecular reactions the occurrence of heterogeneous reactions is usually detected by making experiments at different S/V ratios, and also by special treatment of the surface of the reaction vessel.

The latter effect is often achieved by "aging", i.e. by making a large number of experiments in the same vessel. This quite often improves the reproducibility of the results. "Aging" is explained by the appearance on the walls of a thin film of carbon deposits, which are inert towards the given reaction.

Heterogeneous reactions can be entirely eliminated by a special technique[5] for studying the kinetics of first-order reactions in a stream of an inert gas, which completely prevents reactant molecules from striking the walls of the reaction vessel. In this technique the reaction is conducted under streamline flow conditions in the initial (diffusion) portion of the zone in which a current of the reactant mixes with an accompanying coaxial flow of the inert gas. By this means kinetic measurements are made only on the homogeneous reaction.

Heterogeneous reactions can be eliminated also by means of a shock tube, which has recently become widely used. In this method a detonation wave effects rapid heating of the initial gaseous mixture, while the walls of the vessel remain cold.

Radical-Chain Processes

Molecular reactions are often complicated also by radical-chain processes, and therefore methods for the detection and suppression of radical reactions are of primary value. The most convincing evidence for the participation of free atoms and radicals in a reaction is their direct detection and measurement of their concentrations. Various physical and chemical methods (electron spin resonance, mass spectrometry, the mirror technique, etc.) are used for this purpose. In the study of molecular reactions, however, it is not so important to detect radicals as to prove their absence. This is a more complicated task, since a failure to detect radicals still does not mean that there are absolutely none in the system. Nevertheless, the inhibition method, consisting in adding substances which can react readily with radicals and thereby remove them from the system, has become widely used for assessing the possible part played by radical processes. The most frequently used inhibitors are nitric oxide, propene, toluene, and cyclohexene. If the rate of a reaction is not affected by the addition of inhibitors, this is regarded as an argument in support of its molecular character. Even when an inhibiting effect is present, it is sometimes considered that the "residual" inhibited reaction is molecular, since secondary radical processes are then completely suppressed.

To ascertain the possible effect of heterogeneous and radical processes on the kinetics and the mechanism of molecular reactions it is now standard practice to conduct experiments at various S/V ratios and also with additions of inhibitors, and if no appreciable change in reaction velocity is detected, it can be more or less confidently stated that the reaction is molecular.

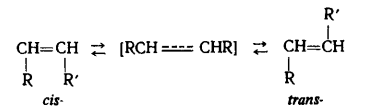
Careful analysis of the reaction products and the use of isotopes are extremely useful in the detection of radical processes. When radicals are present, many secondary products are usually formed. If, however, the reaction is conducted in a mixture, say of an undeuteriated and a completely deuteriated reactant, radical reactions will yield partly deuteriated products. In the absence of free radicals the products of the reaction should be either undeuteriated or completely deuteriated compounds. This method is applicable, of course, only to decompositions and isomerisations, and only if no deuterium exchange takes place either between molecules of the initial reactant or between molecules of the reaction products.

However, it must be borne in mind that short-lived biradicals can sometimes take part in a reaction, these being able to isomerise into molecules in a time less than that between collisions. In this case attempts to detect such biradicals by means of inhibitors will be unsuccessful, but this does not prove their absence. Additional difficulties are thereby created for the experimental investigation of the reaction mechanism. Determining the stereochemical structure of the reaction products may prove of some assistance here, since molecular reactions, unlike radical reactions, are usually stereospecific.

IV. ANALYSIS OF EXPERIMENTAL DATA

1. *cis–trans*-Isomerisation of Ethylenic Compounds

The *cis–trans* isomerisation of ethylenic compounds is the only example of a molecular reaction whose activated complex contains a single activated bond:



cis- *trans-*

The activation energy of reactions of this type, calculated additively, is

$$E = Q_{\pi\text{-C=C}} - Q^{\neq}_{\pi\text{-C=C}} = 61-17=44 \text{ kcal} .$$

Certain existing experimental values would appear to agree fairly well with this calculation, as can be seen from Table 3.

Table 3. Experimental values of the activation energy and of the logarithms of the pre-exponential factor for the *cis–trans* isomerisation of alkenes.

Alkene	Reaction	lg$A$*	E, kcal	Ref.
CHD=CHD	*cis* → *trans*	13.00	65.0	11
CHCl=CHCl	*trans* → *cis*	12.70	42.0	6
CHCl=CHCl	*trans* → *cis*	12.68	55.3	9
CHCl=CHCl	*cis* → *trans*	12.76	56.0	9
$CH_3CH=CHCH_3$	*cis* → *trans*	13.78	62.8	15
$CH_3CH=CHCH_3$	*cis* → *trans*	11.00	52.0	14
$CH_3CH=CHCH_3$	*cis* → *trans*	14.54	65.0	18
$CH_3CH=CHCH_3$	*cis* → *trans*	14.00	64.2	16
$CF_3CF=CFCF_3$	*cis* → *trans*	13.53	56.4	20
p-$CH_3OC_6H_4CH=CHC_6H_5$	*cis* → *trans*	10.23	35.5	22
p-NO_2—$C_6H_4CH=CHC_6H_5$	*cis* → *trans*	10.23	34.0	22
$C_6H_5CH=CHCOOCH_3$	*cis* → *trans*	10.54	41.6	21
$C_6H_5CH=CHCN$	*cis* → *trans*	11.60	46.0	23
$C_6H_5CH=CHCN$	*trans* → *cis*	11.80	46.0	23
$C_6H_5CH=CHC_6H_5$	*cis* → *trans*	12.78	42.8	24
$CH_3CH=CHCOOCH_3$	*cis* → *trans*	13.20	57.8	70
$CH_3CH=CHCN$	*cis* → *trans*	11.00	51.3	71

* Here and subsequently the units of A are s^{-1} and cm^3 $mole^{-1}$ s^{-1} for first-order and second-order reactions respectively.

However, careful analysis shows that the matter is complicated by several secondary factors, which throw doubt on the reliability of the results. It has recently become obvious that many *cis–trans* isomerisations, which have previously been regarded as unimolecular homogeneous reactions, are actually initiated by free radicals or are heterogeneous.

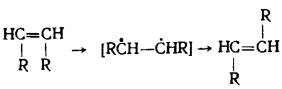
An example of such a reaction is the isomerisation of 1,2-dichloroethylene. In this case it was discovered[6] that, in order to obtain reproducible results, the reaction vessel had to be "aged", but even in an "old" vessel the reproducibility of the rate constant rarely became better than 50%.[7] A considerable departure from the first order was found[8] during the first 5 min of an experiment. The reaction velocity depends also on the surface–volume ratio S/V of the reaction vessel[9]. Finally, Steel[10] showed that the isomerisation of 1,2-dichloroethylene is strongly inhibited by toluene and propene, so that it is a radical-chain reaction. The isomerisation rate constant has been measured[9] in excess of toluene. This constant, when extrapolated to $S/V = 0$, is ascribed to a true unimolecular reaction, the activation energy then being 56 kcal.

The above complications explain the contradictions in published experimental results, and prevent an unambiguous conclusion from being drawn on the reaction mechanism.

A similar situation is found in the isomerisation of dideuterioethylene. The rate of this reaction depends[11] on the surface area of the reaction vessel, and increases on the addition of oxygen, ethanethiol, azomethane, and nitric oxide. The first-order rate constant increases with pressure over a wide range (9–312 mmHg). The activation energy at $p = \infty$ is 65 kcal. The isomerisation of dideuterioethylene in the presence of nitric oxide is of the first order with respect to the latter, and the activation energy is 27.5 kcal[12].

Many investigators have studied the *cis–trans* isomerisation of but-2-ene. In 1936 Kistiakowsky and Smith found[13] that the activation energy of this reaction had the unexpectedly low value of $E = 18$ kcal, which was difficult to explain. Later measurements by Anderson et al.[14], who used an improved method, gave a value of 52 kcal. In these experiments (over the pressure range 200–400 mmHg) some increase in pressure was observed during the reaction, probably caused by secondary reactions. Rabinovitch and Michel[15] found that, at pressures exceeding 10 mmHg, the reaction was complicated in character (autocatalytic) and sensitive to additions of oxygen, azomethane, and propene. Below this pressure, however, isomerisation was regarded[15] as unimolecular with an activation energy of 62.8 kcal. Other authors[16,17] have reached similar conclusions. The kinetics of the isomerisation of but-2-ene has been studied also at considerably higher temperatures in a shock tube[18]. On extrapolating the early results[16,17] to the conditions of their own experiments, these workers found[18] the activation energy to be 65 kcal.

Thus at present the mechanism of *cis–trans* isomerisations cannot be regarded as finally established. Complications due to the occurrence of heterogeneous reactions and the possible influence of free radicals, observed by several workers, compel a very cautious approach to the expressions obtained for the isomerisation rate constants. If recent results are correct, the activation energies of *cis–trans* isomerisations will be larger than those assumed earlier. These quantities are close to the mean energy of the π-C=C bond in alkenes, and it may therefore be supposed that isomerisation is accompanied by the formation of an unstable biradical intermediate:



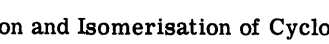
This possibility had been pointed out earlier by Kondrat'ev[19]. The intermediate biradical is in a singlet state, so that the reaction takes place without change in the multiplicity, as is indicated by the "normal" values of the pre-exponential factors.

With this reaction mechanism *cis–trans* isomerisation by definition is not a molecular reaction, and its consideration is in general outside the scope of the present review. Nevertheless, certain other reactions are discussed, where the mechanism is also a matter of controversy.

2. Decomposition and Isomerisation of Cyclobutanes

Two types of chemical changes—(1) decomposition into two alkene molecules and (2) *cis–trans* isomerisation—are possible in the case of cyclobutane derivatives.

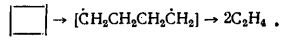
If the decomposition of cyclobutane is a single-stage unimolecular reaction, the structure of the corresponding activated complex can be represented



This involves the cleavage of two σ-C=C bonds in the four-membered ring, with the formation of two π-C=C bonds. The additive activation energy of this reaction is $E = 60 + 79 - (12 + 28 + 2 \times 17) = 65$ kcal, which agrees with most of the experimental results in Table 4.

However, we have tacitly assumed that activated π-bonds are not conjugated, and we have not introduced appropriate corrections. This can be justified by the fact that the decrease in energy of the system resulting from conjugation is to a considerable extent balanced by the increase due to the high deformation energy for the four-membered ring. Indeed, the deformation energy in cyclobutadiene, for example, is so large that this compound is probably absolutely unstable, and all attempts at its synthesis have failed.

A single-stage mechanism is supported by the fact that the rate of this reaction depends neither on the surface–volume ratio S/V nor on additions of inhibitors of radical reactions. Nevertheless, several workers assume that the decomposition of cyclobutanes takes place in two stages, with the intermediate formation of an unstable biradical:

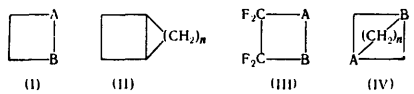


If the first stage is rate-determining, the activation energy should be equal to the energy of rupture of a carbon–carbon bond in cyclobutane, i.e. 60 kcal. This value is also close to experimental values of the activation energy.

It is therefore difficult to draw a final conclusion on the mechanism of the reaction. However, interesting work[25,26] on the decomposition and isomerisation of *cis-* and *trans-*1,2-dimethylcyclobutanes shows that, if an intermediate biradical is formed, its decomposition is more rapid than rotation about the carbon–carbon bond. Indeed, this work has revealed firstly that the rate of *cis–trans* isomerisation of cyclobutane is far lower than its rate of decomposition, although the activation energy of isomerisation is also rather smaller; and secondly that, in the decomposition of 1,2-dimethylcyclobutanes with the formation of but-2-ene and ethylene, non-equilibrium proportions of the *cis-* and *trans-*isomers are formed, the butene which corresponds in configuration to the original cyclobutane always being produced preferentially. These facts undoubtedly suggest that the lifetime of the hypothetical biradical is extremely short, probably shorter than the time of rotation about the carbon–carbon bond. Experimental data on the kinetics of the *cis–trans* isomerisation of cyclobutanes are listed in Table 5.

It is interesting also to note the appreciable differences in decomposition kinetics between cyclobutane and its derivatives containing a double bond in the β-position relative to the ring: the activation energy of decomposition of the latter is about 12 kcal smaller than that of cyclobutane.

Table 4. Kinetic data on the decomposition of cyclobutane and its derivatives (I)–(IV).



(I) (II) (III) (IV)

Compound type	A	B	n	Reaction products	lgA	E, kcal	Ref.
I	CH_2	CH_2	—	$2C_2H_5$	15.60	62.5	31
I	CH_2	$CHCH_3$	—	$C_2H_4+C_3H_6$	15.38	61.2	32
I	CH_2	$CHCH_3$	—	$C_2H_4+C_3H_6$	15.64	62.0	33
cis-I	$CHCH_3$	$CHCH_3$	—	$2C_3H_6$	15.48	60.4	25
cis-I	»	$CHCH_3$	—	$C_2H_4+CH_3CH=CHCH_3$	15.57	63.0	25
trans-I	$CHCH_3$	$CHCH_3$	—	$2C_3H_6$	15.45	61.6	26
trans-I	»	$CHCH_3$	—	$C_2H_4+CH_3CH=CHCH_3$	15.46	63.4	26
I	CH_2	CHC_2H_5	—	$C_2H_4+CH_2=CHC_2H_5$	15.56	62.0	34
I	CH_2	$CHCH(CH_3)_2$	—	$C_2H_4+CH_2=CHCH(CH_3)_2$	15.63	62.6	35
I	CH_2	CHC_3H_7-n	—	$C_2H_4+CH_2=CHC_3H_7$-n	15.53	61.6	36
I	CH_2	$CHC(CH_3)=CH_2$	—	$C_2H_4+CH_2=CHC(CH_3)=CH_2$	14.64	51.0	28
I	CH_2	$C=CH_2$	—	$C_2H_4+CH_2=C=CH_2$	15.68	63.3	40
I	CH_2	$C=CH_2$	—	$C_2H_4+CH_2=C=CH_2$	15.09	61.5	41
I	CH_2	$C=O$	—	$C_2H_4+CH_2=C=O$	14.56	52.0	23
I	CH_2	$CHCHO$	—	$C_2H_4+CH_2=CHCHO$	14.43	53.3	44
I	CH_2	$CHCOCH_3$	—	$C_2H_4+CH_2=CHCOCH_3$	14.53	54.5	45
I	CH_2	$CHCOC_2H_5$	—	$C_2H_4+CH_2=CHCOC_2H_5$	14.50	54.2	46
I	CH_2	$CHCOOCH_3$	—	$C_2H_4+CH_2=CHCOOCH_3$	14.84	57.3	47
II	—	—	2	$CH_2=CH(CH_2)_2CH=CH_2$	15.40	36.0	37
II	—	—	3	C_3H_4+ cyclo-C_5H_8	14.84	60.7	38
II	—	—	3	$CH_2=CH(CH_2)_3CH=CH_2$	15.40	64.0	38
III	CF_2	CF_2	—	$2C_2F_4$	16.00	73.3	48
III	CF_2	CF_2	—	$2C_2F_4$	15.95	74.1	49
		reverse reaction			10.40	24.0	48
		ditto			11.22	26.3	50
		»			11.01	25.4	51
cis-III	CFCl	CFCl		$2C_2F_3Cl$	15.50	69.3	52
trans-III	CFCl	CFCl		$2C_2F_3Cl$	15.09	65.3	52
		reverse reaction			10.63	26.6	52
	reaction	$C_2F_3+C_2F_4\rightarrow$III,	A=CF_2,	B=CFCl	10.93	26.3	50
cis-III	$CFCF_3$	$CFCF_3$		$2C_3F_6$	15.36	64.2	53
trans-III	$CFCF_3$	$CFCF_3$		$2C_3F_6$	15.77	64.2	53
IV	CH	CH	0	$CH_2=CHCH=CH_2$	14.02	40.58	56
IV	CCH_3	CCH_3	0	$CH_2=C(CH)_3C(CH_3)=CH_2$	14.45	43.3	42
IV	CH	CH	2	$CH_2=CH(CH_2)_2CH=CH_2$	15.17	55.0	54
					12.81	33.5	39
					15.51	55.9	55

Table 5. Kinetic data on the *cis–trans* isomerisation of the cyclobutane derivatives (I) and (III)*.

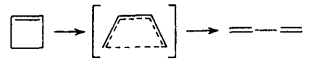
Compound	Reaction	lg A	E, kcal	Ref.
I, A=B=$CHCH_3$	*cis* → *trans*	14.81	60.1	25
ditto	*trans* → *cis*	14.57	61.3	26
III, A=B=$CFCF_3$	*cis* → *trans*	15.36	64.2	53
ditto	*trans* → *cis*	15.77	64.2	53
III, A=B=CFCl	*trans* → *cis*	15.10	60.1	52
ditto	*cis* → *trans*	14.86	60.2	52

* See Table 4.

With a biradical mechanism this decrease in the activation energy of decomposition is attributed to the resonance (stabilisation) energy of an allylic radical $\cdot CH_2CH_2CH_2\dot{C}HCH:CH_2$.[27,28] However, this energy is considerably smaller than for allyl itself $CH_2:CH.CH_2\cdot$, where it is 22 kcal‡.

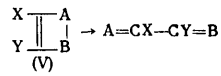
3. Isomerisation of Cyclobutenes

The isomerisation of cyclobutene and its derivatives into dienes has been studied in detail by Frey and Walters[56–65]. These are first-order reactions, and their rate is affected neither by change in the surface–volume ratio nor by additions of inhibitors. The view that these are true unimolecular reactions is entirely justified. Isomerisation involves the cleavage of one C–C bond in the four-membered ring and one π-bond, while three (activated) cumulative π-bonds and one σ-bond are formed:



The additive activation energy of this reaction is $E = 60 + 61 - (12 + 3 \times 17 + 3 \times 8) = 34$ kcal.

Table 6. Kinetic data on the isomerisation of cyclobutenes (V).



(V)

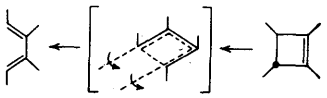
X	Y	A	B	lgA	E, kcal	Ref.
H	H	CH_2	CH_2	13.08	32.5	57
—	—	—	—	13.26	32.7	58
CH_3	H	CH_2	CH_2	13.79	35.1	59
CH_3	CH_3	CH_2	CH_2	13.84	36.04	60
CH_3	H	CH_2	$CHCH_3$	13.65	33.0	61
CH_3	H	$CHCH_3$	CH_2	13.52	33.39	61
H	H	CH_2	$C(CH_3)_2$	13.93	36.09	62
CH_3	H	CH_2	$C(CH_3)_2$	13.90	37.03	62
H	H	$CHCH_3$	CH_2	13.53	31.55	63
H	C_2H_5	CH_2	CH_2	13.76	34.83	65
CH_3	CH_3	$CHCH_3$	$CHCH_3$	13.85 (*trans*-)	33.59 (*trans*-)	64
—	—	—	—	14.10 (*cis*-)	37.36 (*cis*-)	64
F	F	CF_2	CF_2	14.12	47.08	66
		reverse reaction		12.03	35.38	66
				14.31	45.51	67
				14.13	43.18	64
				14.00	39.5	69

This value shows excellent agreement with available experimental data (Table 6), except for the reactions of dicyclic compounds and perfluorocyclobutene, the activation energies of which are 10–13 kcal higher. In the case perfluorocyclobutene the presence of fluorine atoms probably greatly affects the energies of the bonds in the molecule. Such deviation from a simple additive scheme is a

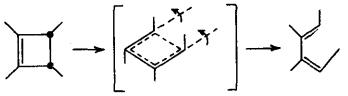
‡ The stabilisation energy of a radical can be estimated as the difference between the mean energy and the energy of rupture of a carbon–hydrogen bond in the molecule[29]. For propene this will give[30] $E_{stab} = 99 - 77 = 22$ kcal.

general phenomenon in the reactions of perfluorinated compounds, which requires the introduction of appropriate corrections into the scheme.

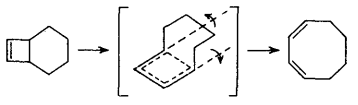
Special interest attaches to the isomerisation of dicyclic compounds, where the departure from additivity is due to the peculiar stereochemistry of the process. In fact the isomerisation of substituted cyclobutenes involves rotation of the terminal groups formed, where "unidirectional" rotation (the *conrotatory* process) is energetically more favourable. Thus, *trans*-1,2,3,4-tetramethylcyclobutene yields 3,4-dimethylhexa-*trans*-2,*trans*-4-diene:



whereas, *cis*-1,2,3,4-tetramethylcyclobutene gives 3,4-dimethylhexa-*cis*-2,*trans*-4-diene[64]:



In dicyclic molecules, however, such unidirectional rotation is impossible, and isomerisation is accompanied by rotation in the opposite direction (*disrotatory* process)[64]:



Since "opposite" rotation is energetically less favourable, the activation energy is appreciably higher in these cases.

There is a qualitative quantum-mechanical explanation of these peculiarities in terms of the symmetry of the molecular orbitals of the electrons taking part in the reaction[68]. In a conrotatory process two σ-electrons and two π-electrons of the initial molecule pass into the two lowest orbitals ψ_1 and ψ_2 of the resulting butadiene:

$$\sigma^2\pi^2 \rightarrow \psi_1^2\psi_2^2.$$

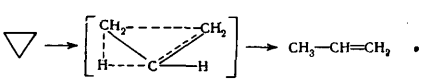
With a disrotatory process two of these electrons should pass into a higher level ψ_3 in order to maintain the symmetry of the orbitals:

$$\sigma^2\pi^2 \rightarrow \psi_1^2\psi_3^2 \ .$$

Thus the departure from additivity in the isomerisation of dicyclic molecules finds a simple explanation in the method of molecular orbitals.

4. Isomerisation of Cyclopropanes

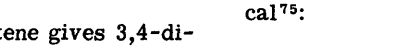
Two types of isomerisation—structural isomerisation with the formation of alkenes and geometrical *cis–trans* isomerisation—occur in cyclopropane and its derivatives, as also in cyclobutane. A theoretical treatment of and kinetic data on the structural isomerisation of cyclopropanes into alkenes will be found in several papers[72-92,202]. Two mechanisms have been suggested for this reaction. Smith[72] suggested that isomerisation involves formation of a transition state containing five atoms in the same plane:



An alternative mechanism, with intermediate formation of the short-lived biradical trimethylene, was put forward by Rabinovitch et al.[73]:

Additive calculation of the activation energy of isomerisation and also several other arguments[74,81] tip the balance in favour of the biradical mechanism of isomerisation. In fact the calculated activation energy for the first mechanism $E = 50 + 99 - (4 + 2 \times 45 + 17) = 38$ kcal differs markedly from the experimental value of 65 kcal. This implies that the reaction does not take place by the first mechanism.

The scheme proposed by Rabinovitch for the alternative biradical mechanism must be supplemented by reaction *2*, the reverse reaction to formation of the trimethylene radical[75]:



The isomerisation rate constant for this extended mechanism is $k = k_1k_3/(k_2 + k_3)$, where k_1, k_2, and k_3 are the rate constants of the corresponding reactions. When $k_3 \ll k_2$, we have $k \simeq k_3k_1/k_2 = k_3K_{eq}$, where K_{eq} is the equilibrium constant for the formation of trimethylene from cyclopropane. According to Benson[75]

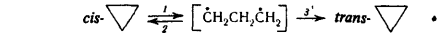
$$k_1 = 10^{16.0}\exp(-64200/RT)$$

$$k_2 = 10^{13.0}\exp(-8200/RT)$$

$$k_3 = 10^{13.2}\exp(-9500/RT) \ .$$

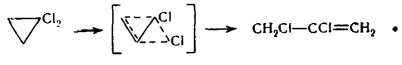
The expression for k_1 was obtained on the assumption that the rate of reaction *1* was equal to the rate of geometrical isomerisation of cyclopropane.

Rabinovitch and his coworkers found[73] that the rate of geometrical isomerisation of dideuteriocyclopropane exceeded its rate of structural isomerisation about sixteenfold. This is perfectly understandable when it is remembered that the intermediate trimethylene biradical is common to the two reactions:



Comparison of data on the kinetics of the geometrical isomerisation of cyclopropanes (Table 8) with those on the structural isomerisation of the same compounds (Table 7) shows that the activation energy of *cis–trans* isomerisation is the lower. This is due to the lower potential barrier to internal rotation in the biradical than to its isomerisation into propene. Hence in this case $k_3' \gg k_2$ and $k_{geom} = k_1k_3'/(k_2 + k_3') \simeq k_1$, in agreement with Benson's conclusions[75].

It is interesting that 1,1-dichlorocyclopropane isomerises into 2,3-dichloropropene with migration of a chlorine atom, not of a hydrogen atom[76]:



From the experimental results the authors[76] conclude that this reaction has a single-stage mechanism with an activation energy of 57.8 kcal, which agrees with the additive value of 55 kcal.

5. Isomerisation of Vinylcyclopropanes

A peculiar type of isomerisation with expansion of the ring is observed with compounds containing a C=C double bond in the β-position to the ring. The simplest compound

of this type is vinylcyclopropane, which isomerises into cyclopentene:

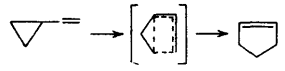
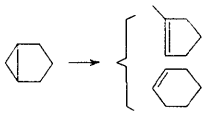
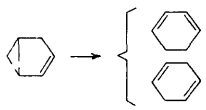
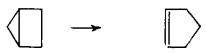


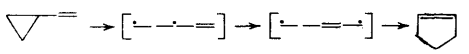
Table 7. Kinetic data on the structural isomerisation of cyclopropanes (VI).



VI A	VI B	Reaction products	lg A	E, kcal	Ref.
CH_2	CH_2	C_3H_6	15.30	65.1	77
			15.17	65.0	78
			14.84	64.2	79
			15.85	67.2	203
			15.26	65.9	204
CH_2	$CHCH_3$	C_4H_8	15.45	65.0	80
			14.46	63.2	81
CH_2	$C(CH_3)_2$	C_5H_{10}	15.05	62.6	82
$CHCH_3$ (*cis*)	$CHCH_3$ (*cis*)	*cis*-$CH_3CH{=}CHC_2H_5$	14.05	61.8	83
			13.92	61.4	84
		trans-$CH_3CH{=}CHC_2H_5$	14.13	61.8	83
			13.96	61.2	84
		$(CH_3)_2C{=}CHCH_3$	13.28	59.7	83
			14.08	62.3	84
		$CH_2{=}C(CH_3)C_2H_5$	13.21	59.6	83
			13.93	61.9	84
$CHCH_3$ (*trans*)	$CHCH_3$ (*trans*)	*cis*-$CH_3CH{=}CHC_2H_5$ *trans*-$CH_3CH{=}CHC_2H_5$	14.40	63.6	84
			14.30	62.9	84
$C(CH_3)_2$	$C(CH_3)_2$	$(CH_3)_2CHCH{=}C(CH_3)_2$	15.83	64.4	85
CHC_2H_5	CHC_2H_5	$CH_2{=}CHCH(C_2H_5)_2$	14.95	63.8	86
		$CH_3CH{=}C(C_2H_5)_2$	14.84	63.4	86
CH_2	$CHCH{=}C(CH_3)_2$	$CH_2{=}CHCH_2CH{=}C(CH_3)_2$	14.61	56.65	87
		cis-$(CH_3)_2CH{=}CHCH{=}CHCH_3$	13.33	53.0	87
		trans-$(CH_3)_2C{=}CHCH{=}CHCH_3$	13.25	52.1	87
CH_2	CHF	C_3H_5F	14.58	61.01	88
CH_2	$CHCl$	$CH_2ClCH{=}CH_2$	14.8	56.2	92
CH_2	CCl_2	$CH_2ClCCl{=}CH_2$	15.13	57.8	76
CHD	CHD	$C_3H_4D_2$	15.20	65.5	73
			15.12	65.4	204
CH_2	$CHCF_3$	$C_3H_5CF_3$	14.60	65.6	205
CH_2	$CHCH_2CF_3$	$C_4H_7CF_3$	14.38	63.6	205
			13.89	61.17	89
			13.29	57.4	89
			14.28	50.2	90
			14.09	50.2	90
			14.58	46.6	91

This reaction involves the cleavage of one π-bond and one σ-C–C bond in the three-membered ring. The additive activation energy of this reaction is $E = 50 + 61 - (4 + 17 + 17 + 22) = 51$ kcal.

Two mechanisms have been suggested for reactions of this type—via a four-membered activated complex, as indicated above[95], and a biradical mechanism involving the formation and isomerisation of a biradical[96]



The first mechanism is supported by two arguments: firstly the pre-exponential factor in these reactions is smaller by $10^{1.5-2}$ than in the isomerisation of cyclopropanes into alkenes, which involves the intermediate formation of biradicals (see subsection 4); secondly, the activation energy of the isomerisation of vinylcyclopropane into pentadienes, which has a biradical mechanism, exceeds that for the present reaction by 6–7 kcal (see Table 7).

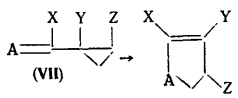
Table 8. Kinetic data on the geometric isomerisation of cyclopropanes (VI). *cis*-VI → *trans*-VI

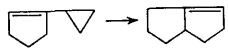
VI A	VI B	lg A	E, kcal	Ref.
CHD	CHD	16.00	64.2	73
$CHCH_3$	$CHCH_3$	15.25	59.4	83
CHC_2H_5	$CHCH_3$	15.08	58.9	93
1,2,3-trimethylcyclopropane		15.78	60.9	94

Available experimental data (Table 9) show excellent agreement with the additive activation energy, which suggests that the reaction takes place by the first mechanism.

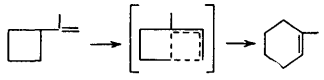
It is interesting that the activation energy of the isomerisation of perfluorovinylcyclopropane is considerably smaller because of the greater deformation energy of this compound compared with cyclopropane. It has been estimated[103] as $\Delta Q_{def} = 43–50$ kcal, compared with ~ 28 kcal in the case of cyclopropane[155].

Table 9. Kinetic data on the isomerisation of vinylcyclopropanes (VII).



VII A	X	Y	Z	lg A	E, kcal	Ref.
CH_2	H	H	H	13.61	49.7	97
$C(CH_3)_2$	H	H	H	13.50	49.6	98
CH_2	CH_3	CH_3	H	14.40	54.6	87
CH_2	H	CH_3	H	14.14	50.2	99
CH_2	CH_3	H	H	14.11	49.35	100
CHC_2H_5	H	H	H	13.89	50.9	96
CH_2	H	H	CH_3 (*trans*)	13.79	49.88	95
				13.67	48.64	101
CH_2	cyclo-C_3H_5	H	H	14.29	51.06	102
perfluorovinylcyclopropane C_5F_8				13.895	34.6	103
				14.01	51.29	102

Substituted cyclobutanes undergo analogous isomerisation with an activation energy of 51 kcal[28]:



6. Decomposition of Esters

Esters containing a carbon atom in the β-position relative to the carboxyl decompose into an acid and an alkene:

$$RCOOR' \rightarrow RCOOH + \text{Alkene}\ .$$

The activated complex of this reaction is either four-membered or six-membered:

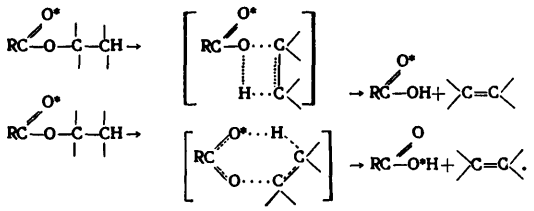


Table 10. Kinetic data on the decomposition of esters.

$$R^1-C(=O)-OR \rightarrow R^1-C(=O)-OH + >C=C<$$

R	R′	Alkene	lgA	E, kcal	Ref.
C_2H_5	H	C_2H_4	11.33	44.1	104
			11.57	44.03	105
C_2H_5	CH_3	C_2H_4	12.49	47.8	104
C_2H_5	C_2H_5	C_2H_4	12.72	48.5	106
iso-C_3H_7	H	C_2H_4	12.33	44.2	104
iso-C_3H_7	CH_3	C_2H_4	13.00	45.0	104
			12.88	44.8	206
t-C_4H_9	H	iso-C_4H_8	11.10	34.0	107
t-C_4H_9	CH_3	iso-C_4H_8	13.34	40.5	108
t-C_4H_9	C_2H_5	iso-C_4H_8	12.80	39.2	108
$C_2H_5C(CH_3)_2$	CH_3	C_5H_{10}	13.50	40.1	109
$C_6H_5CHCH_3$	CH_3	$CH_3CH=CHCH_3$	13.12	46.6	110
$CH_2=CHCH_2CHCH_3$	CH_3	$CH_2=CHCH=CHCH_3$ + $+CH_2=CHCH_2CH=CH_2$	13.00	44.4	111
$CH_3COCH_2CHCH_3$	CH_3	$CH_3COCH=CHCH_3$	11.88	37.4	111
$C_6H_5CH_2CHC_6H_5$	CH_3	$C_6H_5CH_2CH=CHC_6H_5$	13.05	43.3	112
$CH_3CHC_6H_5$	CH_3	$C_6H_5CH=CH_2$	12.81	43.7	115
C_2H_5	$(CH_3)_2C$	C_2H_4	11.24	44.0	114
$C_{27}H_{45}$ (cholesteryl)	CH_3	$C_{27}H_{44}$	12.71	44.1	113

Table 11. Kinetic data[197] on the decomposition of acetates.

$$X-C_6H_4CHCH_2C_6H_4-Y \rightarrow X-C_6H_4CH=CHC_6H_4-Y + CH_3COOH$$
$$\quad\quad\quad

8. Decomposition of Alkyl Halides

A large number of investigations have been made on the mechanism and the kinetics of the thermal decomposition of alkyl halides to form an alkene and a hydrogen halide. The study of reactions of this type is complicated by the fact that, depending on their structure, alkyl halides may decompose either by a molecular or by a chain mechanism. Summarising a large amount of experimental information, Semenov[29] concluded that a molecular mechanism of decomposition was undergone only by those alkyl halides which, having lost a hydrogen atom, were incapable, because of the peculiar structure of the molecule, of forming an alkene by elimination of the halogen atom. Furthermore, the decomposition of alkyl halides is extraordinarily sensitive to the condition of the surface of the reaction vessel[29].

Experimental determination of the rate constants of unimolecular decomposition in particular is therefore difficult. Szwarc[116] used a toluene method to determine the unimolecular decomposition constants of an alkyl bromide, on the assumption that the presence of toluene suppresses radical side-reactions. To eliminate the effect of heterogeneous reactions on the kinetics of the unimolecular decomposition of ethyl chloride, we have studied[5] the reaction kinetics in a stream of an inert gas. Comparison of the rate of decomposition under these conditions with the rate on the packing in a column also enabled the rate constant of the heterogeneous reaction to be determined.

In spite of the above difficulties, a large number of rate constants have now been determined for the elementary reactions in the decomposition of alkyl halides. In all reactions of this type a four-membered activated complex is formed:

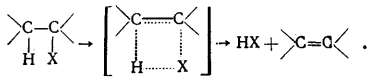


Table 13. Activation energy for the decomposition of alkyl halides (calculated). RX → HX + Alkene

Alkyl	X		
	Cl	Br	I
Primary	55	51	53
Secondary	48	46	45
Tertiary	41	41	37

Analysis of existing experimental results shows that the activation energy of these reactions is appreciably dependent on whether the halogen atom X is attached to a primary, secondary, or tertiary carbon atom. The activation energy for the decomposition of primary alkyl halides is rather higher (5–8 kcal) than for the secondary compounds, and the values for the latter are higher than for tertiary alkyl halides.

In the additive calculation of activation energy this is allowed for by the different mean energies of the activated bonds $C_{prim}...X$, $C_{sec}...X$, and $C_{tert}...X$. The influence of the immediate environment of the carbon atom on the energy of the activated bond C...X is exhibited here quite clearly. This effect is observed only with halogen atoms, and is probably caused by their great electronegativity, as a consequence of which the activated bond is strongly polar in character, approaching an ionic bond in polarity.

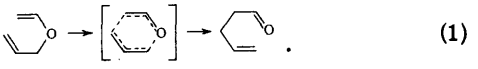
The additive activation energy for the decomposition of alkyl halides can be represented by the formula

$$E = 99 + Q_{C-X} - (45 + 17 + Q^{*}_{H-X} + Q^{*}_{C-X}) = 37 + Q_{C-X} - Q^{*}_{H-X} - Q^{*}_{C-X}.$$

Calculated activation energies for the decomposition of primary, secondary, and tertiary alkyl halides are listed in Table 13. Comparison with the numerous experimental values available (Table 14) shows good agreement with the calculated additive values.

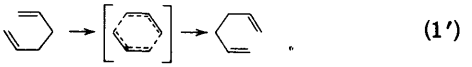
9. Claisen and Cope Rearrangements

Intramolecular rearrangements accompanied by inversion of an allyl group are widely known in organic chemistry. In the case of ethers such reactions are termed Claisen rearrangements. The reaction can be represented by the scheme



(1)

The Cope rearrangement can be represented by a similar scheme. The only difference is that here we have a carbon atom instead of the oxygen atom:



(1′)

The additive activation energies are—for the Claisen rearrangement

$$E = 2 \cdot 61 + 80 - (3 \cdot 17 + 18 + 27 + 28 + 4 \cdot 12) = 30 \text{ kcal}$$

and for the Cope rearrangement

$$E = 2 \cdot 61 + 79 - (4 \cdot 17 + 2 \cdot 28 + 4 \cdot 12) = 29 \text{ kcal}.$$

These values agree excellently with available experimental data (Table 15).

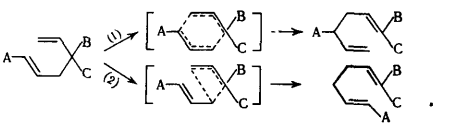
In the case of these rearrangements the experimental evidence for the structure of the activated complex, i.e. for the reaction mechanism, is quite complicated, and indeed a six-membered structure for the cyclic transition state has been confirmed only in isolated cases. Sometimes, however, the possibility is admitted[74] that a four-membered activated complex can be formed:



(2)

for the Cope rearrangement. A completely analogous scheme applies to the Claisen rearrangement.

To choose between these two mechanisms it is necessary to use a compound containing substituents attached both to the extreme carbon atom in the molecule (at position 6) and at position 3. Only in this case do reactions (1) and (2) yield products differing in structure:



The additive calculation of activation energy provides new opportunities for establishing the mechanism of a reaction. In the present case the activation energies calculated for six-membered and four-membered activated complexes differ markedly. For reaction (2), for example, the activation energy is $E = 79 + 61 - (2 \times 17 + 2 \times 28) = 50$ kcal.

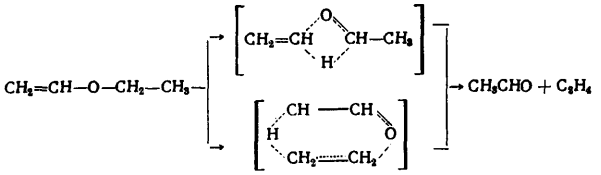
Table 14. Kinetic data on the decomposition of alkyl halides. R–X → HX + Alkene

Alkyl halide RX	lgA	E, kcal	Ref.
Ethyl chloride	13.16	56.46	117
	13.46	56.62	118
	13.45	55.00	119
	14.03	58.43	120
1-Chloropropane	13.50	55.08	121
	13.45	55.00	119
1-Chlorobutane	13.63	55.15	121
	14.00	57.00	119
1-Chloropentane	13.81	55.33	121
	14.61	58.3	122
1,6-Dichlorohexane	14.50	58.00	123
1-Chlorododecane	14.10	55.7	123
1,10-Dichlorodecane	13.35	53.0	123
2-Chloropropane	13.40	50.5	124
	13.64	51.1	117
2-Chlorobutane	13.62	49.6	126
	14.07	50.75	127
	13.75	50.1	128
3-Chloropentane	12.29	45.0	123
4-Chlorododecane	11.95	43.4	123
1,2-Dichlorohexane	13.42	50.0	123
2,5-Dichlorohexane	12.63	46.2	123
2,2-Dichloroheptane	12.80	45.0	123
5,7-Dichlorododecane	14.25	49.5	123
6,7-Dichlorododecane	13.60	49.3	123
Chlorocyclopentane	13.47	48.3	129
Chlorocyclohexane	13.50	49.2	129
2-Chloro-2-methylpropane	12.40	41.4	130
	13.73	45.0	131
	13.90	46.2	132
2-Chloro-2-methylbutane	13.82	44.2	131
2-Chloro-2,3-dimethylbutane	13.38	42.3	131
3-Chloro-3-methylheptane	12.38	38.0	123
3-Chloro-3-methylundecane	11.30	36.0	123
2-Chlorohept-1-ene	13.55	55.0	123
4-Chlorohept-3-ene	14.00	57.0	123
4-Chlorohex-2-ene	10.75	34.0	123
Ethyl bromide	13.19	53.7	117
	12.86	52.3	133
	13.25	53.7	150
	13.45	53.9	135
1-Bromopropane	12.90	50.7	140
	13.00	50.7	133
1-Bromobutane	13.18	50.9	140
1-Bromopentane	13.09	50.5	137
1-Bromohexane	13.13	50.5	137
1-Bromo-2-methylpropane	13.05	50.4	138
3-Bromopropene	12.33	45.5	139
2-Bromopropane	13.62	47.8	117
	12.60	47.7	133
	12.74	47.0	136
2-Bromobutane	12.63	43.8	141
	13.04	45.5	142
	13.53	46.5	134
3-Bromopentane	13.51	45.44	143
Bromocyclopentane	11.90	41.4	125
	12.84	43.7	145
Bromocyclohexane	13.51	46.1	146
4-Bromopent-1-ene	12.94	44.7	135
2-Bromo-2-methylpropane	13.50	41.5	132
	14.00	42.0	147
	13.23	41.0	142
2-Bromo-2-methylbutane	13.60	40.5	148
Ethyl iodide	13.36	50.0	149
	14.80	53.7	150
2-Iodopropane	14.49	48.0	154
	13.20	42.9	151
	13.67	45.1	117
	14.46	48.2	155
	12.96	43.5	152
2-Iodobutane	14.90	47.9	154
2-Iodo-2-methylpropane	12.52	36.4	153
	13.73	38.1	117

The analogous calculation for the Claisen rearrangement via a four-membered complex gives 51 kcal. These values differ by more than 20 kcal from the experimental values of the activation energy. The agreement with experiment of activation energies calculated for the six-membered complex, and the sharp divergence between the corresponding values for the four-membered complex, show quite obviously that the reaction takes place by the first mechanism.

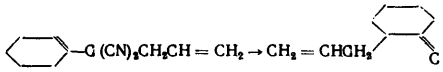
10. Decomposition of Unsaturated Ethers

Several unsaturated ethers decompose with the formation of alkenes and aldehydes. For example, ethyl vinyl ether when heated breaks down into acetaldehyde and ethylene. Two possible mechanisms—



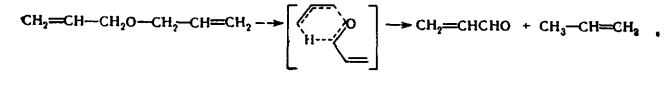
have been suggested and discussed[161,162] for this reaction. Additive calculation of the activation energy for the first mechanism, involving formation of a four-membered activated complex, gives $E = 80 + 99 - (18 + 27 + 2 \times 45) = 44$ kcal. For the second route, with formation of a six-membered activated complex, $E = 90 + 80 + 61 - (2 \times 45 + 18 + 27 + 2 \times 17 + 2 \times 12) = 47$ kcal.

Table 15. Kinetic data on allylic rearrangements.

Reaction	lgA	E, kcal	Ref.
$CH_2=CHCH_2CH_2CH=CHCH_3 \rightarrow CH_2=CHCH_2CHCH=CH_2$ (CH₃)	9.09	32.5	144
$CH_2=CHCH_2CHCH=CH_2 \rightarrow CH_2=CHCH_2CH_2CH=CHCH_3$ (CH₃)	9.84	32.5	144
$CH_2=CHCH_2C(CN)_2C=CHCH_3 \rightarrow CH_2=CHCH_2CHC=C(CN)_2$ (C₂H₅; CH₃, C₂H₅)	10.94	25.78	157
$CH_2=CHCH_2C(CO_2C_2H_5)C=CH-CH(CH_3)_2 \rightarrow CH_2=CHCH_2CHC(CH_3)=CCO_2C_2H_5$ (CN, CH₃; CH(CH₃)₂, CN)	10.36	28.62	157
	10.80	26.16	157
$CH_2=CHCH_2CH_2CH=C=CH_2 \rightarrow CH_2=CHCH_2C(=CH_2)-CH=CH_2$	9.93	28.47	158
$CH_2=CHCH_2OCH=CH_2 \rightarrow CH_3=CHCH_2CH_2CHO$	11.70	30.6	159
$CH_2=CHCH_2OC=CH_2 \rightarrow CH_2=CHCH_2CH_2COCH_3$ (CH₃)	11.37	29.3	160

Activation energies calculated for both mechanisms agree with the experimental values $E_{exp} = 42.3$–48.5 kcal (Table 16). However, analysis of the entropies of activation shows that the reaction involves formation of a six-membered complex[161]. There is also a direct experimental confirmation of this conclusion: the decomposition of isopropyl vinyl ether yields acetaldehyde and propene[163], whereas reaction involving a four-membered complex should have given ethylene and acetone.

A peculiar mechanism is observed in the decomposition of diallyl ether to form propene and acrylaldehyde[165]:



The activated complex in this case differs from the preceding one only in the relative position of the activated

bonds: therefore the calculated activation energy is also 47 kcal, which agrees satisfactorily[165] with the experimental value of 42.3 kcal.

11. Diels–Alder Reactions

Reactions of this type, which are termed also diene syntheses, are extremely important in organic chemistry and are widely used in the synthesis of various organic compounds. According to present-day ideas Diels–Alder reactions take place in a single act involving a six-membered activated complex:

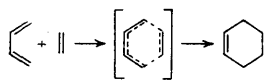
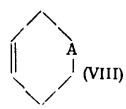


Table 16. Kinetic data on the decomposition of unsaturated ethers.

Reaction	lg A	E, kcal	Ref.
$CH_2=CHOC_2H_5 \rightarrow CH_3CHO + C_2H_4$	11.43 11.60	43.8 44.4	161 162
$CH_2=CHO\text{-iso-}C_3H_7 \rightarrow CH_3CHO + C_3H_6$	12.58	43.6	163
$CH_2=CHO\text{-n-}C_4H_9 \rightarrow CH_3CHO + C_4H_8$	11.15	42.38	164
$CH_2=CHCH_2OCH_2CH=CH_2 \rightarrow CH_2=CHCHO + C_3H_6$	11.95	42.3	165
$CH_2=CHCH_2OC_2H_5 \rightarrow CH_3CHO + C_3H_6$	12.89	48.5	165

Table 17. Kinetic data on Diels–Alder reactions.



(VIII)

Initial compounds	Reaction products	lgA	E, kcal	Ref.
$2CH_2=CHCH=CH_2$	VIII, $A=CHCH=CH_2$	11.14 9.96	26.8 23.7	166 167
VIII, $A=CHCH=CH_2$	$2CH_2=CHCH=CH_2$	15.20 15.70	62.0 61.8	168 169
$CH_2=CHCH=CH_2+C_2H_4$	VIII, $A=CH_2$	10.48	27.5	166
VIII, $A=CH_2$	$CH_2=CHCH=CH_2+C_2H_4$	15.02 15.16	66.7 66.2	168 170
$2CH_2=C(CH_3)CH=CH_2$ *	dimer	11.73 10.90	28.9 24.9	171 172
$2CH_2=CHCH=CHCH_3$	dimer	10.19	26.0	173
VIII, $A=CHCH_3$	$CH_2=CHCH=CH_2+CH_2=CHCH_3$	15.13	66.6	168
2 cyclo-C_5H_6 **	dimer	5.0–7.1	14.7–17.4	174

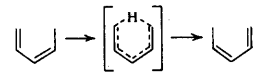
* Reaction in the liquid phase.
** Data on the kinetics of the reaction in various solvents.

All six π-electrons of the initial system are involved in the reaction. The activated complex contains four activated π-C=C bonds and two σ-C–C bonds. Three of the activated π-bonds form a cumulative chain, while one π-bond is conjugated.

Additive calculation gives a value for the activation energy of $E = 3 \times 61 - (4 \times 17 + 2 \times 28 + 3 \times 8 + 12) =$ 23 kcal, which agrees well with experimental data (Table 17). Rather larger deviations are observed with reactions in which dicyclic compounds are formed. In this case the additivity of the mean bond energies in the molecules probably breaks down.

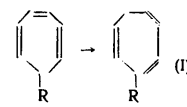
12. Diene Rearrangements

Dienes undergo an interesting type of reaction, accompanied by migration of a hydrogen atom:

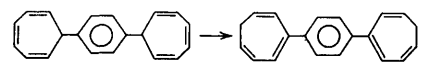


The additive activation energy of this process is $E = 2 \times 61 + 99 - (2 \times 45 + 4 \times 17 + 4 \times 8) = 31$ kcal. Here the activated complex contains two activated C–H bonds and a chain of four cumulative π-bonds. Thus the cumulation of four π-bonds must be taken into account in this case. The calculated activation energy agrees excellently with existing experimental data (Table 18).

Table 18. Kinetic data on diene rearrangements.

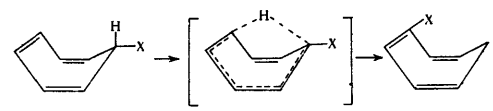


(I)

Reaction	lgA	E, kcal	Ref.
$CH_2=CHCH=CHC_2H_5 \rightarrow CH_3CH=CHCH=CHCH_3$	10.80	32.5	175
$CH_2=CCH_3CH=CHCH_3 \rightarrow CH_3CCH_3=CHCH=CH_2$	11.24	32.76	176
I, R=D	11.2	31.5	177
I, R=CH_3	12.60	33.3	178
I, R=OR′	10.04	26.4	179
I, R=C_6H_5 *	10.08	27.6	180
Cyclo-octa-1,3,6-triene → cyclo-octa-1,3,5-triene	11.74	28.9	182
$CHD_2CH=CHCH=CHD \rightarrow CD_2=CHCH=CHCH_2D$	11.45	36.3	183
	12.5	30.6	181

* Reaction in the liquid phase.

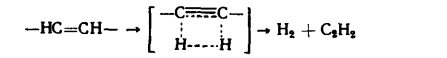
A particular type of diene rearrangement, which, however, has been most thoroughly studied, is the isomerisation of substituted cycloheptatrienes:



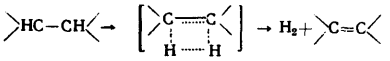
Although the structure of cycloheptatrienes differs from that of normal alkadienes, the activation energies of isomerisation are similar in the two cases. This fact yet again supports the concept underlying the additivity principle, that the energy of the transition state is determined solely by the activated bonds, while the presence of other chemical bonds, not altering in the activated complex and not involved in the reaction, has no effect on the activation energy within the limits of accuracy of the additive calculation.

13. Dehydrogenation

In most cases the dehydrogenation of molecules takes place by a chain mechanism. A classic example is the decomposition of ethane into ethylene and hydrogen. The mechanism of the dehydrogenation of ethylene with the formation of acetylene is a matter of controversy: some papers[184] assume a molecular mechanism, and others[185] a chain mechanism. The spread of experimental values for the activation energy of this reaction—from 20[186] to 86[187] kcal—is extremely wide. For the molecular mechanism

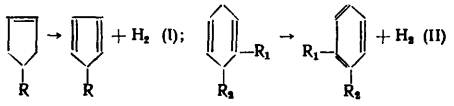


the additive activation energy is $E = 2 \times 99 - (2 \times 45 + 48 + 9) = 51$ kcal. According to the additive principle the dehydrogenation of alkanes to alkenes



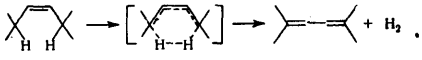
should be characterised by a lower activation energy $E = 2 \times 99 - (2 \times 45 + 48 + 17) = 43$ kcal, which agrees e.g. with data on the dehydrogenation of cyclopentane ($E_{exp} = 44$ kcal[188]).

Table 19. Kinetic data on the dehydrogenations (I) and (II).



Reaction	lgA	E, kcal	Ref.
I, R=H	13.34 13.01	59.9 58.8	189 190
I, R=O	12.72	48.5	191
II, $R_1=R_2=H$	12.36 12.02	43.8 42.7	192 90
II, $R_1=CH_3$; $R_2=H$	12.69	44.7	193
II, $R_1=H$; $R_2=CH_3$	12.47	42.95	194

Several studies have been made of the dehydrogenation of cycloalkenes, where hydrogen atoms are detached not from neighbouring carbon atoms but from those in the β-position with respect to the double bond:

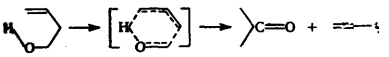


Reactions of this type are probably molecular.

Additive calculation gives for the activation energy $E = 2 \times 99 + 61 - (2 \times 45 + 48 + 3 \times 17 + 3 \times 8) = 46$ kcal, which agrees well with existing experimental results (Table 19). The data on the dehydrogenation of cyclopentene constitute an exception, and it is possible that in this case the reaction occurs partly by a chain mechanism.

14. Decomposition of Unsaturated Alcohols

In concluding this survey of experimental data let us consider the decomposition of an unsaturated alcohol into an alkene and an aldehyde or a ketone. Such decomposition has been most thoroughly studied with alcohols whose hydroxyl is in the γ-position relative to the double bond. The reaction is assumed to involve the formation of a six-membered activated complex:

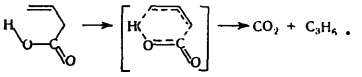


The activation energy calculated for this mechanism $E = 105 + 79 + 61 - (55 + 45 + 2 \times 17 + 28 + 18 + 2 \times 12) = 41$ kcal agrees excellently with existing experimental data (Table 20).

Table 20. Kinetic data on the decomposition of unsaturated alcohols.

Reaction	lgA	E, kcal	Ref.
$CH_2=CH(CH_2)_2OH \rightarrow H_2CO + C_3H_6$	11.65	41.0	195
$CH_2=CHCH_2CH(CH_3)OH \rightarrow CH_3CHO + C_3H_6$	11.93	40.8	195
$CH_2=CHCH_2C(CH_3)_2OH \rightarrow CH_3COCH_3 + C_3H_6$	12.14	40.7	195
$CH_2=C(C_6H_5)(CH_2)_2OH \rightarrow CH_3C(C_6H_5)=CH_2 + H_2CO$	11.80	38.9	195
$C_6H_5CH=CH(CH_2)_2OH \rightarrow C_6H_5CH_2CH=CH_2 + H_2CO$	11.58	42.8	195
$C_6H_5CH=CHCH_2C(C_2H_5)_2OH \rightarrow C_6H_5CH_2CH=CH_2 + (C_2H_5)_2CO$	12.04 12.14	41.75 41.8	196 195

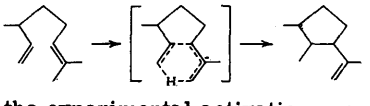
It is interesting that but-3-enoic acid decomposes by an analogous mechanism to form propene and carbon dioxide:



In this case, too, the experimental activation energy $E_{exp} = 39.3$ kcal[197] is close to the calculated value.

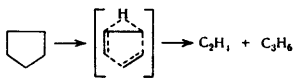
V. EFFECT OF CONJUGATED AND CUMULATIVE BONDS ON THE KINETICS OF MOLECULAR REACTIONS

Even a cursory analysis of the experimental information on the kinetics of molecular reactions shows that π-bonds are involved in the reaction in the vast majority of cases. It is therefore natural to expect that energy effects due to the peculiarities of behaviour of π-electrons would be revealed in the height of the potential barrier to the reaction. This is in fact so, and here we shall examine the effect of conjugation and cumulative π-bonding on the kinetics of molecular reactions. The influence of conjugation is shown most distinctly by comparing the experimental activation energy with the additive value calculated without correcting for conjugation. For the isomerisation of 3,7-dimethylocta-1,6-diene into 1-isopropenyl-2,3-dimethylcyclopentane, the activated complex of which contains two conjugated π-bonds,



for example, the experimental activation energy is $E_{exp} = 35.2$ kcal[198], whereas the additive value calculated without regard to conjugation is 58 kcal.

Similarly, in the decomposition of cyclopentane into ethylene and propene, where conjugation of two activated π-bonds also occurs,

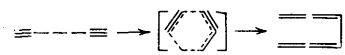


the calculated activation energy without correction for conjugation is 76 kcal, while the experimental value is 49.6 kcal[188]. In both cases the experimental activation energy is smaller than the calculated value by 23–26 kcal.

The calculated activation energy exceeds the experimental value by the same amount for the decomposition of unsaturated ethers (subsection 10) and unsaturated alcohols (subsection 14), where there is conjugation of activated π-C=C and π-C=O bonds.

Attributing the decrease in activation energy to stabilisation of activated π-bonds by conjugation, we must conclude that the mean energy of a conjugated activated π-bond is about 12 kcal larger than that of the corresponding unconjugated bond.

A correction of the same magnitude must be introduced also into every conjugated π-bond of acetylenic type. For the isomerisation of hexa-1,5-diyne



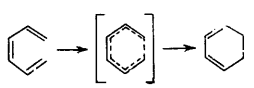
for example, $E = 79 + 2 \times 56 - (2 \times 28 + 2 \times 9 + 2 \times 17 + 4 \times 12) = 35$ kcal. This reaction is the first and slowest stage in the isomerisation of hexa-1,5-diyne into dimethylenecyclobutene ($E_{exp} = 34.4$ kcal[200]).

The effect of conjugation becomes especially important when several conjugated π-bonds are present in the activated complex. In this case the gain in energy may exceed the potential barrier to the reaction. For the allylic Claisen and Cope rearrangements (Section IV, 9), for example, the conjugation of four π-bonds gives a gain of 48 kcal with a potential barrier of about 30 kcal!

Thus the effect of conjugation in the activated complex can be allowed for by means of the additive correction $\Delta Q^{\neq}_{conj} = 12$ kcal for every conjugated activated π-bond.

An analogous effect is observed when a chain of $n \geqslant 3$ cumulative π-bonds is present. The energy of the system of π-bonds is also diminished in this case, with a corresponding lowering of the potential barrier. An example is the isomerisation of dienes (Section IV, 12), where there is a system of four cumulative π-bonds. Here the activation energy calculated additively without correcting for cumulation exceeds the experimental value by 32–33 kcal, about 8 kcal for each cumulative π-bond.

A still stronger effect of cumulation is observed in the cyclisation of hexatriene:



In this case $E = 3 \times 61 - (5 \times 17 + 27 + 5 \times 8) = 27$ kcal and $E_{exp} = 29.9$ kcal[201]. Here the activated complex contains a system of five cumulative π-bonds, and the corresponding decrease in energy is ~ 40 kcal. Thus the effect of cumulation can be allowed for by means of the additive correction $\Delta Q^{\neq}_{cum} = 8$ kcal for every cumulative activated π-bond when the number of π-bonds $n \geqslant 3$.

Summarising the above discussion, we can draw the following conclusions:

1. The activation energy is very greatly affected by the behaviour of the π-electrons in the activated complex.
2. The conjugation of π-bonds produces a marked decrease in the energy of the activated complex, and consequently diminishes the activation energy.
3. The presence of a system of three or more cumulative π-bonds also substantially lowers the potential barrier to the reaction.
4. The effects of conjugation and cumulation are readily allowed for in calculations of activation energy by introducing the appropriate additive corrections.

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The immense volume of published experimental work, the great variety of types of molecular reactions having activation energies over the range 15–70 kcal, and the absence of rigorously established mechanisms for many reactions—all this produces an unfavourable first impression. The purpose of the present Review was at least partly to remove this impression, and to show that in the apparently impenetrable, frequently unconnected experimental results several paths can nevertheless be found.

Summarising the paper as a whole, we can draw several important conclusions. It must first be noted that the structure of the activated complex is of decisive importance for the kinetics. It is extremely useful in ascertaining its nature to regard the activated complex as a molecule some of whose atoms are bound together by activated bonds. It is significant that the activated bonds determine the principal features of the structure of the activated complex: other chemical bonds, not directly involved in the reaction, usually play a very small part. For this reason reactions involving activated complexes having the same type of structure, and differing only in the substituents, are characterised in most cases by a similar activation energies.

Activated bonds of the same type, like ordinary chemical bonds, have roughly the same mean energies in different activated complexes: i.e. additivity of the bonds is maintained not only in molecules but also in activated complexes. This makes it very easy to calculate quite accurately the activation energy of diverse, even extremely complicated chemical reactions. The additive method of calculating activation energy proves to be extremely useful in considering the mechanism of molecular reactions.

The presence of conjugated and cumulative π-bonds in the activated complex has a marked effect on the activation energy. Conjugation and cumulation lower the activation energy. Both effects are easily allowed for in the additive calculation of activation energy.

The applicability of a simple additive scheme for calculating activation energy is restricted, of course, to reactions for which the ordinary chemical bonds are additive. This is evidently not satisfied with perfluorinated compounds and molecules containing fused rings.

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