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The Pre-exponential Factors for Unimolecular Gas-phase Reactions

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The principal concepts and methods whereby the pre-exponential factors for unimolecular gas-phase reactions may be found have been examined. The methods are based on the transition state theory which accounts successfully for all experimental data. The reactions have been classified taking into account the typical structure of the activated complex. The question of the effect of molecular structure on the value of the pre-exponential factor has been examined for each group of reactions. The general postulates have been illustrated by examples. The data employed embrace about 800 reactions.
The bibliography includes 177 references.

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I. INTRODUCTION

Extensive information is now available concerning the pre-exponential factor A for unimolecular reactions of polyatomic molecules. The fundamental principles of the theory, which permitted a successful explanation of the experimental data, were formulated many years ago with the aid of the transition state method [1]. However, a detailed quantitative treatment with extension of the theory to different classes of compounds became possible only in the 1960's, in the first place due to the large-scale introduction in practice of the computational method of the Rice–Ramsperger–Kassel–Marcus (RRKM) theory and in the second place due to the marked increase in the number of experimental data. The data of recent years are the most accurate and frequently refer to long series of similar compounds, which is also important. The aim of the present review is to give a general and systematic account of the available data on gas-phase reactions.

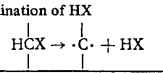
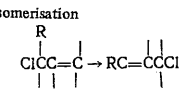
II. THE VALUE OF THE PRE-EXPONENTIAL FACTOR

In 1928 Polanyi and Wigner [2] were the first to examine the question of the magnitude of the pre-exponential factor in unimolecular reactions using for this purpose mainly data for reactions in solutions [3] and introduced the concept of the "normal" pre-exponential factor, which has similar magnitude to molecular vibration frequencies (10^{12}–10^{14} s^{-1}). It is remarkable that at that time only three gas-phase reactions were known (decomposition of azomethane and N_2O_5 and the racemisation of pinene), which can now be classified, making certain assumptions, as unimolecular;

Table 1. The range of values of pre-exponential factors and certain other characteristics of unimolecular reactions.

No.	Class of compound	Reaction	Group according to Table 2	Number of compounds for which the following parameters are available				
				$\lg A$ (s^{-1})	$k(p)$	IE*	k (e)	Calcn. based on RRKM theory
1	2	3	4	5	6	7	8	9
1	alkanes	dissociation of C–C bond	1	—, —, 10 (Refs. 6 & 7)	1 (Ref.8)	—	2 (Ref.9)	5 (Refs.8 & 9)
		dissociation of C–H bond $CH_4 \rightarrow CH_3 + H$	2	—, —, 1 (Ref.6)	—	—	1 (Ref.9)	1 (Refs.8 & 9)
		loss of H_2 $CH_4 \rightarrow CH_2 + H_2$	—	—, 1, — (Ref.10)	—	—	—	—
2	unsaturated hydrocarbons	dissociation of C–C bond	1	—, —, 5 (Refs.6,7 & 11)	—	—	7 (Ref.12)	7 (Ref.12)
3	aliphatic-aromatic hydrocarbons	dissociation of C–C bond	1	—, —, 5 (Refs.6,7 & 13)	—	—	—	—
		dissociation of C–H bond	2	—, 6, – (Refs.6 & 14)	—	—	—	—
4	ketones and diacetyl	dissociation of C–C bond $RCOR' \rightarrow R' + R\dot{C}O$	1	—, 3, 9 (Refs.15–24)	—	—	—	—
5	alkyl cyanides	dissociation of C–C bond $R\dot{C}CH \rightarrow R\cdot + \rangle\dot{C}CN$	1	—, 1, 2 (Refs.15 & 25)	—	—	—	—
		loss of H_2 $CH_3CH_2\dot{C}N \rightarrow CH_2{=}CHCN + H_2$	3	—, 1, — (Ref.25)	—	—	—	—
		loss of HCN $CH_3CH_2CN \rightarrow C_2H_4 + HCN$	3	—, —, 1 (Ref.25)	—	—	—	—
6	free alkyl radicals	dissociation of C–C bond	1	—, 7, 3 (Ref.26)	—	4 (Refs.27, 28 & 29)	7 (Refs.9 & 30)	7 (Refs.9, 28–30)
		dissociation of C–H bond	2	—, 3, 2 (Ref.26)	—	1 (Ref.9)	2 (Ref.9)	2 (Refs.8 & 9)
		isomerisation	4	2, —, — (Refs.31 & 32)	—	—	—	—
7	acetyl radicals	dissociation of C–C bond $R\dot{C}O \rightarrow R\cdot + CO$	1	1, —, 3 (Ref.26)	—	—	—	—
8	alkoxy-radicals	dissociation of C–C bond $RC(O\cdot) \rightarrow R\cdot + \rangle C{=}O$	1	3, 1, 1 (Ref.26)	—	—	—	—
9	$ROCH_2\cdot$ radicals (R = CH_3 or H)	dissociation of R–O bond	1,2	—, 2, — (Ref.26)	1 (Ref.8)	—	—	1 (Ref.8)
10	amines and amides	dissociation of C–N bond	1	—, 2, 2 (Refs.15 & 33)	—	—	—	—
		loss of CH_4	3	—, —, 1 (Ref.22)	—	—	—	—
		loss of NH_3	3	—, —, 1 (Ref.22)	—	—	—	—
11	azo-compounds	dissociation of C–N bond $R{-}N{=}N{-}R \rightarrow R\dot{N}_2 + R$	1	1, 2, 10 (Refs.15, 22 & 34)	1 (Refs.35 & 36)	1 (Ref.36)	—	1 (Refs.35 & 36)
12	aliphatic nitro- and halogenonitro-compounds	dissociation of C–N bond $RNO_2 \rightarrow R + NO_2$	1	—, —, 28 (Ref.37)	3 (Reg.38)	—	—	—
13	difluoroamines	dissociation of C–NF_2 bond	1	—, —, 3 (Ref.39)	—	—	—	—
14	difluoro-aminoalkyl radicals	dissociation of C–N bond $-\dot{C}-C(-NF_2)- \rightarrow \rightarrow \rangle C{=}C\langle + NF_2$	1	1, 7, — (Ref.36)	—	—	—	—
15	hydrazine and its derivatives	dissociation of N–N bond	1	—, 3, 1 (Refs.15 & 26)	1 (Ref.40)	—	—	1 (Ref.41)
16	tetrazenes $R_2N{-}N{=}N{-}NR_2$	dissociation of N–N bond	1	—, 1, 1 (Ref.42)	—	—	—	—
17	nitramines $R_2N{-}NO_2$	dissociation of N–N bond	1	—, —, 3 (Refs.43 & 44)	—	—	—	—
18	nitrosamines $R_2N{-}NO$	dissociation of N–N bond	1	—, —, 1 (Ref.48)	—	—	—	—
19	dialkyl peroxides	dissociation of O–O bond	1	—, 1, 6 (Refs.45,46 & 47)	—	—	—	—
20	diacyl peroxides $RC(=O){-}O{-}O{-}C(=O)R$	dissociation of O–O bond	1	—, —, 3 (Ref.49)	—	—	—	—

Table 1 contd.

No.	Class of compound	Reaction	Group according to Table 2	Number of compounds for which the following parameters are available				
				lg$A$ (s^{-1})	k (p)	IE*	k (e)	Calcn. based on RRKM theory
1	2	3	4	5	6	7	8	9
21	hydroperoxides	dissociation of O–O bond	1	—, 3, 4 (Refs.45 & 50)	—	—	—	—
22	nitrites RO—NO	dissociation of O–N bond	1	—, 1, 4 (Refs.22 & 45)	—	—	—	—
23	nitrates RO—NO_2	dissociation of O–N bond	1	—, —, 3 (Ref.45)	—	—	—	—
24	inorganic oxides N_2O_4, N_2O_5, NO_3F, Cl_2O_7	loss of NO_2, OF, or ClO_3	1	—, —, 4 (Ref.15)	1 (Ref.51)	—	—	1 (Ref.52)
25	organomercury compounds	dissociation of Hg–C bond	1	—, 1, 4 (Refs.14,15,20,21 & 53)	1 (Ref.53)	—	—	—
		dissociation of Hg–Hal bond	2	—, 1, 2, (Refs.14,15,20 & 21)	—	—	—	—
26	compounds MR_n M=Zn, Cd, Sb, Bi, Pb, Sn, Ge, Si	dissociation of M–C bond	1	1, 4, 5 (Refs.15,54–57)	—	—	—	—
27	sulphones RSO_2—R	dissociation of C–S bond	1	—, —, 3 (Ref.58)	—	—	—	—
28	sulphides Rh CH_2—SCH_3	dissociation of C–S bond	1	—, 1, —(Ref.59)	—	—	—	—
29	$\dot{R}SO_2$ radicals	dissociation of C–S bond	1	—, 1, 1 (Ref.33)	—	—	—	—
30	cyclohexadienes	dissociation of C–H bond	2	—, 2, — (Ref.60)	—	—	—	—
31	organic chloro-derivatives of different classes	dissociation of C–Cl bond	2	—, 2, 2 (Refs.14,25,61–63)	—	—	—	—
32	organic bromo-derivatives of different classes	dissociation of C–Br bond	2	—,12,— (Refs.14,15,25,61–63)	—	—	—	—
33	organic iodo-derivatives of different classes	dissociation of C–I bond	2	—, 4, — (Refs.15,64 & 65)	—	—	—	—
34	inorganic oxides and fluorides FNO_3, F_2SO_3, $FClO_3$, $FClO_2$, $ClNO_2$, SF_4	elimination of F, O, or Cl	2	—, 5, 2(Refs.15, 66–69)	—	—	—	—
35	acetaldehyde	elimination of H	2	—	—	—	1 (Ref.70	1 (Ref.70)
36	chloroalkyl radicals	loss of Cl	2	—, 7, — (Ref.26)	—	—	4 (Ref.71)	4 (Refs.71–73)
37	halogenomethanes	elimination of HX 	—	—, 5, — (Refs.15,66 & 67)	1 (Ref.74)	—	—	1 (Ref.75)
38	cyclic hydrocarbons, cyclo-olefins	dehydrogenation	3,4	—, 8, — (Refs.6,60,66 & 77)	—	—	—	—
39	fluoroalkanes	elimination of HF	3	—, 3, — (Refs.78–82)	—	1(Ref.83)	17 (Refs.84–87)	4(Refs.86 & 87)
40	AlR_3	elimination of isobutene	3	1, —, — (Ref.88)	—	1 (Ref.88)	—	—
41	chloroalkanes	elimination of HCl	3	17, 46, 1 (Refs.89–94)	1 (Ref.95 & 96)	2 (Refs.95 & 97)	3 (Refs.97–99)	4 (Refs.52,95–97, 100–102)
			4	—, 1, — (Ref.94)	—	—	—	—
42	bromoalkanes	elimination of HBr	3	—, 17, — (Refs.90 & 103)	1 (Ref.104)	—	3(Ref.101)	3(Ref.101)
43	iodoalkanes	elimination of HI	3	1, 5, 2 (Refs.90,103,105 & 106)	—	—	—	1 (Ref.64)
		dissociation of C–I bond	2		—	—	—	1 (Ref.64)
44	neo-$C_5H_{11}Cl$	γ-elimination of HCl	—	—, 1, —(Ref.107)	—	—	—	—
45	chloroalkenes	isomerisation 	3	2, —, —(Ref.90)	—	—	—	—

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Table 1 contd.

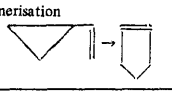
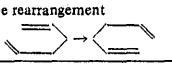
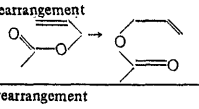
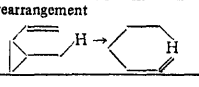
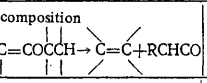
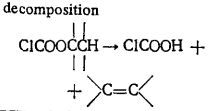
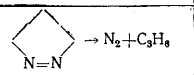
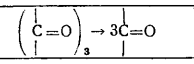
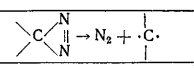
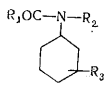
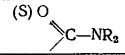
No.	Class of compound	Reaction	Group according to Table 2	Number of compounds for which the following parameters are available				
				lg$A$ (s^{-1})	k (p)	IE*	k (e)	Calcn. based on RRKM theory
1	2	3	4	5	6	7	8	9
46	alcohols	loss of H_2O	3	—, 2, — (Ref.103)	—	—	—	—
47	mercaptans	loss of H_2S	3	—, 1, — (Ref.108)	—	—	—	—
48	acetic acid	loss of H_2O	3	—, 1, — (Refs.25 & 109)	—	—	—	—
		loss of CH_4	3	1, —, — (Ref.25)	—	—	—	—
49	alkyl azides	loss of HN_3	3	—, 1, 2 (Refs.110 & 111)	—	—	—	—
50	halogenosilanes	$XCCSiR_3 \rightarrow \rangle C{=}C\langle + XSiR_3$	3	2,2, — (Ref.103)	—	—	—	—
51	acetic anhydride	$(CH_3CO)_2O \rightarrow$ $\rightarrow CH_2{=}CO + CH_3COOH$	3	—, 1, — (Ref.103)	—	—	—	—
52	vinylcyclopropanes	isomerisation 	3	—, 6, 4 (Refs.15 & 112)	—	—	—	—
53	methyl thiocyanate	isomerisation $CH_3SCN \rightarrow CH_3NCS$	3	—, —, 1 (Ref.15)	—	—	—	—
54	alkyl isothiocyanates	elimination of HNCS $RNCS \rightarrow \rangle C{=}C\langle + HNCS$	3	—, 3, — (Ref.113)	—	—	—	—
55	alkyl isocyanides	isomerisation $CH_3NC \rightarrow CH_3CN$		—, 1, 1— (Ref.114)	2 (Refs.115 & 116)	2 (Refs.115 & 116)	—	2 (Refs.115 & 116)
56	mononitroalkanes	elimination of HNO_2 $HCCNO_2 \rightarrow \rangle C{=}C\langle + HNO_2$	4	7, 9, 0 (Ref.117)	—	—	—	—
57	trimethylacetyl choride	$Me_3CC(=O)Cl \rightarrow C_4H_8 + CO + HCl$	4	1, —, — (Ref.118)	—	—	—	—
58	dienyls and diynyls	Cope rearrangement 	4	13, —, — (Refs.6 & 119)	—	—	—	—
59	allyl vinyl ethers	non-aromatic Claisen rearrangement	4	4, —, — (Ref.6)	—	—	—	—
60	allylic esters	rearrangement 	4	8, 6, — (Ref.6)	—	—	—	—
61	1-alkyl-2-vinylcyclo-propanes	rearrangement 	4	5, —, — (Ref.6)	—	—	—	—
62	linear conjugated polyenes	cyclisation	4	4, —, — (Ref.6)	—	—	—	—
63	unsaturated cyclic systems	isomerisation	4	3, —, — (Ref.6)	—	—	—	—
64	esters	decomposition $RCOOCCH \rightarrow RCOOH +$ $+ \rangle C{=}C\langle$	4	9, 77, 4 (Refs.88, 103 & 120)	—	—	—	—
65	unsaturated esters	rearrangement	4	8, 6, —(Refs.112 & 120)	—	—	—	—
66	acetals	decomposition $RCH(OCOR')_2 \rightarrow$ $\rightarrow RCHO + (R'CO)_2O$	4	12, —, — (Refs.25 & 103)	—	—	—	—
67	*cis*-1,3-dienes	1,5-migration of hydrogen	4	10, 6, — (Refs.6 & 121)	—	—	—	—
68	γ-unsaturated alcohols, β-unsaturated acids, β-ketoacids	elimination of ketone (aldehyde, CO)	4	6, 2, —(Refs.15 & 103)	—	—	—	—

Table 1 contd.

No.	Class of compound	Reaction	Group according to Table 2	Number of compounds for which the following parameters are available				
				lg$A$ (s^{-1})	k (p)	IE*	k (ε)	Calcn. based on RRKM theory
1	2	3	4	5	6	7	8	9
69	alkyl vinyl ethers	decomposition 	4	5, —, — (Refs.103 & 112)	—	—	—	—
70	dicarbonates	decomposition	4	—, 15, — (Refs.103 & 120)	—	—	—	—
71	chloroformates	decomposition 	4	1, 3 — (Ref.103)	—	—	—	—
72	cyclopropane and its derivatives	structural isomerisation	5	1,4,23 (Refs.6,15,112,122-125)	7 (Refs.122,126, 127 & 128)	1 (Ref.126)	2 (Refs.129&130)	3 (Refs.52,72,104,126, 127,131 & 132)
		geometrical isomerisation	5	—,—,4(Refs.6 & 59)	11 (Ref.26)	11 (Ref.26)	—	1 (Ref.126)
73	bicyclic compounds containing the cyclopropane ring	rearrangement with opening of cuclopropane ring	5	—,2,2 (Refs.6,112 & 124)	—	—	—	—
74	oxiran and its derivatives	structural isomerisation	5	—,1,2 (Refs.6,133,134 & 135)	2 (Refs.70 & 134)	1 (Ref.70)	1 (Ref.133)	1 (Ref.70)
75	cyclobutane and its derivatives	decomposition	5	—,—,23(Refs.5 & 112)	3 (Refs.126 136-140)	1 (Ref.126)	—	3 (Refs.52,126 & 136)
		geometrical isomerisation	5	—,—,6 (Refs.6 & 112)	—	—	—	—
76	bicyclic compounds containing the cyclobutane ring	structural isomerisation with opening of cyclobutane ring	5	1,1,3 (Refs.6 & 112)	—	—	—	—
77	oxetan and its derivative	structural isomerisation	5	—,—,2 (Refs.6,141 & 142)	—	—	—	—
78	cyclobutene and its derivatives	structural isomerisation	5	—,20,2(Refs.6 & 112)	3 (Refs.126, 143-146)	1 (Ref.146)	—	3 (Refs.126,132,146,147)
79	bicyclic compounds containing the cyclobutene ring	isomerisation	5	—, 1,3 (Ref.6)	—	—	—	—
80	1-pyrazolines		5	—,—,10 (Ref.148)	—	1 (Ref.149)	—	—
81	cyclic radicals	decomposition	5	—,—,2 (Ref.6)	—	—	—	—
82	trimers		—	—,—,4 (Refs.15 & 25)	—	—	—	—
83	olefins	*cis-trans*-isomerisation	5	6,7,1, (Refs.15,112 & 150)	1 (Ref.132)	—	—	1 (Refs.52 & 132)
84	diazirines		5	—, 3,1, (Refs.151 & 154)	2 (Refs.151 & 153)	—	—	—
85	cyclic compounds	retrodiene reactions	5	—,5,2, (Refs.6,76,155 & 156)	—	—	—	—
86	*ortho*-substituted acetanilides 	rotation about C-N bond	—	4,4 — (Ref.157)	—	—	—	—
87	amides and thioamides 	rotation about C-N bond	—	1,3,— (Refs.15 & 158)	—	—	—	—
88	FN=NF	*cis-trans*-isomerisation	5	—,1, — (Ref.159)	—	—	—	—
89	alkyl halides	rotation about C-C bond	—	4,9, —(Refs.160 & 161)	—	—	—	—
90	$O=N-NMe_2$ $O=N-OCMe_3$	rotation about N-N and N-O bonds	—	—,2, —(Ref.15)	—	—	—	—

Note. Column 7 lists data on all types of kinetic isotope effects in both thermally and chemically activated systems. The first, second, and third numerals in column 5 indicate the numbers of reactions with lg A less than 12, in the range 12–14, and greater than 14 respectively.

they all have lg $A > 14$. All earlier theories of unimolecular reactions (the Rice–Ramsperger, Kassel, and Slater theories) yielded a normal value of A,[4,5] which to a considerable degree helped to confirm the validity of this concept.

In 1952 the proportion of reactions with normal values of A were 60% according to Kondrat'ev's data[4] and that of reactions with lg $A > 14$ was 16%. At present about 800 unimolecular reactions are known, for which the parameters of the Arrhenius equation have been determined (Table 1). Of these 47% have lg $A = 12$–14, 33% have lg $A > 14$, and 20% have lg $A < 12$. On the whole, pre-exponential factors lie in the range between 10^9 and 10^{17} s^{-1}. The absolute number of reactions with A exceeding 10^{14} or below 10^{12} s^{-1} is very large. Therefore the concept of the "normal" pre-exponential factor is now of purely conventional significance; it reflects the frequently encountered situation where the structure of the activated compound differs little from that of the initial molecule.

III. CALCULATION OF THE PRE-EXPONENTIAL FACTOR

The high or low experimental values of A can only be accounted for with the aid of statistical theories of unimolecular reactions based on the activated complex (AC) method. The modern RRKM theory[9,162,163] yields the following expression for the rate constant at a high pressure:

$$k_\infty = \alpha \frac{kT}{h} \frac{Q^{\neq}}{Q} e^{-E_a/RT}, \qquad (1)$$

which is the same as the classic Eyring formula and is equivalent to the formulation[1]

$$k_\infty = \alpha \frac{kT}{h} e^{\Delta S_0^{\neq}/R} \cdot e^{-\Delta H_0^{\neq}/RT}, \qquad (2)$$

where α is the statistical factor for the reaction, $Q^{\neq}$ and Q are the partition functions of the activated complex and the initial molecule, E_a is the true activation energy, i.e. the height of the potential barrier at 0°K, and $\Delta S^{\neq} = S_0^{\neq} - S_0$ and $\Delta H_0^{\neq} = \Delta U_0^0 + (H_T - H_0^0)^{\neq} - (H_T - H_0^0)$ are the entropy and enthalpy of formation of one mole of activated complex.

The relation between E_a and the activation energy E at a temperature T is illustrated in Fig. 1 (E_{vibr} and $E_{vibr}^{\neq}$ are the vibration energies of the active internal degrees of freedom of the reactant and the activated complex, $E_{t\text{-}r}$ is the energy of the internal translational and rotational motions in the activated complex, r and t are the numbers of internal rotations, and E_0 and $E_0^{\neq}$ are the zero-point energies of the initial molecule and the activated complex respectively).

If it is assumed that the experimental activation energy U, determined from the Arrhenius equation

$$k_\infty = Ae^{-U/RT}, \qquad (3)$$

is equal to E, then the following relations are valid:

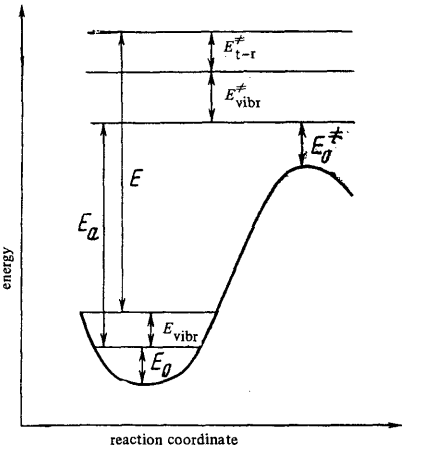
$$U = E_a + E_{t\text{-}r}^{\neq} + E_{vibr}^{\neq} - E_{vibr} = E_a + (r - t + 2)RT/2 + RT^2(d\ln Q^{\neq}/dt - d\ln Q/dT), \qquad (4)$$

$$k_\infty = \alpha \frac{ekT}{h} e^{\Delta S^{\neq}/R} e^{-U/RT}, \qquad (5)$$

$$\ln A = 1 + \ln\alpha + \ln\frac{kT}{h} + \frac{\Delta S^{\neq}}{R}, \qquad (6)$$

$$\ln A = \ln\frac{\alpha ekT}{h} + \ln\frac{Q^{\neq}}{Q} + T\left(\frac{d\ln Q^{\neq}}{dt} - \frac{d\ln Q}{dt}\right). \qquad (7)$$

When account is taken of the changes in the moments of inertia of the overall rotation owing to the greater size of the activated complex, then the term $\frac{1}{2}\ln(I_A^{\neq}I_B^{\neq}I_C^{\neq}/I_AI_BI_C)$ must be added to the right-hand side of Eqn. (7). All the difficulties of the theoretical calculation of A from Eqn. (7) reduce to the necessity of determining the vibration frequencies and the moments of inertia of the overall and internal rotations in the activated complex. Since the same partition function can be obtained with the aid of a wide variety of frequency sets, there is always a considerable uncertainty in the choice of the structure of the activated complex.



Schematic representation of the energy levels in a unimolecular reaction.

The RRKM theory provides the greatest scope for overcoming this uncertainty. On the basis of a single model of the activated complex, it is possible to calculate within the framework of this theory a wide variety of characteristics of unimolecular reactions, which are susceptible to experimental determination. They include the following[5,9].

1. The pressure dependence of the rate constant $k(p)$.
2. The primary and secondary isotope effects in thermally activated systems: $(k_H/k_D)_{prim}$ and $(k_H/k_D)_{second}$.
3. The reverse isotope effect in the region where k varies with p: $(k_H/k_D)_{rev}$.
4. The dependence of the rate of reaction on the excess energy above the threshold value: $k(\epsilon)$.
5. The isotope effect in chemically activated systems: $k(\epsilon)_H/k(\epsilon)_D$.

Unfortunately not all these characteristics are sufficiently sensitive to changes in the vibration frequency in the activated complex. Measurements of the dependence of k on p and of the isotope effects in thermally activated systems are the most useful[9,146,164]. It was shown recently[126,146] that in reactions with a reverse isotope effect the position of the point of intersection of the $k(p)$ curves for isotopic molecules depends greatly on the structure of the

activated complex and thus may be used successfully to test activated complex models.

Reactions involving the decomposition of the molecule into two radicals have yet another extremely important characteristic which makes it possible to infer the structure of the activated complex: the rate constant for the recombination of radicals (see p. 718). Similarly the rate constant for the addition of an atom or a radical to an olefin helps us to understand the structure of the activated complex in the reverse reaction involving the decomposition of the free radical into an olefin and an atom (or a radical).

Calculations for activated complex models based on the RRKM theory using, in addition to the pre-exponential factor, at least one other experimental characteristic have been made for approximately 60 reactions (Table 1). However, in the majority of cases this involves the calculation of the rate of decomposition of chemically activated species, i.e. a characteristic which is relatively insensitive to the activated complex parameters [9]. There are comparatively few calculations concerning the $k(p)$ relation and the isotope effect.

The most complete attempts to determine the structure of the activated complex by adjusting the calculated $k(p)$ curves to coincide with experimental plots have been made for ethane [8,9], hexafluoroethane [165], ethyl chloride [52,95-97,100,101], methyl isocyanide [115,166], ethyl isocyanide [116], cyclopropane [52,126,131,132], 1,1-dichlorocyclopropane [167], cyclobutane [52,126], cyclobutene [126,132,146,147], methylcyclobutene [136], azomethane [35,36], and alkyl [9,28] and certain other radicals [71]. In many cases [100,136,167] it was established that the detailed structure of the activated complex is very difficult to determine, since different models yield similar results. Probably this difficulty will increase with increase of the complexity of the molecular structure and of the activation energy [136,167].

Models using two characteristics, $k(p)$ and the reverse isotope effect at low pressures, have been optimised for the following reactions: decomposition and isomerisation of cyclopropane [126,165] and cyclobutane [126,146], isomerisation of methyl isocyanide [112] and ethyl isocyanide [116], and decomposition of ethyl chloride [100]. One may assume that the interpretation of the structure of the activated complex for these reactions and also for the decomposition of ethane, hexafluoroethane, azomethane, and alkyl radicals has been made fairly reliably. Examples of activated complex models will be quoted below.

One should note that the accuracy of the geometrical structure and of the vibration frequencies of the activated complex achieved in these calculations greatly exceeds the accuracy required for the calculation of the pre-exponential factor. Therefore, from the standpoint of the estimation of A, the importance of calculations based on the RRKM theory consists primarily in a convincing demonstration of the validity of the transition state method for reactions of polyatomic molecules at high pressures and the fact that, for all fundamental types of unimolecular reactions (which will be dealt with below), a detailed analysis has been made of activated complex models in individual examples.

Recently successful attempts have been made to develop semiempirical methods for the calculation of A. [103,168-170] In the main they refer to reactions proceeding via a cyclic transition state. The methods are based on approximate hypotheses concerning the structure of the activated complex and employ experimental values of $\Delta S^{\neq}$ [from Eqn. (5)] in order to find the contributions of the individual structural elements of the activated complex to the total entropy of activation. Either the values of the contributions or the methods of their determination are then standardised.

Mulyava and Shevchuk [168] proposed a method based on the additivity of bond entropies in molecules and activated complexes for the calculation of $\Delta S^{\neq}$. Using the bond classification of the kind usual in additive schemes [171,172] and the concept of the activated bond in the activated complex [173], they calculated the corresponding bond entropies and also corrections for symmetry, cyclisation, conjugation of double bonds, and the presence of cumulative double bonds. A fairly high accuracy in the calculation of $\Delta S^{\neq}$ was demonstrated on a number of examples, but for its large-scale application the method probably requires a more detailed formulation. A similar procedure for the estimation of $\Delta S^{\neq}$ but with a less detailed subdivision into components was proposed by Szabó and Berces [174].

The method of calculation of A for cyclic activated complexes proposed by O'Neal and Benson [103] is less formal. On the basis of a physically clear albeit approximate activated complex model, these workers proposed simple rules for the calculation of individual structural contributions to activation entropy from molecular characteristics. The method is applicable to calculations for more than one hundred reactions and yields an excellent agreement with experiment. Within the framework of this method, it is easy to predict the effect of substituents on $\Delta S^{\neq}$ for the reaction (the method is described in greater detail on p. 720).

The success of the approximate methods of calculation of $\Delta S^{\neq}$ for cyclic activated complexes can be accounted for to some extent by the comparatively low sensitivity of this quantity to changes in the activated complex parameters. In order to predict A to within a factor of three, it is sufficient to take into account the most fundamental changes in the types of motion on formation of the activated complex, i.e. those associated with low-frequency vibrations and internal rotation. Probably the same accuracy can be achieved also in the estimation of A for bond dissociation reactions [170,175].

IV. CLASSIFICATION OF REACTIONS

In terms of the pre-exponential factor and the typical structure of the activated complex, reactions can be divided into the five main groups indicated in Table 2.

Table 2. Classification of reactions.

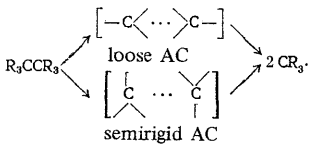
No.	Group of reactions	Reactions investigated	Reactions with lg$A$ in the range			Number of series with different numbers of reactions				
			<12	12–14	>14	1–5	6–10	11–15	16–20	20
1	decomposition into two radicals	171	7	40	124	17	4	2	—	2
2	decomposition into an atom and a radical	52	—	43	9	7	3	1	—	—
3	elimination or isomerisation via a four-membered ring	130	24	93	13	17	2	—	1	1
4	ditto via a five- or six-membered ring	227	98	125	4	8	1	5	2	1
5	reactions via a biradical transition state (ring opening, *cis-trans*-isomerisation)	146	8	50	88	7	5	1	—	3

The assignment of reactions to particular groups is specified in column 4 of Table 1. The classification does not embrace about 50 reactions. The characteristic features of each group of reactions will be examined in subsequent sections.

Table 2 also shows the distribution of reactions with respect to homologous reaction series. Evidently in gas-phase reactions there are comparatively few long reaction series. Nevertheless, large series in which the effect of structure on A is shown (and for which the most reliable experimental data are as a rule available) are in fact the most valuable for understanding the structure of the activated complex and for developing semiempirical methods for calculating A. Studies undertaken specially to investigate the greatest possible number of reactions with the same mechanism and the same reaction centre probably merit attention.

V. DISSOCIATION OF THE MOLECULE INTO TWO RADICALS OR INTO AN ATOM AND A RADICAL

In the decomposition of a molecule into two radicals via homologous bond dissociation, for example the reaction $R_3C-CR_3 \rightarrow 2CR_3$, two types of activated complex structures are distinguished—the loose and semirigid structures. The following notation can be introduced:



(8)

A characteristic feature of the loose activated complex is a considerable extension of the bond undergoing dissociation and free (or almost free) three-dimensional rotation of the separating fragments. The structure of such a complex is close to that of the reaction products. The reverse radical recombination process occurs in almost every collision in the case of a loose activated complex and the recombination rate constant k_r is of the order of $10^{10.5}$ litre mole^{-1} s^{-1}. The recombining radicals are held at a considerable distance by polarisation forces and are oriented arbitrarily reliative to one another [1,15]. The barriers to recombination via a loose activated complex are very small. A loose activated complex is typical in the dissociation of strong bonds between small radicals. It has been demonstrated rigorously for the decomposition of ethane, hexafluoroethane, and certain other compounds.

If $k_r < 10^{10}$ litre mole^{-1} s^{-1}, then the activated complex can be assigned to the semirigid type. In its formation from the molecule, the R_3C-C rocking vibrations do not pass to free rotation but merely undergo a decrease in their frequency. A complete liberation of the rotations of CR_3 radicals does not occur until the critical point has been passed. The formation of a semirigid activated complex from radicals requires a specific orientation of the latter and the transformation of rotational into vibrational motion. Therefore recombination via a semirigid complex involves a loss of entropy.

Judging from the recombination rate constants (Table 3), in most cases the decomposition of molecules into two radicals proceeds via a semirigid activated complex.

In the formation of an activated complex of any type from the initial molecules in reaction (8), the following changes in internal degrees of freedom are possible.

1. A decrease of the frequency of deformation vibrations associated with the dissociating bond (C-C). Two of these pass into the out-of-plane vibrations of the CR_3 radicals formed in the activated complex. The decrease of frequency in this process can be measured with the aid of the secondary α-deuterium isotope effect [164,176]. Judging from the available data, one can assume without much error that in all cases the frequency changes by a factor of two.

The frequencies of the four rocking vibrations of R_3C-C characterising the rocking of the CR_3 groups relative to one another decrease by a factor of 2–3 in a semirigid complex and by a factor of 6–10 in a loose complex. The latter decrease is almost equivalent to free rotation of the fragments about axes perpendicular to the internal axis of inertia. The decrease of the rocking vibration frequencies makes the principal contribution to the entropy of a loose activated complex.

Table 3. Rate constants for the recombination of radicals [45].

Radicals	$\lg k_r$ (litre mole^{-1} s^{-1})	Bond strength, kcal mole^{-1}
R + R R + OR	10—11	80—90
R + NO R + NO_2	9—10	50—60
RO + NO RO + NO_2 RO + OH RO + OR	7—9	35—40

2. The freeing of internal rotation relative to the dissociating bond when the rotation was hindered in the ground state. The increase of activation entropy owing to the freeing of the hindered internal rotation depends little on the partition function for free rotation and factors such as the size of the rotating groups or the symmetry number do not play a significant role. The barrier to internal rotation has the main effect. The maximum contribution to $\Delta S^{\neq}$, which may occur when the height of the barrier is in excess of 10 kcal mole^{-1}, is about 3 Gibbs mole^{-1}.

3. The change in the frequency of torsional vibrations relative to the R-C bonds, i.e. the change in the rotational motion of the groups R adjoining the reaction centre. The decrease of the torsional vibration frequency, which may accompany a change in the geometry of the R_3C fragment and a decrease of the repulsion between the groups R and which can be very large in principle, occurs comparatively rarely, since usually adjacent groups inhibit fairly strongly their mutual rotation both in tetrahedral and in planar CR_3 structures.

On the other hand an increase of the frequency of the torsional vibrations of an adjacent group (and hence a decrease of A) are frequently observed in the decomposition of free radicals or olefins, when the barrier to internal rotation relative to the terminal bond being formed increases owing to the conjugation of the free valence produced. Usually one bond is involved in such conjugation and therefore the effect is small.

When account is taken of all three factors enumerated above, it is usually possible to explain satisfactorily the experimental data.

The decomposition of the molecule into an atom and a radical, $R_3CX \rightarrow R_3C\cdot + \cdot X$, is analogous to the decomposition into two radicals. The difference is that in the

elimination of an atom the number of deformation vibrations which are altered in the activated complex is a factor of two less than in the elimination of a radical and moreover the effect associated with rotation relative to the bond undergoing dissociation is missing. For the majority of reactions investigated, the activated complex has a semirigid structure and the entropy change $\Delta S^{\neq}$ is small. A loose activated complex has been postulated only for the decomposition of methane [9]. However, in this case too A exceeds 10^{14} s^{-1} only slightly owing to the small total number of parameters which are altered.

Table 4. Dissociation of the C–C bond.

Compound	Activated complex	lg$A$ (s^{-1})
$H_3C—CH_3$	loose	16.3—17
$F_3C—CF_3$	ditto	17.6
$Me_3C—CMe_3$	semirigid	16.3
$CH_3—CH_2CH=CH_2$	ditto	15.8
$CH_3—CH_2Ph$	»	14.5
$CH_3—CH_2CHCH_3$	»	13.5—15

Example 4. Dissociation of the C–C bond. In C–C bond dissociation reactions, A varies from $10^{13.5}$ to 10^{17} s^{-1}. Typical cases are presented in Table 4. [6]

The ethane and hexafluoroethane decomposition reactions provide a classic example of a loose activated complex and have the highest values of A. In the case of hexamethylethane the complex is semirigid, but A is also very high. Possibly in this case the rotation of adjacent groups, i.e. the decrease of the frequencies of the torsional vibrations of the CH_3 groups in the transition state, has an effect. Much lower values of A are observed in the decomposition of unsaturated and aliphatic-aromatic compounds and also of free radicals, owing to conjugation and the increase of the barriers to internal rotation in the radical formed (Table 5 presents a model which explains quantitatively the observed pre-exponential factors).

Example 2. Azo-compounds. The high values of A (10^{17} s^{-1}) observed in the decomposition of azo-compounds can be explained by the simultaneous dissociation of two C–N bonds and by a loose structure of the activated complex. Table 6 presents a model of such a transition state for the decomposition of azomethane [35] (lg$A$ = 17.3). A free activated complex probably occurs also in the decomposition of $C_2H_5N_2C_2H_5$.

However, for large groups R in R–N=N–R, free activated complexes are unlikely and therefore the corresponding values of A should not exceed 10^{15} s^{-1}. The values of A of the order of 10^{17} s^{-1} quoted in the literature for large molecules of azo-compounds are probably erroneous. Recent data confirm this [34].

Example 3. Peroxides, hydroperoxides, nitrites, and nitrates (Table 7). A general characteristic of all these compounds is a comparatively rigid structure of the activated complex (recombination rate constant 10^7–10^9 litre $mole^{-1}$ s^{-1}) and the fact that the dissociation of O–O or O–N bonds results not only in a freeing of rotation about these bonds but also in a decrease of the barrier to the internal rotation of the group R, i.e. the effect of adjacent groups is bound to be shown to some extent in this case. It can be particularly appreciable for peroxides. Unfortunately accurate calculations have not been made for these compounds. The attempts to explain the high values of A in the decomposition of peroxides without taking into account the rotation of R were unsuccessful [47].

Table 5. Models of the transition states for the dissociation of the C–C bond [8, 28, 52] (vibration frequency, cm^{-1}).

Vibration	$C_2H_6 \rightarrow [—C\cdots C—]$		$H_3C—CH_2CH=CH_2 \rightarrow [{}^{1}H_3C\cdots{}^{2}CH_2\cdots{}^{3}CH\cdots{}^{4}CH_2]$		$H_3C—CH_2CHCH_3 \rightarrow [{}^{1}H_3C\cdots{}^{2}CH_2\cdots{}^{3}CH—{}^{4}CH_3]$	
	molecule	AC	molecule	AC	molecule	AC
$^{1}C—{}^{2}C$ stretch, CH_3 def.	993 1375 1375	0 840 840	1055	0	1055	0
$^{1}CH_3—{}^{2}C$ rock.	820	144	765	190	1442	724
(either $^{1}C—{}^{2}CH_2$	820	144	1165	290	1152	576
rock. or	1155	144	960	240	972	486
$^{1}C—{}^{2}C—{}^{3}C$ skelet.)	1155	144	435	375	435	215
$^{1}C—{}^{2}C$ tors.	275	142	225	56	194	97
$^{2}C—{}^{3}C$ tors.	—	—	102	250	102	250
$^{2}C—{}^{3}C$ stretch.	—	—	845	1200	1008	1350

Example 4. Aliphatic nitro-compounds. In the study of the pyrolysis of aliphatic nitro- and α-halogenonitro-compounds, data were obtained for bond dissociation in the longest reaction series in the group of reactions involving decomposition into two radicals [37]. Here all the theoretically predicted contributions to the increase of $\Delta S^{\neq}$ and in particular the effect of the free rotation of the alkyl groups in the radical formed have been detected and measured experimentally (Table 8).

Table 6. Decomposition of azomethane

$$CH_3—N=N—CH_3 \rightarrow \left[—C\cdots N=N\cdots C—\right] \rightarrow N_2 + 2CH_3.$$

Vibration	Molecule	Activated complex
C–N stretch.	922	0
	1 100	0
N=N stretch.	1576	2 000
CH_3 def.	1370 (2)	580 (2)
CH_3 rock.	1013 (4)	free rock.
skelet. def.	593	550 (2)
	350	
	300	
$I_A \cdot I_B \cdot I_C$	$2.85 \cdot 10^{-115}$	$4.33 \cdot 10^{-115}$

In all cases the activated complexes have a semirigid structure (the $CH_3 + NO_2$ recombination rate constant is $10^{9.5}$ litre $mole^{-1}$ s^{-1}). In nitromethane the barrier to internal rotation about the C–N bond is very low and the only factor which alters $\Delta S^{\neq}$ is the decrease of the deformation vibration frequencies of CH_3–N and C–NO_2. In all

Table 7.

Compound	Activated complex	$\lg A$ (s^{-1})
Peroxides	R—O···O—R	15.4—16.1
Hydroperoxides	R—O···O—H	13.4—13.7
Nitrites	R—O···NO	14.1—14.4
Nitrates	R—O···NO_2	14.4—14.7

Table 8. Decomposition of aliphatic nitro-compounds.

No.	Compound	No. of substances investigated	Contribution by different factors				$\Delta S^{\neq}$, gibbs moles^{-1}
			rocking vibration	$^{*}NO_2$ rot.	NO_2 rot	R rot.	
1	$CH_3—^{*}NO_3$	1	+	—	—	—	3.06
2	$X_3C^{*}NO_2$, $X_2C(NO)_2^{*}NO_2$, $XC(NO_2)_2^{*}NO_2$ (X = Cl, Br, I)	9	+	+	—	—	6.2—8.4
3	$X_2C(NO_2)^{*}NO_2$, $XC(NO_2)_2^{*}NO_2$, $X_2(NO_2)C—^{*}NO_2$ (X = H, F, NO_2)	5	+	+	+	—	9—10.4
4	$RCXNO_2—^{*}NO_2$, (X = H, F, NO_2)	7	+	+	+	+	13.7—15
5	RCX_2NO_2 (X = Cl, Br)	3	+	+	—	—	6.2—8.0

other compounds the effect associated with the freeing of hindered internal rotation is shown. In the absence of large halogen atoms (Cl, Br, and I) from the α-position (third row in Table 8), $\Delta S^{\neq}$ increases slightly, which may be attributed to a decrease of the torsional vibration frequencies of the NO_2 groups in the radicals formed [$\cdot C(NO_2)_3$, $\cdot CH(NO_2)_2$, $\cdot CHFNO_2$]. A similar but much larger effect is observed for the alkyl group the rotation of which in the transition state becomes completely free (fourth row in Table 8). This conclusion has been confirmed by a number of independent findings[38].

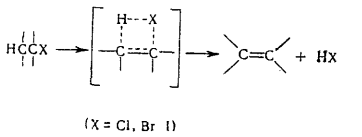
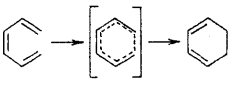
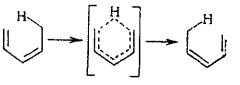
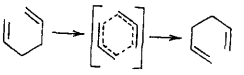
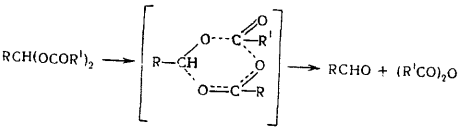
VI. REACTIONS INVOLVING A CYCLIC TRANSITION STATE

In reactions which proceed via a cyclic activated complex, the loss of free or partly hindered internal rotation has the greatest influence on A. There is no fundamental difference between the third and fourth groups of the proposed classification (Table 2). The difference is merely quantitative. In a four-membered transition state, only one or two internal rotations can be lost and in a six-membered state the loss of 2–4 rotations is possible. Accordingly, in the fourth group of reactions (Table 2), low values of A are encountered much more frequently than in the third group. Certain cases where it is possible to follow clearly the change in A owing to the increase of the number of restricted internal rotations are presented in Table 9.

In a cyclic transition state the decrease of entropy due to the disappearance of internal rotations is partly compensated by the appearance of low-frequency out-of-plane ring vibrations. It is not possible to determine by any simple method the frequency of these vibrations taking into account all the ring atoms. Therefore O'Neal and Benson[103], who developed a method for the calculation of A in four- and six-centre unimolecular reactions, proposed for the activated complex a model with a so called loose cyclic structure in the formation of which internal rotations are transformed into semifree partial torsional bond vibrations, It is assumed further that the order of the bonds being loosened and formed changes by 1/2 with a corresponding change in the deformation, stretching, and torsional vibration frequencies. This hypothesis standardises the method of calculation of $\Delta S^{\neq}$. To simplify the calculation, the activation entropy is divided into four parts:

1. $\Delta S^{\neq}_{vibr}$—the entropy change owing to the change in the deformation and stretching vibration frequencies. For each principal cyclic framework, $\Delta S^{\neq}_{rot}$ is constant.

Table 9. Four- and six-membered rings.

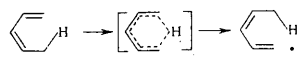
Reaction	No. of rotations lost	$\lg A$ (s^{-1})
 (X = Cl, Br I)	1	12—13
	2	11—11.8
	2	11—12
	3	10—11.5
	4	9—10.5

2. $\Delta S^{\neq}_{rot-vibr}$—the entropy arising owing to the restriction of the free internal rotations (which are converted into torsional vibrations about bonds with an order of 3/2).
3. $\Delta S^{\neq}_{sym}$—the overall symmetry correction: $\Delta S^{\neq}_{sym} = R \ln \sigma$, where σ is the statistical factor of the reaction.
4. $\Delta S^{\neq}_{cor}$—a correction term which must be introduced into $\Delta S^{\neq}_{r-t}$ in order to take into account the barriers to internal rotation in the initial molecule. The effect of substituents on A is in fact taken into account in terms of $\Delta S^{\neq}_{cor}$.

Despite the considerable simplifying assumptions made in the calculation of activation entropy, in most cases the calculated A differ by not more than a factor of two from the average experimental values[103]. Within the framework of a single reaction series, where the main variable parameter is $\Delta S^{\neq}_{cor}$, the accuracy of the prediction of A may be very high.

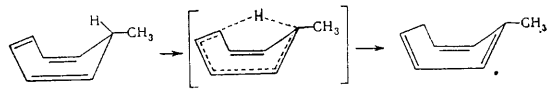
In many cases a purely qualitative examination of the direction of change in the barrier to rotation makes it possible to explain fine effects of the structure and substituents on A. The examples quoted, the experimental data for which were taken from Refs. 6 and 103, illustrate this.

Example 5. 1,5-Migration of hydrogen. Ten cases of hydrogen migration [reaction (9)] have been investigated[9]. Two rotations are lost in the activated complex and $\lg A = 11-11.8$:

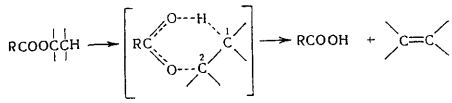


(9)

However, for 7-methylcyclohepta-1,3,5-triene, where there is no internal rotation, $\lg A$ has the normal value of 12.6:



Example 6. Esters. The value of A. In the transition state for the reaction

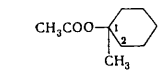
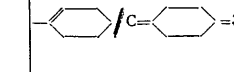
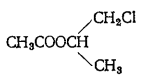


the rotations about the O–$\overset{2}{C}$ and $\overset{1}{C}$–$\overset{2}{C}$ bonds disappear, which explains the decrease of the pre-exponential factor to 10^{11}–$10^{11.8}$ s^{-1}. The substituents in the 1- and 2-positions increase the barrier to internal rotation and smooth out the differences between the initial state and the activated complex. Substituents in the 2-position may be expected to have a greater effect, since they influence also the $\overset{1}{C}$–$\overset{2}{C}$ bond and what is particularly important, the O–$\overset{2}{C}$ bond, which has a very low barrier to internal rotation (Table 10).

Table 10. Effect of substituents on A for the decomposition reactions of esters.

Substituent	lg A
1-Phenyl	12.0
2-Phenyl	12.4
1,2-Diphenyl	12.7
1-Alkyl (linear)	12.0
1-Alkyl (branched)	12.6
1,1-Dialkyl	12—13

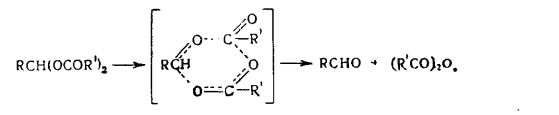
Table 11.

Reactant	Observed ratio	Statistical ratio
	 =3	0.67
	$\frac{CH_3CH=CHCl}{CH_2=CHCH_2Cl} = 1.1$	0.67

Example 7. Esters. Mode of Cleavage. When the elimination reaction can occur in two ways, the pathway for which the transition state includes bonds with highest barriers to internal rotation is preferred. On the basis of this simple postulate, one can explain all cases where the composition of the products differs from their relative proportions based on a purely statistical distribution (Table 11).

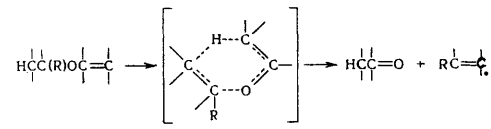
In the first example quoted in Table 11, the transition state involves preferentially the $\overset{1}{C}$–$\overset{2}{C}$ bond of the cyclohexane ring instead of the C–CH_3 bond and the second includes the C–CH_2Cl bond instead of C–CH_3.

Example 8. Acetals.



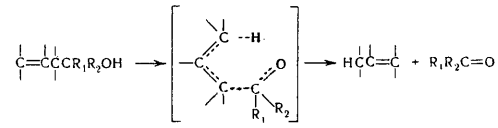
R	lg A
H	9.23
alkyl	10.3
CCl_3	11.1

Example 9. Alkyl vinyl ethers.



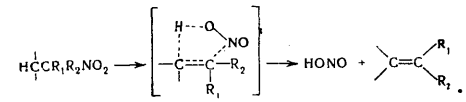
R	lg A
H	11.60
CH_3	12.58

Example 10. β-Hydroxyolefins.



R_1	R_2	lg A
H	H	11.65
H	CH_3	11.93
CH_3	CH_3	12.40

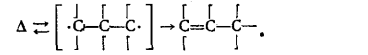
Example 11. Mononitroalkanes [117].



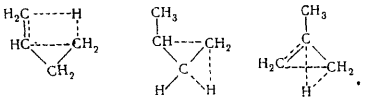
R_1	R_2	A/σ
H	H	11.5—11.8
H	alkyl	11.9—12.2
alkyl	alkyl	12.5—12.8

VII. REACTIONS INVOLVING A BIRADICAL TRANSITION STATE

The first elementary step in the geometrical isomerisation of olefins and cyclic hydrocarbons and also in the decomposition and structural isomerisation of the latter consists in the dissociation of a C–C bond and proceeds via an activated complex which has the properties of a biradical [112,169,170]. In many cases an excited biradical is probably an intermediate, which can lead to the formation of products and to the reverse reaction



The reversibility of the first stage hinders the interpretation of the kinetic data [126]. For certain structural isomerisations, it is postulated that the dissociation of a C–C bond and hydrogen migration can occur in a single elementary step via a transition state which differs from the biradical state [132]. From this standpoint, the following activated complex structures are possible for the structural isomerisation of methylcyclobutane:



Product but-1-ene but-2-ene isobutene

However, it is assumed that the cyclisation, associated with hydrogen transfer, involves a very loose structure and does not prevent rotation about the C–C bond.

In most cases the pre-exponential factors for these reactions are enhanced (up to $10^{15.5}$ s^{-1}), the main reason for which is the appearance of internal rotations about single bonds in the linear system produced.

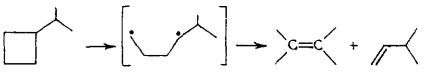
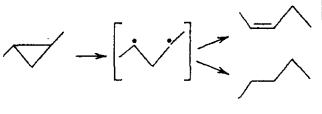
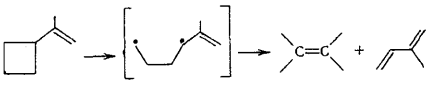
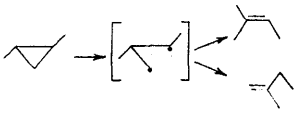
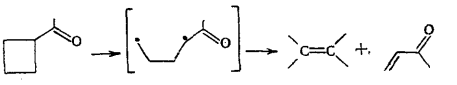
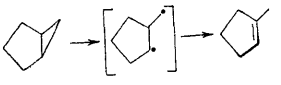
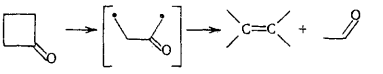
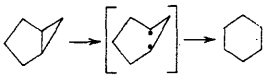
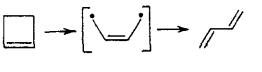
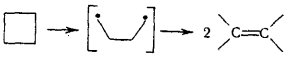
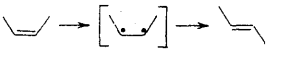
The presence of substituents prevents internal rotation and limits the increase of A. A double bond in the α-position relative to the free valence has a similar effect, since conjugation leads to an increase of the barrier to internal rotation. On the basis of these general considerations, even when the treatment is confined for simplicity to the hypothesis of a purely biradical structure of the activated complex, it is possible to understand the typical values of A observed in these reactions, which are listed in Table 12.

Quantitative calculations based on the RRKM theory have been made for only a few reactions of this type [52,126,132], but these confirm satisfactorily the decisive role of internal rotations. Pre-exponential factors have been evaluated by semiempirical calculations of activation entropies for reactions involving a biradical state [169,170,175]. A recent handbook [177] describes methods for the semiempirical calculation of A for all types of unimolecular reactions.

In conclusion one may note yet again that, despite the large number of theoretical treatments of unimolecular reactions, the real possibility of estimating pre-exponential factors of decomposition and isomerisation rate constants for polyatomic molecules at high pressures is nowadays based almost entirely on the classical formula (1) of the transition state theory. The more detailed RRKM statistical theory, the general validity of which has been confirmed by the success of its application, yields for k_∞ a formula identical with Eqn. (1). The possibility of taking into account anharmonic interactions in the activated molecule by postulating an activated complex with a somewhat predetermined structure in the RRKM theory) and the explanation on this basis of the high values of the pre-exponential factor constitute a brilliant achievement of the statistical theory. As a result, among problems concerning unimolecular reactions, that of the pre-exponential factor is the most completely resolved. Its solution is based on hypotheses concerning the structure of activated complexes in various elementary processes, which have arisen as a result of long experience gained in the application of the transition state theory to real systems. Despite their qualitative nature, in the vast majority of cases these hypotheses are sufficient to estimate correctly the critical values of A for reactions of the given type and to predict the dependence of A on molecular structure. Recently, in connection with the development of the RRKM theory, the possibility of a quantitative approach to the modelling of the activated complex structure has also appeared.

In the calculation of the pre-exponential factor, one may restrict the treatment to specifying the geometrical structure, the vibration frequencies, and the barriers to internal rotation in the activated complex, which can be frequently done using the corresponding characteristics

Table 12.

No.	Reaction	lg A	No.	Reaction	lg A
1		15.45	7		15.63
2		14.05 14.13	8		14.61
3		13.28 13.21	9		14.50
4		13.89	10		14.50
5		13.29	11		13.26
6		15.62	12		14.10

of the reactants and the reaction products or any of their analogue among stable compounds. When the reaction mechanism is well known, A can be in its turn an important source of information about the structure of the activated complex. This factor has been used successfully to develop empirical and semiempirical methods for the calculation of A, which nowadays play a dominant part in the interpretation and prediction of pre-exponential factors[168,170,177]. The scope of these methods depends entirely on the accumulation of experimental data and their reliability depends on fundamental studies involving the calculation of activated complex structures (for example within the framework of the RRKM theory). Together with considerable achievements in this field, the experimental and particularly theoretical studies which have been made are still inadequate and require further development.

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