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Pre-exponential Factor in Hydrogen Abstraction Reactions

M.V.Bazilevskii and E.A.Trosman

The principal rules governing the variation in the pre-exponential factor in reactions involving the abstraction of hydrogen by atoms and radicals are examined using the activated complex theory. 205 references.

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I. INTRODUCTION

The homolytic removal of a hydrogen atom is one of the reactions that have been studied most fully. The great number of quantitative kinetic measurements allow this reaction to be used for verifying theories of chemical kinetics and such attempts have been made repeatedly. Stepukhovich[1] showed that the values of the pre-exponential factor for some reactions of this type can be given with an accuracy of within an order of magnitude in the framework of the simplest version of activated complex (AC) theory. Other reviews[2-13] dealing with the reactivity of individual radicals have set out from the same position.

The present review systematises the absolute values of the pre-exponential factors for reactions in which hydrogen is abstracted by radicals or atoms, studied up to 1969. These experimental results are discussed from the position of AC theory. Unlike the reviews mentioned above we have excluded trivial geometric factors, so as to investigate the role of finer effects. In particular, the effect on the reaction rate of changes in the frequencies of the deformation vibrations of the reaction centre is examined (Johnston[14] was the first to report the significant part played by this factor). The importance of steric effects is discussed.

In investigations of this type we encounter the peculiar status of the work. On the one hand, the AC theory has recently come under criticism, justified in many respects[15-17]. On the other, at present there are no other theories for explaining such complex reactions. The situation is complicated by the absence of reliable potential surfaces (except for the $H + H_2$ reaction).

The last circumstance decides the matter. Non-empirical numerical calculations of transition probabilities are quite impossible without potential surfaces. The AC theory allows rather far-reaching conclusions to be drawn,

using only the most general ideas about the structure of the transition state. After comparison with experiment these conclusions seem quite plausible. Hence there is no choice at present. In explaining the regularities in rates of reaction AC theory is still the only working tool of the chemist, who has to use it, whilst taking note of its imperfections.

2. EVALUATION OF THE PRE-EXPONENTIAL FACTOR ACCORDING TO ACTIVATED COMPLEX THEORY

The principal equation of AC theory[18]

$$\kappa = \varkappa \frac{kT}{h} \cdot \frac{F^{\neq}}{F^{AB}} \cdot \exp(-E/kT) \qquad (1)$$

expresses the reaction rate in terms of the partition functions of the transition state $F^{\neq}$ and reagents F^{AB}. For comparison with the experimental values of the Arrhenius parameters the temperature dependence must be clearly distinguished. With an accuracy of up to an order of magnitude the temperature dependence of the pre-exponential factor in Eqn. (1) can be disregarded and the factor identified with the Arrhenius pre-exponent A:

$$A = \varkappa \frac{kT}{h} \frac{F^{\neq}_{transl}}{F^{AB}_{transl}} \cdot \frac{F^{\neq}_{rot}}{F^{AB}_{rot}} \cdot \frac{F^{\neq}_{int}}{F^{AB}_{int}} \qquad (2)$$

(here the partition functions $F^{\neq}$ and F^{AB} are expanded). It is assumed that the error involved hardly exceeds the error in AC theory itself. Furthermore, the experimental values of A are usually accurate only to an order of magnitude. Further discussion is based on Eqn. (2). In this section the relative role and methods of evaluating the individual factors in this formula are briefly examined.

a. Geometrical Factor

The contribution of the translational and rotational degrees of freedom in Eqn. (2) will be termed the geometrical factor. It is determined by the geometry of the AC and is readily calculated if the position of the saddle point on the potential surface is known. A change in the geometry within rather wide limits has little effect on the value of the geometric factor. Therefore the geometry can generally be evaluated without a knowledge of the potential surface, by assuming a reasonable distance between the reagents in the AC. The values of the other geometric parameters can be obtained without serious error by interpolation between the reagents and the products or even by putting them equal to the corresponding parameters of the reagents.

b. Internal Degrees of Freedom

To calculate the contribution of the internal degrees of freedom in Eqn. (2) the form of the potential surface close to the saddle point must be known. In this region the potential is approximatelv a quadratic function of the coordinates q_i:

$$V = \frac{1}{2} \sum U_{ij} q_i q_j . \qquad (3)$$

The force constants U_{ij} are determined from the conditions for the best agreement between (3) and the calculated potential surface. Usually calculation can only give the variation of the energy with a limited number of coordinates q. For the remaining degrees of freedom the force constants are evaluated by more or less plausible extrapolation.

After this the normal vibrations and their frequencies ω_i are determined with the aid of standard procedures well known from the theory of vibrational spectra[19].

In the system of "natural" coordinates q_i (changes in bond lengths and valence angles), unlike the cartesian system, the kinetic energy is a non-diagonal quadratic of the generalised momenta p_i:

$$K = \frac{1}{2} \sum T_{ij} p_i p_j . \qquad (4)$$

The coefficients T_{ij} in Eqn. (4) and U_{ij} in Eqn. (3) form the matrices T and U. The squares of the frequencies are given to sufficient accuracy by the eigen values of the TU matrix:

$$\omega^2 = \frac{1}{4\pi^2} Q^{-1} TUQ \qquad (5)$$

where ω^2 is the diagonal matrix of the numbers ω_i^2 and Q the unit matrix, which is directly related to the matrix which determines the form of the normal vibrations.

The frequencies found by Eqn. (5) were also used to calculate the vibrational partition functions in Eqn. (2). One of the values of ω_i^2 is always negative, corresponding to an imaginary frequency. It describes the spatially-unrestricted motion along the reaction coordinate with a maximum (not a minimum) potential at the saddle point.

This procedure has been used by Johnston[20-23].

c. Transmission Factor

Strictly speaking, the quantity κ in Eqn. (2) can be found only by completely solving the problem of the motion of a system of atomic nuclei (which are present in the reactants) in the field of a multidimensional potential with subsequent averaging over the distribution of the initial conditions. When such a solution is obtained the semi-empirical AC theory is generally not needed. Therefore the inclusion of the values of κ in Eqn. (1) is formal and is significant only when this quantity is close to unity.

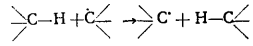
In several studies[24-32] the classical equations of motion for two- and three-dimensional potential surfaces were integrated numerically. These complex calculations, which require a knowledge of all the surfaces, give a set of trajectories for the motion of representative points depending on the initial conditions. They are discussed in Nikitin's book[33]. The technique of such classical calculations has been developed sufficiently well to investigate comparatively complex systems. For example, Bunker and Pattengill[34] calculated the trajectories for the reactions H + CH_4 and its isotopic analogues (using of course, an empirical potential).

Quantum calculations for empirical potential surfaces[35-38] and also more qualitative quantum estimations[39] show that the classical approximation does not introduce serious errors in those instances where the highest vibrational levels made a negligible contribution to the rate of reaction. There is evidently only one communication about the complete quantum calculation for the reaction H + H_2.[40]

In the language of AC theory such calculations imply calculation of the interaction of the reaction coordinates with the other degrees of freedom. Eqn. (1) is based on

the hypothesis of the absence of interaction. More precisely, the Hamiltonian of the AC theory is the adiabatic Hamiltonian for the vibrational degrees of freedom. The adiabatic approximation postulates the absence of vibrational transitions in motion along the reaction coordinate: the reagents in vibrational states with definite quantum numbers are converted into products in states with the same quantum numbers.

The applicability of the adiabatic approximation is determined by two factors. The sharper the change in the parameters of the potential surface (first the vibrational frequencies and the curvature of the reaction coordinate) along the reaction coordinate and the greater the rate of diffusion along it, the higher the probability of vibrational transitions. On the other hand, this probability decreases with increase in the vibrational quanta, that is, the frequency. In this respect the hydrogen abstraction reactions considered in our review occupy a favourable position. In this case the frequencies usually change little (thus in the reactions



the frequencies of the bonds being broken and being formed are almost the same, whereas the absolute values of the frequencies for the X–H bonds are high). It can be expected that the adiabatic description is applicable here, at least while the temperature is not too high, that is, the rate of relative motion is low and the highest vibrational levels are weakly populated.

There has recently been a series of papers which specially investigated range of applicability of the AC theory[41,42] and also of the calculated reaction probabilities (in particular, for H + H_2,[43-45]) in the adiabatic approximation. Their results agree with the qualitative conclusion drawn above. It must be added that when the adiabacity breaks down and vibrational transitions are observed this effect is levelled to a considerable degree by the averaging of the reaction probabilities over the vibrational states of the products in the concluding stage of the calculation of the overall rate constants. In other words, AC theory can remain a successful semiempirical method of investigating the overall rate constants even if its approximate nature is unsatisfactory for describing the elementary transition probabilities.

If it is assumed that the reaction coordinate is an adiabatically independent degree of freedom then the chief contribution to the value of κ is from a quantum correction for tunnelling through the one-dimensional potential barrier. In essence this is a correction to the classical state sum for the reaction coordinate; it is naturally included in AC theory.

In the calculation the potential barrier (that is, the section of the potential surface along the reaction coordinate around the saddle point) is approximated by an analytical expression: by a truncated parabola[46] or an Eckart potential[20,47]. The latter expression is more admissable[20,47,48]. Le Roy and coworkers[49] calculated κ by using the quantum partition function of an inverted harmonic oscillator (with imaginary virtual frequency)—this corresponds to a non-truncated parabolic model.

In any case the correction κ is determined by the effective mass μ^* for motion along the reaction coordinate, by the curvature of the potential barrier close to the saddle point, and by the energy of the reacting molecules. The characteristic parameter is

$$\lambda = \frac{hc}{kT}\frac{(\omega^*)}{i},$$

where ω^* is the imaginary frequency mentioned above, in cm^{-1}:

$$\omega^* = \frac{1}{2\pi}\sqrt{\frac{U^*}{\mu^*}}$$

(U^* is the negative force constant). κ increases with λ. For a hydrogen abstraction reaction, when the reaction coordinate near the saddle point is close to an antisymmetric vibration, $\mu^* \simeq \frac{1}{2}$ a.m.u. For this reaction (and probably for it alone) the tunnelling correction is rather significant at the experimental temperatures.

Table 1. Transmission coefficients for certain reactions.

T, °K	Reaction					
	H+H_2	H+D_2	H+T_2	D+D_2	CF_3+H–CD_3	CF_3+D–CHD_3
200	44.9	12.9	7.0	10.2	—	—
250	13.1	5.3	3.5	4.5	—	—
300	6.6	3.3	2.4	2.9	18.4	6.0
350	4.2	2.4	1.9	2.2	9.3	3.9
400	3.1	2.0	1.7	1.9	6.0	2.9
450	2.5	1.8	1.5	1.7	—	—
500	2.2	1.6	1.4	1.5	3.4	2.1
1000	1.3	1.2	1.1	1.1	1.5	1.3

Table 1 gives the tunnelling corrections calculated from the Eckart potential for the reaction H + H_2 and its isotopic analogues[48], and also for the reaction CF_3 + CHD_3 [21]. In the first instance the best of the potential surfaces at present available is used. The surface for the second reaction, calculated empirically, must be regarded as a rough approximation.

The figures given in Table 1 are probably too high[20,21]. Quantum calculations on a two-dimensional potential surface give somewhat smaller values of κ [35]. Generally, according to Rankin and Light's results[36], allowance for the quantum effects in hydrogen transfer reactions below 500°K is equivalent to an effective decrease in the height of the potential barrier by 1 kcal $mole^{-1}$.

Hence the existing calculated and theoretical estimates do not give reason for assuming that the errors in determining rate constants by AC theory are too high. However, this conclusion is valid only for thermal processes with relatively low reactant energies in the "chemical" temperature interval 300–500°K. At very high temperatures the assumption that the reaction coordinate is an independent degree of freedom is ineffective. At low temperatures the quantum corrections are significant.

Allowance for tunnelling within the framework of AC theory can increase the calculated value of the constant several times.

3. THE ACTIVATED COMPLEX MODEL

Johnston and coworkers have shown[20-22] that under certain conditions a considerable simplification of the real structure of the reactants and AC by replacing atomic groups by effective point masses, facilitates the calculation and has hardly any effect on the accuracy of the predicted pre-exponential factor.

For the reaction

$$M{-}H + R \rightarrow M \ldots H \ldots R \rightarrow M + HR$$

we have taken the AC model shown in Fig. 1. The fragments M and R are each regarded as an entity: their

internal degrees of freedom are obviously not taken into account. With each of the fragments is associated its coordinate system, positioned at its centre of gravity; the Z axis is directed along the M–H and H–R bonds respectively. Clearly there are nine internal degrees of freedom of the reaction centre to be considered:

1. The stretching vibrations of the bonds M–H (s_M) and H–R (s_R).
2. The deformation vibrations of the angles $HMX_M(\gamma_{MX})$, $HMY_M(\gamma_{MY})$, $HRX_R(\gamma_{RX})$, and $HRY_R(\gamma_{RY})$.
3. The deformation vibrations of the angle MHR in the XZ plane (γ_{HX}) and in the YZ plane (γ_{HY}).

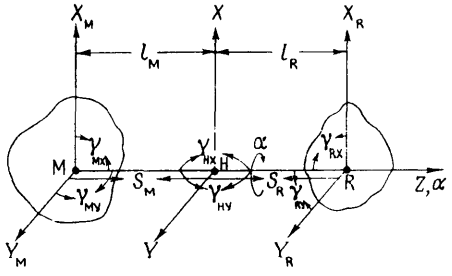


Figure 1. Model of an activated complex.

4. The internal rotation of the fragments M and R (α) relative to the axis α, coincident with the direction of the M–H and H–R bonds.

The following assumptions will be used subsequently:

I. The AC is linear—the bonds MH and HR lie in the same straight line (along axis α, common for both fragments).

II. In the calculation of the vibrational partition functions the systems of principal axes of inertia of the fragments M and R coincide with those coordinate systems introduced for these fragments in Fig. 1.

III. The above nine degrees of freedom do not interact with the internal degrees of freedom of the fragments.

IV. The stretching vibrations (s) of the reaction centre do not interact with the deformation vibrations (γ).

V. The internal rotation (α) is free and does not interact with either the stretching or the deformation vibrations.

These simplifications allow attention to be concentrated on the principal factors which determine the pre-exponential factor. Assumption (I) is almost always adopted in investigating hydrogen abstraction reactions. Assumptions (II)–(V) facilitate the assessment of the vibrational partition functions.

Refinement of the model should evidently not change the general qualitative conclusions. Quantitatively this investigation has the effect of dealing with each reaction separately only when the potential surface is known sufficiently reliably.

Since they do not depend on the form of the potential surface we tried to evaluate the rotational partition functions more accurately. Assumption (II) was not used in their calculation.

In evaluating the vibrational frequencies of the reaction centre in our model the matrix of the kinematic coefficients T_{ij} is needed (4). It has a simple form (Table 2) when assumptions (I)–(V) are used.

The following symbols are used: m_H, m_M, m_R are the masses of the hydrogen atom and the fragments M and R; I^M_X, I^M_Y, I^R_X, I^R_Y the principal moments of inertia of the fragments M or R relative to the corresponding axes; l_M and l_R the distances MH and HR;

$$\frac{1}{l_{MR}} = \frac{1}{l_M} + \frac{1}{l_R}.$$

Table 2 gives the part of the matrix to the right of the diagonal. Internal rotation is not considered, because of its separability.

4. ISOLATION OF THE GEOMETRIC FACTOR AND ITS EVALUATION

Eqn. (2) can be rewritten in the form:

$$A = A_0 A_1 \tag{6}$$

$$A_0 = \frac{kT}{h} \cdot \frac{F^{\neq}_{transl}}{F^{MH}_{transl} F^{R}_{transl}} \cdot \frac{F^{\neq}_{rot}}{F^{MH}_{rot} F^{R}_{rot}} \cdot F^{\neq}_{\alpha}, \tag{7}$$

$$A_1 = \varkappa \frac{\prod_i^7 F^{\neq}_i}{F^{M}_{\gamma MX} \cdot F^{M}_{\gamma MY} \cdot F^{M}_{sM}} \cdot \frac{F^{\neq}_{Mint}}{F^{M}_{int}} \cdot \frac{F^{\neq}_{Rint}}{F^{R}_{int}} \cdot \varphi_\alpha \tag{8}$$

In expression (7) $F^{\neq}_{\alpha}$ is the partition function for the free internal rotation α; the remaining symbols are obvious. In Eqn. (8), $F^{\neq}_i$ are the partition functions for the seven vibrations of the reaction centre (one stretching, six deformation); $F^{M}_{\gamma MX}$, $F^{M}_{\gamma MY}$, and F^{M}_{sM} those for the two deformation and one stretching vibrations of the C–H bond in the molecule. The remaining partition functions correspond to the internal degrees of freedom of the fragments M and R in the AC and in the reagents. The factor $\varphi_\alpha \leq 1$ is inserted into Eqn. (8) as a correction to the partition function $F^{\neq}_{\alpha}$ when the internal rotation is really restricted. When it is free, $\varphi_\alpha = 1$.

The quantity A_0 depends solely on the geometry of the AC and is independent of the form of the potential surface. It is not very sensitive to the detailed structure of the AC and therefore can be calculated reliably. The value of A_1, which is determined by the form of the potential surface, can only be estimated with a greater or lesser degree of accuracy.

Let us examine in greater detail the value of A_0 for the reaction of non-linear radicals and molecules. We obtain the first approximation by assuming that one of the reagents (the radical) is small in comparison with the other (the molecule) and the distance between the fragments M and R in the AC is not too great (<3 Å). Then

$$\frac{m_R}{m_R + m_{MH}} \ll 1; \quad \frac{I^R_X I^R_Y I^R_Z}{I^{\neq}_X I^{\neq}_Y I^{\neq}_Z} \ll 1; \quad \frac{I^R_\alpha}{I^R_\alpha + I^{MH}_\alpha} \ll 1.$$

Here m_{MH} is the mass of the molecule. The moments of inertia with subscripts X, Y, and Z are the principal moments of inertia of the radical (superscript R), molecule (superscript M), or AC (superscript ≠). The subscript α denotes calculation of the moment of inertia relative to the rotation axis α. We can assume that:

$$m^{\neq} \approx m_{MH}; \quad I^{\neq}_X I^{\neq}_Y I^{\neq}_Z \approx I^{MH}_X I^{MH}_Y I^{MH}_Z. \quad I^{\neq}_\alpha = \frac{I^R_\alpha I^{MH}_\alpha}{I^R_\alpha + I^{MH}} \approx I^R_\alpha$$

Table 2. Matrix of the kinematic coefficients for a reaction centre.

	s_M	s_R	γ_{HX}	γ_{MX}	γ_{RX}	γ_{HY}	γ_{MY}	γ_{RY}
s_M	$\frac{1}{m_H}+\frac{1}{m_H}$	$-\frac{1}{m_H}$	0	0	0	0	0	0
s_R		$\frac{1}{m_H}+\frac{1}{m_R}$	0	0	0	0	0	0
γ_{HX}			$\frac{1}{m_H l_{MR}^2}+\frac{1}{m_M l_M^2}+\frac{1}{m_R l_R^2}$	$-\frac{1}{m_H l_{MR} l_M}-\frac{1}{m_H l_M^2}$	$-\frac{1}{m_H l_{MR} l_R}-\frac{1}{m_R l_M^2}$	0	0	0
γ_{MX}				$\frac{1}{I_Y^M}+\frac{1}{m_H l_M^2}+\frac{1}{m_M l_M^2}$	$\frac{1}{m_H l_M l_R}$	0	0	0
γ_{RX}					$\frac{1}{I_Y^R}+\frac{1}{m_H l_R^2}+\frac{1}{m_R l_R^2}$	0	0	0
γ_{HY}						$\frac{1}{m_H l_{MR}^2}+\frac{1}{m_M l_M^2}+\frac{1}{m_R l_R^2}$	$-\frac{1}{m_H l_{MR} l_M}-\frac{1}{m_M l_M^2}$	$\frac{1}{m_H l_{MR} l_R}-\frac{1}{m_R l_R^2}$
γ_{MY}							$\frac{1}{I_X^M}+\frac{1}{m_H l_M^2}+\frac{1}{m_M l_M^2}$	$\frac{1}{m_H l_M l_R}$
γ_{RY}								$\frac{1}{I_X^R}+\frac{1}{m_H l_R^2}+\frac{1}{m_R l_R^2}$

where $I_\alpha^{\neq}$ is the reduced moment of inertia[50]. After these simplifications we obtain an approximate value of A_0:

$$A_0' = \text{const} \cdot \left(\frac{1}{m_R}\right)^{3/2} \left(\frac{I_\alpha^R}{I_X^R I_Y^R I_Z^R}\right)^{1/2} \frac{\sigma^R}{\sigma_\alpha^R}, \quad (9)$$

where σ^R is the complete symmetry number of the radical and σ_R^α the symmetry number for internal rotation. The temperature T is included in the constant factor.

A_0' is completely independent of the nature of the molecule MH. Since A_0 Eqn. (7), is determined by the order of magnitude of the pre-exponential factor A, Eqn. (9) gives a basis for unifying reactions for molecules with a single radical into a reaction series. In such series the pre-exponential factor should be approximately constant (excluding instances where the molecules are small). The breakdown of the constancy of A in a reaction series shows a change in the structure of the reaction centre and is associated with A_1 not being constant. Table 12 gives A_0' for various radicals.

Refinement of Eqn. (9) for small molecules, which brings it back nearer to form (7), yields the expression:

$$A_0 = A_0' \cdot \left(\frac{m_R + m_{MH}}{m_{MH}}\right)^{3/2} \cdot \left(\frac{I_X^{\neq} I_Y^{\neq} I_Z^{\neq}}{I_X^{MH} I_Y^{MH} I_Z^{MH}}\right)^{1/2} \cdot \left(\frac{I_\alpha^M}{I_\alpha^M + I_\alpha^R}\right)^{1/2} \cdot \frac{\sigma^{MH}}{\sigma^{\neq}} \quad (10)$$

where σ^{MH} and $\sigma^{\neq}$ are the symmetry numbers of the molecules in the AC. It is easy to obtain formulae, analogous to Eqns. (9) and (10), for reactions of atoms and also of linear radicals and molecules.

5. CONTRIBUTION OF THE INTERNAL DEGREES OF FREEDOM TO THE VALUE OF THE PRE-EXPONENTIAL FACTOR

We will write A_1 of Eqn. (8) in the form:

$$A_1 = \varkappa \cdot A_{11} \cdot A_{12}, \quad (11)$$

$$A_{11} = \frac{\prod_{i=1}^{Z} F_i^{\neq}}{F_{\gamma MX}^M F_{\gamma MY}^M F_{sM}^M}, \quad (12)$$

$$A_{12} = \frac{F_{M\,int}^{\neq}}{F_{int}^M} \cdot \frac{F_{R\,int}^{\neq}}{F_{int}^R} \varphi_\alpha . \quad (13)$$

The transmission factor $\varkappa$ takes into account the quantum effects of motion along the reaction coordinate and of the interaction between this coordinate and the remaining degrees of freedom. The value of A_{11} characterises the contribution to the pre-exponential factor of the vibrations of the reaction centre. The value of A_{12} is connected with changes in the internal degrees of freedom of the fragments M and R and can be regarded as a steric effect. The relative role of the factors entering into Eqn. (11) will be examined below.

a. Dependence of the Reaction Coordinate on the Symmetry of the AC

We will write the 2×2 unit of the upper left corner of the matrix of the kinematic coefficients T (Table 2).

$$T = \begin{pmatrix} \frac{1}{m_H} + \frac{1}{m_M} & -\frac{1}{m_H} \\ -\frac{1}{m_H} & \frac{1}{m_H} + \frac{1}{m_R} \end{pmatrix}$$

In the region of the saddle point it is determined by the reaction coordinate and the stretching vibration orthogonal to it. According to Eqn. (5), the form and frequency of the normal vibrations also depend on the matrix of the force constants U:

$$U = \begin{bmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{bmatrix}$$

For a symmetric reaction centre we can put

$$m_R = m_M = M, \quad U_{11} = U_{22} = U, \; U_{12} = u.$$

Then the frequencies of the symmetric and antisymmetric vibrations are

$$\omega_s = \frac{1}{2\pi} \sqrt{\frac{U_s}{\mu_s}},$$

$$\omega_a = \frac{1}{2\pi} \sqrt{\frac{U_a}{\mu_a}},$$

where

$$\frac{1}{\mu_s} = \frac{1}{M}; \frac{1}{\mu_a} = \frac{2}{m_H} + \frac{1}{M}; U_s = U + u; U_a = U - u .$$

At the saddle point U_a is negative and the frequency ω_a is imaginary. The reaction coordinate is an antisymmetric vibration. Since $M \gg m_H$, the effective mass μ_α is close to $\frac{1}{2} m_H$ and, as shown above, the transmission factor can acquire a rather greater value. It also increases when the barrier thickness is reduced, that is, with increase in $|U_\alpha|$.

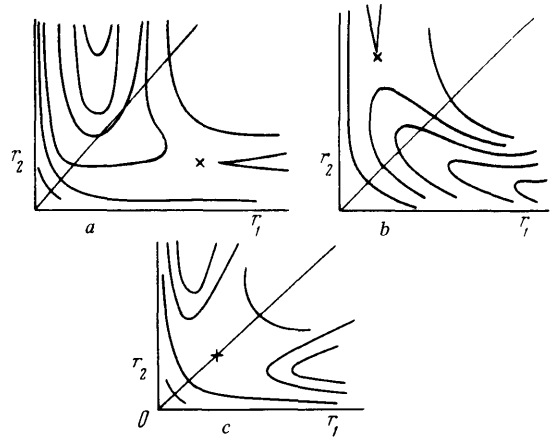


Figure 2. Types of potential surfaces for the transition states M...H...R. *a*) Attractive surface; *b*) repulsive surface; *c*) symmetric surface. $r_1 = s_{RH}$; $r_2 = s_{MH}$.

A reduction in symmetry, as is easily checked, leads to an increase in effective mass for the reaction coordinate and (at strictly the same conditions)—to a decrease in $\varkappa$ owing to the decrease in the quantum corrections. In the limiting cases the following two normal degrees of freedom are obtained:

(a) $U_{22} < 0$; $U_{11} \gg |U_{22}| \simeq |U_{12}|$: the s_{MH} vibration and the relative (counter) motion of MH and R.

(b) $U_{11} < 0$; $U_{22} \gg |U_{11}| \simeq |U_{12}|$: the s_{RH} vibration and the relative (towards opposite sides) motion of M and RH.

In considering the symmetric case in which all the force constants are essential three types of transition

states are obtained. They correspond to three types of potential surface[31,32]:
(a) "Attractive surface": the saddle point is situated on the initial linear part of the reaction coordinate; (b) "repulsive surface": the col point is situated on the final linear part of the reaction coordinate; (c) "symmetric surface": the saddle point is situated at the centre of the curvilinear part.

These surfaces are shown schematically in Fig. 2. For the first two types of AC the reaction coordinate is a relative translational motion. Only in the third "symmetric" type is it an antisymmetric vibration.

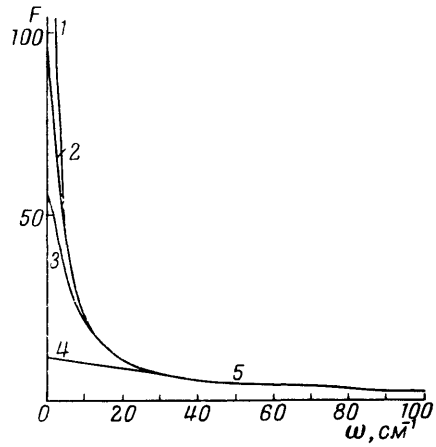


Figure 3. Variation of the vibrational partition functions with frequency (cm^{-1}). Curve *1*) calculated by Eqn. (15); curves *2*)–*4*) calculated by Eqn. (17) for specific values: *2*) for $I = 224$ (a.m.u.)Å^2 corresponds to I_X for the $(C_6H_5)_2CH$ fragment in $AK(C_6H_5)_2CH\ldots H\ldots R$; *3*) for $I = 79.4$, corresponds to the antisymmetric vibration in the XZ plane of $C_6H_5CH_2$ fragments in the activated complex $C_6H_5CH_2\ldots H\ldots CH_2C_6H_5$; *4*) for $I = 3.25$, corresponds to I_X for the CH_3 fragment in $CH_3\ldots H\ldots R$; *5*) calculated by Eqn. (14), the quantum and classical curves coincide in the range of frequencies shown.

b. Deformation Vibrations of the Reaction Centre

We have already noted that the values of the pre-exponential factor A calculated by the AC method are not very sensitive to the choice of model of the transition state. The explanation is that almost all the vibrational frequencies of the AC are high and for the corresponding degrees of freedom at the temperatures which are realised in the usual chemical experiment the higher vibrational levels are almost non-populated. Changes in these frequencies over a very wide range of values has little effect on the value of A. This very circumstance, which is quite general, means that in kinetic studies it is possible to use the AC model, which is quite unacceptable to the spectroscopist, from whose standpoint a change in any frequency by, let us say, 100 cm^{-1} already seems very great.

Fig. 3 shows the variation of the vibrational partition function with the frequency:

$$F_{vib} = \left[1 - \exp\left(-\frac{hc\omega}{kT}\right)\right]^{-1} \quad . \tag{14}$$

At frequencies of 100–300 cm^{-1} and 300–500°K this changes from the quantum kinetic inactive region to the classical:

$$F_{vib} = \frac{kT}{hc\omega} \quad . \tag{15}$$

In subsequent discussion deformation vibrations are important. For these the role of the effective mass μ is played by the effective moment of inertia I; in the one-dimension case, when U is the corresponding force constant,

$$\omega = \frac{1}{2\pi}\sqrt{\frac{U}{I}} \tag{16}$$

The classical state sum equals[51]

$$F_{vib} = \frac{kT}{hc\omega}\,\mathrm{erf}\left[\pi^2 c\omega\left(\frac{2I}{kT}\right)^{1/2}\right] \tag{17}$$

where erf is the error integral.

Eqn. (17) corresponds to a harmonic oscillator with an amplitude bounded between the limits $(-\pi, \pi)$. At very low frequencies they are converted into a one-dimensional rotational partition function $(8\pi^3 IkT)^{1/2}/h$ and at high frequencies it agrees with the classical formula (15) (Fig. 3). This model describes in the simplest manner the conversion of the vibrational degree of freedom into rotational. It was used for estimating the pre-exponential factor in recombinations, where the AC are assumed to be very loose[52].

The kinetically active frequencies are found to lie in the classical region. Frequencies in the quantum region are generally not of interest.

It is evident that the lowest values of the frequencies must be sought among the deformation vibrations. In our model (Fig. 1 and Table 2) the matrix T for six deformation vibrations is broken down into two three-dimensional blocks: vibrations in the XZ and YZ planes.

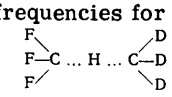
Let us consider the symmetric example (M = R) for motion in the XZ planes. We will introduce the symbols: $m_M = m_R = M$, $l_M = l_R = l$, $I_X^M = I_X^R = I_X$. The vibrations γ_{MX} and γ_{RX}, on mixing, form symmetric $\frac{1}{\sqrt{2}}(\gamma_{MX} + \gamma_{RX})$ and antisymmetric $\frac{1}{\sqrt{2}}(\gamma_{MX} - \gamma_{RX})$ vibrations with kinematic coefficients:

$$\frac{1}{I_s} = \frac{1}{I_X} + \frac{1}{l^2 M} + \frac{2}{l^2 m_H} \text{ and } \frac{1}{I_a} = \frac{1}{I_X} + \frac{1}{l^2 M} \, . \tag{18}$$

The antisymmetric vibration does not mix with the γ_{HX} vibration. It has the most effective moment of inertia, since the term which contains the small quantity m_H in the denominator is lost. According to Eqn. (16), when the force constants are approximately the same the antisymmetric frequency ω_α should be least. These qualitative discussions are still valid when the fragments M and R are different but their mass is sufficiently great and the reaction centre is symmetric or almost symmetric, that is, the M–H and H–R bonds are almost the same.

The closest vibrations of normal molecules to γ_{MX} and γ_{RX} are the in-plane deformation vibrations of the C–H bonds in aromatic molecules. Their frequencies are 400–1000 cm^{-1} [53,54]. These quantities should be reduced by approximately 50% since in comparison with the bonds in the normal molecules the CH bonds in the AC are longer, and their force constants are reduced (in some studies[20-22] it has been assumed that the force constants are reduced by 50%). The frequency ω_α of the antisymmetric vibration is further reduced as a result of

the interaction of γ_{MX} and γ_{HX}. Hence we estimate ω_α to be 100–400 cm^{-1}, lying at the boundary between the classical and quantum regions. We note that allowance for the interactions which we neglected in our model can only decrease the value of the least frequency, that is, the figure obtained can be regarded as the upper bound of the frequency ω_α. The frequencies for the AC



have been calculated[21].

An empirical potential surface was used and the estimates of the force constants were doubly approximate. Nevertheless it is helpful to compare the results of this calculation with our estimates obtained without any calculation. The values found for the vibrational frequencies of the reaction centre are 304 cm^{-1} for the symmetric stretching vibration, 1026 and 470 cm^{-1} for the two doubly degenerate, almost symmetric, deformation vibrations in the XZ and YZ planes, and $\omega_\alpha = 147$ cm^{-1} for the doubly degenerate, (almost) antisymmetric vibrations. The two antisymmetric vibrations contribute a factor of 4.3 to the vibrational partition function (the full value of this sum is ~10). In the calculation mentioned allowance was made for all interactions of the normal coordinates, including interaction with the vibrations within the fragments CF_3 and CD_3. Strictly speaking, these frequencies belong not to the above vibrations of the reaction centre but to the normal vibrations which contain these vibrations as one of their components (probably the main one). Consequently, these results confirm numerically that our model is suitable for approximate evaluations.

If the force constant U in Eqn. (16) is approximately the same for different AC then the upper bound of the deformation frequency ω_α corresponds to small values of the moment of inertia I_X in expression (18). This happens, for example, when the fragments M and R (or even one of them) are CH_3 groups, that is, only the hydrogen atoms contribute to the moment of inertia I_X. Then the effective moment of inertia I_α is also small. As an example, we give the calculated[22] least values of the frequencies for the reactions Cl + HM. For M = CH_3, CH_2Cl, $CHCl_2$, and CCl_3 they are 457, 233, 187, and 159 cm^{-1} respectively.

When the fragments M and R, or one of them, are atoms, the corresponding deformation vibrations generally disappear. Therefore the lowest frequencies for the reactions of radicals with the same molecules should be less.

Hence for a symmetric reaction complex (surface of type *c* in Fig. 2)the contribution of the deformation vibrations (mainly due to two antisymmetric vibrations) can, according to Eqn. (12), lead to values of $A_{11} \simeq 10-100$.

Considerably greater effects must be expected for potential surfaces of types *a* and *b* (Fig. 2). For these the value of one of the force constants U in formula (16) can be expected to be very small. The frequency is reduced accordingly. At the limit this corresponds to the change of the (almost) antisymmetric deformation vibrations into rotation of the fragment M or R according to Eqn. (17). Since there are thus two degrees of freedom (in the planes XZ and YZ) values of $A_{11} \simeq 10^3-10^4$ can be obtained.

We must remember that, as shown above (Section 2c), the adiabatic resolution of the variables is of little effect for low frequencies. Although the change in frequency along the reaction coordinate is also smaller in this instance, the problem of whether AC theory can describe the contribution of kinetically active low-frequency vibrations is unresolved. The conclusion about the increase in the pre-exponential factor remains in force but the estimates given of the magnitude of this effect could be greatly changed on making allowance for the exchange of energy between the reaction coordinate and the rotational degrees of freedom.

c. Internal Degrees of Freedom of the Reactants

The value of A_{12} in expression (13) is usually close to unity. This is because even if any frequencies of the fragments M and R are altered in the AC as compared with the isolated reactants, all the same these frequencies are kinetically inactive. There are exceptions when the structure of the fragments is rather complex:- there are bulky substituents. Then internal rotations which are restricted in the reactants can be freed in the formation of the AC, or on the other hand rotations which are free in the reactants can become restricted. An example of this is the restriction of the free rotation around the M...H...R bond in the AC. Such steric effects can make significant contributions to the pre-exponential factor.

6. SUMMARY OF THE EXPERIMENTAL VALUES OF THE PRE-EXPONENTIAL FACTOR

Tables 3–10 give the experimental values of the pre-exponential factors recalculated per single active (in bold type in the tables) hydrogen atom (A, litre $mole^{-1}$ s^{-1}). Reactions in the gas phase and liquid phase are considered (in the latter instance, in non-polar media). Results from existing reviews on hydrogen abstraction reactions[55-59] and from the individual papers listed in the references are used.

The absolute values of A for the reactions of a fluorine atom were obtained from results on competing fluorination and the reference value of A = 10^{10} litre $mole^{-1}$ s^{-1} for the reaction F + C_2H_6. This value was calculated by assuming that the fluorine atoms react with C_2H_6 at every collision[2].

Absolute values of A in the reactions of Cl atoms were obtained from results on competitive chlorination; in the reactions of Cl with various isotopic modifications of H_2 and CH_4 the standard adopted was the value of A = 4.1×10^{10} litre $mole^{-1}$ s^{-1} for the reaction Cl + H_2 [2], in other instances the reference quantity was A = 0.6×10^{10} litre $mole^{-1}$ s^{-1} for the reaction Cl + CH_4 [2].

For the reactions of Br atoms the absolute values of the pre-exponential factor were obtained from results on competitive bromination and the absolute value of A = 1.67×10^7 litre $mole^{-1}$ s^{-1} for the reaction Br + CH_3Br [2].

In determining the absolute values of A for the reactions of alkyl and halogenoalkyl radicals the reference quantities used were A for their recombinations. For the reaction CH_3 + CH_3 A was taken as 2.2×10^{10} litre $mole^{-1}$ s^{-1} [60], and for CF_3 + CF_3 A = 2.3×10^{10} litre $mole^{-1}$ s^{-1} [61]. For the recombination of other alkyl and halogenoalkyl radicals we took A = 10^{11} litre $mole^{-1}$ s^{-1} [59].

The absolute values of A for the reactions of 2-cyano-2-methylethyl radical were calculated from our results[62]. A = 2×10^9 litre $mole^{-1}$ s^{-1} was used as the reference quantity for the recombination of $C(CH_3)_2CN$ radicals[63].

7. CALCULATION OF MOMENTS OF INERTIA

The principal moments of inertia I_X, I_Y, and I_Z are determined as the eigenvalues of the I matrix of the inertia tensor. The direction cosines of the principal axes

Table 3. Pre-exponential factor of reactions involving the abstraction of hydrogen by atoms.

Atom	Molecule	T, °K	$10^{-10}A$, litre mole^{-1} s^{-1}	Reference
1	2	3	4	5
H	H_2	400	6.0	64
	HD	400	1.3	64
	DH	400	1.2	64
	D_2	400	2.1	64
	D_2	368—468	0.2	65
D	D_2	300—750	2.5	66
	H_2	400	2.3	64
	H_2	250—750	2.2	66
	HD	400	1.0	64
	DH	400	0.9	64
	D_2	400	3.1	64
	CH_4	1220—1790	5.0	67
	CH_4	372—436	0.0003	68
H	CH_4	500—803	0.02	69
	CH_4	673—753	1.4	70
D	CH_4	620—738	0.3	71
H	CH_3CH_3	323—523	0.2	72
	$CH_3CH_2CH_3$	330—793*	3.3	73
	$CH_3CH_2CH_3$	330—490	0.3	74
	$CH_3(CH_2)_2CH_3$	323—523	0.01	72
	$CH_3(CH_2)_2CH_3$	753—793*	0.8	72
	$(CH_3)_3CH$	753—793*	1.0	72
	$(CH_3)_3CH$	323—523	0.04	75
O	H_2	409—928	2.0	76
	CH_4	300—900	0.4	76
	C_2H_6	320—590	0.3	76
F	H_2	178—373	5.9	77, 78
	CH_4	178—373	3.1	78
	CH_3CH_3	178—373	1.3	9
	$CH_3CH_2CH_3$	178—373	0.6	9
	$CH_3CH_2CH_3$	178—373	0.6	9
	$CH_3(CH_2)CH_3$	178—373	0.5	9
	$CH_3(CH_2)_2CH_3$	178—459	0.6	9, 78
	$(CH_3)_3CH$	178—373	0.5	9
	$(CH_3)_3CH$	178—459	0.7	9, 78
	$(CH_3)_4C$	178—373	0.5	9
	cyclo-C_6H_{12}	178—373	0.5	9
Cl	H_2	—	4.1	2
	HD	243—350	3.3	79
	HT	234—345	3.0	80
	D_2	273—305	3.0	81
	CH_4	200—600	0.6	8, 82
	CH_3CH_3	273—588	1.5	2
	$CH_3CH_2CH_3$	200—600	1.7	8
	$CH_3CH_2CH_3$	200—600	3.6	8
	$CH_3(CH_2)_2CH_3$	200—600	1.4	8
	$CH_3(CH_2)_2CH_3$	200—600	2.4	8, 78
	$(CH_3)_3CH$	200—600	1.3	8
	$(CH_3)CH$	200—600	2.1	8, 78
	$(CH_3)_4C$	200—600	1.4	8
	cyclo-C_3H_6	200—600	0.9	8
	cyclo-C_4H_8	200—600	3.2	8
	cyclo-C_6H_{10}	200—600	2.3	8, 82
	CH_3Cl	273—573	1.1	82, 83
	CH_2Cl_2	273—573	1.3	83
	$CHCl_3$	273—573	0.7	83
	$CDCl_3$	253—573	0.5	83, 84
	C_2H_5Cl	200—600	0.7	82, 8
Cl	C_2HCl_5	273—573	0.5	83, 85
	$ClCH_2(CH_2)_2CH_3$	308—419	1.2	86
	$FCH_2(CH_2)_2CH_3$	273—419	1.3	86
	$ClCH_2CH_2CH_2CH_3$	308—419	1.1	86
	$ClCH_2CH_2CH_2CH_3$	308—419	2.4	86
	$FCH_2CH_2CH_2CH_3$	273—419	1.9	86
	$FH_2CCH_2CH_2CH_3$	273—419	2.6	86
	H_2	273—1071	14.0	2
Br	D_2	—	10.0	2
	CH_4	210—503	1.5	87
	CH_4	311—421	5.0	10
	CH_3Cl	477—614	1.3	10
	CH_3Br	210—503	1.7	87
	CH_3CH_3	332—573	1.2	10
	$(CH_3)_4C$	330—573	1.5	10
	$CH_3CH_2CH_3$	286—418	2.5	10
	$CH_3(CH_2)_2CH_3$	267—371	4.1	10
	$(CH_3)_3CH$	311—421	2.0	10
	$CHCl_3$	420—455	1.5	88
I	H_2	667—800	5.0	11
	D_2	667—800	5.0	12
	$CH_3CH_2CH_3$	580—613	5.0	89
	$(CH_3)_3CH$	525—583	7.6	90
	$CH_3—CH_2—CH=CH_2$	465—572	0.1	91
	CH_3CHO	495—541	2.0	92

* The reaction is not selective at high temperature. The corresponding values of A are obtained by dividing the experimental value by the total number of hydrogen atoms.

Table 4. Pre-exponential factors for the reactions: $CH_3 + CH_3-X$.

Molecule	T, °K	$10^{-7}A$, litre mole^{-1} s^{-1}	Reference
1	2	3	4
CH_4	473—623	17	93
	623—793	16	94
CH_3F	—	9.3	55
CH_3Cl	—	16	55
CH_3Br	—	70	55
CH_3OH	406—473	2.0	95
	413—523	6.7	96
	403—523	0.8	97
CH_3OD	403—523	6.6	96, 98
CD_3OH	403—523	6.7	96, 98
	406—473	6.0	95
	403—523	0.5	97
CH_3NH_2	393—448	3.3	99
CD_3NH_2	393—448	2.6	99
CH_3ND_2	393—448	4.7	99
$CH_3N_2CH_3$	383—453	1.3	99
	383—458	1.3	100
	383—453	1.2	101
$CH_3N_2D_2$	383—453	1.7	100
CH_3CN	373—573	6.7	102
CH_3SH	403—473	2.5	103
$CH_3—CH_3$	433—493	27	104, 105
	578—689	18	106, 107
$CH_3CH_2CH_3$	433—423	12	107
	568—792	1.1	108
$(CH_3)_4C$	458—581	16	109
	423—573	1.3	110, 111
$(CH_3)_3CC(CH_3)_3$	343—613	0.7	112
$(CH_3)_3C(CH_3)_2CC(CH_3)_3$	343—617	0.7	112
$(CH_3)_3CD$	568—729	0.1	113
$CH_3CH=CH_2$	343—613	1.4	112
$CH_3—CH=CH—CH_3$	343—613	1.1	112
$(CH_3)_2C=CH_2$	343—613	1.8	112
$(CH_3)_2C=C(CH_3)_2$	343—613	2.5	112
$CH_3C\equiv CCH_3$	343—613	5.4	112
CH_3OCH_3	343—613	3.3	112
	413—523	6.7	96
CH_3OOCH_3	393—523	6.1	114
CH_3COCH_3	413—523	4.8	96
	403—473	3.8	103
	343—613	5.0	112
	386—573	4.7	115
		4.5	116
	393—523	5.7	117
	373—573	6.7	118
CD_3COCD_3	413—523	7.0	96
	393—523	3.7	114
$CH_3COCOCH_3$		0.9	55
CH_3OCOCH_3	450—489	3.7	114
$(CH_3)_3COOC(CH_3)_3$	450—489	4.3	119
$N(CH_3)_3$	400—440	25.0	120
	343—613	5.8	112
$(CH_3)_2NCOCH_3$	396—433	2.8	121
CH_3CONH_2	398—430	2.6	122
$CH_3C_6H_5$	395—532	4.5	122
$CH_3C_6H_5$	343—613	3.3	112
$CH_3COC_6H_5$	33—533	1.0	123
o-$CH_3C_6H_4CH_3$	557—687	1.7	124
	373—473	2.3	125
m-$CH_3C_6H_4CH_3$	273—368	0.8	126
	373—473	4.8	125
	273—368	0.8	126
p-$CH_3C_6H_4CH_3$	373—473	1.1	125
	273—368	0.8	126
p-$FC_6H_4CH_3$	606—733	0.4	127
o-$FC_6H_4CH_3$	604—734	0.6	127
m-$FC_6H_4CH_3$	602—753	0.5	127
$C_6H_5(CCH_3)_3$	273—368	0.5	126

$(I_i,\ m_i,\ n_i)$ form a matrix of eigenvectors **I**. The matrix elements I_{ik} were calculated by the formula

$$I_{ik} = \Sigma m_n(x_n^2\delta_{ik} - x_{ni}x_{nk}) - m(a^2\delta_{ik} - a_ia_k), \qquad (19)$$

where x_n is the radius vector of the atom n, a the radius vector of the centre of inertia, m_n the mass of atom n, and $m = \Sigma m_n$ the mass of the entire system.

This standard procedure was used to calculate the moments of inertia of the molecules and radicals. Tables 11 and 12 give the results. Fig. 4 shows the geometric characteristics employed in the calculation and the choice of coordinate axes.

Since the geometry of the AC is not known precisely, it is desirable to use a simple approximate method for calculating its moments of inertia. Assuming that the radical is small in comparison with the molecule and the

distance between the fragments M and R is not too great we will model the fragment R by the point mass $m_R = \Sigma m_n$ equal to it in mass and located at its centre of inertia R with radius vector r. We choose as coordinate system the principal axes of the molecule with the direction cosines from Table 12. Then Eqn. (19) takes the form:

$$I_{ik}^{\neq} = I_i^M \delta_{ik} + m_R (r^2 \delta_{ik} - r_i r_k) - (m_{MH} + m_R) \cdot (a^2 \delta_{ik} - a_i a_k) .$$

In the system of coordinates used

$$a_i = \frac{m_R}{m_R + m_{MH}} r_i ,$$

whence

$$I_{ik}^{\neq} = I_i^M \delta_{ik} + \mu (r^2 - r_i r_k); \ \mu = \frac{m_{MH} \cdot m_R}{m_{MH} + m_R} .$$

By using perturbation theory, we obtain to the first order:

$$I_i^{\neq} = I_i^{MH} + \mu (r^2 - r_i^2) \qquad (20)$$

Table 5. Pre-exponential factors for the reactions $CH_3 + CH_2X^1X^2$ and $CH_3 + H-C\swarrow$.

Molecule	T, °K	$10^{-7}A$, litre mole^{-1} s^{-1}	Reference
1	2	3	4
$CH_3CH_2CH_3$	578—723	36	107, 113
$CH_3CD_2CH_3$	629—723	7.0	104
$CH_3(CH_2)_2CH_3$	523—723	13	104
	668—744	19	110
$CH_3(CH_2)_3CH_3$	668—744	12	110
$CH_3(CH_2)_4CH_3$	668—744	15	110
CH_3CH_2OH	403—523	20	98
	463—613	20	128
cyclo- C_3H_6	668—744	12	110
	427—713	17	129
cyclo- C_4H_8	427—713	6.3	129
cyclo- C_5H_{10}	427—713	6.6	129
cyclo- C_6H_{12}	427—713	6.6	129
cyclo- C_7H_{14}	427—713	6.3	129
CH_3=CH·CH_2CH_3	343—613	5.5	112
CH_2=CH—$CH_2CH_2CH_3$	343—613	5.8	112
CH≡C—CH_2CH_3	343—613	27	112
$(CH_3)_2NH$	383—448	6.9	101
$CH_3CH_2NH_2$	393—453	8.0	121
$CH_3CH_2NH_2$	283—453	8.0	130
$(CH_3CH_2)_2NH$	396—533	15	121
$(CH_3CH_2)_3N$	396—533	3.3	121
$NH_2(CH_2)_2NH_2$	363—448	2.0	131
$(CH_3CH_2)_2O$	318—353	25	132
$(CH_3CH_2)_2CO$		2.5	132
CH_3CH_2CN	373—573	1.0	102
$C_6H_5CH_2CH_3$	273—368	1.5	126
$(C_6H_5)_2CH_2$	273—368	3.2	126
$(C_6H_5)_2(CH_2)_2$	273—368	1.3	126
CH_2Cl_2		10	133
$(CH_3)_3CH$	578—732	30	107, 113
	343—613	6.3	112
$(CH_3)_2CH$-$CH(CH_3)_2$	343—613	6.5	112
$(CH_3)_2CH(CH_3)CHCH(CH_3)_2$	343—613	4.3	112
$(CH_3)_2CH$—OH	297—613	6.3	112
$(CH_3)_2CH$—OH	408—523	1.5	96, 98
$(CH_3)_2CH$—O—$CH(CH_3)_2$	408—523	1.6	96
	453—513	8.0	112
$(CH_3)_2CHOOCH(CH_3)_2$	394—432	1.6	134
$C_6H_5C(CH_3)_2H$	273—368	2.7	126
n-$C_4H_9C_6H_4C(CH_3)_2H$	273—368	2.1	126
$(C_6H_5)_2CH$	273—368	3.9	126
C_6H_5—CHC_5H_{10}	273—368	3.0	126
$CHCl_3$		6.0	133
CF_3H		2.3	135
CF_3CF_2H		14	135
n-C_3F_7H		91	135

Formula (20) allows the moments of inertia of the AC to be found easily from the data of Tables 11 and 12. When there is a large radical and a small molecule, the moment of inertia of the molecule is replaced by the moment of inertia of the radical and the radius vector of the radical by that of the molecule.

When the moments of inertia I_i^{MH} in formula (20) are the same or very similar to one another, the error in the individual values of $I_i^{\neq}$ can be rather high (then perturbation theory with allowance for degeneracy leads to the full task of diagonalisation of the I matrix) but the product $\Pi I_i^{\neq}$ is also determined with acceptable accuracy in this instance (cf. the calculation for methane). Table 13 compares the calculations by Eqn. (20) with the full calculations.

In the complete calculation the geometry of the fragments M and R is unchanged in the AC. The distance between the carbon atoms of the reaction centre C—H—C was assumed equal to 2.4 Å. For a reaction centre X—H—Y, where although one of the atoms X and Y is not a carbon atom, the lengths of the bonds X—H and Y—H in the AC were evaluated by the Pauling formula[23,199],

Table 6. Pre-exponential factors for the reactions: $CH_3 + H-COX$.

Molecule	T, °K	$10^{-8}A$, litre mole^{-1} s^{-1}	Refs.	Molecule	T, °K	$10^{-8}A$, litre mole^{-1} s^{-1}	Refs.
HCOH	392—448	0.8	120	C_2F_5COH	673—717	79	136
H—$OCCH_3$	392—448	7.9	120	C_3F_7COH	673—717	160	136
H—COC_2H_5	392—448	10	120		393—523	1.8	117
HCO n-C_3H_7	392—448	6.3	120	$HCOOCH_3$	348—443	0.5	137
HCO iso- C_3H_7	392—448	40	120	$HCOOC_2H_5$	350—450	0.3	138, 139
HCO n-C_4H_9	392—448	13	120	HCOO n C_3H_7	392—448	0.1	120
HCO s-C_4H_9	392—448	200	120	HCOO i-C_3H_7	350—450	0.8	120, 139
HCO i-C_4H_9	392—448	20	120	HCOO n C_4H_9	393—453	0.4	120
HCO t-C_4H_9	392—448	100	120	$HCONH_2$	443—520	0.3	140
CH_3CH-$CHCOH$	392—448	200	120	$HCON(CH_3)H$	434—560	0.8	140
CF_3COH	673—717	13	136	$HCON(CH_3)_2$	393—571	0.3	140

Table 7. Pre-exponential factors for the reactions $CH_3 + H-N\swarrow$, $CH_3 + H-O-$, and $CH_3 + H-S-$.

Molecule	T, °K	$10^{-7}A$, litre mole^{-1} s^{-1}	Refs.	Molecule	T, °K	$10^{-7}A$, litre mole^{-1} s^{-1}	Refs.
NH_3	383—453	2.3	141	$(C_2H_5)_2NH$	398—430	60	142
ND_3	383—453	3.3	141	$(C_3H_7)_2NH$	398—430	100	142
H_2NNH_2	383—453	2.5	100, 141	$(CH_2)_2NH$	383—448	1.5	101
CH_3NH_2	363—448	0.2	99	CH_3OH	403—523	3.0	96
CD_3NH_2	368—448	0.3	99		403—523	2.9	97
$(CH_3)_2NNH_2$	383—448	10	100	C_2H_5OH	403—523	8.0	96
$C_2H_5NH_2$	383—453	0.5	130	iso-C_3H_7OH	403—523	0.1	96
CH_3ONH_2	383—448	2.5	99	iso-C_3H_7OD	403—523	0.1	96
$H_2NCH_2CH_2NH_2$	363—448	0.5	131	CD_3SH	403—523	10	103
$(CH_3)_2NN(CH_3)H$	383—448	0.5	100	H_2S	323—473	13	143
$(CH_3)_2NH$	398—430	52	142				

$l_{H-X}^{\neq} = l_{H-X} - 0.6 \ln n$, where l_{H-X} is the length of the H—X bond in the ordinary molecule and n the bond order (assumed to be 0.5).

8. ANALYSIS OF THE VALUES OF A_i FOUND FROM EXPERIMENT

Having determined the value of A_0 from formulae of the type of Eqn. (10) with moments of inertia calculated by the method described in the previous section, "experimental" values of A_i can be obtained. According to Eqn. (6) the experimental values of the pre-exponential factor must be separated from A_0. Table 14 gives the values of A_i thus found. The values of A_0 were calculated for 373 °K.

In discussing the values of A_1 caution is necessary because both the experimental results and the AC theory itself, which form the basis of the discussion, are imprecise. We will examine the effects which seem to be unquestioned: either they are of the order of 10^2-10^3, or (for effects of the order of 10^1) they are repeated with sufficient regularity in several reaction media.

According to Eqn. (11), A_1 is the product of three factors. The transmission factor κ can be either greater or less than unity owing to the competition of two effects: tunnelling and the interaction between the reaction coordinate and the remaining degrees of freedom (strictly,

Table 8. Pre-exponential factors for hydrogen abstraction by trifluoromethyl radicals.

Molecule	T, °K	$10^{-7}A$, litre mole^{-1} s^{-1}	Refs.	Molecule	T, °K	$10^{-7}A$, litre mole^{-1} s^{-1}	Refs.
CH_4	391—673	14	144	$CH_3CH_2CH_3$	540—570	23	149
	426—568	23	145		300—392	28	158
	357—534	24	146	$CH_3(CH_2)_2CH_3$	300—392	3.5	159
CD_4	379—560	3.8	146		540—570	7.0	149
CHD_3	601—900	11	21		357—435	5.0	155
CH_3Cl	417—673	46	145	cyclo-C_5H_{10}	540—570	3.5	149
CH_3Br*	423—533	14	142	cyclo-C_6H_{12}	292—364	4.7	151
CH_3Br**	423—533	48	142	$(CH_2)_2NH$	433—503	2.0	158
CH_3I	327—583	1.4	142	$(CH_3)_2CHCH(CH_3)_2$	540—570	3.5	149
CH_2Cl_2	358—722	8.4	147	$(CH_3)_3CH$	350—392	14	159
$CHCl_3$	367—999	14	147		291—673	15	144
	390—524	97	146		338—537	300	146
$CDCl_3$	338—537	60	146	CH_3OCOH	393—523	26	117
CH_3CH_3	601—900	7.0	11	CH_3OCOD	393—523	20	117
	668—797	21	148	CH_3COH	291—673	6.9	144
$C(CH_3)_4$	540—570	4.8	149	CF_3COH	291—673	54	144
CH_3CH_3	668—797	8.0	148		300—434	90	160
$CH_3C_6H_5$	300—383	4.3	150	C_2F_5COH	300—434	13	160
$CH_3C_6H_5$	300—400	1.3	151	C_3F_7COH	300—580	47	161
	571—627	7.0	149		300—434	12	160
$CH_3C_6F_5$	300—383	1.9	150	CD_3OH	357—435	0.3	155
o-$CH_3C_6H_4CH_3$	310—341	8.0	152	CH_3OD	650—798	400	156
CH_3COCF_3	298—623	0.7	153	CH_3NH_2	303—433	0.4	157
CH_3COCH_3	302—442	1.0	154	$(CH_3)_2NH$	300—434	3.2	158
	540—570	5.0	149	$(CH_3)_2ND$	300—434	7.5	158
CH_3OH	357—435	0.3	155	$(CH_3)_2NH$	300—434	2.0	158
CD_3OH	357—435	0.5	155	H_2S	368—434	8.0	162
CH_3OD	680—798	11	156		330—370	20	163
CH_3CO_2H	393—523	3.3	117		333—384	33	164
CH_3NH_2	303—433	1.7	157	D_2S	353—484	40	165
CH_3ND_2	303—433	4.0	157	NH_3	286—513	1.2	165
$(CH_3)_2ND$	300—434	7.3	158	ND_3	286—513	0.9	165
$(CH_3)_3N$	300—434	11	158	SiF_3H	383—563	135	166

* High value.
** Low value.

the transmission factor). The vibrational factor A_{11} is greater than or equal to unity. The steric factor A_{12} can be either greater or less than unity.

The last two factors are not present in reactions of atoms with diatomic molecules. On the basis of the data in Table 14 in this instance $A_1 \simeq \kappa \leqslant 1$. Consequently, the opposing effects which contribute to κ are either insignificant or compensated. When a factor of 2 – 5 is taken for the tunnelling, the transmission factor proper is 0.1 – 0.5. Thus or otherwise, κ is of the order of unity ($\kappa \simeq 0.3-1$), that is, the simple AC theory does not contradict experiment in any instance. Subsequently we will take $\kappa = 1$.

For the remaining reactions it is possible with sufficient confidence to distinguish those instances in which the steric effect is absent ($A_{12} \simeq 1$). These are reactions with molecules of simple structure. From Table 14 we find $A_1 \simeq A_{11} \geqslant 1$ for them. Table 15 gives values of A_1 for typical pairs of reactants.

From the results of Table 15: (1) In the reactions of one molecule with a series of radicals A_{11} is least for the radical CH_3; (2) in the reactions of one radical with a series of molecules it is least for the CH_4 molecule.

Table 9. Pre-exponential factors for hydrogen abstraction reactions of alkyl, halogenoalkyl, phenyl, and alkoxy radicals.

Radical	Molecule	T, °K	$10^{-7}A$, litre mole^{-1} s^{-1}	Reference
1	2	3	4	5
C_2H_5	CH_4		16	58
	C_2H_6		11	58
	$C(CH_3)_4$	323—573	3.0	167
	$N(CH_3)_3$	363—431	0.3	168
	$CH_3(CH_2)_2CH_3$	323—573	5.0	167
	$CH_3(CH_2)_4CH_3$	360—525	3.4	169
	$CH_3(CH_2)_5CH_3$	400—476	10	170
	$CH_2{=}CH{-}CH_2(CH_2)_3CH_3$	357—473	16	170
	$CH_2{=}CH{-}CH_2(CH_2)_4CH_3$	298—456	13	170
	$CH_3CH_2CH_2CH{=}CHCH_2CH_2CH_3$	359—439	16	170
	$CH{\equiv}C{-}CH_2(CH_2)_3CH_3$	298—454	8.0	170
	cyclo-C_6H_{10}	300—526	31	170
	$CH_3COCH_2CH_3$		10	56
	$(CH_3CH_2)_2CO$		6.2	56
	$(CH_3CH_2)_2CO$	363—433	6.2	168
	$(CH_3CD_2)_2CO$		20	56
	$(CH_3CD_2)_2CO$		8.3	56
	$(CD_3CD_2)_2CO$	298—587	10	171
	$(CH_3CH_2)_2N_2$		4.0	56
		301—425	13	172
	$(CH_3CH_2)_2Hg$		1.0	56
	cyclo-C_6H_{12}	371—564	4.4	169
	$(CH_3)_3CH$	323—573	8.3	167
	CH_3CH_2COH	323—778	18	173
	C_3H_7OCOH	340—440	8.0	120
	H_2NNH_2	363—430	1.3	124
	CH_3COCH_3	403—503	1.9	117
	$(CH_3CH_2CH_2)_2CO$	328—530	0.6	174
n-C_3H_7	n-C_3H_7COH	371—634	20	175
	$CH_3CH_2CH_2COH$	464—573	5.0	175
iso-C_3H_7	n-C_3H_7OCOH	347—451	16	176
	$(CH_3)_2CHCOH$	556—650	2.5	177
	$(CH_3)_2CDCOCD(CH_3)_2$		0.4	59
	$(CH_3)_2CDCOCD(CH_3)_2$		33	59
	iso-C_3H_7COH	390—627	16	177
	iso-C_3H_7OCOH	367—454	2.5	176
	$(CH_3)_2CHNNCH(CH_3)_2$		1.3	59
n-C_4H_9	n-C_4H_9COH	334—503	7.9	178
s-C_4H_9	s-C_4H_9COH	297—621	5.0	179
iso-C_4H_9	n-C_4H_9OCOH	348—459	1.6	180
	iso-C_4H_9COH	451—580	50	181
	$(CH_3)_2CHNNCH(CH_3)_2$	298—441	1.6	182
t-C_4H_9	t-C_4H_9COH	392—448	3.2	120
C_6H_5	CH_4	561—697	20	124
		453—623	3.6	183
	cyclo-C_3H_6	561—657	6.3	124
	$(CH_3)_3CH$	561—697	63	124
	$CH_3COC_6H_5$	561—697	13	124
		453—623	1.3	183
CH_3O	CH_4	403—523	16	97
	CH_3CH_3	463—536	4.0	184
	$(CH_3)_4C$	463—536	4.0	184
	$CH_3(CH_2)_2CH_3$	463—536	0.6	184
	cyclo-C_3H_6	463—536	21	184
	$(CH_3)_3CH$	463—536	8.0	184
	$CH_3CH_2CH_3$	463—536	8.0	184
	CH_3COOCH_3	450—483	1.3	119
	CH_3OCOH	450—489	160	114
C_2H_5O	$C_2H_5COOCH_2CH_3$		2.5	58
CH_2F	$(CH_2F)_2CO$	294—585	1.25	185
C_2F_5	CH_4	423—544	10	186
	C_2F_5CHO	300—588	19	161
C_3F_7	CH_4	370—455	2.4	187
	CH_3CH_3	379—455	29	187
	cyclo-C_6H_{12}	296—566	1.2	188
	$(CH_3)_2CO$	300—579	11	189
	C_3F_7CHO	300—588	1.8	161
CCl_3	$CH_3(CH_2)_3CH_3$	423—630	0.3	190
	$CH_3(CH_2)_3CH_3$	423—630	0.2	190
	$FCH_2(CH_2)_2CH_3$	423—630	0.8	190
	$FCH_2CH_2CH_2CH_3$	423—630	0.5	190
	$CF_3CH_2(CH_2)_2CH_3$	423—630	0.1	190
	$CF_3CH_2CH_2CH_2CH_3$	423—630	0.8	190
	$CF_3CH_2CH_2CH_2CH_3$	423—630	0.5	190
	$CF_3(CH_2)_3CH_3$	423—630	0.8	190
$C(CH_3)_2CN$	$(CH_3)_3C_6H_3$	353—383	0.1	62
	$(CH_3)_2NC_6H_5$	353—383	0.5	62
	$(CH_3CH_2)_3N$	353—383	0.1	62
	$(C_6H_5)_2CH_2$	353—383	4.4	62
	$(C_6H_5CH_2)_2O$	353—383	54	62
	$(C_6H_5CH_2)_3N$	353—383	10	62

The quantity A_{11} is a minimum for the reaction CH_3 + CH_4, where it is ~1. As the hydrogen atoms in the radical and molecule are replaced it gradually increases, reaching values of 10^2-10^3 for complete replacement. This is a qualitative conclusion, following from an analysis of a large number of reactions, which we think reliable. It can be explained with the aid of the arguments given in sections 5 and 6.

Considering the reaction complex to be approximately symmetric, we assume that the value of A_{11} is determined by the contribution of two antisymmetric deformation vibrations. By using Fig. 3 we estimate their frequencies ω_α:

A_{11}	1	10	100	1000
ω_α	200	50—100	20—30	5—10 cm^{-1}

Table 10. Pre-exponential factors for reactions involving abstraction of hydrogen by radicals from H–X molecules.

Radical	Molecule	T, °K	$10^{-8}A$, litre $mole^{-1}$ s^{-1}	Reference
CH_3	H—H	403—663	0.5	191
	H—D	403—663	1.1	192
	H—**D**	403—663	2.3	192
	D—D	403—663	1.4	191
CD_3	H—H	403—663	1.6	191
		403—663	4.7	192
	H—D	403—663	2.5	192
	H—**D**	403—663	1.4	192
	D—D	403—663	0.4	191
CH_3	H—Cl		2.5	117
CF_3	H—H	375—447	3.6	193
		—	2.4	194
	D—D	375—447	1.4	193
	H—D	375—447	6.0	193
CF_3	H—D	375—447	2.2	193
	H—Cl	313—578	2.4	194
	D—Cl	313—578	2.4	194
	H—Br	328—607	7.1	164, 195
	H—I		8.0	164
		343—562	5.4	194
C_2H_5	H—H	323—573	3.2	167
		327—560	10	196
C_2F_5	H—H	410—610	23	289
		419—586	79	197
	D—D	430—592	14	197
C_3F_7	H—H	430—592	36	198
			22	58
	D—D	438—570	48	197
C_6H_5	H—H	453—623	30	183

For the reaction of $CH_3 + CH_4$ calculations[20-22] give $\omega_\alpha \simeq 200$ cm^{-1}. For a tenfold decrease in ω_α the moment of inertia I_a must be increased a hundredfold. The last quantity is mainly determined by the value of I_X for the corresponding radical or molecule, Eqn. (18). According to Table 11 the values of I_X for the radicals CH_3, CF_3, CCl_3, and Ph are respectively 2, 50, 170, and 170. Hence an observable effect within the framework of our model is naturally explained by a change in the kinematic coefficients for corresponding AC.

A natural exception is the radical $C(CH_3)_2CN$ for which the value A_{11} is anomalously low. We will assume that the AC for the reaction of this radical (for example, with toluene) is more "rigid" than the typical AC for the reactions considered above, that is, one or both C–H bonds of the reaction centre are shorter for it. Most probably there is a shortening of the newly formed bond in accordance with the Hammond rule, since the $(CH_3)_2CCN$ radical is much less active than other radicals considered—for example, the activation energies for the reactions of CH_3, CF_3, and $(CH_3)_2CCN$ with toluene are 8, 6, and 11 kcal $mole^{-1}$ respectively. Then an increase in the moment of inertia I_X seems to be compensated by an increase in the force constant for the R–H bond being formed. This assumption agrees with the more detailed discussion given below.

Now let us examine the effect which is evidently due to the steric factor A_{12}. In the reaction for hydrogen abstraction from the carbonyl group of the aldehydes the value of A_1 is in many instances anomalously high (Tables 14 and 15). This can be explained as follows. During the course of the reaction the hybridisation of the carbonyl carbon atom changes from trigonal to digonal. The angle between the R–C and C=O bonds in R–C(=O)–H alters from 120° to 180°. Here the internal rotation of the substituent R or its fragments, restricted in the initial aldehyde by steric interaction with the oxygen atom, is freed. In the AC such an "aldehydic" effect should appear, even if only partly. In addition the effect of the moment of inertia, considered above, must be considered. From Table 14, clearly when the substituent R has a simple structure and a steric effect cannot be expected, the value of A_1 for RCHO and for molecules with a tertiary hydrogen atom are approximately the same. An anomalous increase in the pre-exponential factor is observed for aldehydes having a substituent of complex structure.

Table 11. Calculated values of the principal moments of inertia (a.m.u.).Å² and of $Å_0$ for radicals and molecules.

Compound	I_X	I_Y	I_Z	A_0'
CH_3	1.8	1.8	3.6	$4.5 \cdot 10^6$
CH_2CH_3	22.3	5.0	34.1	$1.9 \cdot 10^5$
$CH_3CH_2CH_2$	54.4	13.3	61.2	$4.5 \cdot 10^4$
$(CH_3)_2CH$	13.8	60.5	67.8	$3.1 \cdot 10^4$
$CH_3CH_2CH_2CH_2$	221	23.9	240	$7.6 \cdot 10^3$
$CH_3CHCH_2CH_3$	125	35.1	117	$1.5 \cdot 10^4$
$(CH_3)_2CHCH_2$	105	62.5	60.5	$1.2 \cdot 10^4$
$(CH_3)_3C$	63.7	63.7	118	$1.7 \cdot 10^4$
$C(CH_3)_2CN$	132	60.5	126	$4.9 \cdot 10^3$
C_6H_5	172	83	38.8	$1.0 \cdot 10^3$
CCl_3	173	172	307	$8.8 \cdot 10^3$
CF_3	48.2	48.2	94.1	$8.4 \cdot 10^3$
C_2F_5	213	138	263	$1.2 \cdot 10^3$
C_3F_7	429	270	508	$3.9 \cdot 10^2$
CH_4	3.25	3.25	3.25	$4.4 \cdot 10^6$
CH_2CH_3	24.9	6.5	24.9	$4.4 \cdot 10^5$
$(CH_3)_2CH_2$	17.8	57.6	65.7	$8.2 \cdot 10^3$
$(CH_3)_3CH$	63.8	63.8	169	$8.3 \cdot 10^3$
$(CH_3)_4C$	107	108	111	$8.4 \cdot 10^3$
$(CH_3)_3N$	56.1	59.5	100	$1.3 \cdot 10^4$
$(CH_3)_2NH$	15.2	54.0	61.4	$2.8 \cdot 10^4$
CH_3COCH_3	102	60.4	48.4	$1.2 \cdot 10^4$
$C_6H_5CH_3$	199	92.6	288	
$BrCH_3$	53.1	3.25	53.1	
$C_6H_5CH_2CH_3$	415	114	334	
$C_6H_5COCH_3$	547	411	139	
$(C_2H_5)_3N$	269	120	338	
$CH_3(CH_2)_2CH_3$	142	133	22.2	
CH_3COH	55.0	9.75	48.4	$3.4 \cdot 10^4$
C_2H_5COH	104	32.2	78.2	
n-C_3H_7COH	203	35.2	177	
iso-C_3H_7COH	134	60.1	171	
s-C_4H_9COH	250	23.9	191	
iso-C_4H_9COH	217	168	79.7	
t-C_4H_9COH	180	106	175	
CF_3COH	169	97.7	175	
C_2F_5COH	353	280	250	
C_3F_7COH	635	341	659	
$(C_6H_5)_2CH_2$	225	1430	1300	
$(C_6H_5CH_2)_2O$	193	344	1760	
$(C_6H_5CH_2)_3N$	2760	749	3150	

Let us discuss yet another effect. As shown above, the value of A_1 for the radical $C(CH_3)_2CN$ in reactions with small molecules is anomalously low. However, it becomes rather and possibly even too great ($\sim 10^3$) in reactions with complex molecules: diphenylmethane, dibenzyl ether, tribenzylamine (Table 14). This result can be interpreted in two ways. On the one hand, it could be supposed that in the latter instance, steric interactions in the AC make its structure looser than the structure of the AC for reactions with simple molecules, where there is no such interaction[62]. Then the pre-exponential factor is increased owing to a decrease in the force constants for the C–H bonds in the reaction complex, which involves a decrease in the antisymmetric frequencies ω_a. Hence a relative increase in the activation energy is to be expected.

Table 12. Calculated values of the coordinates of the centre of mass a_i, Å, and of the direction cosines of the principal axes for radicals and molecules.

Compound	a_X	l_1	l_2	l_3	a_Y	m_1	m_2	m_3	a_Z	n_1	n_2	n_3
CH_3	0.00	0.728	−0.686	0.000	0.00	0.686	0.728	0.000	0.00	0.000	0.000	1.000
CH_3CH_2	0.00	1.000	0.000	0.000	0.78	0.000	1.000	0.000	0.35	0.000	0.000	1.000
$CH_3CH_2CH_2$	0.55	0.815	−0.580	0.000	1.19	0.580	0.815	0.000	0.00	0.000	0.000	1.000
$(CH_3)_2CH$	0.00	1.000	0.000	0.000	−0.52	0.000	1.000	0.000	0.00	0.000	0.000	1.000
$CH_3CH_2CH_2CH_2$	0.00	1.000	0.000	0.000	2.11	0.000	0.950	−0.311	−0.73	0.000	0.311	0.950
$CH_3CHCH_2CH_3$	0.34	0.897	0.427	0.113	0.70	−0.366	0.863	−0.349	−0.31	−0.247	0.271	0.930
$CH_3CH(CH_3)CH_2$	−0.33	0.805	0.339	0.486	1.40	−0.207	0.929	−0.306	−0.19	−0.556	0.146	0.819
$(CH)_3C_3$	0.00	0.729	−0.684	0.000	0.00	0.685	0.729	0.000	0.00	0.000	0.000	1.000
$(CH_3)_2C(CN)$	0.00	1.000	0 000	0.000	0.45	0.000	1.000	0.000	0.00	0.000	0.000	1.000
C_6H_5	0.00	1.000	0.000	0.000	0.00	0.000	1.000	0.000	1.44	0.000	0.000	1.000
CCl_3	0.00	0.729	−0.685	0.000	0.00	0.685	0.729	0.000	0.41	0.000	0.000	1.000
CF_3	0.00	0.729	−0.685	0.000	0.00	0.685	0.729	0.000	0.28	0.000	0.000	1.000
C_2F_5	0.00	1.000	0.000	0.000	0.87	0.000	1.000	0.000	0.00	0.000	0.000	1.000
C_3F_7	0.24	0.095	−0.292	−0.337	1.21	0.160	0.916	−0.367	−0.43	0.416	0.247	0.807
CH_4	0.00	0.730	−0.683	0.0	0.00	0.683	0.730	0.000	0.00	0.000	0.0	1.000
CH_3CH_3	0.00	1.000	0.000	0.0	0.72	0.000	0.943	−0.333	−0.25	0.000	0.333	0.943
$(CH_3)_2CH_2$	0.00	1.000	0.000	0.0	0.00	0.000	0.817	0.577	0.00	0.000	−0.577	0.817
$(CH_3)_3CH$	0.00	0.842	−0.540	0.0	0.00	0.540	0.842	0.000	−0.39	0.000	0.0	1.000
$(CH_3)_4C$	0.00	1.000	0.000	0.0	1.44	0.000	1.000	0.000	−0.49	0.000	0.0	1.000
$(CH_3)_3N$	0.00	0.979	−0.197	−0.047	1.36	0.198	0.980	0.013	−0.06	0.043	−0.022	0.999
$(CH_3)_2NH$	0.00	1.000	0.000	0.0	−0.49	0.000	0.749	0.662	−0.29	0.000	−0.662	0.749
CH_3COCH_3	0.00	1.000	0.000	0.0	1.36	0.000	0.760	0.650	−0.55	0.000	−0.650	0.760
$C_6H_5CH_3$	0.00	1.000	0.000	0.0	2.30	0.000	0.943	−0.333	−0.81	0.000	+0.333	0.943
$BrCH_3$	0.00	1.000	0.000	0.0	1.53	0.000	0.943	−0.333	−0.54	0.000	+0.333	0.943
$C_6H_5CH_2CH_3$	−0.18	0.984	−0.174	−0.032	1.90	0.165	0.966	−0.201	−0.78	0.066	0.192	0.979
$C_6H_5COCH_3$	0.00	1.000	0.000	0.000	1.66	0.000	0.975	0.223	−2.16	0.000	0.223	0.975
$(C_2H_5)_3N$	−0.19	0.949	−0.306	0.070	1.68	0.308	0.951	−0.012	−0.26	−0.063	0.327	0.997
$CH_3(CH_2)_2CH_3$	0.00	1.000	0.000	0.000	1.44	0.000	0.714	0.700	−1.27	0.000	−0.700	0.714
CH_3COH	0.00	1.000	0.000	0.000	0.08	0.000	0.996	0.091	−0.46	0.000	−0.091	0.996
C_2H_5COH	0.00	1.000	0.000	0.000	0.30	0.000	0.782	−0.623	−0.93	0.000	0.623	0.782
C_3H_7COH	0.00	1.000	0.000	0.000	0.74	0.000	0.773	−0.634	−1.29	0.000	0.634	0.773
s-C_4H_9COH	0.20	0.910	0.276	0.309	0.97	−0.062	0.827	−0.558	−1.14	−0.41	0.489	0.770
iso-C_4H_9COH	−0.20	0.971	0.171	−0.170	0.41	−0.027	0.775	0.630	−1.53	0.240	−0.607	0.757
t-C_4H_9COH	0.01	0.984	−0.023	−0.176	0.91	0.016	0.999	−0.041	−0.74	0.177	0.037	0.984
iso-C_4H_7COH	0.02	1.000	0.000	0.000	0.89	0.000	1.000	0.000	−0.42	0.000	0.000	1.000
CF_3COH	0.03	0.972	−0.025	0.233	0.98	0.045	0.996	−0.077	−0.76	0.230	0.085	0.969
C_2F_5COH	0.00	1.000	0.000	0.000	0.95	0.000	0.940	0.341	−1.47	0.000	−0.341	0.940
C_3F_7COH	0.00	1.000	0.000	0.000	1.48	0.000	0.748	−0.664	−1.84	0.000	0.664	0.748
$(C_6H_5)_2CH_2$	0.00	1.000	0.000	0.000	−0.75	0.000	0.933	0.358	−0.77	0.000	−0.358	0.933
$(C_6H_5CH_2)_2O$	0.93	0.815	−0.476	−0.330	1.25	0.370	0.866	−0.336	−1.67	0.445	0.152	0.882
$(C_6H_5CH_2)_3N$	0.64	0.906	−0.391	0.164	2.46	0.400	0.916	−0.025	−0.79	−0.140	0.085	0.986

Table 13. Values of $(\pi I_i^{\neq})^{1/2}$ for certain activated complexes.

Activated complex	$(\pi I_i^{\neq})^{1/2}$, (a.u.)$^{3/2}$Å^3 complete calculation geom. activated complex	Calculation by Eqn.(20)
CH_3+H—CH_3	$1.3\cdot10^2$	$0.87\cdot10^2$
CH_3+H—$CH_2C_6H_5$	$4.9\cdot10^3$	$3.1\cdot10^3$
CH_3+H—$CH(C_6H_5)_2$	$2.9\cdot10^4$	$2.8\cdot10^4$
$C(CH_3)_2CN$+H—CH_3	$2.6\cdot10^3$	$2.1\cdot10^3$
$C(CH_3)_2CN$+H—$CH_2C_6H_5$	$1.6\cdot10^4$	$1.4\cdot10^4$
$C(CH_3)_2CN$+H—$CH(C_6H_5)_2$	$5.7\cdot10^4$	$4.7\cdot10^4$

Actually in these reactions show a clearly expressed compensation effect.

On the other hand, a change in the hybridisation of the carbon atom of the molecule from tetrahedral to trigonal can lead to the freeing of internal vibrations: similar to what is observed in aldehydes.

In the first instance A_{11} increases, in the second, A_{12}. In each specific reaction either the first or the second can predominate; they can also act simultaneously. In the next section we will investigate the reaction with diphenylmethane as an illustration.

9. STERIC EFFECTS IN THE REACTIONS OF THE 2-CYANO-2-METHYLETHYL RADICAL WITH DIPHENYLMETHANE

The model calculation given below clearly shows the complex picture of steric interactions in the reaction

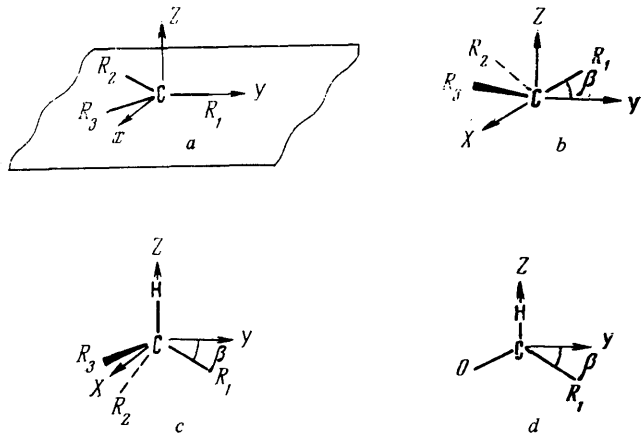


Figure 4. Configurations of molecules and radicals. The Z axis coincides with the direction of the molecule's CH bond that is being broken; one of the bonds of the central carbon atom (in the molecule or radical) lies in the YZ plane. All the angles β for the exit of C−R bonds from the XY plane for a given system are the same. *a*) $\beta = 0°$, alkyl radicals; *b*) $\beta = 15°$, CF_3 or CCl_3 radicals, *c*) $\beta = 19°\ 28'$, removal of H from a tetrahedral carbon atom; *d*) $\beta = 30°$, removal of H from a trigonal carbon atom (aldehydes). Standard values were adopted for the bond lengths and angles in the molecules and radicals.

Table 14. Experimental values of A_1, the contribution of the internal degrees of freedom to the pre-exponential factor.

Radical or atom	Molecule	A_0, litre mole^{-1} s^{-1}	A_1
1	2	3	4
H	H_2	$7.8\cdot10^{10}$	0.8
	HD	$4.4\cdot10^{10}$	0.3
	HD	$3.4\cdot10^{10}$	0.4
	D_2	$3.9\cdot10^{10}$	0.5
D	H_2	$6.0\cdot10^{10}$	0.4
	D_2	$2.8\cdot10^{10}$	1.1
	HD	$2.5\cdot10^{10}$	0.4
	HD	$1.9\cdot10^{10}$	0.5
H	CH_4*	$3.7\cdot10^{10}$	0.9
	$CH_3CH_2CH_3$	$4.3\cdot10^{9}$	4.2
	$(CH_3)_3CH$	$3.9\cdot10^{9}$	2.5
O	H_2	$8.2\cdot10^{10}$	0.2
	CH_4	$9.3\cdot10^{9}$	0.4
	CH_3CH_3	$6.5\cdot10^{8}$	4.6
F	H_2	$5.5\cdot10^{10}$	0.9
	CH_4	$9.0\cdot10^{9}$	3.4
	$C(CH_3)_4$	$1.4\cdot10^{8}$	36
	$CH_3CH_2CH_3$	$3.2\cdot10^{8}$	19
	$(CH_3)_2CH$	2.0	35
CH_3	H_2	$2.1\cdot10^{9}$	0.8
	HCl	$2.9\cdot10^{8}$	0.9
	CH_4	$1.9\cdot10^{8}$	0.9
	CH_3Br	$2.4\cdot10^{8}$	3.0
	CH_3CH_3	$6.7\cdot10^{7}$	3.4
	$CH_3C_6H_5$	$1.37\cdot10^{7}$	0.8
	$(CH_3)_4C$	$1.5\cdot10^{7}$	0.9
	CH_3COCH_3	$4.9\cdot10^{7}$	1.1
	$CH_3COC_6H_5$	$1.6\cdot10^{7}$	1.1
	$(CH_3)_3N$	$1.7\cdot10^{7}$	2.5
	$CH_3CH_2CH_3$	$2.9\cdot10^{7}$	13
	$CH_3CH_2C_6H_5$	$8.8\cdot10^{6}$	1.7
	$C_6H_5CH_2C_6H_5$	$7.0\cdot10^{6}$	4.6
	$(CH_3CH_2)_3N$	$9.0\cdot10^{6}$	3.7
	$(CH_3)_3CH$	$1.6\cdot10^{7}$	10
	$(CH_3)_2NH$	$2.1\cdot10^{7}$	25
	CH_3COH	$3.6\cdot10^{7}$	22
	C_2H_5COH	$2.2\cdot10^{7}$	46
	$n\text{-}C_3H_7COH$	$1.8\cdot10^{7}$	35
	$iso\text{-}C_3H_7COH$	$1.5\cdot10^{7}$	270
	$s\text{-}C_4H_9COH$	$1.8\cdot10^{7}$	1100
	$iso\text{-}C_4H_9COH$	$1.4\cdot10^{7}$	150
	$t\text{-}C_4H_9COH$	$1.1\cdot10^{7}$	930
	CF_3COH	$1.2\cdot10^{7}$	110
	C_2F_5COH	$8.9\cdot10^{6}$	900
	C_3F_7COH	$7.8\cdot10^{6}$	2100
CF_3	H_2	$2.7\cdot10^{8}$	1.2
	HD	$1.7\cdot10^{8}$	3.6
	HD	$1.6\cdot10^{8}$	1.3
	HCl	$2.6\cdot10^{6}$	65
	HBr	$3.4\cdot10^{6}$	29
	HI	$3.0\cdot10^{6}$	23
C_3F_7	H_2	$6.7\cdot10^{8}$	4.3
	D_2	$1.2\cdot10^{8}$	32
	CH_4	$1.6\cdot10^{6}$	15
	CH_3CH_3	$7.7\cdot10^{5}$	380
	CH_3COCH_3	$3.2\cdot10^{4}$	3600
	C_3F_7COH	$4.1\cdot10^{3}$	4500
Cl	H_2	$7.5\cdot10^{10}$	0.6
	D_2	$2.7\cdot10^{10}$	1.1
	HD	$2.7\cdot10^{10}$	1.2
	CH_4	$9.4\cdot10^{9}$	0.7
	CH_3CH_3	$6.0\cdot10^{8}$	2.5
	$C(CH_3)_4$	$1.0\cdot10^{8}$	140
	$CH_3CH_2CH_3$	$2.0\cdot10^{8}$	180
	$(CH_3)_3CH$	$1.5\cdot10^{8}$	140
Br	H_2	$8.4\cdot10^{10}$	1.7
	CH_4	$9.5\cdot10^{9}$	3.5
	CH_3CH_3	$5.5\cdot10^{8}$	22
	$(CH_3)_4C$	$9.5\cdot10^{8}$	16
	$CH_3CH_2CH_3$	$2.0\cdot10^{8}$	130
	$(CH_3)_3CH$	$1.2\cdot10^{8}$	170
I	H_2	$11\cdot10^{10}$	0.5
	D_2	$4.7\cdot10^{10}$	1.1
	$CH_3{-}CH_2CH_3$	$1.8\cdot10^{8}$	276
	$(CH_3)_3CH$	$1.1\cdot10^{9}$	690
	CH_3COH	$3.5\cdot10^{8}$	57
CF_3	CH_4	$1.8\cdot10^{7}$	7.5
	CH_3CH_3	$2.6\cdot10^{6}$	3.1
	CH_3COCH_3	$2.0\cdot10^{5}$	51
	$C(CH_3)_4$	$1.2\cdot10^{5}$	410
	$CH_3C_6H_5$	$1.1\cdot10^{5}$	710
	$(CH_3)_3N$	$1.5\cdot10^{5}$	480
	CF_3COH	$9.5\cdot10^{4}$	5700
	C_2F_5COH	$6.1\cdot10^{4}$	4900
	C_3F_7COH	$4.7\cdot10^{4}$	4200
	$(CH_3)_3CH$	$1.0\cdot10^{5}$	1400
	$(CH_3)_2NH$	$2.9\cdot10^{5}$	110
C_2H_5	H_2	$4.0\cdot10^{8}$	0.8
	D_2	$2.4\cdot10^{8}$	4.2
	CH_4	$3.7\cdot10^{7}$	4.3
	CH_3CH_3	$3.5\cdot10^{6}$	30
	$C(CH_3)_4$	$8.1\cdot10^{5}$	37
	$(CH_3)_3N$	$1.1\cdot10^{6}$	79
	C_2H_5COH	$1.5\cdot10^{6}$	82
$n\text{-}C_3H_7$	CH_3COOH_3	$4.4\cdot10^{5}$	44
	$n\text{-}C_3H_7COH$	$4.2\cdot10^{5}$	480
$iso\text{-}C_3H_7$	$iso\text{-}C_3H_7COH$	$2.1\cdot10^{5}$	760
$s\text{-}C_4N_9$	$s\text{-}C_4H_9COH$	$8.2\cdot10^{4}$	620
$iso\text{-}C_4H_9$	$iso\text{-}C_4H_9COH$	$1.0\cdot10^{5}$	5000
$t\text{-}C_4H_9$	$t\text{-}C_4H_9COH$	$1.1\cdot10^{5}$	350
C_6H_5	CH_4	$1.6\cdot10^{7}$	13
C_6H_5	$(CH_3)_3CH$	$7.7\cdot10^{4}$	8300
	$C_6H_5COCH_3$	$8.4\cdot10^{4}$	1600
CCl_3	$CH_3(CH_2)_2CH_3$	$9.1\cdot10^{4}$	29**
C_2F_5	H_2	$4.9\cdot10^{8}$	10
	D_2	$1.1\cdot10^{8}$	12.7
	CH_4	$9.8\cdot10^{6}$	11
	C_2F_5COH	10^{4}	18000
$C(CH_3)_2CN$	$C(CH_3)_2CNCH_3C_6H_5$***	$5.3\cdot10^{4}$	23
	$(CH_3CH_2)_3N$	$2.5\cdot10^{4}$	57
	$C_6H_5CH_2C_6H_5$	$1.8\cdot10^{4}$	2400
	$(C_6H_5CH_2)_2O$	$1.7\cdot10^{4}$	3100
	$(C_6H_5CH_2)_3N$	$9.4\cdot10^{3}$	10000

* In calculating A_1, the value $A = 3.2\times10^{10}$ litre mole^{-1} s^{-1}, obtained[200] as the mean of the available[58-60,200] values of A, was used.

** In calculating A_1, the value $A = 0.3\times10^{7}$ litre mole^{-1} s^{-1}, corresponding to the loss of H from a methyl group in the n-C_5H_{10} molecule, was used.

*** The experimental value of A for mesitylene[62] was used.

$(CH_3)_2CCN + H_2CPh_2$. The energy of the steric interactions between the reagents in the linear AC is investigated as a function of their relative orientation and the positions of the individual groups. Our results give information about the contribution of the internal rotations to the pre-exponential factor.

Table 15. Values of A_1 for some typical reactions.

Radical	Molecule										
	CH_4	C_2H_6	CH_3COCH_3	$(CH_3)_4C$	CH_3Ph	CH_3COPh	$(CH_3)_3N$	$-CH_3$	$-CH_2-$	$>CH-$	aldehydes
CH_3	0.9	3.4	1.1	0.9	0.8	1.1	2.5	1—3	~5	~10	100—1000
C_2H_5	4.3	30	—	37	—	—	3	3—30	~25	~80	~80
n-C_3H_7	—	—	43	—	—	—	—	~40	—	—	~500
iso-C_3H_7	—	—	—	—	—	—	—	—	—	—	~800
CF_3	7.5	—	50	400	710	—	475	50—500	~1000	1400	100—5000
CCl_3	—	—	—	—	—	—	—	~30	—	—	—
$C(CH_3)_2CN$	—	—	—	—	23	—	—	~20	~60	—	—
C_2F_5	11	—	—	—	—	—	—	~10	—	—	20000
C_3F_7	15	380	3600	—	—	—	—	15	—	—	~5000
Ph	13	—	—	—	—	1600	—	—	—	8300	—

Fig. 5 shows the geometry of the AC and the reactants. For the radical all the angles are assumed to be tetrahedral. The rotations of the methyl groups are characterised by the angles Ψ_1 and Ψ_2. The rotation of the phenyl rings in the molecule were described by angles ρ_1 and ρ_2 between the plane of the corresponding ring and the plane of the angle ω between the C – Ph bonds. The angles between the C – H bond being broken and the CH and C – PH σ-bonds were assumed to be the same for all three bonds (~107°). The rotation around the C... H... bond was characterised by the angle α (Fig. 5*a*). The relative position of the methyl and phenyl groups at $\alpha = 0$ for various values of the remaining angles are shown schematically in Fig. 6.

The interaction energy U was regarded as the sum of the pairwise intermolecular interactions $U_{rr'}$ between the atoms (not bound by valence) r of the radical and r' of the molecule. The interaction due to changes during the reaction with the hydrogen atom were not taken into account. The generally accepted approximation

$$U_{rr'} = A\exp(-al) - Bl^{-6},$$

where $l \equiv l_{rr'}$, the distance between the atoms, was used. The empirical coefficients A, a, and B were evaluated for various pairs of atoms from published data[201-205]. The steric interaction energy is

$$U = \Sigma U_{rr'}$$

First let us examine the effect of the angle ω in the isolated diphenylmethane molecule. Fig. 7 shows the interaction energy between the phenyl rings as a function of the angles of their rotation ρ_1 and ρ_2. Rotation of the rings is impossible, and only torsional vibrations about the equilibrium position at $\rho_1 = \rho_2 = 90°$ are admissible. As ω is varied from 109° to 120° the energy at the minimum changes from 8 to 3 kcal mole^{-1} and the potential well as a whole becomes much more shallow. The absolute value of the energy does not affect the pre-exponential factor (it makes a contribution solely to the activation energy). The decrease in the curvature of the potential surface $U(\rho_1, \rho_2)$ corresponds to a decrease in the force constants for the torsional vibrations, that is, to some freeing of the internal motions which was postulated above. For aldehydes, when the angle between the bonds is changed by 60, not 11, degrees, this effect is probably more significant.

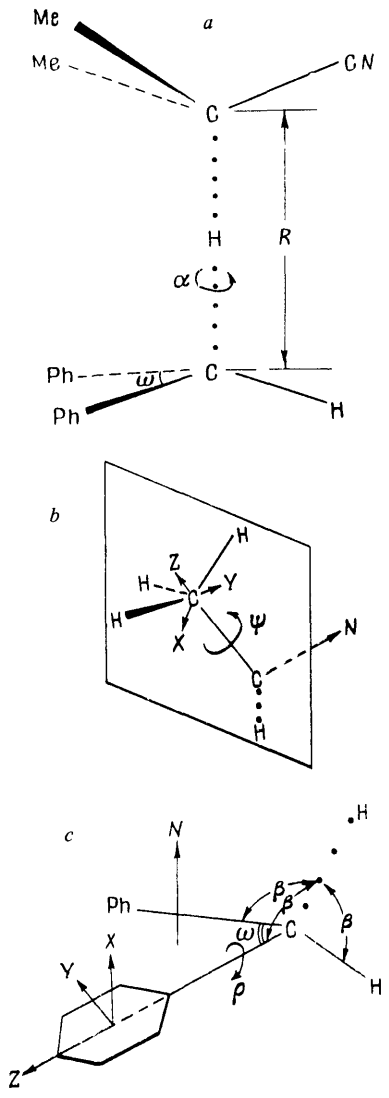


Figure 5. Geometric parameters of activated complexes for the reactions. *a*) Model of an activated complex: the C – CN bond of the radical and the C – H bond of the molecule lie in the plane of the diagram. The rotation angle α is reckoned from this plane; for the configuration shown $\alpha = 0$; *b*) rotation of methyl groups in the radical. The coordinate system is rigidly attached to the methyl group: the Z axis is directed along the C – C bond, the Y axis lies in the plane passing through one of the C – H bonds and the rotation axis; Ψ is the angle between the X axis and the normal N to the plane represented on the diagram (in the Figure, $\Psi = \pi/2$); *c*) rotation of the phenyl rings in the molecule. The coordinate system is rigidly attached to the ring, which lies in the YZ plane; the rotation angle ρ is the angle between the X axis and the normal to the plane of the PhCPh angle (in the Figure, $\rho = 0$), the angles β equal 106° 47′.

Subsequently it was assumed that in the AC a more favourable (and in energetic and in statistical respects) configuration with $\omega = 120°$ is realised. All the values of ρ_1 and ρ_2 were taken from the region situated close to the minimum.

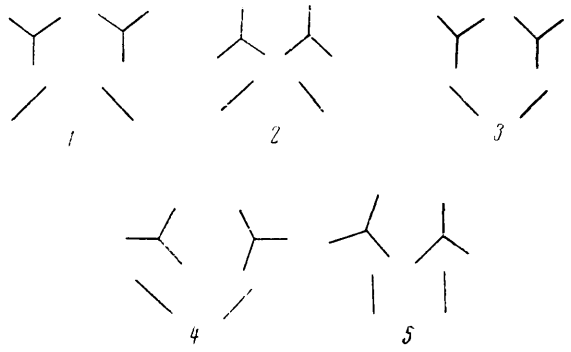


Figure 6. Schematic representation of the various configurations of the activated complex at $\alpha = 0$; ⟩⟨ denotes a methyl group, / the plane of the phenyl ring. *1*) $\Psi_1 = \Psi_2 = 0$, $\rho_1 = 120$, $\rho_2 = 60$; *2*) $\Psi_1 = 60°$, $\Psi_2 = 300°$, $\rho_1 = 120°$, $\rho_2 = 60°$; *3*) $\Psi_1 = \Psi_2 = 0°$, $\rho_1 = 60°$, $\rho_2 = 120°$; *4*) $\Psi_1 = 30°$, $\Psi_2 = 330°$, $\rho_1 = 60°$, $\rho_2 = 120°$; *5*) $\Psi_1 = 30°$, $\Psi_2 = 60°$, $\rho_1 = \rho_2 = 90°$.

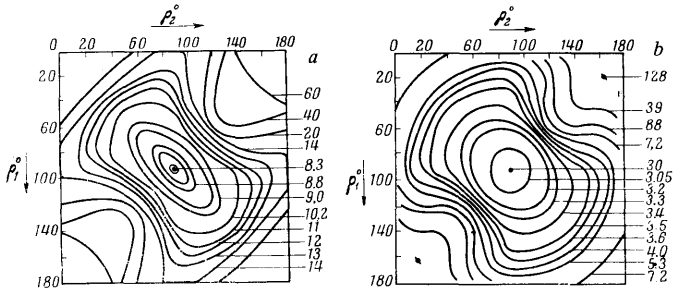


Figure 7. Potential surfaces for the interaction of the rings in diphenylmethane; energy in kcal mole^{-1}. *a*) $\omega = 109° 28'$; *b*) $\omega = 120°$.

Fig. 8 gives the relation between the intermolecular steric interaction in the AC from angle α in the fixed position of the methyl groups ($\Psi_1 = 60°$, $\Psi_2 = 300°$) and a distance of $R = 2.2$ Å between the carbon atoms of the reaction centre. Curves 1–5 correspond to different pairs $\rho_1 - \rho_2$. Of the five conformations considered rotation around the C–H–C bond seems possible for only one: $\rho_1 = 120°$, $\rho_2 = 60°$. For all the other instances steep and deep potential wells are characteristic.

The conformation with $\rho_1 = 120°$, $\rho_2 = 60°$ was investigated more thoroughly. Potential curves $U(\alpha)$ at various orientations of the methyl groups were constructed for these values of ρ. From Fig. 9, clearly for most of the conformations considered the rotation is strongly restricted or quite impossible. Hence the internal rotation α is practically free only for the conformations rigidly held about the values $\rho_1 = 120°$, $\rho_2 = 60°$, $\Psi_1 = 60°$, $\Psi_2 = 300°$. In other words, the rotation of the methyl groups is restricted, and the region of admissible values of ρ is greatly restricted. These motions might be made freer—with the same reagents at certain fixed values of angle α, that is, at the price of restricting the internal rotation around the C–H–C bond. The internal rotation as a whole in such an AC is greatly restricted.

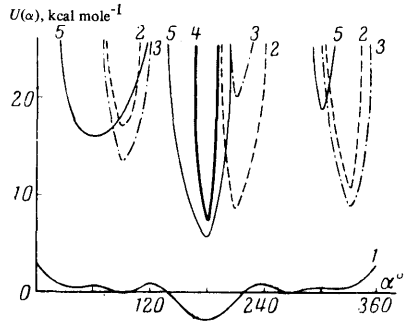


Figure 8. Variation of the energy of the intermolecular steric interaction in an activated complex with the angle α in a fixed arrangement of the methyl groups ($\Psi_1 = 60°$, $\Psi_2 = 300°$). *1*) $\rho_1 = 120°$, $\rho_2 = 60°$, *2*) $\rho_1 = \rho_2 = 40°$; *3*) $\rho_1 = 20°$, $\rho_2 = 80°$; *4*) $\rho_1 = \rho_2 = 90°$; *5*) $\rho_1 = 160°$, $\rho_2 = 100°$.

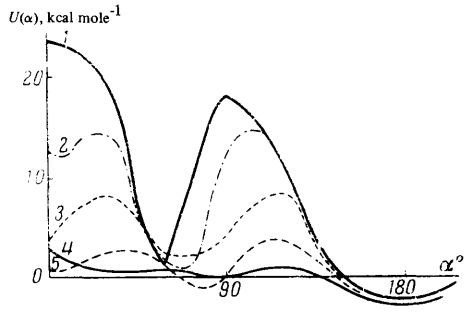


Figure 9. Variation of the potential curves $U(\alpha)$ with the orientation of the methyl groups for the conformations $\rho_1 = 120°$, $\rho_2 = 60°$. *1*) $\Psi_1 = \Psi_2 = 0$; *2*) $\Psi_1 = 15°$, $\Psi_2 = 345°$; *3*) $\Psi_1 = 30°$, $\Psi_2 = 330°$; *4*) $\Psi_1 = 60°$, $\Psi_2 = 300°$; *5*) $\Psi_1 = 45°$, $\Psi_2 = 315°$.

The calculations quoted relate to a rigid AC with the distance $R = 2.2$ Å. The variation with R of the potential curves $U(\alpha)$ is illustrated in Fig. 10. The deep minima characteristic for small R are gradually smoothed out. At $R = 2.5$ Å, the "poorest" of the curves given in Fig. 9 already permits restricted rotation; for $R = 2.7-2.8$ Å the rotation is free.

Of course, this result is obtained for optimal values of $\rho_1 = 120°$, $\rho_2 = 60°$. For other pairs ρ_1, ρ_2 free internal rotations occur at $R \geq 3$ Å. It can be considered

that in the range 2.6–3.0 Å the rotations Ψ and α are already sufficiently free, but the motion of the phenyl rings is still restricted in comparison with the isolated diphenylmethane molecule.

Now we can discuss more specifically the values of A_1 found for the $(CH_3)_2CCN$ radical. $A_1 \simeq 20$ for reactions with toluene†, for example. This is a low value: for the reaction $CF_3 + CH_3-Ph$, $A_1 \simeq 700$. In the previous section we assumed that the AC for the first reaction is more rigid, owing to the shortening of the R–H bond. Then an increase in the force constants explains the decrease in A_1. The value $R \simeq 2.6$ Å was taken[20-22] for reactions of CH_3 and CF_3 radicals. Consequently, we can take $R \simeq 2.4-2.5$ Å for the AC in the reaction $(CH_3)_2CCN + H_3C-Ph$. Calculations analogous to those given above show that in this system there is no steric interaction even at $R = 2.2-2.3$ Å.

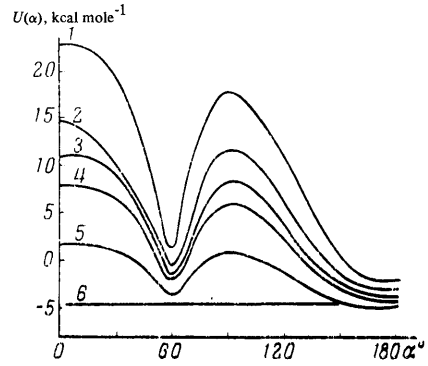


Figure 10. Variation of the potential curves $U(\alpha)$ with R at fixed positions of the methyl groups in the radical ($\Psi_1 = 0°$, $\Psi_2 = 0°$) and of the phenyl rings in the molecule ($\rho_1 = 120°$, $\rho_2 = 60°$). R, Å: *1*) 2.2; *2*) 2.25; *3*) 2.3; *4*) 2.35; *5*) 2.5; *6*) 2.8.

However, for AC of reactions with diphenylamine at $R < 2.5$ Å the steric effects are considerable. We therefore assume that in the AC represented in Fig. 5 R is increased to the value $R \leqslant 2.6$ Å, at which the change in internal motions compared with those of the reagents can be neglected. Such a system has a reaction centre close to the reaction centres of active radicals, for example, CF_3. Correspondingly (owing to the decrease in the force constants) the value of A_1 has increased to $A_1 = 2400$.

It is most probable that the increase in R takes place owing to the stretching of the C–H bond in diphenylmethane in accordance with the Hammond rule. A change to the favourable trigonal hybridisation with $\omega = 120°$ is facilitated thereby. The high values of A in the reactions of the isobutyronitrile radical with dibenzyl ether ($A_1 \simeq 3000$) and tribenzylamine ($A_1 \simeq 10\,000$) can probably be explained in approximately the same way but the details of the action of the "steric factors" should, of course, change.

It is impossible to maintain that this explanation is absolutely true, although it seems plausible. Information about the true values of R for various AC is not available and empirical calculations of the interaction energies are very approximate. The figures obtained (distances and angles) have an illustrative nature in every instance. But steric factors undoubtedly play an important part in the reactions of rather complex molecules.

Our calculations show certain specific mechanisms by means of which the internal degrees of freedom can affect the value of the pre-exponential factor.

† More precisely, the value of A_1 given in Table 14, relates to mesitylene, not toluene.

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Karpov Physicochemical Institute,
Moscow