28 (1955).
189. I. K. Taimni and R. Rakshpal, Analyt. Chim. Acta, 25, 438 (1961).
190. I. K. Taimni and R. Rakshpal, J. prakt. Chem., 27, 171 (1965).
191. G. Preuner and I. Brockmöller, Z. phys. Chem., 81, 151 (1913).
192. F. D. Richardson and J. H. E. Jeffes, J. Iron Steel Inst., 171, 165 (1952).
193. L. A. Aslanov, Yu. P. Simanov, A. V. Novoselova, and Yu. M. Ukrainskii, Zhur. Neorg. Khim., 8, 2635 (1963) [Russ. J. Inorg. Chem., 1381 (1963)].
194. A. E. Vol, "Stroenie i Svoistva Dvoinykh Metallicheskikh Sistem" (Structure and Properties of Binary Metallic Systems), Vol. II, Fizmatgiz, Moscow, 1962, p. 455.
195. S. Meyer, Wied. Ann., 69, 241 (1899).
196. G. Spengler and A. Weber, Chem. Ber., 92, 2163 (1959).
197. G. Krüss, Annalen, 225, 40 (1884).
198. V. D. Ponomarev and E. A. Buketov, Geologiya, Gornoe Delo, Metallurgiya. Sbornik Nauchnykh Trudov Kazakh. Gorno-Met. Inst., No. 16, 369 (1959).

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KINETICS OF RECOMBINATION AND DISPROPORTIONATION REACTIONS OF ALKYL RADICALS

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The present review is an attempt to collect and systematise information from numerous Russian and non-Russian papers on the kinetic study of recombination and disproportionation reactions of free radicals.

Recombination and disproportionation of alkyl radicals

$$R_1+R_2- \begin{cases} \longrightarrow R_1R_2 & (1) \\ \longrightarrow P+O, & (2) \end{cases}$$

(R_1 and R_2 are alkyl radicals, P is a paraffin molecule, and O is an olefin molecule) are the main types of reactions in which chains are broken, or free valencies disappear, in numerous organic reactions that proceed by a radical chain mechanism in the gas or liquid phase. On the other hand, these reactions are thermodynamically linked with the dissociation of alkanes and the molecular dismutation of alkanes and alkenes, which are possible routes to radical initiation in conversions of hydrocarbons at high temperatures. Actually, the radical chain mechanism results from the competition between these reactions and chain-propagation reactions.

In the experimental study of substitution reactions

$$R+M \rightarrow RH+R_1, \quad (3)$$

the difficulty of setting up an experimental model of reaction (3) is encountered, since under experimental conditions with sufficiently complicated radicals (beginning with C_2H_5), reactions (1) and (2) occur to a great extent, and these require virtually no activation energy. This makes difficult the determination of the absolute rate constant of reaction (3) from experimental results. However, the relative value of the rate constant of reaction (3) may be determined experimentally, when it is expressed in the form of the rate constants of the recombination k_1 and disproportionation k_2 of radicals. The rate of disappearance of radicals by recombination and disproportionation in reactions (1) and (2) is

$$W = (k_1 + k_2)(R)^2. \quad (4)$$

Eliminating the concentration of radicals (R) from Eqn. (4) and Eqn. (5) for the rate of reaction (3):

$$W_3 = k_3(R)(M), \quad (5)$$

we obtain the relation

$$\frac{k_3}{(k_1+k_2)^{\frac{1}{2}}} = \frac{W_3}{W^{\frac{1}{2}}(M)}. \quad (6)$$

Since the right-hand side of Eqn. (6) contains values that can be calculated from the experimental kinetic curves for the accumulation of products (RH, R_1R_2, P, O) and for the disappearance of M, the relative value of the rate constant of reaction (3) can be calculated from experimental results.

As will be seen, by comparing reactions of the same radical R with different molecules it is possible to determine the relative values of the rate constants of radical reactions (3) without finding the concentrations of free radicals (R), which up to now has presented considerable difficulties. The essential feature of this determination forms the basis of the now well developed method of competitive reactions[1,2]. In the simplest type in the method of competitive reactions we are concerned with competing reactions of the same order, for example

$$R + M_1 = RM_1, \quad (7)$$

$$R + M_2 = RM_2. \quad (8)$$

The ratio of the rate constants of reactions (7) and (8)

$$\frac{k_7}{k_8} = \frac{W_7(M_2)}{W_8(M_1)}, \quad (9)$$

is determined from experimental measurements of the reaction rates W_7 and W_8 and the concentrations of the molecules taking part in the reactions. If the value of one of the rate constants (k_7 or k_8) can be determined (or calculated) by some independent method, the absolute value of the other constant can be determined from Eqn. (9).

However, it is not always possible successfully to choose a suitable competing reaction, and then Eqn. (6) must be used to determine the absolute rate constant of reaction (3). The solution of this problem requires independent experiments to measure absolute rate constants of the radical recombination (1) and disproportionation (2) reactions; at present these experiments present serious difficulties and must be supplemented by theoretical calculations.

Experimental difficulties are one of the reasons for the view long held that radical recombination reactions occur with every collision[3]. It should be mentioned that even

now in many experimental papers dealing with radical recombination reactions it is assumed that $k = 10^{14}$ mole$^{-1}\times$ $\times$ cm^3 s^{-1} (i.e. the steric factor $s = 1$ and $E = 0$)[4]†.

However, although the absence of a true activation energy E has been confirmed by numerous experimental results, the assumption that every collision is effective can be shown to be doubtful. This is confirmed by the fact that the steric factors for the addition of H atoms to alkenes, and also the factors for addition and replacement reactions of H and CH_3 radicals with various molecules (alkanes and alkenes), calculated by the transition-state method as applied to radical reactions[5,6,7], have low values. It may therefore be assumed that recombination reactions of CH_3, or more complex radicals, must also have low steric factors; otherwise, it would have to be accepted that reactions in which two free valencies disappear have special steric features compared with radical replacement reactions, in which the free valency is retained, but there are no grounds for this[8]. Moreover, if the preexponential factors A of the rate constants of recombination reactions are taken as equal to 10^{14} mole^{-1} cm$^3\times$ $\times$ s^{-1}, examination of the frequency factors of decomposition reactions on the basis of entropy changes leads to values that are too high for the preexponential factors (from 10^{17} s^{-1} for n-alkyl radicals to 10^{20} s^{-1} for t-butyl radicals[4,9]). Interpretation of the negative temperature coefficient found for the rate of recombination of CH_3 radicals[3] also unambiguously indicates that the steric factor s is less than unity and its value decreases with increase of temperature[10].

Approximate evaluation of steric factors for recombination reactions of the simplest radicals shows that their values are less than unity even for the recombination of H atoms and CH_3 radicals (900°K)[8]. If it is assumed that ternary collisions are necessary for the successful recombination of these particles, as in the combination of hydrogen atoms, then the steric factor will be still lower. When one of the recombining H atoms is replaced by a CH_3 radical, the steric factor of the recombination reaction decreases at first sharply, but then more gradually as the radicals become more complex (C_2H_5, C_3H_7). In the recombination of CH_3 radicals, the steric factor decreases still further, by one order of magnitude in comparison with its value in the H + CH_3 reaction. However, calculation gives a lower value (10^{-5}) than that found experimentally ($\sim 10^{-3}$) by Brodskii[11].

The calculation of the absolute rate constants of reactions (1) and (2), and especially the preexponents of these reactions, is therefore of interest, since unfounded assumptions connected with a difference of several orders between the preexponents of reactions (1), (2), and (3) lead to the competing relations between different radical reactions appearing in a distorted light. However, we shall first examine somewhat more widely the question of the calculation of the kinetic parameters of bimolecular reactions, since recombination and disproportionation reactions belong to this class.

The calculation of the rate constants of bimolecular reactions must be based on a detailed analysis of the collision process between the particles and the accompanying redistribution of energy, and it is complicated by the fact that the interaction forces between the particles have been little studied. This calculation of intermolecular forces can only be made for a small number of the simplest atoms and molecules. It is virtually impossible with complex particles, since their electronic molecular wave functions and potential energy surfaces are not known with sufficient accuracy. Therefore, only the approximate calculation of the reaction rate constant on the basis of a simplified collision model can be considered; quantum-mechanical methods of calculating the cross section may be used for these. One of these approximate calculations was made by Bauer and Wu for the exchange reaction $H_2 + X = HX + H$, where X is a Cl or Br atom[12]; an approximate value of 10^{-2} (300°K) was found for the steric factors of these reactions, which is in good agreement with calculations by the activated-complex method[8] and also with experimental results[13].

In recent years electronic computers are being increasingly used for quantum-mechanical calculations. However, the calculations could only be carried out in the simplest of cases and with approximate methods and models. A number of papers deal with the computer calculation of the probabilities of exchange reactions AB + C = = A + BC, which has permitted a more detailed study of the effect of vibrational excitation of the initial molecule on the effective activation energy (minimal initial translational energy necessary for the reaction to occur)[14,15].

The question of the calculation of the rate constants of bimolecular reactions on the basis of quantum-mechanical collision theory has been considered by Eliason and Hirschfelder[16]; by making a number of assumptions, they related the rate constant of a bimolecular reaction to the reaction cross section by means of a Laplace transformation, and they obtained an expression in terms of transition-state theory.

Attempts have also been made to calculate the rate constant of an elementary bimolecular reaction without making the assumption of equilibrium between the activated complex and the starting molecules[17,18]; the results are approximately equal to those obtained by transition-state theory.

Recently, phenomenological and statistical thermodynamics of irreversible processes are becoming more widely used in kinetic investigations. An important step in the construction of a logical theory of irreversible microscopic processes is the deduction of general expressions for kinetic coefficients from correlation functions[19]. However, their application to chemically reacting systems meets with great mathematical difficulties. Thus, a more nearly correct calculation of the rate constant of bimolecular reactions encounters serious mathematical difficulties, and a number of assumptions leads to a result similar to that obtained by transition-state theory[20,21]. The activated-complex theory makes it possible to determine the steric factor in the expression for the preexponential factor of the rate constant ($A = sZ$), which for bimolecular reactions has the form[5]:

$$s = \gamma \frac{kT}{h} \frac{1}{Z} \frac{Q^*}{Q_A Q_B} \exp\left[-\frac{1}{2} + T\frac{d}{dT}\ln\left(T\frac{Q^*}{Q_A Q_B}\right)\right] \quad (10$$

(the generally accepted symbols have been used in this equation[7]; in what follows it is assumed that $\gamma = 1$).

† For this reason, in the method of competing reactions for studying the kinetics of reactions in which radicals are replaced by various organic molecules, the radical recombination reaction was used as a convenient standard of comparison, since then the relative values of the steric factors and activation energies agree with their absolute values.

Approximation expressions for the temperature coefficient of s for reactions in which complex particles participate may be obtained[7,22] by logarithmic differentiation of Eqn. (10):

$$s_T/s_{T_1} = (T_1/T)^{3.5} \quad (11)$$

and for reactions in which H atoms participate:

$$s_T/s_{T_1} = (T_1/T)^2. \quad (12)$$

In the transition from higher to lower temperatures (900–300°K) the steric factors of the corresponding reactions increase within the limits of two orders (for CH_3 and more complex particles) or one order (for H atoms). Experimental results obtained by the study of recombination of CH_3 radicals confirm this conclusion[3,10].

Because of the absence of spectroscopic data, the calculation of the rotational and vibrational partition functions of radicals and activated complex required by formula (10) meets with considerable difficulties. The necessary assumptions that enable satisfactory results to be obtained have previously been discussed in detail[7]. The results of calculation of steric factors of addition and replacement reactions of H atoms and CH_3 radicals with saturated and unsaturated hydrocarbons on the basis of Eqn. (10) leads to good agreement with experiment[7,23]. In later papers by non-Russian authors, preexponential factors in reactions between the simplest molecules and radicals have been evaluated in the same way.

The preexponential factors for twelve bimolecular reactions between simple inorganic molecules and radicals (including the atoms N, O, F, Cl) have been calculated by the transition-state method by Herschbach and coworkers[24]. In these reactions, the number of atoms in the activated complex did not exceed 5 or 6, and its structural and mechanical properties were calculated from the properties of the initial and final molecules. For the reaction $NO + O_3 = NO_2 + O_2$ the normal vibrational frequencies for the complex $NO{-}O_3$ were calculated from the assumed geometry and the force constants of NO_2 and O_3 molecules. The values of the steric factors found for these reactions were low (10^{-1}–10^{-3}) and are in satisfactory agreement with experimental results‡; however, usually the calculated preexponents were less than those obtained experimentally, which confirms the necessity of regarding the activated complex as a molecule in which a somewhat elongated bond is being formed[21].

In a number of reactions in which a hydrogen atom is detached ($R + M \rightarrow RH + R_1$; R = H, CH_3, CD_3, Br) the bonds formed in the activated state were assumed to be longer than those in the corresponding hydrocarbons; in finding the length of the bonds formed the authors[25,26] followed Pauling's empirical rule[27] for the relation between the covalent radii of bonds and their order:

$$R(1) - R(n) = 0.3 \log n, \quad (13)$$

where $R(1)$ is the radius of the corresponding single bond, $R(n)$ is the radius of the bond formed, which by hypothesis is always considered to be a bond of half order ($n = \frac{1}{2}$)[25,26]. Formula (13) shows that the length of the C–C bond in the activated complex increases by about 0.18 Å.§

The application of Pauling's empirical rule (13) enabled the structure of the activated complexes to be determined and Q_{rot} to be approximately calculated (in the calculation it was assumed that the H atoms are localised in the nuclei of the C atom with which they are linked).

The vibrational partition function has been approximately evaluated[24]. On the basis of these and a number of other assumptions, the preexponential factors for reactions in which H atoms are abstracted have been found within a factor of ten. Values of the steric factor (10^{-1}–10^{-3}) in a number of available instances are in good agreement with those found by calculation from formula (10) and by experiment[23].

The preexponential factor of a reaction of the type $RH + Cl = R + HCl$ (where $R = CH_3$ (has been obtained from partition functions calculated by the classical method[29] and is in agreement with the experimental value¶. This method of calculation has the advantage that it requires less detailed information on reagents and activated complexes; in particular, and this is very important, data on the normal vibrational frequencies of the reagents and the activated complex are not required. Calculation of the classical partition function, of course, requires a knowledge of the potential energy surface. The authors assume that it corresponds approximately with the potential energy surface for the reaction $H_2 + Cl = HCl + H$. The bonds in the activated complex (C–H and H–Cl) were assumed to be longer than in the corresponding compounds, in accordance with Pauling's empirical rule (see above). The preexponential factor of this reaction was evaluated on the basis of these assumptions.

The method of calculating preexponential factors considered has been generalised for reactions of the type $CF_3 + RH \rightarrow CF_3H + R$, (where RH = C_2H_6, n-C_3H_8, n-C_4H_{10}) and the case has been considered in which the activated complex may be represented as an aggregate of three rigidly linked groups, each with its own reaction centre (three-centre problem X–Y–Z)[31]. Information on the potential energy surface may be obtained from the force constants of the particles. The preexponential factor A may then be expressed in terms of the force constants and other characteristics of the reacting particles and the activated complex (bond length, symmetry number, etc.). The unknown valence force constants for the selected geometric structure of the activated complex were roughly evaluated[31] by Badger's empirical rule[32], and the deformation force constants were obtained from a comparison with simpler known examples. The calculated preexponents of these reactions agree with the experimental values; it has been shown that the quantum correction in this classical evaluation of the partition function is not great, being less than 1.4 when $\omega < 1000$ cm^{-1} at 400°K.[31]

In radical polymerisation reactions a number of questions may be interpreted in the light of the calculations of steric factors[33]. It has been found that the steric factor of the

‡ The preexponential factors are also calculated by making an analogy between the entropies of the activated complexes of the reactions considered and the corresponding hydrocarbon molecules similar to them in structure, but the results are not always confirmed by experiment[24].

§ This rule has also been used for other types of bonds[26,28,29].

¶ Some divergencies from experimental results which have been found by Knox and Trotman-Dickenson in the evaluation of the preexponents of the rate constants of analogous reactions on the basis of transition-state theory are due to a somewhat simplified approach to the calculation of the partition functions of the initial particles and activated complexes[20].

propagating reaction in the molecular and radical polymerisation of ethylene greatly diminishes only in the early stages of polymerisation, but then the formation of trimer, tetramer, etc. occurs at a constant value of s (10^{-5}–10^{-6}). Similar relationships are observed in radical polymerisation reactions of propene, in which the steric factor of initial chain growth is particularly low (10^{-7}–10^{-9}). This explains why polymerisation of unsaturated molecules is frequently interrupted at the dimerisation stage [34], and also indicates that polymers of different chain length are equally reactive [35]. A comparison of the steric factors in radical and molecular polymerisations† shows that under the same conditions radical polymerisation must proceed more rapidly than molecular, because of the low activation energy in the propagating reaction (4–7 kcal instead of 38 kcal for molecular polymerisation).

Thus, numerous calculations of preexponential factors of addition and substitution reactions between simple molecules and radicals based on transition-state theory show that these reactions have low steric factors ($s \simeq \simeq 10^{-1}$–10^{-5}), in agreement with experimental results.

We shall now consider the kinetic characteristics of radical recombination and disproportionation reactions [23,37-43].

A current model for radical recombination reactions enables activation energies to be calculated and also permits a more nearly correct calculation of steric factors of these reactions, and rate constants can be evaluated from these.

Let us consider the recombination reaction A + B = AB. If A and B are atoms, the potential energy surface is two-dimensional, i.e. it is a curve similar to a Morse curve. Since the approaching atoms have a relative angular momentum, it is still necessary to calculate their centrifugal energy of rotation for each quantum state and for each distance between them. From this the position of the activated state on the potential energy surface can be determined; the energy maximum equal to the sum of the rotational and potential energies will correspond to this position. From this and the most probable value of the rotational quantum number j^* for the activated complex, the most probable interatomic distance (effective collision diameter) in the transition state can be calculated. As calculations show [21], the value of the effective collision diameter r^* is several times greater than the equilibrium interatomic distance in the molecule AB (for H–H, $r^* = 4$–5 Å), and therefore the energy of dispersion interaction may be used as an approximate evaluation of the energy barrier. The rate constants of recombination reactions of some simple radicals have been calculated from the theory of absolute reaction rates by the use of this method with some assumptions [44-47].

The steric factors of radical recombination reactions can be calculated from more detailed information on the activated state, and the activation energies can also be calculated by the solution of two transcendental simultaneous equations which may be obtained from the accepted model of the recombination reaction. Actually, the energy barrier E is the difference between the centrifugal energy ϵ_j and the polarisation energy ϵ_p of the approaching radicals; when account is taken of the dissociation energy of the molecule D and its vibrational energy ϵ_v the energy barrier is given by:

$$E(r, j) = \varepsilon_j - (D - \varepsilon_v) - \varepsilon_p. \quad (14)$$

In the activated state Eqn. (14) has a maximum, that is, the following condition holds:

$$\frac{\partial E(r, j)}{\partial r} = 0,$$

from which the equation for r follows:

$$r = r(j). \quad (15)$$

The probability of the activated state $\omega(r, j)$ is calculated in the usual manner

$$\omega(r, j) = (2j+1) \exp\left(-\frac{E}{kT}\right).$$

The most probable values of j^* for the activated complex may be calculated from the condition

$$\frac{\partial \omega(r, j)}{\partial j} = 0 \quad (16)$$

and then the interatomic distances r^* of the separating particles in the transition state may be evaluated. The height of the barrier (Eqn. 14) that must be overcome by radicals to form a stable molecule may be evaluated from the values of r^* and j^* found. The parameters in Eqn. (15) and Eqn. (16) characterise the physicochemical properties of the radicals (their polarisabilities and ionisation potentials) and the bond of the activated complex formed (its dissociation energy, vibrational constant, and equilibrium distance).

It is well known that free radicals have ionisation potentials that differ little from the ionisation potentials of the molecules from which they are obtained. Concordant values of the ionisation potentials of many alkyl radicals have been obtained by electron-impact, photoionisation, and other methods [48]. Since the occupied electronic radical orbitals are not lower than the orbitals of the related molecules, it may be assumed that they are geometrically similar to one another [49]. This suggests that the polarisability of the radical is intermediate between the polarisabilities of the alkane and alkene molecules (the values for the latter are close [50]).

$$\alpha(\mathrm{R}) \simeq \frac{\alpha(\mathrm{C}_n\mathrm{H}_{2n+2}) + \alpha(\mathrm{C}_n\mathrm{H}_{2n})}{2}.$$

Values of the dissociation energy of the corresponding bonds may be found in the literature [48,51]. The numerical value of the vibrational force constant differs little from the stretching vibration of the corresponding C–C (or C–H) bond. Data required for calculating the parameters in the equations above, and also the parameters themselves, have been published [23,37].

Table 1 is concerned with recombination reactions, mainly of alkyl radicals.

The transcendental Eqns. (15) and (16) have been solved on a Ural-1 electronic computer. The following conclusions may be drawn from the results obtained.

1. With regard to the energy barrier, radicals entering into the reactions are practically equivalent, since the activation energy of the recombination reaction E is 200–300 cal.

† Low steric factors in polymer chain-lengthening reactions mean low preexponents, and therefore reaction rates are not so high, although the reactions have low activation energies. Recently it has been found [36] that in methyl methacrylate polymerisation reactions the steric factor is 10^{-4}.

TABLE 1. Steric factors and rate constants for the recombination and disproportionation of alkyl radicals.

Reaction No.	Reaction	900°K				300°K			
		recombination		disproportionation		recombination		disproportionation	
		s_1	k_1	s_2	k_2	s_1	k_1	s_2	k_2
1	$H+CH_3$	$2.3\ 10^{-2}$	$2.0\ 10^{-11}$	—	—	$3.6\ 10^{-1}$	$1.8\ 10^{-10}$	—	—
2	$H+C_2H_5$	$5.5\ 10^{-3}$	$7.3\ 10^{-12}$	$2.7\ 10^{-3}$	$3.5\ 10^{-12}$	$8.5\ 10^{-2}$	$6.6\ 10^{-11}$	$2.4\ 10^{-2}$	$1.9\ 10^{-11}$
3	$H+C_3H_7$	$1.7\ 10^{-3}$	$3.1\ 10^{-12}$	$1.1\ 10^{-3}$	$2.1\ 10^{-12}$	$2.6\ 10^{-2}$	$2.8\ 10^{-11}$	$1.0\ 10^{-2}$	$1.1\ 10^{-11}$
4	$H+C_4H_9$	$5.9\ 10^{-4}$	$1.2\ 10^{-12}$	$5.4\ 10^{-4}$	$1.0\ 10^{-12}$	$9.2\ 10^{-3}$	$1.1\ 10^{-11}$	$4.9\ 10^{-3}$	$5.9\ 10^{-12}$
5	CH_3+CH_3	$1.1\ 10^{-3}$	$4.9\ 10^{-13}$	—	—	$9.1\ 10^{-2}$	$2.3\ 10^{-11}$	—	—
6	$CH_3+C_2H_5$	$2.3\ 10^{-4}$	$1.3\ 10^{-13}$	$3.5\ 10^{-5}$	$1.9\ 10^{-14}$	$1.9\ 10^{-2}$	$6.1\ 10^{-12}$	$1.7\ 10^{-3}$	$5.2\ 10^{-13}$
7	$CH_3+C_3H_7$	$5.6\ 10^{-5}$	$3.8\ 10^{-14}$	$7.7\ 10^{-6}$	$5.3\ 10^{-15}$	$4.5\ 10^{-3}$	$1.8\ 10^{-12}$	$3.6\ 10^{-4}$	$1.5\ 10^{-13}$
8	$CH_3+C_4H_9$	$2.2\ 10^{-5}$	$1.5\ 10^{-14}$	$6.4\ 10^{-6}$	$4.4\ 10^{-15}$	$1.8\ 10^{-3}$	$7.0\ 10^{-13}$	$3.0\ 10^{-4}$	$1.2\ 10^{-13}$
9	$CH_3+C_5H_{11}$	$1.2\ 10^{-5}$	$9.5\ 10^{-15}$	$3.5\ 10^{-6}$	$2.7\ 10^{-15}$	$9.6\ 10^{-4}$	$4.5\ 10^{-13}$	$1.7\ 10^{-4}$	$7.5\ 10^{-14}$
10	$C_2H_5+C_2H_5$	$1.0\ 10^{-5}$	$6.4\ 10^{-15}$	$2.2\ 10^{-6}$	$1.4\ 10^{-15}$	$8.0\ 10^{-4}$	$3.0\ 10^{-13}$	$1.0\ 10^{-4}$	$3.9\ 10^{-14}$
11	$C_2H_5+C_3H_7$	$3.3\ 10^{-6}$	$2.5\ 10^{-15}$	$9.2\ 10^{-7}$	$6.9\ 10^{-16}$	$2.6\ 10^{-4}$	$1.2\ 10^{-13}$	$4.3\ 10^{-5}$	$1.9\ 10^{-14}$
12	$C_2H_5+C_4H_9$	$2.0\ 10^{-6}$	$1.5\ 10^{-15}$	$5.7\ 10^{-7}$	$4.2\ 10^{-16}$	$1.6\ 10^{-4}$	$7.0\ 10^{-14}$	$2.7\ 10^{-5}$	$1.1\ 10^{-14}$
13	$C_2H_5+C_5H_{11}$	$1.6\ 10^{-6}$	$1.3\ 10^{-15}$	$4.7\ 10^{-7}$	$3.7\ 10^{-16}$	$1.3\ 10^{-4}$	$6.1\ 10^{-14}$	$2.2\ 10^{-5}$	$1.0\ 10^{-14}$
14	$C_3H_7+C_3H_7$	$1.2\ 10^{-6}$	$1.0\ 10^{-15}$	$3.4\ 10^{-7}$	$2.8\ 10^{-16}$	$9.9\ 10^{-5}$	$4.7\ 10^{-14}$	$1.6\ 10^{-5}$	$7.7\ 10^{-15}$
15	$C_3H_7+C_4H_9$	$1.0\ 10^{-6}$	$8.0\ 10^{-16}$	$2.8\ 10^{-7}$	$2.3\ 10^{-16}$	$8.0\ 10^{-5}$	$3.8\ 10^{-14}$	$1.3\ 10^{-5}$	$6.2\ 10^{-15}$
16	$C_3H_7+C_5H_{11}$	$8.3\ 10^{-7}$	$7.1\ 10^{-16}$	$2.3\ 10^{-7}$	$2.0\ 10^{-16}$	$6.7\ 10^{-5}$	$3.4\ 10^{-14}$	$1.1\ 10^{-5}$	$5.5\ 10^{-15}$
17	$C_4H_9+C_4H_9$	$7.5\ 10^{-7}$	$5.6\ 10^{-16}$	$2.1\ 10^{-7}$	$1.6\ 10^{-16}$	$6.0\ 10^{-5}$	$2.6\ 10^{-14}$	$9.9\ 10^{-6}$	$4.4\ 10^{-15}$
18	$C_4H_9+C_5H_{11}$	$5.5\ 10^{-7}$	$4.5\ 10^{-16}$	$1.8\ 10^{-7}$	$1.4\ 10^{-16}$	$4.4\ 10^{-5}$	$2.1\ 10^{-14}$	$8.5\ 10^{-6}$	$3.9\ 10^{-15}$
19	$C_5H_{11}+C_5H_{11}$	$3.3\ 10^{-7}$	$2.8\ 10^{-16}$	$1.1\ 10^{-7}$	$9.4\ 10^{-17}$	$2.6\ 10^{-5}$	$1.3\ 10^{-14}$	$5.2\ 10^{-6}$	$2.6\ 10^{-15}$
20	$2iso\text{-}C_3H_7$	$2.5\ 10^{-6}$	$2.0\ 10^{-15}$	$3.7\ 10^{-6}$	$3.0\ 10^{-15}$	$2.0\ 10^{-4}$	$9.4\ 10^{-14}$	$1.7\ 10^{-4}$	$8.3\ 10^{-14}$
21	$2iso\text{-}C_4H_9$	$1.8\ 10^{-10}$	$1.3\ 10^{-19}$	$1.3\ 10^{-10}$	$1.0\ 10^{-19}$	$1.4\ 10^{-8}$	$6.1\ 10^{-18}$	$0.6\ 10^{-8}$	$2.6\ 10^{-18}$
22	$2s\text{-}C_4H_9$	$1.4\ 10^{-9}$	$1.1\ 10^{-18}$	$5.2\ 10^{-9}$	$3.9\ 10^{-18}$	$1.1\ 10^{-7}$	$5.2\ 10^{-17}$	$2.5\ 10^{-7}$	$1.1\ 10^{-16}$
23	$2t\text{-}C_4H_9$	$1.6\ 10^{-9}$	$1.2\ 10^{-18}$	$1.2\ 10^{-8}$	$0.9\ 10^{-17}$	$1.3\ 10^{-7}$	$5.6\ 10^{-17}$	$5.7\ 10^{-7}$	$2.5\ 10^{-16}$

2. The distance r^* between the radicals in the activated complex is several times greater than the distance separating the radicals in the corresponding hydrocarbon and is equal to 4–5 Å for all reactions (900°K).

3. At normal temperatures ($\sim$300°K) the value of r^* increases by about 1 Å, which increases the temperature dependence of the steric factors.

4. A change of 10–20% in the values of the parameters in Eqn. (15) and Eqn. (16) leads to virtually the same solutions, which indicates the lack of sensitivity of the equations and the possibility of using them in the calculation of kinetic characteristics.

Therefore, in the study of radical recombination reactions the preexponents of the rate constants of these reactions are particularly significant, since the exponential factor is always of the order of unity — $\exp(-E/RT) \simeq 0.7$. Here it is easy to follow the effect of the structure of the reacting particles on the change in their reactivity, since the difference between the activity of the radicals in combining is due only to a change in steric factors.

The steric factors of recombination reactions of alkyl radicals were calculated from Eqn. (10). In contrast to previous calculations[8] (the length of the bond formed in the activated complex of recombination reactions was taken to be 15–20% greater than the bond in the corresponding hydrocarbon) values of r^* obtained by solving the equations above were used. This led to a tenfold to fifteenfold increase in the steric factors compared with values previously calculated.

The results of the calculation (Table 1) show that the steric factor is of the order of unity only for the recombination of such simple radicals as H and CH_3 (300°K). At higher temperatures the value of s decreases by two orders ($s \simeq 1\times10^{-2}$). For more complex radicals in reactions of the type (H + R = HR), the value of s decreases at first by an order and then more gradually.

The value of the steric factor for the recombination of two CH_3 radicals is 9×10^{-2} (300°K), or 10^{-3} (900°K). As one of the combining radicals becomes more complex, the value of s decreases, and for the recombination of CH_3 and C_5H_{11} radicals it reaches a limiting value ($s_{300} \simeq 10^{-3}$; $s_{900} \simeq 10^{-5}$).

A similar picture is observed for the recombination of C_2H_5 radicals; the steric factors for their recombination are 8×10^{-4} (300°K) and 10^{-5} (900°K), which are lower by two orders than the factors for the recombination of two methyl radicals. For this group of reactions the value of s decreases gradually as the radicals become more complex, and the limiting value is lower than in reactions in which CH_3 radicals take part ($s_{900} \simeq 10^{-6}$, $s_{300} \simeq 10^{-4}$).

In the recombination of C_3H_7 radicals there is a slight reduction in the steric factor ($s_{300} \simeq 10^{-4}$, $s_{900} \simeq 10^{-6}$), which scarcely changes as the combining radicals become more complex.

Recombination reactions of more complex radicals have about the same values of s ($s_{300} \simeq 4\times10^{-5}$, $s_{900} \simeq 10^{-7}$).

Recombination reactions of the isomeric radicals iso-C_3H_7, s-C_4H_9, and t-C_4H_9 have lower steric factors. Evidently, this is because the branched structure of the radical inhibits the formation of the dimer.

Thus, as the reacting radicals become more complex the steric factors of their recombination reactions decrease. Therefore, more complex radicals are less reactive; the value of the steric factor may be taken as a measure of the activity of the radicals. The results of the calculation of steric factors show that the activity of free alkyl radicals decreases with increasing chain length up to a certain limit (C_3–C_4), after which there is almost no further change; secondary and tertiary radicals also show a decrease compared with primary radicals. According to Semenov[51], this is connected with the interaction of an electron of the free valency with electrons of the adjacent C–C and C–H σ-bonds. This leads to a change in the shape of the radicals and to comparatively small changes in electron density due to overlap and interaction of the electron clouds of the free electron and the electrons of the σ-bonds. It is this type of interaction that reduces the activity of alkyl radicals in the transition from CH_3 to C_4H_9, and also when hydrocarbon branching increases up to a certain limit.

The recombination rate constants were evaluated from the values found for the steric factors, numbers of binary collisions z of reacting radicals, and activation energies of these reactions; the values of these constants together

with the calculated steric factors are given in Table 1. It is of interest to compare the theoretical and experimental values of the kinetic parameters considered.

Avramenko and Postnikova [53] made a kinetic study of the recombination of the simplest CH_3 radicals at low temperatures, when the steric factor of this reaction has the low value of ~ 0.1 (the calculated value of s_{300} is 9.1×10^{-2}). As the temperature is raised, the value of the rate constant falls, because of the temperature dependence of the preexponential factor. The calculated steric factor for the recombination reaction of CH_3 radicals falls to 10^{-3} at high temperatures; this agrees with the experimental value obtained by determining the temperature dependence of the rate constant by means of tracer atoms [11].

A negative temperature dependence was also found for the recombination of CH_3 and C_2H_5 radicals in a study of the mechanism of high-temperature cracking of ethane; this indicates a low steric factor for this reaction [54]. The experimental value of the steric factor ($\sim 10^{-3}$) is close to the calculated value (2.3×10^{-4}) (Table 1).

In a number of instances the concentrations of reacting radicals have been obtained from experimental results [44,45,55]; this enables the rate of accumulation of dimer, $W = k_1(R)^2$, to be evaluated from the calculated rate constant of the radical recombination reaction. Comparison shows that the calculated rates of recombination and disproportionation of C_2H_5, C_3H_7, and C_5H_{11} radicals are in good agreement with the experimental values (Table 2).

It is interesting to study the change in the reactivity of radicals with the introduction of substituents and also with the introduction of a new partner in the recombination reaction. Theoretical examination of the recombination of CF_3 radicals, and also of the combination of CF_3 and CH_3 radicals [37], shows that these reactions are energetically similar to the reactions described above ($E \simeq 200$–300 cal, $r^* \simeq 5$ Å). The calculated steric factor for the recombination of CF_3 radicals is considerably lower (4.6×10^{-6}, 900°K) than the factor for the analogous reaction with CH_3 radicals. For the recombination of CF_3 and CH_3 radicals s has an intermediate value (5.2×10^{-4}). It follows from these results that replacement of H atoms in CH_3 radicals by F atoms (with a greater atomic volume and the more polar C–F bond) leads to a sharp reduction in the steric factor, but differences between the recombination reactions of CH_3 and CF_3 radicals have not been observed experimentally [56]. The experimental activation energy for CF_3 radicals ($E \simeq 2.1$ kcal [57]) does not agree with the value calculated from the accepted model. If it is assumed that the activation energy is low, as in other cases, a value of 10^{-2} is obtained for the steric factor, which is greater than the value found, $s \simeq 4 \times 10^{-4}$ (300°K)‡.

Experimental results show that CF_3 radicals remove hydrogen from methane and ethane molecules more easily than CH_3 radicals [59,60]. Only relative steric factors of these reactions can be determined experimentally, and since the calculated value of s for the recombination of CF_3 radicals is considerably less than that for the recombination of CH_3 radicals, this may be a simple explanation of the experimentally observed increased activity of CF_3 radicals in reactions with saturated molecules (the activation energies of both substitution reactions are close).

TABLE 2. Calculated and experimental rates of recombination and disproportionation of alkyl radicals.

$2R \rightarrow R_2(I)$, $\rightarrow P+O(2)$	W (molecules cm^{-3} s^{-1}) $\times 10^{-12}$											
	W_1	W_1^{exp}	W_2	W_2^{exp}	W_1	W_1^{exp}	W_2	W_2^{exp}	W_1	W_1^{exp}	W_2	W_2^{exp}
	320° K				370° K				420° K			
$C_2H_5+C_2H_5$ [44]	0.39	0.44	0.06	0.0585	20.4	24	4.55	3	2.22	2.47	0.46	3
	370° K				390° K				420° K			
$C_3H_7+C_3H_7$ [45]	46	45.4	7.8	6.2	46	42.2	—	—	59	56	10	6.6
	336° K				420° K							
$C_5H_{11}+C_5H_{11}$ [55]	1.4	0.3	0.3	0.12	2.46	—	0.56	0.23	—	—	—	—

When radicals collide, in addition to recombination, the competing process in which they are disproportionated with the formation of two molecules is observed. In disproportionation reactions, as in exchange reactions, a hydrogen atom migrates from one particle to another. However, ordinary exchange reactions are exothermic by not more than 25 kcal, but the heat given out in disproportionation reactions is considerably greater (50–60 kcal). Disproportionation reactions would therefore be expected to have a low activation energy, and as a result are encountered no less frequently than radical recombination reactions. This may be demonstrated by an experimental study of the products of these reactions, which include saturated and unsaturated molecules as well as dimer.

Free radicals are mainly obtained by photolysis or pyrolysis of suitable compounds, by mercury photosensitisation of saturated molecules, or by the addition of a hydrogen atom to an alkene. Sources of the radicals include molecules of metal alkyls, ketones, aldehydes, and also other compounds. The following reaction scheme may be used to study the mechanism and kinetics of recombination and disproportionation reactions [52,61]:

$$M + h\nu \rightarrow 2R\,(\text{or } R_1 + R_2) \qquad (17)$$

$$2R \begin{cases} \rightarrow R_2\,(k_1) \\ \rightarrow P + O\,(k_2). \end{cases}$$

Clearly,

$$k_2 = \frac{W_O}{(R)^2} \text{ or } \frac{W_P}{(R)^2} \text{ and } k_1 = \frac{W_{R_2}}{(R)^2} \qquad (18)$$

$$\Delta = \frac{k_2}{k_1} = \frac{W_O}{W_{R_2}} \text{ or } \frac{W_P}{W_{R_2}}.$$

The ratio Δ may be found by analysis of the reaction products, the dimer R_2, P, or O, with subsequent determination of the rates of formation W of the corresponding compounds. However, the reaction scheme may be more complex than that considered above. Frequently alkene and alkane molecules are formed by the following reactions

$$R + M = r + RH\,(k_3) \qquad (19$$

$$r = O + R' + X, \qquad (20$$

where r is the radical formed by removal of a hydrogen atom from the molecule M. If at the temperatures under

‡ On the basis of experimental results on the rates of the radical recombination reactions $2CH_3 = C_2H_6$ (a), $CH_3 + CF_3 = CH_3CF_3$ (b), and $2CF_3 = C_2F_6$ (c), the relative change in activation entropy of reaction (b) in relation to reactions (a) and (c) $\Delta S_b^* - \frac{1}{2}(\Delta S_a^* - \Delta S_c^*)$ has been calculated. Calculation of this by the theory of absolute reaction rates with the use of known values of the internal rotation barriers for ethane and substituted ethanes gives a value close to the experimental ratio of the preexponents [58].

study it is still necessary to take reaction (19) into account, then

$$W_P = k_2(R)^2 + k_3(R)(M)$$
$$W_{R_2} = k_1(R)^2.$$

Therefore

$$\frac{W_P}{W_{R_2}} = \frac{k_2}{k_1} + \frac{k_3(M)}{\sqrt{k_1 W_{R_2}}}.$$

Since W_P, W_{R_2}, and (M) may be measured experimentally, the ratio Δ is found graphically using plots of W_P/W_{R_2} against (M). Extrapolation of the straight line obtained to (M) = 0 will give an intercept on the ordinate equal to k_2/k_1. Sometimes additional difficulties are encountered, because alkane and alkene molecules are formed in the initial photolytic step[52].

When radicals are formed in the presence of an excess of hydrogen atoms by addition of the latter to alkenes, the value of Δ may be found by determining the relative amounts of P and R_2 in the products, provided that the reaction $R + H_2 = RH + H$ plays an insignificant part at the experimental temperatures[62]. This method of investigation has two disadvantages[63]. The first is that a careful mass-spectrometric analysis of the dimer (which is not an easy task) must be carried out to determine which radicals are present in the reacting system. Moreover, radicals formed by the addition of H-atoms to alkenes have a considerable excess of internal energy (~ 40 kcal), which makes them unstable with regard to decomposition into simpler particles. For these reasons, results obtained by this method should be viewed critically.

Numerous experimental results that have been quoted very frequently in recent years for the ratio of the rate constants of disproportionation and recombination reactions have been obtained by a study of the systems mentioned. The main reason for the divergence of experimental values of Δ appears to be the use of different methods of initiation, leading to the production of radicals with different internal energies. The reasons for the divergence of experimental results obtained by different workers is discussed by Thynne[64].

The parameters s and E for radical disproportionation reactions have been obtained from Eqn. (18) with the use of experimental values of Δ and on the assumption[4] that each collision leading to the combination of two radicals is effective ($s = 1$, $E = 0$). Since the experimental ratios of the rate constants are of the order $1-10^{-1}$, it is concluded that the steric factors of radical disproportionation reactions are within the same limits; it is assumed that the activation energies of these reactions are approximately equal to the activation energies of recombination reactions[65]. However, it has been shown in a number of experimental and theoretical papers that s is less than unity in radical recombination reactions (Table 1). Such an approach to the numerical evaluation of the preexponential factors of disproportionation reactions on the basis of experimental values of Δ and the assumption that $k_1 = 10^{14}$ mole^{-1} cm^3 s^{-1} for all alkyl radicals is therefore unsound. In this connection, the calculation of absolute rate constants of radical disproportionation reactions and, in the first instance, more detailed evaluation of preexponential factors are of interest.

Available experimental results on radical disproportionation reactions (the systematic study of which began in the last decade) do not allow the setting up of any definitive reaction model. Combination and disproportionation reactions of deuterated ethyl radicals have been observed in the photolysis of 2,2,4,4-tetradeuterodiethyl ketone[66]; two possible mechanisms for the disproportionation of ethyl radicals were considered: the "head-to-tail" mechanism

$$CH_3-CH_2- + H-CH_2-CH_2- = C_2H_6 + C_2H_4, \quad (21)$$

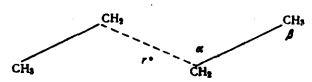
and the "head-to-head" mechanism

$$CH_3-CH_2- + H-CH-CH_3 = C_2H_6 + C_2H_4. \quad (22)$$

On the basis of a study of the isotopic composition of the products (the ethylene consisted of 90% $C_2H_2D_2$), it was concluded that the radicals preferentially disproportionate by the "head-to-tail" mechanism ($CH_3-CD_2...H-CH_2-CD_2$). Similar results were obtained in the pyrolysis of the same ketone[67]. Mass-spectrophotometric analysis of the products showed that CH_3CD_2H and $CH_2=CD_2$ are mainly obtained in the disproportionation of ethyl radicals.

The possible mechanism of the disproportionation of alkyl radicals has again been discussed in a number of recent papers. Bradley draws attention to the similarity of the values of the rate constants of radical recombination and disproportionation reactions[40]. It has previously been noted that the activated complex in recombination reactions consists of two freely rotating radicals[46]. Since the rate constants of recombination and disproportionation reactions are close, it is reasonable to assume that the radicals also rotate freely in the activated complex in disproportionation reactions. From this it can be concluded that the transition states are identical. However, the "head-to-tail" mechanism cannot allow such freedom to the radicals in the activated state undergoing disproportionation, and since the energy surfaces corresponding to radical recombination reactions scarcely change with the radicals considered (this is demonstrated quantitatively by calculations of the activation energies of these reactions), it must be assumed that rearrangement of the activated molecule for disproportionation occurs after passage through the transition state. Because disproportionation is a highly exothermic process, the energy barriers to rearrangement cannot exceed the initial activation energy of the radicals, and therefore cannot be expressed experimentally as temperature coefficients of the reaction.

For the reaction between ethyl radicals Bradley considers the rearrangement of an activated molecule formed by the "head-to-head" mechanism, which has the following form in the case of radical recombination reactions:



The central C–C bond is ruptured in the reaction and a hydrogen atom is transferred from one half of the activated butane molecule to the other. The author concludes from an examination of the activated butane molecule that a β-hydrogen atom migrates to the methylene group of the other radical, and this converts the system into the reaction products, ethane and ethylene; as a result of intramolecular movements, the hydrogen in the β-position of one radical comes closer to the methylene group of the other radical than do the other hydrogen atoms. Bradley presents a number of proofs of the proposed mechanism[40].

Kerr and Trotman-Dickenson have proposed a similar explanation of the mechanism of disproportionation of alkyl

radicals[4,41]. Because of the closeness of the rate constants of reactions (1) and (2), they assume that radicals in the activated complex of disproportionation reactions are no less free than in the complex of recombination reactions. The structure of the activated complex in a "head-to-tail" disproportionation reaction does not allow such freedom to the radicals. It is considered that a dimer is formed initially and this then decomposes by a four-centre reaction. Since such dimerisation is a highly exothermic process, the activation energy required for decomposition is available.

This view of the mechanism of disproportionation of alkyl radicals has been confirmed by the work of Matsuoka and coworkers[42]. They investigated recombination and disproportionation reactions of ethyl radicals obtained by photolysis. The dependence of $\log\Delta$ of $1/T$ is linear in the temperature range -78° to + 85°C (some side reactions were excluded by the use of low temperatures). The observed negative temperature coefficient of this reaction may be explained by assuming that the radical disproportionation results from deformation vibrations of the active butane molecule which is formed by the union of two ethyl radicals. This leads to the migration of a hydrogen atom in the β-position from one radical to the methyl group of the other. This process competes with the intermolecular dispersion of energy of an incipient C–C bond which leads to butane as the product of the radical recombination reaction.

Quite recently Bradley and Rabinovitch have critically reexamined the mechanism of radical disproportionation[43]. They point out that, because of the rigidity of the activated complex, the previously accepted "head-to-tail" mechanism cannot correspond to the transition state of the disproportionation reaction, for which a looser structure is assumed. It may be assumed from the similarity between the activated complexes of radical disproportionation and recombination reactions that the corresponding saddle points are energetically and configurationally similar, and some reaction complexes may pass through both configurations. However, the experimental divergence between the values of k_1 and k_2, which differ by almost a factor of ten for most reactions of alkyl radicals, indicates that caution must be used in drawing an analogy between the mechanisms of these reactions. Moreover, possible amendments to the mechanism of radical reactions§ obviously change the existing point of view on the mechanisms of these reactions.

The well-known experimental fact that $E_{rec} - E_{dis} \simeq 0$ may be used to evaluate the rate constants of disproportionation reactions of alkyl radicals[65]. It is also assumed that the transition state in a disproportionation reaction is formed by a "head-to-head" mechanism; the reaction products then result from the transfer of a hydrogen atom in the β-position from one radical to the other[40]. Moreover, by analogy with exchange reactions (the distance between the particles in the activated complex has been found theoretically and experimentally for the simplest of these reactions[20,21]), it has been assumed that for migration of a hydrogen atom the disproportionating radicals must approach one another to a distance r^*, which is of the same order as the length of the interatomic bond in the corresponding hydrocarbon.

§ Rice recently pointed out another possible mechanism for radical recombination reactions, which consists in the coupling of combining radicals by means of three-centre H-atom bonds[68].

The rate constants for the disproportionation of alkyl radicals have been calculated from Eqn. (10) with the use of these assumptions. The data necessary for the calculation of the preexponents of these reactions have been published[23,37,39].

The results obtained show that disproportionation reactions have lower steric factors and rate constants than recombination reactions (Table 1). The reaction between a hydrogen atom and an ethyl radical, which is one of the simplest disproportionation reactions, has a steric factor much less than unity (2.4×10^{-2}) at room temperature. Disproportionation reactions in which hydrogen and more complex radicals participate have lower steric factors. At higher temperatures ($\sim$ 900°K) these values of s become still lower (Table 1), in accordance with Eqn. (11).

Replacement of a hydrogen atom by a CH_3 radical in the reaction between methyl and ethyl radicals leads to a reduction of the steric factor by about one order (1.7×10^{-3}, Table 1). As the reacting radicals become more complex (reactions 6–9, Table 1), the steric factor decreases more gradually, reaching a limiting value in these reactions of $\sim 10^{-4}$ (300°K) or $\sim 4\times10^{-6}$ (900°K).

A similar situation is observed with ethyl radicals (see reactions 10–13 in Table 1); the steric factor for the disproportionation of ethyl radicals is 10^{-4}.

We have made supplementary calculations in connection with the discussion above on the possible mechanism of disproportionation of ethyl radicals. Different directions of approach of two ethyl radicals which may disproportionate by the "head-to-tail" mechanism, and local changes of up to 20% in bond lengths and angles change the final result by less than a factor of 1.5. Similar calculations on the basis of the "head-to-head" mechanism, which is also accepted for other radical disproportionation reactions, lead to virtually the same values of the rotational partition coefficient of the activated complex. Thus, the difference between these two mechanisms cannot materially affect the value of the preexponential factors[37].

For reactions in which more complex radicals participate (reactions 14–19 in Table 1), the values of the steric factors scarcely change from one disproportionation reaction to another ($s_{300} = 10^{-5}$ and $s_{900} = 10^{-7}$). These may be considered as limiting values of the steric factors, which no longer depend on the complexity of the disproportionating radicals. The reduction in the reactivity of isomeric radicals (Table 1) appears to be due to the partial screening of the free valency caused by the branched structure of the radicals.

The rate constants of disproportionation reactions have been evaluated (Table 1) from calculated values of the steric factors and the numbers of binary collisions with the use of the assumption mentioned above on the values of the activation energies of these reactions.

When more extensive experimental results have been obtained, it should be possible to put forward a more precise mechanism for radical disproportionation reactions and to examine the energy barrier in these reactions both qualitatively and quantitatively. At present, because of the lack of precision of initial and experimental data which has been pointed out, a more precise calculation of the rate constants of disproportionation reactions would be premature.

The ratio of the rate constants for the disproportionation and recombination of alkyl radicals can be calculated

from the results that have been obtained. Most of the experimental results (which have been discussed in detail by Stepukhovich[23] and Ulitskii[37]) are given in terms of Δ; experimental and calculated values can therefore be compared. As Table 2 shows, the theoretical ratios of the rate constants of radical disproportionation and recombination reactions are close to the corresponding experimental values.

A number of attempts have been made to correlate values of Δ with some characteristics of the processes under consideration. If such a correlation were established, known values of Δ for some reactions could be used approximately to evaluate the ratios of the rate constants for other reactions.

If, as Ausloos and Steacie assume[69], the rate constants for the recombination of different butyl radicals are equal, values of the ratio Δ will be proportional to the rate constants of the disproportionation reactions (k_2). Let $\Delta = ak_2$, the value of a being selected to make ak_2 equal to 5 for s-C_4H_9 radicals. The number of hydrogen atoms which could be eliminated from the radical to form an alkene product is indicated for comparison in the fourth column of Table 3. Clearly there is a similarity between the numbers in the third and fourth columns. This indicates (under conditions such that the rate constants of the recombination reactions are equal) that the main factor determining the rate of disproportionation of butyl radicals is the number of hydrogen atoms that could be eliminated from the radical to form a stable alkene.

Kerr and Trotman-Dickenson have shown[70] from experimental results that values of $\Delta(CH_3, Alk)$ are simply related to the analogous $\Delta(Alk, Alk)$ for the corresponding reaction of two identical alkyl radicals. They examined recombination and disproportionation reactions between the same and different radicals (CH_3, C_2H_5, iso-C_3H_7, and t-C_4H_9). The corresponding values of $\Delta(CH_3, Alk)$ and $\Delta(Alk, Alk)$ are shown in Table 4. The second column of this table shows the number of hydrogen atoms which can migrate in a disproportionation reaction in which CH_3 and Alk radicals participate; thus in a ethyl radical the number is 3, in an isopropyl radical 6, and in t-C_4H_9 it is 9 (the number is denoted by the symbol $|H|$). The fourth and sixth columns of Table 4 show what are termed reduced values of the ratios of the rate constants of radical disproportionation and recombination reactions ($\Delta/|H|$). A linear relationship of the following type may be established for these values:

$$\log \frac{\Delta(CH_3, Alk)}{|H|} = 0.55 \log \frac{\Delta(Alk, Alk)}{|H|} - 0.95.$$

By means of this equation, known reduced ratios of the rate constants of reactions between the same radicals may be used to find analogous values for disproportionation and

TABLE 3. Ratio of the rate constants of disproportionation (k_2) and recombination (k_1) of butyl radicals near 100°C (it it assumed that k_1 is the same for all these reactions[69]).

Radical	k_2/k_1	$ak_2=2.2\frac{k_2}{k_1}$	$\|H\|$
t-C_4H_9	4.59	10.1	9
iso-C_3H_9	0.418	0.92	1
s-C_4H_9	2.27	5.0	5

TABLE 4. Ratio of the disproportionation and recombination rate constants of reactions between the same and different alkyl radicals[70].

Radical	$\|H\|$	$\Delta(CH_3, Alk)$	$\frac{\Delta(CH_3, Alk)}{\|H\|}$	$\Delta(Alk, Alk)$	$\frac{\Delta(Alk, Alk)}{\|H\|}$
C_2H_5	3	0.06	0.02	0.13	0.043
iso-C_3H_7	6	0.22	0.036	0.65	0.11
t-C_4H_9	9	0.70	0.078	4.6	0.51

recombination reactions between CH_3 radicals and other alkyl radicals. This relationship may be expressed in the more general form:

$$\log \frac{\Delta(Alk', Alk'')}{|H|} = 0.55 \log \frac{\Delta(Alk', Alk')}{|H|} + C,$$

which links the reduced rate constants of these reactions between like and unlike radicals (C is a constant which is equal to 0.95 when Alk = CH_3). Too much significance should not be attached to these linear relationships, since they are constructed from three experimental points¶. Moreover, the experimental results of Boddy and Robb[62] do not show such a correlation.

Obviously, correlations between values of $\Delta(Alk', Alk'')$ and $\Delta(Alk', Alk')$ must link not only the number of hydrogen atoms that can migrate in radical disproportionation, but they must also include other characteristics of radical recombination and disproportionation. In particular, it has been found in a number of examples examined that changes in $\Delta(Alk', Alk'')$ or $\Delta(Alk', Alk')$ and $S_{dis} - S_{rec}$ are symbathic and a relationship can be established between them[40]. Moreover, as Table 1 shows, there are no grounds for assuming that the reactivity of recombining radicals does not change with a change in their structure (this conclusion is true only for sufficiently complex radicals). Therefore, the assumption that the rate constants for the recombination of different radicals are equal is not always justified, and the assumption that the correlations depend only on radical disproportionation processes cannot always be considered valid.

The ratios of the rate constants for the disproportionation and recombination of alkyl radicals found in different experiments are close. The calculated values of analogous ratios of the rate constants agree with the experimental values (Table 5). Since the calculated and experimental values of steric factors of radical recombination reactions are low, and the ratios of the rate constants of reactions (1) and (2) are close to unity, the steric factors for the disproportionation of alkyl radicals are also low, and these determine the kinetics of the reactions.

Since it is concluded that the steric factors for the recombination and disproportionation of alkyl radicals are low, these reactions may be classified as fairly slow bimolecular reactions, and not as rapid bimolecular reactions (as has been done in the literature). At high temperatures (in the cracking of hydrocarbons and other thermal conversions) the steric factors are particularly low and the kinetics of the processes are determined entirely by these factors. Therefore, the not too high reaction

¶ With these relationships $\Delta(Alk', Alk'')$ can be calculated from a knowledge of $\Delta(Alk', Alk')$ with an uncertainty covered by a factor of 3–4.[71]

TABLE 5. Calculated and experimental values of $\Delta = \frac{k_2}{k_1}$.

Reaction	Δ(theor.)	Δ(expt.)	Reaction	Δ(theor.)	Δ(expt.)
$H+C_2H_5$	0.29	—	$C_2H_7+C_2H_7$	0.16	0.125[45] 0.16[78] 0.157[79]
$H+C_3H_7$	0.4	—	$C_2H_7+C_4H_9$	0.16	—
$H+C_4H_9$	0.53	—	$C_2H_7+C_5H_{11}$	0.16	—
$CH_3+C_2H_5$	0.08	0.04[69] 0.06[72,73]	$C_4H_9+C_4H_9$	0.17	0.9[80] 0.57—1.04[70] 0.7[41]
$CH_3+C_3H_7$	0.08	0.05[74] 0.14[75]	$C_4H_9+C_5H_{11}$	0.19	—
$CH_3+C_4H_9$	0.17	0.15[75]	$C_5H_{11}+C_5H_{11}$	0.2	0.2[76]
$CH_3+C_5H_{11}$	0.17	0.1[76]	2iso-C_3H_7	0.88	0.6[81,82]
$C_2H_5+C_2H_5$	0.13	0.14[44,73,77] 0.15[70]	2iso-C_4H_9	0.43	0.418[80] 0.165[83]
$C_2H_5+C_3H_7$	0.16	—	2s-C_4H_9	2.1	2.27[80]
$C_2H_5+C_4H_9$	0.16	—	2t-C_4H_9	4.5	4.59[80] 4.38[83] 3.2[71]
$C_2H_5+C_5H_{11}$	0.16	—			

rates of radical recombination and disproportionation reactions under these conditions are determined not only by the low radical concentrations in the reaction zone but also by low values of the preexponents.

1. A. F. Trotman-Dickenson et al., J. Chem. Phys., 19, 163 (1951); J. H. Knox and A. F. Trotman-Dickenson, in "Reactions of Free Radicals in the Gas Phase", Chem. Soc. (London), Spec. Publ. No. 9, 1957, at p. 43.
2. A. F. Trotman-Dickenson, J. Chem. Soc., 4 (1959).
3. K. U. Ingold and F. P. Loosing, J. Chem. Phys., 21, 368 (1953).
4. J. A. Kerr and A. F. Trotman-Dickenson, Progr. Reaction Kinetics, 1, 105 (1961).
5. A. D. Stepukhovich, Dokl. Akad. Nauk SSSR, 92, 127 (1953).
6. A. D. Stepukhovich and E. I. Etingof, Dokl. Akad. Nauk SSSR, 99, 815 (1954); Zhur. Fiz. Khim., 29, 1974 (1955).
7. A. D. Stepukhovich, Uspekhi Khim., 25, 263 (1956).
8. A. D. Stepukhovich and V. A. Ulitskii, Zhur. Fiz. Khim., 35, 2569 (1961) [Russ. J. Phys. Chem., 1270 (1961)].
9. A. F. Trotman-Dickenson, Trans. Faraday Soc., 54, 1770 (1958).
10. A. D. Stepukhovich, Zhur. Fiz. Khim., 32, 2415 (1958).
11. A. M. Brodskii, Abstract of Doctoral Thesis, Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow, 1959.
12. E. Bauer and T. Y. Wu, J. Chem. Phys., 21, 726 (1953).
13. W. Jost, Z. phys. Chem., B 3, 95 (1929).
14. J. Mazur and R. J. Rubin, J. Chem. Phys., 31, 1395 (1959).
15. F. T. Wall, L. A. Hiller, and J. Mazur, J. Chem. Phys., 29, 255 (1959); 35, 1284 (1961).
16. M. A. Eliason and J. O. Hirschfelder, J. Chem. Phys., 30, 1426 (1959).
17. J. Ross and I. Mazur, J. Chem. Phys., 35, 19 (1961).
18. Khr. Noninski, Khim. i Ind., 32, 134 (1960).
19. "Termodinamika Neobratimykh Protsessov: Sbornik Statei" (Thermodynamics of Irreversible Processes: Collected Papers), Inostr. Lit., Moscow, 1962.
20. V. N. Kondrat'ev, "Kinetika Khimicheskikh Gazovykh Reaktsii" (Kinetics of Chemical Gas Reactions), Izd. Akad. Nauk SSSR, Moscow, 1958.
21. S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes" (Translated into Russian), Inostr. Lit., Moscow, 1948.
22. A. D. Stepukhovich, Dokl. Akad. Nauk SSSR, 107, 436 (1956); "Nauchnyi Ezhegodnik Saratovskogo Gosudarstvennogo Universiteta za 1954 g." (Scientific Yearbook of Saratov State University for 1954), Izd. "Kommunist", Saratov, 1955, p. 614.
23. A. D. Stepukhovich, "Kinetika i Mekhanizm Termicheskogo Krekinga Alkanov" (Kinetics and Mechanism of Thermal Cracking of Alkanes), Izd. Saratovskogo Universiteta, 1965.
24. D. R. Herschbach, H. S. Johnston, K. S. Pitzer, and R. E. Powell, J. Chem. Phys., 25, 736 (1956).
25. D. J. Wilson and H. S. Johnston, J. Amer. Chem. Soc., 79, 29 (1957).
26. H. S. Johnston, Ann. Rev. Phys. Chem., 8, 249 (1957).
27. L. Pauling, J. Amer. Chem. Soc., 69, 542 (1947).
28. H. S. Johnston and K. S. Pitzer, A. I. Ch. E. J., 5, 277 (1959).
29. K. S. Pitzer, J. Amer. Chem. Soc., 79, 1804 (1957).
30. J. H. Knox and A. F. Trotman-Dickenson, J. Phys. Chem., 60, 1307 (1956).
31. O. Sinanogly and K. S. Pitzer, J. Chem. Phys., 30, 422 (1959).
32. L. Pauling, "The Nature of the Chemical Bond" (Translated into Russian), GNTIKhL, Moscow, 1947, p. 173.
33. A. D. Stepukhovich and V. A. Ulitskii, Vysokomol. Soed., 3, 1341 (1961).
34. V. V. Korshak and K. K. Samplavskaya, Dokl. Akad. Nauk SSSR, 59, 497 (1948).
35. Kh. S. Bagdasar'yan, "Teoriya Radikal'noi Polimerizatsii" (Theory of Radical Polymerisation), Izd. Akad. Nauk SSSR, Moscow, 1959.
36. G. V. Schulz, Z. phys. Chem. (Frankfurt), 27, 1 (1961).
37. V. A. Ulitskii, Candidate's Thesis, Saratov State University, Saratov, 1963.
38. V. A. Ulitskii and A. D. Stepukhovich, Zhur. Fiz. Khim., 37, 689 (1963) [Russ. J. Phys. Chem., 359 (1963)].
39. V. A. Ulitskii, in "Materialy Mezhvuzovskoi Konferentsii, Vypusk Fiziki" (Proceedings of the Inter-University Conference, Physical Section), Saratov, 1965.
40. J. N. Bradley, J. Chem. Phys., 35, 748 (1962).
41. A. F. Trotman-Dickenson, Ann. Report Progr. Chem. (Chem. Soc. London), 55, 36 (1958).
42. M. Matsuoka, P. S. Dixon, et al., Proc. Chem. Soc., 304 (1961).
43. J. N. Bradley and B. S. Rabinovitch, J. Chem. Phys., 36, 3498 (1962).
44. A. Shepp and K. O. Kutschke, J. Chem. Phys., 26, 1020 (1957).
45. S. G. Whiteway and C. R. Masson, J. Chem. Phys., 25, 233 (1956).
46. T. S. Ree, H. Eyring, and T. Fueno, J. Chem. Phys., 36, 281 (1962).
47. T. Kang and T. Ree, J. Chem. Phys., 35, 588 (1961).
48. "Energii Razryva Khimicheskikh Svyazei, Potentsialy Ionizatsii i Srodstvo k Elektronu. Spravochnik" (Energies for the Breaking of Chemical Bonds, Ionisation Potentials, and Electron Affinity. A Handbook), Izd. Akad. Nauk SSSR, Moscow, 1962.
49. H. C. Longuet-Higgins, in "Reactions of Free Radicals in the Gas Phase", Chem. Soc. (London), Spec. Publ. No. 9, 1957, p. 5.
50. Landolt-Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik", 6th Edn., Vol. I, Part 3, "Molekeln II (Elektronenhülle)" (Edited by A. Eucken and K. H. Hellwege), Springer, Berlin, 1951.
51. N. N. Semenov, "O Nekotorykh Problemakh Khimicheskoi Kinetiki i Reaktsionnoi Sposobnosti" (Some Problems of Chemical Kinetics and Reactivity), Izd. Akad. Nauk SSSR, Moscow, 1958.
52. A. F. Trotman-Dickenson, "Gas Kinetics", Butterworth, London, 1955.
53. L. I. Avramenko and L. M. Postnikova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1921 (1960).
54. A. M. Brodskii, R. A. Kalinenko, K. P. Lavrovskii, and V. B. Titov, Zhur. Fiz. Khim., 33, 2457 (1959) [Russ. J. Phys. Chem., 474 (1959)].
55. M. H. J. Wijnen, J. Amer. Chem. Soc., 83, 3752 (1961).
56. P. B. Ayscough, J. Chem. Phys., 24, 944 (1956).
57. G. O. Pritchard and J. R. Dacey, Canad. J. Chem., 38, 182 (1960).

58. G. O. Pritchard, H. O. Pritchard, et al., Canad. J. Chem., 38, 319 (1960).
59. G. Porter, Ann. Rev. Phys. Chem., 7, 207 (1956).
60. S. J. W. Price and K. O. Kutshke, Canad. J. Chem., 38, 2128 (1960).
61. J. N. Bradley et al., Proc. Roy. Soc., A 236, 318, 454 (1956).
62. P. J. Boddy and J. C. Robb, Proc. Roy. Soc., A 249, 518 (1959).
63. J. A. Kerr and A. F. Trotman-Dickenson, Trans. Faraday Soc., 55, 572 (1959).
64. J. C. J. Thynne, Proc. Chem. Soc., 68 (1961).
65. J. G. Calvert, Ann. Rev. Phys. Chem., 11, 41 (1960).
66. M. H. J. Wijnen and E. W. R. Steacie, Canad. J. Chem., 29, 1092 (1951).
67. J. R. McNesby et al., J. Phys. Chem., 59, 988 (1955).
68. O. K. Rice, J. Phys. Chem., 65, 1595 (1961).
69. P. Ausloos and E. W. R. Steacie, Canad. J. Chem., 33, 1062 (1955).
70. J. A. Kerr and A. F. Trotman-Dickenson, J. Chem. Soc., 1602 (1960).
71. J. A. G. Dominguez et al., J. Chem. Soc., 3357 (1962).
72. C. A. Heller, J. Chem. Phys., 28, 1255 (1958).
73. J. C. J. Thynne, Trans. Faraday Soc., 58, 676 (1962).
74. P. Ausloos and E. Murad, J. Amer. Chem. Soc., 80, 5929 (1958).
75. J. C. J. Thynne, Proc. Chem. Soc., 19 (1961).
76. M. H. J. Wijnen, J. Amer. Chem. Soc., 83, 3752 (1962).
77. M. J. Smith, P. M. Beatty, et al., Canad. J. Chem., 33, 821 (1955).
78. J. A. Kerr and A. F. Trotman-Dickenson, Trans. Faraday Soc., 55, 921 (1959).
79. J. A. Kerr and J. G. Calvert, J. Phys. Chem., 83, 3391 (1961).
80. J. W. Kraus and J. G. Calvert, J. Amer. Chem. Soc., 79, 5921 (1957).
81. C. A. Heller and A. S. Gordon, J. Phys. Chem., 60, 1315 (1956).
82. C. A. Heller and A. S. Gordon, J. Phys. Chem., 62, 709 (1958).
83. E. L. Metcalfe and A. F. Trotman-Dickenson, J. Chem. Soc., 5072 (1960).
84. R. N. Birell and A. F. Trotman-Dickenson, J. Chem. Soc., 4218 (1960).

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THE USE OF VIBRATIONAL SPECTRA IN THE STUDY OF THE STRUCTURE OF POLYATOMIC MOLECULES

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CONTENTS

1. Introduction 214
2. Elements of the theory of vibrations in polyatomic molecules 216
3. Characteristic vibrations of polyatomic molecules 217
4. Force constants of polyatomic molecules and their determination 222
5. Appendix 227

1. INTRODUCTION

One of the fundamental tasks in modern science is to study the structure and properties of polyatomic molecules. In the past two decades, in addition to traditional chemical methods, an ever-increasing and in many instances decisive part has begun to be played by various physical methods, particularly methods based on the study of the energy levels of polyatomic molecules. These methods include electronic, vibrational, and rotational spectroscopy and radiospectroscopic methods. The great importance of these methods lies primarily in the fact that they make possible the study of the structure and properties of molecules and molecular associates in any state of aggregation without breakdown of the molecules, as usually takes place when chemical methods are used. At present the methods most widely used are electronic and particularly vibrational spectroscopy. This is due both to the fact that historically they appeared before the radiospectroscopic methods and also to the high degree of development and ubiquity of electronic and vibrational spectroscopy and the wide range of varied problems which can be solved by these methods. The rapid development of experimental techniques and the appearance of automatic spectrophotometers have also been of considerable importance.

Unlike electronic absorption spectra and luminescence spectra, the overwhelming majority of vibrational spectra consist of a large number of discrete lines and bands, whose appearance is related to the presence and interaction of various atomic groups in the molecule, so that the very nature of the vibrational spectra gives considerable information on the detailed structure of a complex system.

Vibrational spectroscopy, however, is an indirect method. Experimental measurement of the parameters of the spectrum alone (the number of bands, their position on the frequency scale, intensities, etc.) is useless if a relationship has not been established between the observed quantities and the structure of the polyatomic molecule, that is, if the appropriate theory has not been developed. The need to develop a special theory of vibrational spectra arose in the nineteen-thirties and -forties as a result of the accumulation of experimental material on the infrared absorption spectra (IRS) and Raman spectra (RS) of complex molecules and the resulting desire to interpret these spectra. At that time a solution to the problem of the vibrational energy levels (normal vibrations) of polyatomic molecules had been roughly outlined; the problem involved primarily the development of a theory to explain the general features characteristic of the vibrational spectra of homologous series, to relate the vibrational spectra to the internal structure of molecules, and to carry out the necessary numerical calculations. This theory could be only semi-empirical, since direct quantum-mechanical methods were here quite inadequate.

A decisive step in this direction was taken by El'yashevich[1-6], who proposed a general method for formulating equations for the vibrations of polyatomic molecules in a special system of coordinates, which he called the natural system. An analogous method was developed independently by Wilson[7-10]. The introduction of natural coordinates made it possible to apply to the theory of vibra-