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Application of the Spin Trapping Method in Kinetic Measurements

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The results obtained in recent years by the spin trapping method in the solution of a number of kinetic problems are analysed and a systematic account is given of the rate constants for the addition of alkyl, polychloroalkyl and hetero-radicals as well as certain others to nitroso-compounds and nitrones; the kinetic data obtained by the spin trapping method in the study of the isomerisation, fragmentation, elimination, substitution and addition reactions are surveyed.
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I. INTRODUCTION

The spin trapping (ST) method is used widely and successfully in the study of the mechanisms of reactions involving radicals.[1-16] Its essential feature consists in the fact that the short-lived radicals formed in the reaction add to the ST agent (STA) specially introduced into the reaction mixture, which leads to the formation of stable radicals capable of being identified by EPR.

The range of compounds which can be used as STA is fairly large. The present review includes the results obtained using nitroso-compounds and nitrones as STA.[1-10] When radicals are captured by these compounds, the products are mainly nitroxy-radicals, whose physicochemical properties have been thoroughly investigated.[17-19] The large set of such STA,[1-7] their selectivity,[5,20-23] and their other features[24-28] make it possible to identify radicals of different nature by EPR.

In order to identify the radicals formed during the reaction, it is essential to know the rate constants for their addition to the STA. These data are also required for the quantitative estimation of the rates of individual stages of complex chemical processes. The rate constants for the addition of a wide range of radicals to STA have now been determined and kinetic data characterising different stages of important processes in radical chemistry have been obtained. The present review is devoted to a survey of these results and an analysis of the scope of the ST method in the study of the reaction kinetics.

II. THE SPIN TRAPPING METHOD IN KINETICS

The radicals $\dot{R}_1$ formed in the reaction interact with the STA, giving rise to nitroxy-radicals—spin adducts (SA):

$$\dot{R}_1 + \text{STA} \xrightarrow{k_1} R_1\text{R}\dot{\text{N}}\text{O} \ . \qquad (1)$$

The radicals can participate in the following reactions:

(a) addition

$$\dot{R}_1 + M \xrightarrow{k_2} \dot{R}_2 , \qquad (2)$$

where M is the monomer,

(b) isomerisation

$$\dot{R}_1 \xrightarrow{k_3} \dot{R}_3 , \qquad (3)$$

(c) fragmentation or elimination

$$\dot{R}_1 \xrightarrow{k_4} X + \dot{R}_4 , \qquad (4)$$

(d) substitution

$$XR_5 + \dot{R}_1 \xrightarrow{k_5} \dot{R}_5 + R_1X \ . \qquad (5)$$

These reactions compete with the main reaction (1) if their rates are comparable to that of the latter.

The radicals $\dot{R}_i$, where $i = 1-5$, can recombine or disproportionate:

$$\dot{R}_i + \dot{R}_i \xrightarrow{k_6} \text{non-radical products.} \qquad (6)$$

The use of the ST method implies that the rate of capture of the radicals obtained in reactions (1)–(5) by the STA is higher than the rate of their conversion into non-radical products. The rate constants for the recombination and disproportionation of short-lived radicals are of the order of $k_6 \cong 10^6-10^{10}$ litre mol^{-1} s^{-1}.[29-35] If the concentration of the short-lived radicals $\dot{R}_i$, which depends on the rate of initiation of the reaction, does not exceed $10^{-7}-10^{-8}$ M and $[\text{RNO}]_0 \cong 10^{-2}-10^{-3}$ M (the STA concentrations most frequently used in experiments[1,5]), then it follows from the condition $k_i[\text{RNO}]_0 \gg 10^8-10^{10}\ [\dot{R}_i]$ that, when

$$k_i \gg 10^2 \div 10^6 \text{ litre mol}^{-1}\text{ s}^{-1}, \qquad (7)$$

stage (6) can be neglected (k_i is the rate constant for the addition of the radicals $\dot{R}_i$ to the STA). Consequently if $[\text{STA}]_0 \cong 10^{-2}-10^{-3}$ M and condition (7) holds, it is possible to disregard stage (6). For example, it has been shown[30] that the recombination of alkyl radicals may be neglected when the solution contains 2×10^{-2} M 2,4,6-tri-t-butylnitrosobenzene.

Thus the knowledge of the rate constants for the addition of the radicals $\dot{R}_i$ to STA makes it possible to select initial STA concentrations and to create necessary experimental conditions such that it is possible to disregard the recombination and disproportionation of radicals and hence to simplify appreciably the reaction mechanism in kinetic studies.

The rate constants for the addition of the radicals $\dot{R}_i$ to STA (k_1) have been determined mainly using the methods of competition kinetics. Under these conditions, reactions (2) to (5), for which the rate constants k_i ($i = 2-5$) have been measured, were used as the reactions competing with the addition of the radicals $\dot{R}_1$ to STA. The rate constants k_1 have been determined using the methods of non-stationary kinetics $\{d[R_1\dot{\text{N}}\text{O}]/dt \neq 0\}$ and quasi-stationary concentrations $\{d[R_i\dot{\text{N}}\text{O}]/dt = 0\}$.

The difference between the ST method and the direct detection of the short-lived radicals in the liquid phase by EPR consists in the fact that the time required to obtain a stationary concentration of the nitroxy-radicals amounts in

many cases to many minutes, which permits the measurement of the rate of formation of these radicals. Such experimental conditions are reached when STA effective in relation to the given radical at low rates of initiation are used. It has been demonstrated,[36] in particular, that, for a rate of initiation of 3×10^{-8} mol litre^{-1} s^{-1}, the times taken to attain a stationary concentration of the spin adducts (SA) of the $Cl_3\dot{C}$ radicals with 2-methyl-2-nitrosopropane (MNP) at $[MNP]_0 = 3.73 \times 10^{-3}$ M, nitrosodurene (ND) at $[ND]_0 = 3.27 \times 10^{-3}$ M, and α-phenyl-N-t-butylnitrone (PBN) at $[PBN]_0 = 2.15 \times 10^{-2}$ M are 7.5, 54, and 4 min respectively.

The formation of the nitroxy-radicals A and B is described by Scheme I when reaction (2) is used as one competing with the addition of the radicals $\dot{R}_1$ to the STA:

Scheme 1

$$\dot{R}_1 + RNO \xrightarrow{k_1} R_1RN\dot{O} \quad (A)$$

$$\dot{R}_1 + M \xrightarrow{k_2} \dot{R}_2 ,$$

$$\dot{R}_2 + RNO \xrightarrow{k_2'} R_2RN\dot{O} \quad (B)$$

The rate constant k_1 is in this case determined by the expression

$$\frac{d[A]/dt}{d[B]/dt} = \frac{k_1[NRO]_0}{k_2[M]_0} = \frac{[A]}{[B]} , \quad (8)$$

where [A] and [B] are the concentrations of the STA radicals $\dot{R}_1$ and $\dot{R}_2$ before the attainment of their stationary values.

A method has been proposed[37] for the determination of k_1 on the basis of the measurements of the rate of formation of the radicals $R_1RN\dot{O}$ in the absence and presence of substances with which the radicals $\dot{R}_1$ can interact, for example, by adding to M via reaction (2). The constant k_1 is calculated from the formula

$$\frac{d[A]_{abs}}{d[A]_{pr}} = 1 + \frac{k_2[M]_0}{k_1[RNO]_0} , \quad (9)$$

where $d[A]_{abs}$ and $d[A]_{pr}$ are the increments of the concentrations of the SA of the radicals $\dot{R}_1$ with RNO in the absence and presence of M.

Eqns.(8) and (9) are valid under conditions where $d[\dot{R}_2]/dt = 0$ and $d[\dot{R}_1]/dt = 0$, which hold for short-lived radicals over a fairly short interval (see, for example, Denisov[38]). The choice of the STA is fairly wide. If the rate constant for the addition of the radical to one STA is known, then, by using the method of non-stationary kinetics, it is possible to determine the corresponding constants for other STA from the expression

$$\frac{[A]}{[B]} = \frac{k_1[RNO]_0}{k'[R'NO]_0} . \quad (10)$$

Eqn.(10) is valid for the reactions

$$\dot{R}_1 + RNO \xrightarrow{k_1} R_1RN\dot{O} \quad (A)$$

$$\dot{R}_1 + R'NO \xrightarrow{k'} R_1R'N\dot{O} \quad (C)$$

When Eqns.(8) and (10) are employed, it is essential to know the relative stabilities of the nitroxy-radicals. It is known[17-19,35] that the stability of these radicals is determined by many factors. However, the relative stabilities of the radicals A and B or A and C, identified by EPR, can be estimated directly in the course of the study of the reaction. For this purpose, it is necessary to follow over a time interval the variation of the ratio of the concentrations of the radicals detected by EPR, and then to extrapolate this ratio to the start of the reaction.[39,40]

The nitroxy-radicals formed in the course of the reaction reach stationary concentrations in many instances after a short time interval. For this reason, the measurement of the rate of their formation involves considerable experimental difficulties. In the study of such reactions, the rate constants for the addition of the radicals $\dot{R}_1$ to the STA are determined by the method of quasi-stationary concentrations. The necessary and sufficient conditions for the determination of this constant after the attainment of stationary concentrations by the nitroxy-radicals will be examined in relation to the systems where reaction (2) competes with reaction (1). Such processes can be described by Scheme I supplemented by the recombination and disproportionation stages:

$$\left.\begin{matrix} A + \dot{R}_1 \\ B + \dot{R}_1 \end{matrix}\right\} \xrightarrow{k_{11}} \text{non-radical products;} \quad (11)$$

$$\left.\begin{matrix} A + \dot{R}_2 \\ B + \dot{R}_2 \end{matrix}\right\} \xrightarrow{k_{12}} \text{non-radical products;} \quad (12)$$

$$\left.\begin{matrix} A + B \\ A + A \\ B + B \end{matrix}\right\} \xrightarrow{k_{13}} \text{non-radical products.} \quad (13)$$

If the conditions

$$k_{11}[\dot{R}_1],\ k_{12}[\dot{R}_2] \gg k_{13}([A]_{st} + [B]_{st}), \quad (14)$$

where $[A]_{st}$ and $[B]_{st}$ are the stationary concentrations of A and B, are satisfied, then the addition of the radicals $\dot{R}_1$ to M in the presence of RNO can be described by Scheme I and by reactions (11) and (12) (the methods of calculation of k_{11}, k_{12}, and k_{13} are described below).

At $\dot{R}_1$ and $\dot{R}_2$ concentrations of 10^{-8}–10^{-9} M and for $[A]_{st} + [B]_{st} < 10^{-5}$ M, conditions (14) for certain short-lived radicals are fulfilled, because it is known[41-44] that k_{11} and k_{12} are greater than k_{13} by 5–7 orders of magnitude.

When account is taken of stages (11) and (12), it follows from Scheme I that

$$\frac{[A]}{[B]} = \frac{k_1[\dot{R}_1]}{k_2'[\dot{R}_2]} . \quad (15)$$

On substituting the stationary concentration

$$[\dot{R}_2] = \frac{k_2[M]_0[\dot{R}_1]}{k_2'[RNO]_0 + k_{12}([A] + [B])} , \quad (16)$$

in Eqn.(15), we obtain

$$\frac{[A]}{[B]} = \frac{k_1[RNO]_0}{k_2[M]_0} + \frac{k_{12}([A] + [B])k_1}{k_2k_2'[M]_0} \quad (17)$$

or

$$k_1 = \frac{k_2k_2'[M]_0}{k_2'[RNO]_0 + k_{12}([A] + [B])} \cdot \frac{[A]}{[B]} . \quad (18)$$

It follows from Eqn.(18) that, in order to determine the k_1 for the chemical reactions described by Scheme I and stages (11) and (12), it is essential not only to identify the nitroxy-radicals A and B by EPR but also to know k_{12} and the rate constants for the addition of the radicals $\dot{R}_1$ and $\dot{R}_2$ to the STA. Eqns.(17) and (18) are the most general for the calculation of the rate constants for the addition of the radicals $\dot{R}_1$ to the STA in the case of chemical processes described by Scheme I and stages (11) and (12) when the radicals A and B have attained stationary concentrations. It follows from Eqn.(18) that, when $k_2'[RNO]_0 \gg k_{12}\{[A] + [B]\}$, then a simple expression can be used to calculate k_1:

$$k_1 = k_2 \frac{[M]_0}{[RNO]_0} \cdot \frac{[A]}{[B]} \quad (19)$$

Eqn.(17) is valid also under the condition where $k_1 \gg k_2'$ and $k_1[RNO]_0 \gg k_{11}\{[A] + [B]\}$ (or $k_1 \geq 10^7$–10^8 litre mol^{-1} s^{-1}), i.e. when the radicals $\dot{R}_1$ are much more reactive than the radicals $\dot{R}_2$ in the interaction with the STA. It is desirable that the condition [A]/[B] ≈ 1 (taking into account the multiplicity of the signals in the EPR spectra of the spin-adducts of the radicals $\dot{R}_1$ and $\dot{R}_2$, on the one hand, and STA, on the other) should hold, although the content of the nitroxy-radicals in the reaction mixture can be determined over a fairly wide range of [A]/[B] ratios by means of standard computer programs for the simulation of EPR spectra.[45] Using Eqns.(17) with known values of k_1, k_2, and k_2' and having determined the dependence of the ratio [A]/[B] on $[RNO]_0/[M]_0$,[46] it is possible to calculate k_{12}.

Application of the method of quasi-stationary concentrations[31] to the radicals formed in the processes described by Scheme I and stages (11) and (12) yields

$$[A] + [B] = \frac{k_1[\dot{R}_1] + k_2'[\dot{R}_2]}{k_{11}[\dot{R}_1] + k_{12}[\dot{R}_2]}[RNO]_0 \quad (20)$$

When the conditions

$$k_1 = k_2' \text{ and } k_{11} = k_{12} \quad (21)$$

hold, it follows from Eqn.(20) that

$$[A] + [B] = \frac{k_1}{k_{12}}[RNO]_0 \quad (22)$$

Taking into account Eqns.(21) and (22), we obtain from Eqn.(18)

$$k_1 = \frac{k_2[M]_0}{2[RNO]_0} \cdot \frac{[A]}{[B]} \quad (23)$$

Thus, when conditions (21) hold, Eqn.(23) can be used to calculate k_1.

Eqns.(8), (9), (17)–(19), and (23) have been obtained for examples where the reaction competing with reaction (1) involves the addition of $\dot{R}_1$ to M. Other expressions for the calculation of k_1 can be obtained by similar procedures having selected reactions (3)–(5) as the reactions competing with the addition of $\dot{R}_1$ to the STA. Joint examination of reactions (1) and (3) or (4) yields an expression for the calculation of k_1 similar to Eqns.(8), (9), (17)–(19) and (23) in which $[M]_0 = 1$, $k_2 = k_3$, or $k_2 = k_4$ [B] = [R_3RNO], or [B] = [R_3RNO] respectively. Similarly, when reactions (1) and (5) are considered jointly, one must replace $[M]_0$ by [XR_5] in the above expressions and $k_2 = k_5$ and [B] = [R_5RNO] must be adopted.

Thus the identification by EPR of the spin-adducts of the radicals $\dot{R}_1$ and $\dot{R}_i$ (where i = 2–5) with the STA and the knowledge of the constants k_i are necessary for the determination of the rate constant for the addition of the radicals $\dot{R}_1$ to the STA using the methods of non-stationary kinetics and quasi-stationary concentrations. If Eqn.(9) is used, then it is sufficient to identify the SA of the radicals $\dot{R}_1$ with the STA in order to determine k_1. Another feature which makes this method convenient is the fact that it can be applied also in cases where the radicals $\dot{R}_i$ (i = 2–5), formed as a result of the involvement of $\dot{R}_1$ in secondary reactions [see reactions (2)–(5)], are not trapped by the STA.

For reactions described by Scheme II, i.e.

Scheme II

$$\text{initiator} \xrightarrow{v_i} \dot{R}_1,$$
$$\dot{R}_1 + RNO \xrightarrow{k_1} R_1R\dot{N}O,$$
$$\dot{R}_1 + R_1R\dot{N}O \xrightarrow{k_{11}} \text{non-radical products},$$
$$2R_1R\dot{N}O \xrightarrow{k_{12}} \text{non-radical products},$$

the following expression is valid:

$$\frac{k_1[RNO]_0 - k_{11}[R_1R\dot{N}O]_{st}}{k_1[RNO]_0 + k_{11}[R_1R\dot{N}O]_{st}} = \frac{k_{12}}{v_i}[R_1R\dot{N}O]_{st}^2 \quad (24)$$

It has been suggested[42] that the following expressions be employed to determine k_1, k_{11}, and k_{12}:

$$\left(\frac{d[R_1R\dot{N}O]_{st}}{d[RNO]}\right)_{[RNO]\to 0} = \frac{k_1}{k_{11}}, \quad (25)$$

$$([R_1R\dot{N}O])_{[RNO]\to\infty} = (v_i/k_{12})^{0.5} \quad (26)$$

The rate of initiation is determined by the method of measurement of the initial rate of formation of $R_1R\dot{N}O$.[42,47] Having determined k_1 by Eqn.(25), it is possible to calculate k_{11}. The knowledge of the constants k_{11} and k_{12} and v_i makes it possible, in its turn, to establish the limits of validity of condition (14) and $k_1[RNO]_0 \gg k_{12}[R_1R\dot{N}O]_{st}$ and hence the limits of the applicability of Eqn.(18) or (19) in the calculation of k_1. Since k_{11} may be determined also by other physicochemical methods,[48–51] the agreement between their values calculated by two independent methods can serve as a criterion of the correctness of the rate constants found for the addition of the radicals to the STA.

There exists a fairly wide range of methods for the determination of the rate constants for the addition of short-lived radicals to the STA, which may supplement one another in one form or other.

III. THE RATE CONSTANTS FOR THE ADDITION OF RADICALS TO SPIN TRAPPING AGENTS

1. The Rate Constants for the Addition of Carbon-Centred Radicals

Primary, secondary, and tertiary alkyl radicals are trapped by a large number of STA.[1,4–6,52,53] It is noteworthy that, when 2,4,6-$(Me_3C)_3C_6H_2NO$ (BNB) is used as the STA, the secondary radicals add both to the nitrogen atom, giving rise to nitroxy-radicals, and to the oxygen atom with formation of anilino-radicals.[54,55] Tertiary alkyl radicals add exclusively to the oxygen atom of the NO group in BNB.

Ingold and co-workers[41–43] determined the rate constants for the addition of primary and secondary alkyl radicals to a large number of STA using the cyclisation of $H_2C{=}CH(CH_2)_3\dot{C}H_2$ (I) to the radicals $\dot{C}H_2{-}\overline{CH(CH_2)_3\dot{C}H_2}$ (II) and of $H_2C{=}CH(CH_2)_3\dot{C}HMe$ (III) to the radicals $\dot{C}H_2{-}\overline{CH(CH_2)_3\dot{C}HMe}$ (IV). The authors[42,43] chose cyclisation as the reaction competing with the addition reaction in the determination of the rate constants for the addition of the radicals (I) and (III) to the STA. The rate constants for the cyclisation of the radicals (I) and (III) had been calculated earlier from the EPR spectra.[43,56] The rate constants determined in the above investigations[42,43] for the addition of the radicals to the STA are listed in Table 1, which also includes the rate constants for the addition of the radicals $Ph\dot{C}Me_2$ and $\dot{C}Me_3$ to STA, obtained by Doba et al.[37] and Maeda and Ingold.[43] Table 2 summarises the data on the rate constants for the addition of carbon-centred radicals with functional substituents. It follows from Tables 1 and 2 [cf., for example, No.4 in Table 2 with the data for the radicals (III) in Table 1] the replacement of the alkyl group or hydrogen at the C_β atom by other substituents does not entail an appreciable alteration of the rate constants for the addition of the secondary radicals to the STA.

Table 1. The rate constants (10^{-5} k_1, litre mol^{-1} s^{-1}) for the addition of alkyl radicals to STA.

No.	STA	Radical			
		$H_2C{=}CH(CH_2)_2\dot{C}H_2$*	$H_2C{=}CH(CH_2)_3\dot{C}HMe$**	$PhC\dot{M}e_2$**	$Me_3\dot{C}$***
1	MNP	90.2	61	100	33
2	ND	407.0	406	110	2000
3	BNB	4.7	0.18****; 3.1*****	4.8*****	2.3*****
4	PMNB	—	—	—	1400
5	NB	—	—	—	2000
6	DMPO	25.8	42	1.9	—
7	MBN	31.3	13	12	—
8	PBN	1.33	0.68	0.0027; 10******	0.1
9	4-MeO-PBN	1.16	—	—	—
10	4-Me-PBN	1.24	—	—	—
11	4-CN-PBN	1.68	—	—	—
12	4-NO_2-PBN	2.88	—	—	—
13	$(MeO)_3$-PBN	0.18	—	—	—

Notation: MNP = 2-methyl-2-nitrosopropane, ND = nitrosodurene, BNB = 2,4,6-tri-t-butylnitrosobenzene, PMNB = pentamethylnitrosobenzene, NB = nitrosobenzene, DMPO = 5,5-dimethylpyrroline 1-oxide, MBN = methylene t-butyl nitrone, and PBN = α-phenyl N-t-butyl nitrone.

*At 40 °C.[42]
**At 40 °C.[43]
***At 26 °C.[37]
****Nitroxy-radical.
*****Anilino-radical.
******At 60 °C.[57]

Table 2. The rate constants for the addition to STA of carbon-centred radicals with functional group substituents.

No.	STA*	Radical	10^{-5} k_1, litre mol^{-1} s^{-1}**	Refs.
1	PMNB	cyclo-$\dot{C}_6H_{11}$	160 (26°)	[58]
2	MNP	$(Me_3Co)_2\dot{C}H$	9—45 (25°)	[59]
3	ND	$HO_2C(CH_2)_2\dot{C}H_2$	351 (40°)	[60]
4	ND	$CCl_3(CH_2\dot{C}HMe)_n$***	394 (40°)	[61]
5	Me_2(COMe)CNO	$RCH_2\dot{C}HCCl_2X$****	10 (60°)	[62]
6	PBN	$\dot{P}h$	120 (20°)	[63]
7	ND	$\dot{P}h$	30 000—60 000 (20°)	[64]

*For the significance of the notation, see the footnote to Table 1.
**The temperature (in °C) at which k_1 has been determined is given in brackets.
***n = 1.2.
****X = Cl, F, or H.

2. The Rate Constants for the Addition of $\dot{C}Cl_3$ to Other α-Chloro-radicals

The range of STA which may be used for the identification of $\dot{C}Cl_3$ and other α-chlororadicals is limited.[5,21,65,66] The rate constants for the addition of chloro-radicals to the STA used most frequently for their trapping have been determined[36,67,68] (Table 3).

3. The Rate Constants for the Addition of Hetero-radicals

Table 4 presents the rate constants for the addition of hetero- and other radicals to the STA and also the rate constants for the addition of hydrogen and a hydrated electron.

Table 3. The rate constants for the addition of α-chloro-radicals to STA.

No.	STA*	Radical	10^{-5} k_1, litre mol^{-1} s^{-1}**	Refs.
1	ND	$Cl_3\dot{C}$	91 (20°)	[36]
2	ND	$Cl(CH_2)_2\dot{C}Cl_2$	13 (20°)	[36]
3	ND	$Cl_3CCH_2\dot{C}HCl$	14 (20°)	[68]
4	PBN	$Cl_3\dot{C}$	0.7 (20°)	[36]
5	MNP	$Cl_3\dot{C}$	18.9 (20°)	[36]
6	MNP	$Cl(CH_2)_2\dot{C}Cl_2$	1.7 (20°)	[36]
7	MNP	$Cl_3C\dot{C}HCl$	3.3 (40°)	[67]
8	MNP	$Cl_2HC\dot{C}Cl_2$	3.3 (40°)	[67]
9	MNP	$ClCH_2\dot{C}ClCCl_3$	3.8 (40°)	[67]
10	MNP	$ClCH_2CCl_2\dot{C}Cl_2$	3.8 (40°)	[67]

*For the significance of the notation, see the footnote to Table 1.
**The temperature (in °C) at which k_1 has been determined is given in brackets.

The radicals $Et_3\dot{S}i$ (V) are widely used for the generation of other radicals as a result of the abstraction of a halogen:

$$Et_3\dot{S}i + RHal \xrightarrow{k_{27}} Et_3SiHal + \dot{R} . \quad (27)$$

The constants k_{27} for many halogen-containing compounds have been determined.[81] Various STA are used for the EPR identification of the radicals (V).[54,55,82,83] In the case of BNB, anilino-radicals are produced, while the reaction with PBN gives rise to nitroxy-radicals. The radicals (V) add at high rates to the carbonyl group in ketones:[82]

$$(V) + R'RCO \xrightarrow{k_{28}} R'R\dot{C}OSiEt_3 . \quad (28)$$

The constants k_{28} have been determined for certain ketones and the rate constants for the addition of the radicals (V) to BNB and PBN have also been determined[71,72] (see Table 4, Nos. 5 and 6). Reactions (27) and (28) have been adopted as the stages competing with the addition of the radicals (V) to the STA.

Table 5 lists the rate constants for the addition of the radicals $H\dot{O}$, $HO\dot{O}$, $\dot{C}H_2O$, $Me\dot{C}HOH$, $Me_2\dot{C}OH$, and $MeCH_2\dot{C}HOH$ to substituted PBN.

It is seen from the data in Tables 1—5 that the rate constants for the addition to the most frequently used STA have been determined for a large number of radicals. Although these constants have been obtained in relation to different STA for some of the radicals, nevertheless by employing Eqn. (10) it is also possible to determine the rate constants for the addition of the radicals to other STA. The rate constants for the addition of the radicals to STA vary over a range of several orders of magnitude depending on the STA used. This property of the STA makes it possible to choose a suitable STA permitting the use of simpler expressions, for example Eqn. (19), for the determination of the rate constants for reactions (2)—(5).

It follows from Tables 1–3 that nitroso-compounds are more effective STA for the trapping of aliphatic carbon-centred and phenol radicals than nitrones. Among nitroso-compounds, aromatic compounds are more reactive than alkyl nitroxy-radicals, provided that there is no appreciable steric hindrance. The highest rate constants for the addition of radicals have been obtained for nitrosodurene (Tables 1 and 3, Nos.1–3). However, it does not follow from this that nitrosodurene is also the most reactive STA for other radicals, because the efficiency of the STA depends on many factors, for example on the stability of the SA formed,[84,85] on the thermal and photochemical stabilities of the STA, and other causes.

Table 4. The rate constants for the addition of hetero-radicals and other radicals to STA at 20 °C.

No.	STA	Radical	$10^{-5} k_1$, litre mol^{-1} s^{-1}	Refs.
1	4-Me-PBN	HO·	5 000	[69]
2	PBN	PhCOO·	1—100	[47, 63]
3	PBN	MeO·	1 200	[70]
4	PBN	H·	5 500	[30]
5	PBN	Et_3Si·	430—990	[71]
	PBN	»	60—120	[72]
6	BNB	Et_3Si·	16 000	[72]
7	DMPO	HO·	20 000—27 000	[69]
8	MNP	MeO·	1 300 (—40°)	[73]
9	MNP	PhS·	1 700	[74]
10	PMNB	PhS·	3 200	[74]
11	NB	PhS·	2 200	[74]
12	DMPO	Me_3CO·	5 000	[75]
	DMPO	»	7 300	[76]
13	MNP	Me_3CO·	15	[75]
	MNP	»	11 (40°)	[77]
14	H_2C=N(O)CMe$_3$	Me_3CO·	3 000—5 000	[75]
15	HMPO	Me_3CO·	3 800	[76]
16	DeMPO	Me_3CO·	3 300	[76]
17	PMPO	Me_3CO·	4 100	[76]
18	Me_4-PO	Me_3CO·	86	[76]
19	PBN	e_{aq}^-	100 000	[78]
20	PBN	CO_2^-·	150	[78]
21	PBN	CH_2O·	120	[78]
22	PBN	O_2^-·	50	[78]
23	α-2-pyridine 1-oxide N-t-butyl	HO·	32 000	[79]
24	α-3-pyridine 1-oxide *N*-t-butyl nitrone	HO·	48 000	[79]
25	α-4-pyridine 1-oxide *N*-t-butyl nitrone	HO·	35 000	[79]
26	PBN	EtO·	2 000	[80]

Notation: 4-Me-PBN = 4-*N*-methylpyridine t-butyl nitrone, HMPO = 5-n-hexyl-5-methyl-1-pyrroline *N*-oxide, DeMPO = 5-n-decyl-5-methyl-1-pyrroline *N*-oxide, PMPO = 5-n-propyl-5-methyl-1-pyrroline *N*-oxide, and Me_4-PO = 3,3,5,5-tetramethyl-1-pyrroline *N*-oxide; for the significance of the remaining abbreviations, see the footnote to Table 1.

The high rate constants for the addition of carbon-centred radicals to aromatic sterically unhindered nitroso-compounds can be accounted for by the stabilisation of the SA as a result of the delocalisation of the unpaired electron over the aromatic ring,[86] so that aromatic alkyl hydroxy-radicals should be more stable than dialkyl nitroxy-radicals. However, comparison of the rate constants for the addition of thiyl radicals to NB, PMNB, and MNP (cf.Nos.9–11 in Table 4 and Nos.1, 4, and 5 in Table 1) shows that the efficiency of the STA can also involve factors other than the delocalisation of the unpaired electron in the SA.

In contrast to nitroso-compounds, aliphatic nitrones are more reactive than aromatic nitrones (Table 1, Nos.7–13; in addition, cf.No.14 in Table 4 with Nos.1–3, 5, and 6 in Table 5). It is believed[42] that this is associated, apart from other causes, with the steric factor, because aliphatic nitrones are less sterically hindered than aromatic nitrones. Comparison of the rate constants for the addition of certain radicals to substituted and unsubstituted nitroso-compounds and nitrones shows that the steric structure of the substituents influences significantly the reactivity of the STA (cf. Nos.2–4, 7, 8, and 13 in Table 1, Nos.14–18 in Table 4, and Nos.1–3, 5, and 6 in Table 5).

Table 5. The rate constants ($10^{-7} k_1$, litre mol^{-1} s^{-1}) for the addition of radicals to substituted α-phenyl n-t-butyl nitrones (PBN) at 25 °C.[78]

No.	STA	Radical						
		Me_2CO·*	HO·	HOO·	CH_2OH·	MeCHOH·	Me_2COH·	$MeCH_2CHOH$·
1	PBN	0.55	850	0.5	4.3	1.6	1.0	1.3
2	4-Me-PBN	0.34	470	0.1	2.5	0.1	0.1	0.35
3	4-MeO-PBN	0.55	640	0.1	2.9	0.95	0.15	0.1
4	4-CN-PBN	—	650	0.6	75.0	2.0	—	1.7
5	4-NO_2-PBN	0.9	740	0.3	120.0	3.5	—	0.65
6	4-Cl-PBN	0.65	—	—	—	—	—	—

*According to the data of Janzen and Evans;[75] the solvent was benzene, while in all the remaining cases it was water.

It follows from the data in Tables 4 and 5 that nitroso-compounds and nitrones are just as effective for the identification of oxygen-centred radicals. As for alkyl radicals, aliphatic nitrones are more reactive than aromatic nitrones (cf.No.14 and Table 1 and No.1 in Table 5). Furthermore, the polarity (Table 5) and steric properties (Nos.8–13 in Table 1 and Nos.15–18 in Table 4) influence appreciably the effectiveness of nitrones, as happens for aromatic nitroso-compounds (Table 1, Nos.2–4).

The causes of the differences between the activities of the STA in relation to different radicals are so far not altogether clear. For example, MNP is a relatively ineffective STA, compared with NB and PMNB, in the trapping of the Me_3C radicals (see Table 1, Nos.1, 4, and 5). However, it is seen from the comparison of the rate constants for the addition of thiyl radicals of MNP, NB, and PMNB (Table 4, Nos.9–11) that the difference between the effectiveness of these STA and that of thiyl radicals is insignificant. The strength of the bond between the radicals and the STA apparently has a significant influence on the effectiveness of the STA. Thus the rate constants for the addition of silicon-centred radicals to nitrones are somewhat higher (Table 4, No.5) than the corresponding rate constants for carbon-centred radicals (No.8 in Table 1 and No.4 in Table 3). On the other hand, the rate constants for the addition of silicon-centred radicals to BNB with formation of a silicon–carbon bond are greater by approximately two orders of magnitude than the rate constants for the addition of the same radicals to PBN (Table 4, Nos.5 and 6).

The rate constants for the addition of alkyl radicals of various types to the most effective STA have similar values (Table 1, Nos.1–3 and 5; Table 2, Nos.3 and 4). The radicals containing the HO group at the α-carbon atom are an exception (Table 5), which may be associated, apart from other causes, also with the fact that all these radicals have a planar or nearly planar structure[87,88] and the steric structure of the radicals identified does not therefore play a significant role.

The rate constants for chlorine-containing radicals depend appreciably on the nature of the radical. For example, the rate constants for the addition of the $Cl_3\dot{C}$ radicals to nitroso-compounds are approximately an order of magnitude greater than the corresponding rate constants for the $R\dot{C}Cl_2$ and $R\dot{C}HCl$ radicals (Table 3). This is probably associated with the geometry of the radicals, because it is known[87] that the $Cl_3\dot{C}$ radicals have a more pronounced pyramidal structure than the $R\dot{C}Cl_2$ or $R\dot{C}HCl$ radicals.

According to Ingold and co-workers,[42,43] the relative error in the determination of k_1 for aliphatic carbon-centred radicals is 30%. The error is determined mainly by the difficulty of measuring the relative stabilities of the radicals detected by EPR, because, during the initial period of the reaction, the signal to noise ratio precludes a more accurate determination of the relative SA concentration and the extrapolation of the ratio to zero time owing to the low concentration of the radicals. The absolute values of k_1 listed in Tables 1–5 can differ by a factor of 2–5,[42,43,59,77] which is associated with the accuracy of the determination of the rate constants k_i [i = 2–5, see reactions (2)–(5)] for other reactions competing with the addition of the radicals to the STA, because the k_i enter into the expressions for the determination of k_1 (see Section II).

Table 6 lists the activation energies and pre-exponential factors for the addition of n-alkyl radicals. It follows from these data that the pre-exponential factors are in the range characteristic of the addition of radicals to the double bond within the limits of the accuracy of their determination,[29,31,89,90] while the activation energy for this reaction is low.

Table 6. Parameters of the Arrhenius equation for the reaction involving the addition of radicals to STA.

STA*	Radical	T, °C	E, kcal mol^{-1}	log$A$ (litre mol^{-1} s^{-1})	Refs.
MNP	n-alkyl	40–70	2.0	8.4	[42]
BNB	n-alkyl	40–73	1.0	6.5	[42]
PBN	n-alkyl	27–70	1.2	7.3	[42]
MNP	$CCl_3CH_2\dot{C}HCCl_2F$	−40–27	2.5	—	[62]

*For the significance of the notation, see the footnote to Table 1.

IV. THE USE OF THE SPIN TRAPPING METHOD FOR THE DETERMINATION OF THE KINETIC PARAMETERS OF ISOMERISATION, FRAGMENTATION, ELIMINATION, SUBSTITUTION, AND ADDITION REACTIONS

Section III listed the rate constants for the addition of short-lived radicals to STA. These constants were determined for cases where the reactions selected to compete with addition of the radicals $\dot{R}_1$ to the STA were cyclisation, substitution, or addition reactions whose rate constants were known. Certain data on the rate constants for the isomerisation, fragmentation, elimination, addition, and substitution of the radicals $\dot{R}_1$, obtained by the ST method, are compiled below. On the other hand, the addition of the radicals $\dot{R}_1$ to the STA for which the rate constant has been measured were selected as the reaction competing with the above reactions.

It has been shown in Section II that, in order to be able to determine the rate constants for reactions (2)–(5) by the ST method, it is essential to detect simultaneously by EPR the SA of the radicals $\dot{R}_1$ and $\dot{R}_i$ (i = 2–5) [except in the cases where it is possible to employ Eqn.(9)]. Evidently the STA whose SA with the radicals $\dot{R}_1$ and $\dot{R}_i$ have the simplest EPR spectrum are the most suitable for these purposes. Many nitrones satisfy this condition. On interaction of radicals with these compounds, fairly simple spectra are obtained, and the nitroxy-radicals formed are extremely stable. However, the spectra of the SA of many radicals with nitrones have similar hyperfine interaction (HFI) constants[24,91] and the lines due to individual radicals can therefore frequently overlap. Nevertheless, the large set of the possible nitrones[52,91,92] allows the elimination of these difficulties in many instances. As regards nitroso-compounds, their selection as the STA depends on many factors and therefore requires special study in the investigation of a particular reaction. Nitroso-compounds are known to be selective (see, for example, Freidlina et al.[5]) with respect to individual radicals. For this reason, it is not always possible to detect simultaneously the SA of the radicals $\dot{R}_1$ and $\dot{R}_i$ with the aid of nitroso-compounds. In such cases one can use Eqn.(9) to determine the rate constants for reactions (2)–(5).

When Eqns.(8), (9), (19), and (23) are used to determine k_2, it is necessary to know only the values of k_1. However, the application of these expressions requires that certain conditions be maintained. If these conditions are not fulfilled, then more complex expressions, for example Eqn.(17), may be used to determine k_2, which requires the knowledge of the rate constants for the addition of the radicals $\dot{R}_1$ and $\dot{R}_2$ to the STA. It follows from the data in Tables 1–5 that much information is now available about the rate constants for the addition of short-lived radicals to STA. The main difficulty with which the use of Eqn.(17) for the calculation of k_2 is associated consists in the comparatively small amount of data available for the rate constant k_{12}. However, on the basis of Eqns.(24)–(26), it is possible not only to determine k_{12} but also to establish the validity of condition (14).

1. Determination of the Rate Constants for the Isomerisation Reaction

The present development of the chemistry of radical processes has shown that the chemical processes involving the rearrangement of radicals in the liquid phase [see reaction (3)] are general and can be regarded as one of the principal types of radical reaction together with the fragmentation, elimination, substitution, and addition reactions.[35,90]

The rearrangements of radicals with 1,2-migration of the chlorine atom[93,94] and sulphur-containing groups[95] as well as different types of isomerisation with migration of hydrogen to a more remote radical centre[93,96] occupy an important place in the series of known rearrangements of short-lived radicals. Such rearrangements have been investigated by methods of preparative chemistry,[93–96] EPR,[21,66,67,97–101] and other physicochemical methods.[93,96,102,103]

The STA more effective in relation to the radicals $\dot{R}_1$ and $\dot{R}_2$ investigated, namely MNP and ND, have been used to determine the isomerisation rate constants k_3 (Nos.1 and 2 in Table 1 and Nos.7–10 in Table 3). The rate constants k_3 were determined with the aid of the expression

$$k_3 = k_1 [RNO]_0 \frac{[R_3\dot{R}NO]}{[R_1\dot{R}NO]}$$

[see Eqn.(19)], which has been shown in Section II to be valid subject to the condition $k_3[RNO]_0 \gg k\{[R_3\dot{R}NO] + [R_1\dot{R}NO]\}$, where k is the rate constant for the interaction of the radicals $\dot{R}_3$ with $R_1\dot{R}NO$ and $R_3\dot{R}NO$ [see reaction (12)].

(a) Determination of the rate constant for the isomerisation of polyhalogeno-radicals with 1,2-migration of chlorine. The attempts to determine the rate constant for the rearrangement of the radicals $CCl_3\dot{C}H_2$ to $\dot{C}Cl_2CH_2Cl$ with 1,2-migration of chlorine by the EPR method have been unsuccessful, because it has not been possible to observe signals due to the non-rearranged radicals even at −140 °C.[97,98] On the basis of the results obtained,[98] it has been suggested that these reactions are characterised by low activation energies and that the rate constant for the isomerisation of the primary radicals $CCl_3\dot{C}H_2$ to $\dot{C}Cl_2CH_2Cl$ is apparently $k_{1s} \approx 10^{10}$ s^{-1} at 50 °C.[87,98]

Using the selectivity of nitroso-compounds, Freidlina et al.[5] detected the SA of the radical $CCl_3\dot{C}H_2$ with $Me_2C(COMe)NO$. The rearranged $\dot{C}Cl_2CH_2Cl$ radicals have been detected with the aid of ND as the STA. In subsequent studies,[62,66,67] it was possible to detect simultaneously the SA of the non-rearranged and rearranged radicals in other reactions. These results made it possible to find an approach to the determination of the rate constants for the rearrangement of polyhalogeno-radicals with 1,2-migration of chlorine by the ST method.

The authors[62,66,67] used MNP as the STA for the determination of the rate constant for the isomerisation of polyhalogenoradicals with 1,2-migration of chlorine, because, with the aid of this compound, it is possible to establish the equivalence or non-equivalence of the two β-chlorine atoms in the SA of these radicals with the STA[66,104,105] and thereby assign unambiguously the spectra of the non-rearranged and rearranged radicals when these are present simultaneously in the reaction mixture (Table 7).

Table 7. Parameters of the Arrhenius equation for the reaction involving the isomerisation of the radicals $\dot{R}_1$ to $\dot{R}_3$.[39,60,62,66,67]

No.	$\dot{R}_1$	$\dot{R}_3$	$10^{-4}k_3$, s^{-1}	A, s^{-1}	E, kcal mol^{-1}
1	$CCl_3\dot{C}HCl$	$\dot{C}Cl_2CCl_2H$	1.8*	—	—
2	$ClCH_2\dot{C}ClCCl_3$	$ClCH_2CCl_2\dot{C}Cl_2$	1.0*	—	—
3	$RCH_2\dot{C}MeCCl_3$	$RCH_2CMeCl\dot{C}Cl_2$	3.3	10^{12}	12.5
4	$RCH_2\dot{C}HCCl_2F$	$RCH_2CHCl\dot{C}ClF$	10	10^{12}	10.5
5	$CCl_3\dot{C}H_2$	$\dot{C}Cl_2CH_2Cl$	10^3	10^{12}	8.0
6	$PhC(SPh)_2\dot{C}H_2$	$PhC(SPh)CH_2SPh$	5.6	$8\cdot10^{10}$	8.8
7	$RCO_2CH_2(CH_2)_3\dot{C}H_2$	$RCO_2\dot{C}H(CH_2)_3Me$	13	$3\cdot10^9$	6.3
8	$RCO_2CH_2(CH_2)_4\dot{C}H_2$	$RCO_2\dot{C}H(CH_2)_4Me$	1.8	$2\cdot10^{10}$	8.5
9	$RCO_2CH_2(CH_2)_5\dot{C}H_2$	$RCO_2\dot{C}H(CH_2)_5Me$	0.78	$7\cdot10^9$	8.6

*At 20 °C; in the remaining cases the data refer to 40 °C.

The rate constants for the isomerisation of certain polyhalogeno-radicals with 1,2-migration of chlorine determined in the above studies[62,66,67] and the parameters of the Arrhenius equation characterising these reactions are summarised in Table 7 (Nos.1–5). The knowledge of the isomerisation rate constants leads to the possibility of predicting a whole group of isotypical telomerisation, polymerisation, addition, and substitution reactions in which the intermediate radicals may rearrange with 1,2-migration of chlorine. In particular, the study of the polymerisation of $H_2C{=}CHCCl_2X$, where X = Cl or F,[106] showed that the polymer formed consists mainly of the rearranged —$(CH_2.CHClCClX)_n$— units. Since the rate of isomerisation of the secondary radicals is at least an order of magnitude higher than the rate of their addition to the monomer, the radicals $RCH_2\dot{C}HCCl_2X$ formed have sufficient time to isomerise.

(b) Determination of the rate constant for the isomerisation of the radicals $PhC(SPh)_2\dot{C}H_2$ to $PhC(SPh)CH_2SPh$ with 1,2-migration of the SPh group. The rate constant for the rearrangement of the radicals $PhC(SPh)_2\dot{C}H_2$ to $PhC(SPh).CH_2SPh$ has been determined[39] in the temperature range 10–70 °C (Table 7, No.6). These radicals are obtained on thermal or photochemical isomerisation of acetophenone diphenylmercaptal to 1,2-di(phenylthio)ethylbenzene.[107] The activation energy and the pre-exponential factor obtained proved to be closer to the parameters characteristic of radical isomerisation[62,108,109] than to the parameters of the elimination[31,110] or addition[31] reactions. These results enabled the authors[39] to assume that the isomerisation of the radicals $PhC(SPh)_2\dot{C}H_2$ to $PhC(SPh)CH_2SPh$ with 1,2-migration of the thiyl group proceeds via an intramolecular mechanism.

(c) Determination of the rate constant for the isomerisation of radicals with migration of hydrogen. The SA of the initial $\dot{C}H_2(CH_2)_nCH_2CO_2R$ and the rearranged $Me(CH_2)_n\dot{C}HCO_2R$ radicals with ND have been identified by EPR.[60,101] The non-rearranged radicals were generated by abstracting bromine from $BrCH_2(CH_2)_nCH_2CO_2R$ by triethylsilyl radicals.[101] The radicals $Me(CH_2)_n\dot{C}HCO_2R$ are formed as a result of the rearrangement of the radicals $\dot{C}H_2(CH_2)_nCH_2.CO_2R$ with 1,4-migration (n = 2), 1,5-migration (n = 3), and 1,6-migration (n = 4) of a hydrogen atom.

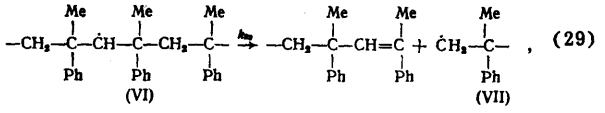
Table 7 (Nos.7–9) presents the temperature variation of the rate constants for the isomerisation of the radicals $\dot{C}H_2(CH_2)_nCH_2CO_2R$ to $Me(CH_2)_n\dot{C}HCO_2R$. These results were obtained over a narrow temperature range (ΔT = 30 to 40 °C) and for a small number of experimental points.[101] Nevertheless it follows from the above data that 1,5-migration is preferred on both kinetic and thermodynamic grounds in reactions where there is a possibility of the rearrangement of the intermediate radicals with migration of hydrogen.

The use of the ST method yielded the kinetic and thermodynamic parameters for the isomerisation of short-lived radicals with migration of chlorine, the thiyl group, and hydrogen. The error in the measurement of the isomerisation rate constants, especially in the rearrangement of radicals with 1,2-migration of chlorine, is apparently half an order of magnitude and is associated with the inaccuracy in the determination of the rate constant for the addition of the non-rearranged radicals to the STA. Nevertheless the results obtained make it possible to take into account the role of the rearrangement stage in complex chemical reactions.

2. Determination of the Rate Constants for the Fragmentation Reaction

The rate constants for the fragmentation of the radicals $R\dot{C}O$ (R = isopropyl, t-butyl, 1-adamentyl, tetra-allyl, and cumenyl) have been measured[57,77] using MNP as the STA.

The fragmentation of polymeric radicals via the mechanism



(29)

has also been studied.[111] Having determined the stationary concentrations (2g) of the SA of the radicals (VI) and (VII) with MNP and having adopted values in the range 3.3×10^6 to 9×10^6 litre mol^{-1} s^{-1} for the rate constants for the addition of the radicals (VI) to MNP, the authors[111] obtained $k_{29} = 5 \times 10^3$–4.1×10^4 s^{-1} at 25 °C.

3. Determination of the Rate Constant for the Abstraction of a Chlorine Atom from CCl_4 by the Telomeric Radicals $CCl_3.(CH_2CHX)_n^{\cdot}$ (n = 1–3; X = H, Me, or Cl) and Their Addition to Olefins

The telomerisation of the olefins $H_2C{=}CHX$ (X = H, Me, or Cl) with CCl_4 takes place at a fairly high concentration of the telogen via a radical chain mechanism:[112–114]

Scheme III

initiator → $\dot{R}$,

$\dot{R} + CCl_4 \rightarrow RCl + \dot{C}Cl_3$,

$\dot{C}Cl_3 + H_2C{=}CHX \rightarrow CCl_3CH_2\dot{C}HX$,

$CCl_3CH_2\dot{C}HX + H_2C{=}CHX \xrightarrow[(a)]{k_p^1} CCl_3CH_2CHXCH_2\dot{C}HX$,

$CCl_3CH_2\dot{C}HX + CCl_4 \xrightarrow[(b)]{k_{tr}^1} CCl_3CH_2CHXCl + \dot{C}Cl_3$, (T_1)

. . . . . .

$CCl_3(CH_2CHX)_n^{\cdot} + H_2C{=}CHX \xrightarrow[(c)]{k_p^n} CCl_3(CH_2CHX)_{n+1}^{\cdot}$,

$CCl_3(CH_2CHX)_n^{\cdot} + CCl_4 \xrightarrow[(d)]{k_{tr}^n} CCl_3(CH_2CHX)_nCl + \dot{C}Cl_3$, (T_n)

$2\dot{C}Cl_3 \xrightarrow{k_5}$ products .

It is seen from this scheme that the relative yield of the telomer-homologue T_n is determined solely by the competition between the stages involving the substitution and addition of the radicals $CCl_3(CH_2CHX)_n^{\cdot}$ [stages (*a*)–(*d*)]. The methods of competitive kinetics made it possible to investigate the reactivity of the radicals. The determination of the partial chain transfer constants $C_n = k_{tr}^n/k_p^n$ is a widely used method for such estimates. An appreciable difference between C_1 and C_n ($n \geq 2$) has been observed in the telomerisation of styrene,[115] ethylene, propene, and vinyl chloride[116] with CCl_4. In order to elucidate the causes of the changes in the quantities C_n, it is essential to calculate k_{tr}^n or k_p^n and to establish thereby the contribution of stages (*c*) and (*d*) to the telomerisation of CCl_4 with olefins.

The rate constants for the abstraction of chlorine from CCl_4 by the radicals $CCl_3(CH_2CHX)_n^{\cdot}$ (where X = H, Me, or Cl) have been determined[61,68,117] by the ST method. The telomeric radicals were generated by the photochemical decomposition of $CCl_3(CH_2CHX)_nI$ in the presence of $Hg(m\text{-}C_2H_2B_{10}H_9\text{-}9)_2$.[118] In the determination of the rate constant $k_5 = k_{tr}^n$ for the abstraction of chlorine from CCl_4 by the radicals $CCl_3(CH_2CHX)_n^{\cdot}$, the authors[61,68,117] used ND as the STA, which is most effective in relation to these radicals, and also the expression†

$$k_{tr}^n = k_5 = k_1 \frac{[ND]_0\,[CCl_3N(\dot{O})Ar]}{[CCl_4]_0\,[CCl_3(CH_2CHX)_nN(\dot{O})Ar]} .$$

In particular, it has been shown[68] that, when a more general expression is used [see Eqn. (18)] to determine k_{tr}^n, the same values of k_{tr}^n are obtained as in the case where the above formula was used. This is associated with the fact that, as numerous results show,[36,41,42,61,68,117] the rates of addition of the radicals $CCl_3(CH_2CHX)_n^{\cdot}$ to ND are much higher than the rate of reaction of these radicals with the SA. The values of k_{tr}^n determined in a number of studies[61,68,117] are listed in Table 8.

Table 8. The chain transfer (k_{tr}, litre mol^{-1} s^{-1}) and propagation (k_p, litre mol^{-1} s^{-1}) rate constants for telomeric radicals at 40 °C.

No.	Radical	$10^{-4}\,k_{tr}$	$10^{-3}\,k_p$	Refs.
1	$CCl_3CH_2\dot{C}H_2$	0,39	45	[117]
2	$CCl_3(CH_2CH_2)_2^{\cdot}$	9,0	30	[117]
3	$CCl_3(CH_2CH_2)_3^{\cdot}$	14.0	19	[117]
4	$CCl_3CH_2\dot{C}HMe$	1.4	8.8	[61]
5	$CCl_3(CH_2\dot{C}HMe)_2^{\cdot}$	20.8	4.2	[61]
6	$CCl_3CH_2\dot{C}HCl$	0.045	168	[68]
7	$CCl_3(CH_2CHCl)_2^{\cdot}$	0.176	98	[68]

Table 9. The rate constants k_5 for the abstraction of hydrogen by the radicals $\dot{P}h$ [122] and $MeO\dot{}$ [123] at 20 °C.

Reaction	$10^{-5}\,k_5$, litre mol^{-1} s^{-1}	Reaction	$10^{-5}\,k_5$, litre mol^{-1} s^{-1}
$\dot{P}h$ + MeOH	1.4	$MeO\dot{}$ + glycerol	13
$\dot{P}h$ + MeCHOH	2.3±0.1	$MeO\dot{}$ + $MeOCH_2OMe$	19
$\dot{P}h$ + Me_2CHOH	4.1±0.1	$MeO\dot{}$ + HCOOMe	48
$MeO\dot{}$ + $MeCH_2OH$	5.0	$MeO\dot{}$ + $MeOCH_2OH$	34
$MeO\dot{}$ + ethylene glycol	6.2	$MeO\dot{}$ + n-pentane	1

Freidlina and co-workers[61,68,117] determined the chain propagation rate constant k_p^n [see Scheme III, stages (*a*) and (*c*)] listed in Table 8 from the values of k_{tr}^n obtained and the partial constants C_n for chain transfer in the telomerisation reactions of propene and vinyl chloride.[116,119–121] It follows from the data in Table 8 that (1) the reactivity of the radicals $CCl_3(CH_2CHX)_n^{\cdot}$ (X = H, Me, or Cl) in reactions with CCl_4 depends significantly on the position of the CCl_3 group relative to the radical centre and on the nature of the substituents at the α-carbon atom, (2) the differences between the values of C_n for the telomerisation of ethylene and propene with CCl_4 are associated mainly with the differences between the rate constants for the abstraction of chlorine from CCl_4 by the radicals $CCl_3CH_2\dot{C}HX$ and $CCl_3(CH_2CHX)_n^{\cdot}$, where $n \geq 2$ and X = Me or H, and (3) the changes in the C_n for the telomerisation of vinyl chloride with CCl_4 are associated with changes in both k_{tr}^n and k_p^n.

†This expression is analogous to Eqn. (19) with $k_5 = k_2$; $[M]_0 = [CCl_4]_0$, $[A] = CCl_3(CH_2CHX)_nN(\dot{O})Ar$, and $[B] = CCl_3N(\dot{O})Ar$, where Ar = 2,3,5,6-Me_4C_6H.

4. Determination of the Rate Constants for the Abstraction of Hydrogen by the Radicals Ṗh and MeȮ

The rate constants in the abstraction of hydrogen from methanol, ethanol, and isopropyl alcohol by phenyl radicals have been determined[122] using PBN as the STA (Table 9). Table 9 presents also the rate constants for the abstraction of hydrogen from various compounds by the radicals MeȮ. These data were obtained on the assumption that the rate constant for the addition of the radicals MeȮ to PBN is 1.2×10^8 litre mol^{-1} s^{-1}.

5. Determination of the Rate Constants for the Addition of Radicals to Compounds Containing the S=C< Groups

It is known[12,15,124,125] that compounds containing the S=C< linkages can be used as STA. The stability of the radicals formed then depends significantly on a series of factors (for further details, see Scaiano and Ingold[12]). Using MNP and $(Me_3C)_2C=S$ as the STA, Scaiano and Ingold determined the rate constants for the addition of methyl radicals to $(Me_3C)_2C=S$. The SA of the radicals Ṁe with MNP and $(Me_3C)C=S$ have been identified by EPR at −40 °C:

$$\dot{M}e + MNP \xrightarrow{k_{30}} \underset{(VIII)}{MeN(\dot{O})CMe_3}, \qquad (30)$$

$$\dot{M}e + (Me_3C)_2C{=}S \xrightarrow{k_{31}} \underset{(IX)}{MeS\dot{C}(CMe_3)_2}. \qquad (31)$$

The value $k_{30} = 1.5 \times 10^5$ litre mol^{-1} s^{-1} was adopted for the rate constant for the addition of the radicals Ṁe to MNP at −40 °C on the basis of the data of Perkins and Roberts.[59,77] The rate constant $k_{31} = 1.1 \times 10^6$ litre mol^{-1} s^{-1} was determined by comparing the rates of formation of the SA of methyl radicals with MNP and $(Me_3)_2C=S$ using the known value of k_{30}. The results obtained showed that alkyl radicals add to compounds containing the S=C< linkage at high rates. Thus the interaction of the radicals Ṗh with S = C(OPh)CH$_2$Ph and S = C(OPh)CHPh$_2$ yields in addition to the radicals PhSĊ(OPh)CH$_2$Ph and PhSĊ(OPh)CHPh$_2$, i.e.

$$\dot{P}h + S{=}C(OPh)CH_2Ph \xrightarrow{k_{32}} PhS\dot{C}(OPh)CH_2Ph, \qquad (32)$$

$$\dot{P}h + S{=}C(OPh)CHPh_2 \xrightarrow{k_{33}} PhS\dot{C}(OPh)CHPh_2, \qquad (33)$$

the radicals S = C(OPh)ĊHPh and S = C(OPh)ĊPh$_2$:

$$\dot{P}h + S{=}C(OPh)CH_2Ph \xrightarrow{k_{34}} S{=}C(OPh)\dot{C}HPh, \qquad (34)$$

$$\dot{P}h + S{=}C(OPh)CHPh_2 \xrightarrow{k_{35}} S{=}C(OPh)\dot{C}Ph_2. \qquad (35)$$

With $k_{34} = k_{35} = 5 \times 10^6$ litre mol^{-1} s^{-1}, the rate constants for the addition of phenyl radicals to S = C(OPh)CH$_2$Ph and S = C(OPh)CHPh$_2$ at 45 °C were found[15] to be $k_{32} = 2.3 \times 10^6$ and $k_{33} = 2.7 \times 10^6$ litre mol^{-1} s^{-1} respectively. It is noteworthy that the values of k_{32} and k_{33} determined by the ST method are virtually identical with the corresponding constants calculated on the basis of the direct identification of the radicals PhSĊ(OPh)CH$_2$Ph and PhSĊ(OPh)CHPh$_2$ by EPR.[15]

The phenylation of benzene has been investigated[63] by the ST method. Having adopted the value of 1.2×10^7 litre mol^{-1} s^{-1} for the rate constant for the addition of phenyl radicals to PBN at 25 °C in methanol, the authors[63] obtained the constant $k_{add} \approx 10^5$ litre mol^{-1} s^{-1} for the addition of phenyl radicals to benzene, which agrees well with the results of the phenylation of benzene by phenyl radicals obtained by Levy et al.[126] and Scaiano and Stewart[127] using other methods.

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Thus the experimental results considered in this review demonstrate the probable usefulness of the application of the ST method in the determination of kinetic data for individual stages of complex chemical reactions of various types. Although the amount of such data is at present small, nevertheless one may hope that further accumulation of experimental rate constants for the addition of radicals to STA as well as the analysis of the dependence of the rate constants for the addition reaction on the steric and polar properties of the radicals and on the nature of the STA will permit a considerable extension of the range of reactions for which kinetic data may be obtained.

REFERENCES

1. C.Lagercrantz, J.Phys.Chem., 1971, **75**, 3466.
2. E.G.Janzen, Acc.Chem.Res., 1971, **4**, 31.
3. E.G.Janzen, in "Free Radicals in Biology", Vol.4 (Edited by W.A.Pryor), 1980, p.115.
4. M.J.Perkins, "Essays in Free Radical Chemistry", Chem.Soc.Special Publ.No.24, The Chemical Society, London, 1972, Ch.5.
5. R.Kh.Freidlina, I.I.Kandror, and R.G.Gasanov, Uspekhi Khim., 1978, **47**, 508 [Russ.Chem.Rev., 1978(3)].
6. V.E.Zubarev, V.N.Belevskii, and L.T.Bugaenko, Uspekhi Khim., 1979, **48**, 1361 [Russ.Chem.Rev., 1979(8)].
7. V.N.Belevskii, Khim.Vys.Energii, 1981, **15**, 3.
8. M.J.Perkins, "Advances in Physical Organic Chemistry", Vol.17, Acad.Press, London–New York–Toronto–Sydney–San Francisco, 1980, p.1.
9. T.Otsu, H.Tanaka, T.Sato, and L.Quach, Makromol. Chem., 1980, **181**, 1897.
10. International Symposium on Spin Trapping and Nitroxyl Radical Chemistry, Canad.J.Chem., 1982, **60**, 1379.
11. C.M.Camaggi, M.Caser, G.Placucci, and M.Guerra, J.Chem.Soc., Perkin Trans.II, 1979, 1675.
12. J.C.Scaiano and K.U.Ingold, J.Amer.Chem.Soc., 1976, **98**, 4727.
13. J.C.Scaiano and K.U.Ingold, J.Amer.Chem.Soc., 1977, **99**, 2079.
14. A.Alberti and A.Hudson, J.Organomet.Chem., 1979, **164**, 219.
15. R.G.Gasanov, R.G.Petrova, T.D.Churkina, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1984, **274**, 343.
16. B.U.Gilbert and R.O.C.Norman, Canad.J.Chem., 1982, **60**, 1379.
17. E.G.Rozantsev, "Svobodnye Iminoksil'nye Radikaly" (Free Iminoxy-Radicals), Izd.Khimiya, Moscow, 1970, p.216.
18. A.L.Buchachenko and A.M.Vasserman, "Stabil'nye Radikaly" (Stable Radicals), Izd.Khimiya, Moscow, 1973, p.408.
19. V.D.Sholle and E.G.Rozantsev, "Organicheskaya Khimiya Svobodnykh Radikalov" (Organic Chemistry of Free Radicals), Izd.Khimiya, Moscow, 1979, p.343.
20. R.G.Gasanov and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1977, **235**, 1309.

21. R.G.Gasanov, I.I.Kandror, M.Ya.Khorlina, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 1758.
22. V.N.Belevskii and S.P.Yarkov, Dokl.Akad.Nauk SSSR, 1980, **254**, 1417.
23. V.N.Belevskii and S.P.Yarkov, Zhur.Org.Khim., 1982, **18**, 1504.
24. E.G.Janzen, Uspekhi Khim., 1974, **43**, 2247 [Russ. Chem.Rev., 1974(12)].
25. B.C.Gilbert and M.Trenwith, J.Chem.Soc., Perkin Trans.II, 1973, 1834.
26. C.Lagercrantz and M.Setaka, Acta Chem.Scand., 1974, **B28**, 619.
27. R.G.Gasanov, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 1134.
28. R.Konaka, S.Terabe, T.Mizuta, and S.Sakata, Canad.J.Chem., 1982, **60**, 1532.
29. E.T.Denisov, "Konstanty Skorosti Gomoliticheskikh Zhidkofaznykh Reaktsii" (The Rate Constants for Homolytic Liquid-Phase Reactions), Izd.Nauka, Moscow, 1971, p.709.
30. S.I.Belpushkin, V.N.Belevskii, and L.T.Bugaenko, Dokl.Akad.Nauk SSSR, 1980, **255**, 903.
31. N.M.Emanuel' and D.G.Knorre, "Kurs Khimicheskoi Kinetiki" (Textbook of Chemical Kinetics), Izd.Vys. Shkola, Moscow, 1974, p.400.
32. G.B.Wetts and K.U.Ingold. J.Amer.Chem.Soc., 1972, **94**, 491.
33. H.G.Korth, R.Sustmann, R.Merenyi, and H.G.Viehe, J.Chem.Soc., Perkin Trans.II, 1983, 67.
34. P.R.Marriott, A.L.Castelhano, and D.Griller, Canad. J.Chem., 1980, **60**, 274.
35. E.C.Nonhebel and J.C.Walton, "Free-Radical Chemistry: Structure and Mechanisms" (Translated into Russian), Izd.Mir, Moscow, 1977, p.606.
36. R.G.Gasanov, L.V.Ivanova, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1980, **255**, 1156.
37. T.Doba, T.Ichikawa, and H.Yoshida, Bull.Chem. Soc.Japan, 1977, **50**, 3158.
38. E.T.Denisov, "Kinetika Gomoliticheskikh Khimicheskikh Reaktsii" (Kinetics of Homolytic Chemical Reactions), Izd.Vys.Shkola, Moscow, 1974, p.47.
39. R.G.Gasanov, R.G.Petrova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 2596.
40. C.Chatgilialoglu and K.U.Ingold. Canad.J.Chem., 1983, **61**, 1077.
41. P.Schmid and K.U.Ingold, J.Amer.Chem.Soc., 1977, **99**, 6434.
42. P.Schmid and K.U.Ingold, J.Amer.Chem.Soc., 1978, **100**, 2493.
43. Y.Maeda an . K.U.Ingold, J.Amer.Chem.Soc., 1979, **101**, 4975.
44. S.Nigan, K.D.Asmis, and R.L.Willson, J.Chem.Soc., Faraday Trans.I, 1976, **72**, 2324.
45. U.M.Oehler and E.G.Janzen, Canad.J.Chem., 1982, **60**, 1542.
46. K.J.Laidler, "Kinetics of Organic Reactions" (Translated into Russian), Izd.Mir, Moscow, 1966, p.331.
47. E.G.Janzen, C.Evans, and Y.Nishi, J.Amer.Chem. Soc., 1972, **94**, 8236.
48. I.V.Khudyakov and V.A.Kuz'min, Uspekhi Khim., 1975, **44**, 1749 [Russ.Chem.Rev., 1975(10)].
49. I.V.Khudyakov and V.A.Kuz'min, Uspekhi Khim., 1978, **47**, 39 [Russ.Chem.Rev., 1978(1)].
50. I.V.Khudyakov, P.P.Levin, and V.A.Kuzmin, Int. J.Chem.Kinet., 1979, **11**, 357.
51. R.G.Kryger, J.P.Lorand, N.R.Stevens, and N.R.Herron, J.Amer.Chem.Soc., 1977, **99**, 7589.
52. E.G.Janzen and I.G.Lopp, J.Magn.Resonance, 1972, **7**, 107.
53. S.Forshult, C.Lagercrantz, and K.Tirssell, Acta Chem.Scand., 1969, **23**, 522.
54. S.Terabe and R.Konaka, J.Amer.Chem.Soc., 1971, **93**, 4306.
55. S.Terabe and R.Konaka, J.Chem.Soc., Perkin Trans.II, 1973, 1252.
56. D.Lal, D.Greller, S.Husband, and K.U.Ingold, J.Amer.Chem.Soc., 1974, **96**, 6355.
57. N.Ohto, E.Niki, and Y.Kamida, J.Chem.Soc., Perkin Trans.II, 1977, 1770.
58. T.Doba, S.Noda, and H.Yoshida, Bull.Chem.Soc. Japan, 1979, **52**, 21.
59. M.J.Perkins and B.P.Roberts, J.Chem.Soc., Perkin Trans.II, 1975, 77.
60. R.G.Gasanov, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 891.
61. R.G.Gasanov, L.V.Ivanova, N.A.Grigor'ev, A.L.Tumanskaya, and R.Kh.Freidlina, Dokl.Akad. Nauk SSSR, 1983, **273**, 1410.
62. R.G.Gasanov, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 2264.
63. E.Janzen and C.A.Evans, J.Amer.Chem.Soc., 1975, **97**, 205.
64. V.E.Zubarev and L.T.Bugaenko, Dokl.Akad.Nauk SSSR, 1978, **242**, 136.
65. R.G.Gasanov, I.I.Kandror, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1976, **226**, 342.
66. R.G.Gasanov, T.T.Vasil'eva, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1978, 817.
67. R.G.Gasanov, L.V.Ivanova, and R.G.Freidlina, Dokl.Akad.Nauk SSSR, 1979, 2810.
68. R.G.Gasanov, L.V.Ivanova, and N.A.Grigor'ev, Dokl.Akad.Nauk SSSR, 1984, 1965.
69. A.Castelhano, M.Perkins, and D.Griller, Canad.J. Chem., 1983, **61**, 298.
70. V.E.Zubarev, V.M.Belevskii, and L.T.Bugaenko, Vestnik Moskov.Gos.Univ., 1975(3), 295.
71. C.Chatgilialoglu, K.U.Ingold, and J.C.Scaiano, J.Amer.Chem.Soc., 1983, **105**, 3292.
72. R.G.Gasanov, L.V.Ivanova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 938.
73. F.P.Sargont, J.Phys.Chem., 1978, **81**, 89.
74. O.Ito and M.Matsuda, J.Amer.Chem.Soc., 1983, **105**, 1937.
75. E.Janzen and C.A.Evans, J.Amer.Chem.Soc., 1973, **95**, 8205.
76. D.L.Haire and E.Janzen, Canad.J.Chem., 1982, **60**, 1514.
77. M.J.Perkins and B.P.Roberts, J.Chem.Soc., Perkin Trans.II, 1974, 297.
78. C.L.Greenstock and R.H.Wiebe, Canad.J.Chem., 1982, **60**, 1560.
79. P.Neta, S.Steenkin, E.Janzen, and R.V.Shetty, J.Phys.Chem., 1980, **84**, 532.
80. V.E.Zubarev, V.N.Belevcky, and L.T.Bugaenko, "Proceedings of the IVth Symposium on Radiation Chemistry, Kesthely (Hungary)", 1976, p.1017.
81. C.Chatgilialoglu, K.U.Ingold, and J.C.Scaiano, J.Amer.Chem.Soc., 1982, **104**, 5123.
82. C.Chatgilialoglu, K.U.Ingold, and J.C.Scaiano, J.Amer.Chem.Soc., 1982, **104**, 5119.
83. H.Chandra, I.M.Davidson, and M.C.R.Symons, J.Chem.Soc., Perkin Trans.II, 1982, 1353.
84. A.Hudson, M.F.Lappert, and B.K.Nicholson, J.Chem.Soc., Dalton Trans., 1977, 551.

85. L.S.Benner and A.L.Balch, J.Organometal.Chem., 1977, **134**, 121.
86. D.Griller and K.U.Ingold, Acc.Chem.Res., 1976, **9**, 13.
87. J.K.Kochi, "Advances in Free Radical Chemistry", Vol.5 (Edited by G.H.Williams), Acad.Press, New York–London–San Francisco, 1975, p.189.
88. P.J.Krusic and J.Meakin, J.Amer.Chem.Soc., 1976, **98**, 228.
89. S.W.Benson, "The Foundations of Chemical Kinetics" (Translated into Russian), Inostr.Lit., Moscow, 1964, p.603.
90. M.N.Semenov, "O Nekotorykh Problemakh Khimicheskoi Kinetiki i Reaktsionnoi Sposobnosti" (Some Problems of Chemical Kinetics and Reactivity), Izd. Akad.Nauk SSSR, Moscow, 1958, p.686.
91. E.Janzen and B.Blackburn, J.Amer.Chem.Soc., 1969, **91**, 4481.
92. E.Janzen and J.Liu, J.Magn.Resonance, 1973, **9**, 510.
93. R.Kh.Freidlina and A.B.Terent'ev, Uspekhi Khim., 1979, **48**, 1548 [Russ.Chem.Rev., 1979(9)].
94. R.Kh.Freidlina, "Advances in Free Radical Chemistry", Acad.Press, London, 1965, Vol.1, p.211.
95. R.Kh.Freidlina, A.B.Terent'ev, and R.G.Petrova, Dokl.Akad.Nauk SSSR, 1963, **149**, 860.
96. R.Kh.Freidlina and A.B.Terent'ev, "Advances in Free Radical Chemistry", Vol.6 (Edited to G.H.W.Williams), Acad.Press, London, 1980, p.1.
97. J.Cooper, A.Hudson, and R.A.Jackson, Tetrahedron Letters, 1973, 831.
98. K.S.Chen, D.Y.H.Tang, L.K.Montgomery, and J.K.Kochi, J.Amer.Chem.Soc., 1974, **96**, 2201.
99. P.S.Skell, R.R.Pavlis, D.C.Lewis, and K.J.Shea, J.Amer.Chem.Soc., 1973, **95**, 6735.
100. R.G.Gasanov and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2242.
101. R.G.Gasanov, R.Kh.Freidlina, and A.B.Terent'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2628.
102. R.G.Gasanov, K.A.Kochetkov, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 1951.
103. R.G.Gasanov, K.A.Kochetkov, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1974, 804.
104. G.A.Razuvaev, G.A.Abakumov, and V.K.Cherkasov, Dokl.Akad.Nauk SSSR, 1973, **212**, 374.
105. C.M.Camaggi, R.J.Holman, and M.J.Perkins, J.Chem. Soc., Perkin Trans.II, 1972, 501.
106. A.P.Suprun, A.S.Shashkov, T.A.Soboleva, G.K.Semin, T.T.Vasil'eva, G.P.Lopatina, T.A.Babushkina, and R.Kh.Freidlina, Dokl.Akad. Nauk SSSR, 1967, **173**, 1356.
107. R.G.Gasanov, R.G.Petrova, and R.Kh.Freidlina, Dokl.Akad.Nauk SSSR, 1976, **227**, 874.
108. B.Maillard and K.U.Ingold, J.Amer.Chem.Soc., 1976, **98**, 1224.
109. E.J.Hamilton and H.Fisher, Helv.Chim.Acta, 1973, **56**, 795.
110. M.G.Katz, A.Horowitz, and I.A.Rajbenbach, Trans. Faraday Soc., 1971, **67**, 2354.
111. T.Ikeda, H.Yamaoka, T.Matsuyama, and S.Okamura, J.Phys.Chem., 1978, **82**, 2329.
112. R.Kh.Freidlina, F.L.Velichko, E.Ts.Chukovskaya, M.Ya.Khorlina, B.A.Krentsel', D.E.Il'ina, N.V.Kruglova, L.S.Mayants, and R.G.Gazanov, "Metody Elementoorganicheskoi Khimii. Khlor. Alifaticheskie Soedineniya" (Methods of Organoelemental Chemistry. Chlorine. Aliphatic Compounds), Izd.Nauka, Moscow, 1973, p.750.
113. R.Kh.Freidlina, E.I.Vasil'eva, E.Ts.Chukovskaya, and B.A.Englin, Symposium, "Uspekhi Khimii Polimerov" (Advances in the Chemistry of Polymers), Izd.Khimiya, Moscow, 1966, p.138.
114. C.M.Starks, "Free Radical Telomerization", Acad. Press, New York–London, 1974, p.4.
115. F.R.Mayo, J.Amer.Chem.Soc., 1948, **70**, 3689.
116. B.A.Englin, N.A.Grigor'ev, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 1568.
117. R.G.Gasanov, L.V.Ivanova, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 1011.
118. B.L.Tumanskii, A.N.Degtyarev, N.N.Bubnov, V.P.Solodovnikov, V.I.Bregadze, N.N.Godovikov, and M.I.Kabachnik, Izv.Akad.Nauk SSSR, Ser. Khim., 1980, 2627.
119. R.Kh.Freidlina, N.A.Grigor'ev, T.A.Onishchenko, and B.A.Englin, Dokl.Akad.Nauk SSSR, 1972, **205**, 602.
120. B.A.Englin, N.A.Grigor'ev, and R.Kh.Freidlina, Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 333.
121. R.Kh.Freidlina et al., Dokl.Akad.Nauk SSSR, 1964, **159**, 1346.
122. E.Janzen, D.E.Nutter, and C.A.Evans, J.Phys. Chem., 1975, **79**, 1983.
123. V.E.Zubarev, Khim.Vys.Energii, 1980(1), 86.
124. J.K.Bolton et al., J.Amer.Chem.Soc., 1975, **97**, 1832.
125. D.Forrest and K.U.Ingold, J.Amer.Chem.Soc., 1978, **100**, 3868.
126. A.Levy, D.Meyerstein, and M.Ottolenghi, J.Phys. Chem., 1973, **77**, 3044.
127. J.C.Scaiano and L.C.Stewart, J.Amer.Chem.Soc., 1983, **105**, 3609.

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