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# THE ABSOLUTE RATE CONSTANTS OF THE ELEMENTARY STAGES OF RADICAL POLYMERISATION

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The elementary stages in a polymerisation radical chain reaction can in most cases be summarised as follows:

$$M \rightarrow M^{\cdot}, \quad (1)$$

$$M^{\cdot} + M \xrightarrow{k_p} MM^{\cdot}, \quad (2)$$

$$2M^{\cdot} \xrightarrow{k_t} P. \quad (3)$$

Reaction (1) is initiation, that is, formation of radicals from inactive molecules of the monomer M, reaction (2) is propagation of the reaction chain, leading to growth of the polymeric radical, and reaction (3) leads to the formation of the final reaction product — inactive polymer — and termination of the reaction chain.

Kinetic study of the polymerisation scheme (1) shows that for long reaction chains the dependence of the steady-stage reaction rate $V_{st}$ on the elementary constants is given by the equation

$$V_{st} = I^{1/2} \frac{k_p}{k_t^{1/2}} [M]. \quad (4)$$

Thus the quantity $k_p/k_t^{1/2}$ can be determined from the reaction rate if the rate of initiation $I$ is known. Methods for measuring rates of initiation have been described in detail[1]. $k_p/k_t^{1/2}$ can also be determined[2] from the dependence of the length of the polymer chain on the rate of polymerisation, given by the equation

$$\frac{1}{P_n} = \frac{k_M}{k_p} + \frac{k_t}{k_p^2} \frac{V_{st}}{[M]^2}, \quad (5)$$

where $P_n$ is the number-average degree of polymerisation, usually determined from the viscosity of the polymer solutions, and $k_M$ is the rate constant for chain transfer via the monomer. Schulz and coworkers[3] proposed equations which can be used to calculate the value of $k_p/k_t^{1/2}$ directly from the viscosity-average degree of polymerisation $P_\eta$. The value of $k_p/k_t^{1/2}$ can also be found by measuring the intensity of light scattering in the reaction vessel during the polymerisation[4].

The individual absolute values of the constants $k_p$ and $k_t$ cannot, however, be determined on the basis of Eqns. (4) or (5) alone. An additional equation relating these quantities depends on kinetic measurements of the lifetime of the radicals under non-steady reaction rate conditions.

There are several methods for making non-steady kinetic measurements. In the case of photochemical initiation, the absolute values of the elementary reaction rate constants can be found by intermittent illumination using a rotating sector. An interesting modification of this method has been proposed[5] for studying reactions in a flow system, initiated by $\gamma$-radiation; the glass tube used as reaction vessel was wound in a spiral round a $^{60}Co$ source placed in a lead cylinder with a longitudinal opening. The extensive use of the intermittent-illumination method for studying chain reactions began about 1945.

The theory of the method has been described in detail[1,6]. The practical details are as follows: measurements are made of the steady-state rates with continuous illumination $V_{st}$ and with the rotating sector $V_{int}$ with light–dark interval $T$ chosen in such a way that $V_{int}/V_{st}$ lies in the range 0.50–0.708. The graph giving the theoretical dependence of $V_{int}/V_{st}$ on $T/\tau$ is then used to find $T/\tau$ and hence the lifetime of the free radicals $\tau$. This is related to the constants $k_p$ and $k_t$ by the equation

$$\frac{k_p}{k_t} = \frac{\tau V_{st}}{[M]}. \qquad (6)$$

The method of intermittent illumination does not require a specially sensitive procedure and is simple in operation, but its accuracy is low compared with other methods.

A modified rotating-sector method combined with dilatometric recording of the steady-state rate has been used[7]. These measurements are made at low degrees of conversion, and in the authors' opinion they give better agreement between the theoretical curves and the experimental points than the ordinary rotating-sector method.

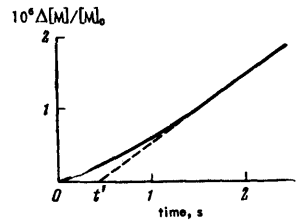
The method of initial non-steady kinetics is based on the determination of the lifetime of the radicals during the establishment of the steady state. The modern form of the theory of this method was put forward by Burnett[8]. The Figure gives the experimental curve for the kinetics of styrene polymerisation and shows clearly the initial non-steady section. The intercept cut off on the time axis by producing the subsequent steady-state section is $t' = \tau \ln 2$. If $\tau$ is known, $k_p/k_t$ can be calculated from Eqn. (6).

These equations refer to quadratic chain termination. It follows from Eqn. (4) that the steady-state rate of polymerisation here is proportional to the square-root of the rate of initiation or, for photochemical initiation, the square root of the incident light intensity. Thus the applicability of Eqn. (4) is verified experimentally from the dependence of the reaction rate on the intensity of illumination. Deviations from the degree of the dependence $n = 0.5$ show that the bimolecular chain termination is accompanied by monomolecular chain termination (with respect to the radical heading the chain), for example, on an impurity X

$$P + X \rightarrow \text{products}. \qquad (7)$$

In the range $n = 0.5$–$0.6$, the corrections to the values of $k_p$ and $k_t$, determined on the assumption that $n$ is equal to exactly 0.50, do not exceed 20%,[9] that is they lie within the limits of the usual accuracy of the determination of kinetic constants. Methods have been proposed for determining these corrections.

Various methods have been proposed for recording the kinetic curve in the initial non-steady stage; these are in




Initial non-steady kinetics for the polymerisation of styrene[11].

fact based on measurement of the increase in temperature in the reaction vessel as a result of the exothermic reaction in the time interval in which it is possible to neglect the loss of heat from the reaction vessel to the thermostat liquid, that is, under so-called pseudo-adiabatic conditions. In the first experiments[10,11], the change in the dielectric constant of the reaction mixture and the change in the refractive index of the liquid were recorded[12]. The increase in temperature was also recorded directly by means of a thermocouple[13] or thermistors[14]. Bengough[15] developed a dilatometric method for recording non-steady kinetics. A method for determining the value of $k_p/k_t$ from light scattering measurements was recently proposed[16].

Study of the initial non-steady kinetics has the indisputable advantage that with the short time interval for a single measurement it is possible to carry out a large number (up to 20) separate measurements on the same specimen, with an appreciable increase in accuracy. The accuracy of the determination of $\tau$ does not exceed 0.1 s, however, and this restricts the applicability of this method, particularly to reactions where the lifetime of the radicals is less than 0.5–0.7 s.

Another group of methods for measuring non-steady kinetics involves the study of reactions after photochemical initiation is stopped. These do not differ in principle from the methods described above, but they exhibit certain characteristic methodological features. In most of them, the rate of the spontaneous thermal reaction is taken into account. To record the reaction rate, Bamford and Dewar[17,18] proposed a viscosimetric method based on the determination of the number-average degree of polymerisation by measurement of the viscosity of the resulting polymer during and after photochemical initiation. Details of the method have been given in a review[19] and a monograph[1]. A modification of the method, which makes it possible to determine the constants directly from the viscosity-average degree of polymerisation and also makes allowance for monomolecular termination, was recently proposed by Okamura and coworkers[20]. The viscosimetric method is rather tedious, involves the solution of cumbersome equations, and has a low accuracy. A method has also been described for determining the chain-growth constant by measuring the rate of emulsion polymerisation under certain conditions[21].

The photochemical after-effect[22] has also been used in the dilatometric determination of polymerisation constants. Benson and North[23] examined some experimental complications associated with the dilatometric measurements (loss of heat from the dilatometer, heating of the reaction mixture as a result of illumination, absence of thermal initiation, presence of monomolecular chain termination, etc.).

We developed a method[24] for determining the value of $k_p/k_t$ from the non-steady kinetics of the photochemical after-effect by measuring the increase in temperature in the period of pseudo-adiabatic conditions. When a slow background reaction, which may be a thermal reaction or a reaction brought about specially by means of constant weak illumination, is taking place in a system, it is found that when the illumination (main initiation) is switched off after a steady-state rate has been attained, the quantity of substance $\Delta M_{qu}$ which has reacted when the reaction is quenched is given by the equation

$$\Delta M_{qu} = k_p n_0 [M](t-\theta) + \frac{k_p}{k_t}[M]\ln\left(\frac{1-q^{-2k_t n_0 (t-\theta)}}{1-q}\right), \quad (8)$$

where $n_0$ is the steady-state concentration of radicals resulting from the background reaction, $\theta$ the moment at which the illumination is switched off, and $q = (V_{st} - V_0)/(V_{st} + V_0)$, where $V_{st}$ and $V_0$ are the steady-state rates of the photoinitiation and the background reaction.

If the reaction vessel in which the background reaction takes place is brought into thermal equilibrium with a thermostat, the increase in temperature for the subsequent switching-on and switching-off of the illumination (main initiation) will be determined by the second term on the right-hand side of Eqn. (8). The total quantity of substance converted at the quenching of the photoinitiated reaction is obtained for $t \to \infty$:

$$\Delta\Delta M = -\frac{k_p}{k_t}[M]\ln\frac{2V_0}{V_{st}+V_0}. \quad (9)$$

This equation can be used to find $k_p/k_t$.

It can be seen that in the photochemical after-affect method, unlike the initial non-steady kinetics method, we record not the duration of the non-steady state, but the quantity of substance converted, which is proportional to the increase in temperature. This quantity is usually determined with a higher accuracy than the duration of the non-steady state. Independent determination of $V_0$ and $V_{st}$ by the dilatometric method also increases the accuracy of the determination of $k_p/k_t$.

The method also makes it possible to carry out measurements where no purely thermal reaction takes place in the system.

An expression identical to (9) was obtained by Bateman and Gee[25] for the quantity of oxygen absorbed at quenching of the photoinitiated oxidation.

Most of the methods for determining the rate constants of the elementary stages of radical polymerisation involve the use of complex highly sensitive instruments, which represent the limits of measuring techniques at the present stage of their development. Methods involving the simpler dilatometric measurements give less reliable results. Almost all methods involve the accurate recording of the start or finish of the photochemical reaction. This feature imposes an additional restriction on the range of materials for which the constants can be measured. This difficulty can apparently be avoided by using a recently-proposed method[26] in which a solution of rapidly-decomposing initiator is sprayed into the monomer, with efficient mixing.

Data on the determination of rate constants for radical polymerisation up to 1958 were collected and critically reviewed by Bagdasar'yan[1]. The present paper will examine chiefly work published in the last five years (up to March 1964), including earlier data for the sake of completeness where necessary.

Sometimes only the overall rate of polymerisation was determined, and information even on the magnitude of $k_p/k_t^{1/2}$ can be obtained from these data only by additional calculation; if the thermal initiator, its concentration, and, most important, the rate of decomposition and efficiency of initiation, determined by an independent method, are known, it is possible to calculate the rate of initiation and the value of $k_p/k_t^{1/2}$. The kinetic behaviour of a number of monomers on polymerisation does not correspond to the kinetic scheme of reactions (1)–(3), and if a new reliable scheme is not proposed, calculation of the constants for these monomers is impossible. Data for individual monomers are given below.

Styrene. Analysis of the most reliable data leads[1] to the following values for the constants† for styrene polymerisation

$$k_p/k_t^{1/2} = 380\exp(-6500/RT), \quad (10)$$

$$k_p = 9.35\times10^6\exp(-7250/RT), \quad (11)$$

$$k_t = 7.1\times10^8\exp(-1500/RT). \quad (12)$$

The values of $k_p/k_t^{1/2}$ recently obtained from the length of the polymer chains[20,27-29] are almost the same as those calculated from Eqn. (10). Henrici-Olivé and Olivé[29], on the basis of their measurements and published data, obtained the expression

$$k_p/k_t^{1/2} = 135\exp(-5700/RT), \quad (13)$$

which is almost the same as (10). Moreover, in these experiments attention was directed to the part played in chain termination by the primary radicals formed by decomposition of the initiator. It was shown[20,27] that at low concentrations of the usual initiators (azoisobutyronitrile, benzoyl peroxide) relative to the monomer, the recombination of the primary radicals with polymeric radicals can be neglected, but with an initiator such as phenylazotriphenylmethane, which gives stable triphenylmethyl radicals with low activity, it is necessary to make allowance for termination by primary radicals even at an initiator concentration of $10^{-4}$ M.[28] An important part is also played by primary radicals in chain termination for initiation of styrene polymerisation by the thermal decomposition of the polymeric peroxides of dibasic organic acids[30].

The value of $k_p$ at 40°, determined by Burnett and Lehrle[31] by the emulsion polymerisation method is only 14% lower than the value calculated from Eqn. (11).

Methyl methacrylate. On the basis of a thorough critical analysis of a large amount of experimental data, Bagdasar'yan[1] obtained the following equations for the constants for methyl methacrylate polymerisation

$$k_p/k_t^{1/2} = 95\exp(-4500/RT), \quad (14)$$

$$k_p/k_t = 1.35\times10^{-2}\exp(-4300/RT). \quad (15)$$

Recent years have seen the appearance of a fairly large number of papers devoted to the kinetics of the polymerisation of methyl methacrylate; studies have been made not only of the initial stage of polymerisation, but also of the kinetics at high degrees of conversion and in solvents with

† The values for all the constants are given in mole litre$^{-1}$ s$^{-1}$.

different viscosities. These data will be discussed later. The results of the determination of the kinetic constants at very low degrees of conversion are compared in Table 1 with the values obtained from Eqns. (14) and (15).

Schulz and coworkers[3] found that in the polymerisation of methyl methacrylate in benzene solution at 30–80° the equation

$$k_p/k_t^{1/2} = 53\exp(-4200/RT), \quad (16)$$

is satisfied.

It can be seen from the above data that the results of recent work show good agreement with Eqns. (14) and (15); the deviation from these equations is determined by the accuracy of the measurements. Values of $k_p/k_t^{1/2}$ were determined[27,34] viscosimetrically from the relationship between molecular weight and characteristic viscosity for non-fractionated polymers, and this method has been supplemented[3] by initiation by means of an initiator labelled with $^{14}C$ and by determination of the molecular weight of individual fractions by an osmotic method. The rate of initiation has been determined using $^{14}C$ [33] and from the rate of the reaction of radicals from the initiator azocyclohexane-1,1′-carbonitrile with diphenylpicrylhydrazyl in chloroform solution[32]. The ratio $k_p/k_t^{1/2}$ was determined from the initial non-steady kinetics using a thermocouple[32,33] and dilatometrically from the photochemical after-effect[34,35].

The ratio of the rate constants for chain termination by disproportionation $k_{dis}$ and by recombination of the radicals $k_{rec}$ was also determined[3]

$$\log(k_{dis}/k_{rec}) = 2.89 - 1000/T, \quad (17)$$

which gives for the difference in the energies of activation $E_{dis} - E_{rec} = 4.6$ kcal mole$^{-1}$. From Eqn. (17) at 60°, $k_{dis}/k_{rec} = 0.78$, which, although it differs from the accepted[1] value of 0.67, produces a change of only 4–5% in the calculated value of $k_p/k_t^{1/2}$. Determination of $k_{dis}/k_{rec}$ from the quantity of radioactive initiator fragments in the polymer gave the value 1.35 at 60°.[36]

North and coworkers[37] studied the polymerisation of methyl methacrylate in the range from -60° to -20° in ethyl acetate solution. The reaction was initiated by ethylsilver, whose rate of decomposition was used to calculate the rate of initiation. The kinetics of the polymerisation are described by the equation;

$$V = 1.7\exp(-5100/RT)\,[MMA]^{3/2}\,[AgC_2H_5]^{1/2}.$$

Extrapolation of Eqn. (17) shows that at these low temperatures, termination takes place chiefly by the recombination of radicals. The values of $k_p/k_t^{1/2}$ determined with this assumption from the length of the polymer chains are greater by a factor of 2.5 than the value expected from Eqn. (14). It is suggested that ethylsilver forms a complex with methyl methacrylate. The reaction is initiated by the reverse decomposition of this complex to metallic silver and a free radical.

Atkinson and Cotten[22] studied the polymerisation of methyl methacrylate in aqueous solution at 25° and obtained the values $k_p = 75$ litre mole$^{-1}$ s$^{-1}$ — Eqns. (14) and (15) give $k_p = 252$ — and $k_t = 1.8 \times 10^4$. Although $k_p$ does not differ greatly from the usual value, the rate of termination in water is greater by three orders of magnitude than that in organic systems.

Ethyl methacrylate. In the range 35–100°, for polymerisation "in bulk" with azoisobutyronitrile initiator, the viscosimetric method gave the value[38] $k_p/k_t^{1/2} = 77.6\exp(-4220/RT)$. The degree of polymerisation was determined from the characteristic-viscosity relationship for fractionated polymers.

n-Propyl methacrylate. The rotating sector method at 30° [39] gave $k_p/k_t = 0.070$, $k_p = 467$, and $k_t = 4.5 \times 10^7$. The rate of initiation was determined from the diphenylpicrylhydrazyl consumption.

n-Butyl methacrylate. $k_p/k_t^{1/2} = 0.116$ at 30° [39] and 0.196 at 60°.[40] The last value was determined without allowance for $k_{dis}/k_{rec}$, but differs from the value calculated from the rate of decomposition of the initiator by only 15–30%. From these two points, $k_p/k_t^{1/2} = 50\exp(-3500/RT)$. At 30° "in bulk" $k_p/k_t = 3.62 \times 10^{-5}$ [39] and in ethyl acetate solution $k_p/k_t = 9.1 \times 10^{-5}$.[35] Making use of the value of $k_p/k_t^{1/2}$, we have $k_p = 147$–$362$ and $k_t = (1.0$–$1.6) \times 10^7$.

Isobutyl methacrylate. Khanna and coworkers[38] obtained the value $k_p/k_t^{1/2} = 55.3\exp(-4000/RT)$. The value obtained at 60°[40] is $k_p/k_t^{1/2} = 0.180$, which is only 14% less than that found by Khanna and coworkers[38] by the same method. In ethyl acetate solution at 30°, $k_p/k_t = 9.1 \times 10^{-5}$,[35] which with the above data gives $k_p = 109$ and $k_t = 1.2 \times 10^7$ at 30°.

t-Butyl methacrylate. Grant and Grassie[41] found for the polymerisation "in bulk" and in benzene solution at 20–90° the value $k_p/k_t^{1/2} = 0.0955$ at 25° and $E_p - \frac{1}{2}E_t = 3.85$ kcal mole$^{-1}$. The value of $k_p/k_t^{1/2}$ was determined viscosimetrically from the length of the polymer chains; it was assumed that $k_{rec} = 0$. The rotating-sector method gave $k_p/k_t = 6.5 \times 10^{-3}\exp(-3300/RT)$, so that $E_p = 4.4$ kcal mole$^{-1}$ and $E_t = 1.1$ kcal mole$^{-1}$; at 30°, $k_p = 410$ and $k_t = 1.4 \times 10^7$.

Comparison of the data for the butyl methacrylates shows that the rotating-sector method gives a value for $k_p$ which is 2–4 times that given by the dilatometric method of Benson and North[34]. It is difficult to give preference to either set of data, particularly since the determination of $k_p/k_t^{1/2}$ and $k_p/k_t$ by the rotating-sector

TABLE 1. Values of $k_p$ and $k_t$ for methyl methacrylate.

| Temperature, °C | $k_p/k_t^{1/2}$ | | $10^4 k_p/k_t$ | |
|---|---|---|---|---|
| | from Eqn. (14) | measured | from Eqn. (15) | measured |
| 22.5 | 0.049 | 0.058[33] | 0.93 | 0.87 [33] |
| 30 | 0.056 | | 1.12 | 4.0 [34] |
| 30 | | | | 1.4* [34] |
| 30 | | | | 1.43*[35] |
| 32 | 0.052 | 0.044[32] | 1.18 | 1.9 [32] |
| 40 | 0.072 | 0.096*[34] | 1.41 | 2.3* [34] |
| 60 | 0.11 | 0.128[37] | | |
| 60 | | 0.144**[37] | | |
| 70 | 0.135 | 0.13**[27] | | |
| 70 | | 0.15*[27] | | |

* In ethyl acetate solution.

** In toluene solution.

method was carried out "in bulk" and the determination of $k_p/k_t$ by the dilatometric method was carried out in the less viscous ethyl acetate solution.

Nonyl methacrylate. The value $k_p/k_t^{1/2} = 24.3 \exp(-2590/RT)$ has been obtained[38] (the structure of the nonyl group is not indicated). The value $k_p/k_t = 1.8 \times 10^{-4}$ was obtained for 3,5,5-trimethylhexyl methacrylate in ethyl acetate solution at 30°.[35] If we assume that the same substance was studied in the two instances and neglect the difference in viscosity, calculation gives $k_p = 620$ and $k_t = 3.45 \times 10^6$ for 30°. The value of $k_p$ is evidently several times too high.

Cetyl methacrylate. The viscosimetric method (by analogy with other methacrylates it was assumed that $k_{rec} = 0$) in the range 50–80° gave the expression[42] $k_p/k_t^{1/2} = 42.3 \exp(-2500/RT)$, which on extrapolation to 30° gives $k_p/k_t^{1/2} = 0.69$. Dobó and Friese[43] by rough calculation obtained $k_t = 3 \times 10^6$ at 24°, from which $k_p = 98$ at 30°.

A detailed study has been made, for the polymerisation of alkyl methacrylates, of the influence of viscosity on the magnitude of the polymerisation rate constants, noted by Bengough and Melville[44] in a study of the polymerisation of vinyl acetate at high degrees of conversion. North and coworkers[34,35] studied this effect by carrying out the polymerisation at a low degree of conversion in solvents with different viscosities, and found that for methyl methacrylate the value of $k_t/k_p$ is inversely proportional to the viscosity throughout the entire range of viscosity studied $\eta = 0.42$–1000 cP, the lower value being less than the viscosity of the monomer. The value of $k_t/k_p$ is proportional to $\eta^{-0.8}$ for butyl methacrylate and to $\eta^{-0.735}$ for nonyl methacrylate. Subsequently, like a number of other authors and following published conclusions[32,33,39], we shall assume that the chain-growth constant for alkyl methacrylates is independent of the viscosity and the length of the side chain (thus in the analysis it is sometimes more convenient to use the reciprocal $k_t/k_p$ instead of the usual ratio $k_p/k_t$). The dependence of the termination rate constant on the length of the side-chain or the solvent, however, is evidently determined by the change in the rate of diffusion of the polymeric radicals and not by polar or steric effects, as has been suggested[27,38].

Since the values of $k_t/k_p$ were given[34,35] for a low viscosity and the values of $k_p/k_t^{1/2}$ were determined "in bulk"[38], the individual rate constants calculated above from these data give merely an indication of the order of magnitude and have no claim to accuracy. It would be of interest to compare the constants obtained at the same viscosity. For this it is necessary to know the viscosity of each monomer, but we have been unable to find this information, apart from data[42] for the viscosity of methyl methacrylate (0.34 cP) and cetyl methacrylate (3.18 cP) at 70°. Calculation based on some rather arbitrary assumptions[45] gives values (Table 2) which reveal certain trends. It is evident that discussion of the influence of structure on the rate of termination for a system where it is determined by diffusion for some substances and lies in the kinetic range for other substances can lead to incorrect conclusions. As far as the values of the constants are concerned, Table 2 shows that at constant viscosity the decrease in the termination rate constant with increase in the dimensions of the ester group is irregular: with increase in the number of carbon atoms from 1 to 4 the termination rate constant decreases by a factor of 4–5,

TABLE 2. Dependence of the rate constants for the polymerisation of alkyl methacrylates on viscosity at 30° (approximate calculation).

| Methacrylate | Viscosity of monomer, cP (estimated) | $k_p$ | | $10^{-7} k_t$ | |
|---|---|---|---|---|---|
| | | for $\eta$ = 0.42 cP | "in bulk" | for $\eta$ = 0.42 cP | "in bulk" |
| Methyl | 0.42 | 270 | 270 | 2.5 | 2.5 |
| n-Propyl | 0.96 | 220 | — | 2.1 | — |
| n-Butyl | 1.23 | 62 | 93 | 0.68 | 0.065 |
| Isobutyl | 1.23 | 51 | — | 0.56 | — |
| Nonyl | 2.58 | 170 | 130 | 0.010 | 0.014 |

whereas further increase up to 9 leads to an increase in the constant by a further factor of 50–60. For a group of medium size (butyl) change in viscosity has a significant influence on the rate of termination, whereas for the bulky nonyl group the viscosity of the surrounding medium is no longer important.

Atherton and North[46] showed that for the copolymerisation of methyl methacrylate and vinyl acetate at 30° and 60° the termination is also determined by diffusion of the polymeric radicals.

According to North[34,35] diffusion termination takes place in three stages. The first stage involves the translational diffusion of two macroradicals into a position in which some segments of each chain are brought into contact. In the second stage, rearrangement or segmental diffusion takes place so that the ends of the two radicals approach sufficiently closely to one another for the third stage — chemical interaction — to take place. This scheme can be represented as follows:

$$P^{\cdot}_A + P^{\cdot}_B \rightarrow [P^{\cdot}_A \ldots P^{\cdot}_B], \quad (18)$$

$$[P^{\cdot}_A \ldots P^{\cdot}_B] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [P_A : P_B], \quad (19)$$

$$[P_A : P_B] \xrightarrow{k_2} \text{products}. \quad (20)$$

It was shown[34] that the first stage is not the limiting stage. A model was proposed for the polymeric radical[35], in which the end of the chain is regarded as a cylinder whose axis coincides with the main C–C axis of the polymer chain and whose radius is determined by the dimensions of the lateral groups. From the dependence of the reaction rate on the size of the alkyl groups it was shown that the model corresponds to the experimental data. On the basis of scheme (18)–(20), Guertin[47] derived equations relating the rate of the individual stages to the rate and degree of polymerisation and also to the rate of initiation $I$, and obtained by calculation from the experimental data for methyl methacrylate[46] the values $k_{-1}/k_2\eta = 0.16$ P and $I\eta/k_1 = 9.16 \times 10^{-18}$ mole$^2$ P$^{-1}$.

Examination of these "hyper-elementary" stages became possible only as a result of the development of kinetic experiment and demonstrates how the fine effects of a chemical reaction can be revealed by modern methods.

Glycidyl methacrylate $CH_2-CHCH_2O-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}=CH_2$.

The length of the polymer chains was determined[48] for polymerisation "in bulk" in the range 40–80°; the value of $k_p/k_t^{1/2}$ was also calculated from the rate of decomposition of the initiators. It was found that $k_{dis}/k_{rec} = 2.7$ and $k_p/k_t^{1/2} = 52.6 \exp(-3800/RT)$, which for 30° gives $k_p/k_t^{1/2} = 0.095$. The same authors[48], on the basis of the assumption that $k_p/k_t$ is proportional to $k_p/k_t^{1/2}$ and

that $E_t$ = 400 kcal mole$^{-1}$, obtained for glycidyl methacrylate, by comparison with the value of $k_p/k_t$ for methyl methacrylate, the values $k_p = 4.13 \times 10^5 \exp(-4000/RT)$ and $k_t = 6.17 \times 10^7 \exp(-400/RT)$. From the data of Arbuzova and Efremova[49] for polymerisation "in bulk" at 70° with benzoyl peroxide initiator, it follows that the rate of polymerisation is approximately proportional to the square root of the initiator concentration. Assuming that the rate constant for the decomposition of benzoyl peroxide is $9.60 \times 10^{-6}$ s$^{-1}$ and that the efficiency of initiation is 0.8,[1] we obtain by calculation $k_p/k_t^{1/2} = 0.242$.

Benzyl methacrylate. Calculation by the same method from Majer's data[50] gives $k_p/k_t^{1/2} = 0.0338$ at 60° and 0.0362 at 70°.

Methyl acrylate. Data from recent papers, published simultaneously, which give the constant determined by the rotating-sector[51] and dilatometric[52] methods, differ little: $k_p = 1.45 \times 10^6 \exp(-4700/RT)$[51] and $k_t$ = $= 3.55 \times 10^8$ [51] and $6.5 \times 10^8$.[52] In one[51] it was assumed that $k_{rec} \simeq 0$, and in the other[52] the rate of initiation was determined from the rate of consumption of diphenylpicrylhydrazyl. The determinations using diphenylpicrylhydrazyl apparently gave slightly high values for $k_p/k_t^{1/2}$.[41]

Butyl acrylate. Melville and coworkers[13,53], from initial non-steady kinetics using a thermocouple, recently obtained the value $k_p/k_t = 6.2 \times 10^{-5}$ at 25°. Benson and North[34], using the dilatometric method at 30°, obtained $k_p/k_t = 12.5 \times 10^{-4}$ "in bulk" (this result coincides with the earliest determination for butyl acrylate[53]) and $8.33 \times 10^{-4}$ in ethyl acetate solution. Having determined the rate of initiation in separate experiments from the rate of consumption of diphenylpicrylhydrazyl, Bengough and Melville[53] obtained $k_p = 2100$ and $k_t = 3.3 \times$ $\times 10^8$ at 25°. These figures are greater, by factors of 4 and 400 respectively, than those adopted[1] on the basis of the values of $k_p/k_t^{1/2}$ found by other methods. For the activation energy it was found by $E_p - \frac{1}{2}E_t = 3.8$ kcal $\times$ $\times$ mole$^{-1}$. It is difficult to give preference to any of the data for butyl acrylate.

Methyl α-cyanoacrylate. For radical polymerisation with azoisobutyronitrile at 60°, $k_p/k_t^{1/2}$ = = 0.145 [55]; 100% efficiency of initiation was assumed in the calculations.

Vinyl chloride. Supplementary to earlier[1] contradictory results, Bengough and coworkers[7] obtained $k_p/k_t = 7.1 \times 10^{-7}$ at 25°, which is smaller by a factor of 10 than the value found by Burnett and Wright[56] by the rotating-sector method.

Vinyl acetate. Recent results[15,57-59] show good agreement with the equations adopted earlier[1]: $k_p = 1.13 \times$ $\times 10^6 \exp(-4200/RT)$ and $k_t = 3.12 \times 10^7$. The rate of polymerisation of vinyl acetate changes in a complex fashion with increase in the degree of conversion[44,60] and increases with increase in the viscosity of the solvent[46]. It was established[60] that in polymerisation "in bulk" the rate of diffusion of the macroradicals begins to exert a significant influence on the value of $k_t$ from a degree of conversion equal to 2%, whereas $k_p$ remains unchanged up to 50% conversion.

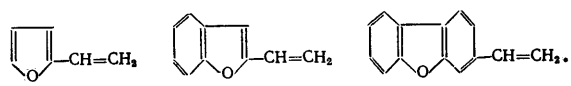
Vinyl benzoate. For polymerisation "in bulk", $k_p/k_t^{1/2} = 0.0255$ at 60° [61] and 0.14 at 79.6°.[62] The first figure[61] is more reliable, since the molecular weights were determined by an osmometric method and the length of the polymer chain was determined using an initiator labelled with $^{14}C$. In the second case[62] the molecular weight was determined from the viscosity of solutions of the polymers from the formula for fractionated polymers, without appropriate corrections.

1-Vinylnaphthalene. The value $k_p/k_t^{1/2}$ = $= 3.92 \times 10^2 \exp(6150/RT)$ was obtained[63] from the dependence of the rate of polymerisation "in bulk" at 50–70° on the concentration of azoisobutyronitrile, with allowance for its rate of decomposition. The constant for chain transfer via the monomer is very high, $k_M = 0.03$. Naphthalene, which generally speaking reacts more readily with radicals than benzene, is activated further by the vinyl group.

Isopropenyl methyl ketone $CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}=CH_2$.

For polymerisation "in bulk" and in toluene solution with benzoyl peroxide at 80°, from the length of the polymer chains, $k_p/k_t^{1/2} = 0.0278$.[64]

2-Vinylfuran, 2-vinylbenzylfuran, and 2-vinyldibenzylfuran



Calculation from the graphs given by Andreeva and Koton[65] on the assumption that Eqn. (4) applies (the dependence of the rate on the concentration of monomer and benzoyl peroxide initiator has not been determined experimentally) gives for polymerisation "in bulk" and in solution at 80–100° the values $k_p/k_t^{1/2} = 0.001$–$0.0025$ for 2-vinylfuran, 0.004–0.008 for 2-vinylbenzylfuran, and 0.006–0.021 for 2-vinyldibenzylfuran.

2-Vinylpyridine. For the rate of polymerisation with azoisobutyronitrile at 50–90°, the equation $V = 1 \times$ $\times 10^9 \exp(-2400/RT)$ s$^{-1}$ has been obtained[66]. Calculation of the rate of initiation with the usual assumptions gives $k_p/k_t^{1/2} = 0.088$ at 50° and 0.281 at 90°, and $E_p - \frac{1}{2}E_t$ = = 5.2 kal mole$^{-1}$; extrapolation to 25° gives $k_p/k_t^{1/2}$ = = $7.4 \times 10^{-3}$. This calculation gives a value which differs from those for other vinylpyridines at 25° by a factor of only 3–4.

4-Vinylpyridine. Using the viscosimetric method at 25°, Onyon[67] obtained the values $k_p = 12$, $k_t = 3 \times 10^6$, and $k_M = 8 \times 10^{-3}$. The value $k_p/k_t = 1.9 \times 10^{-5}$ was obtained for polymerisation "in bulk" and in ethanol solution from the adiabatic increase in temperature[68]. The difference between these data and Onyon's data ($0.4 \times 10^{-5}$) is apparently due to the low accuracy of the viscosimetric method for determining the values of $k_p$ and $k_t$.

2-Methyl-5-vinylpyridine. The polymerisation was carried out[69] in benzene solution at 60–80° with azoisobutyronitrile and benzoyl peroxide. The rate is proportional to the square root of the initiator concentration. Calculation from the graphs gives values of $k_p/k_t^{1/2}$ which differ slightly for each initiator: 0.031 and 0.042 at 80° and 0.020 and 0.034 at 60°; extrapolation to 25° gives the

values 0.008 and 0.021. At 25°,[68] $k_p = 47$, $k_t = 3.5 \times 10^6$, and $k_M = 3.9 \times 10^{-3}$. In the determination of $k_p/k_t^{1/2}$ and $k_M$, the length of the polymer chains was calculated from the viscosity using a formula recalculated for the non-fractionated polymer with allowance for termination by chain transfer.

*N*-Vinylurethane[70]. The degree of polymerisation at 60° with azoisobutyronitrile was determined by an osmometric method. If it is assumed that $k_{rec} = 0$, the efficiency of initiation is $f = 0.59$ and $k_p/k_t^{1/2} = 0.52$ (if it is assumed that $k_{rec} > 0$, the value of $f$ increases; for this initiator, however, $f$ very rarely exceeds 0.6).

Acrylonitrile. The early data[1] are extremely contradictory. The value of $k_p$ at 60° varies in the range 425–1960, and $k_t = 1.2 \times 10^7$–$7.8 \times 10^6$. For a long time it was assumed[71] that termination takes place by disproportionation of the polymeric radicals, but Bailey and Jenkins[72] showed, using tracer methods, that the chains are terminated by recombination of the radicals. Bengough[7] obtained the value $k_p/k_t = 3.4 \times 10^{-6}$ by a combined method in dimethylformamide solution at 25°, and the values $k_p = 52$ and $k_t = 5.0 \times 10^6$ by the thermocouple method "in bulk"[73] at a degree of conversion less than 0.1%, when the polymer has not yet precipitated from its solution in the monomer. These data show satisfactory agreement with our results[68] for dimethylformamide solution: $k_p = 2.35 \times 10^5 \exp(-6400/RT)$, $k_t = 1.8 \times 10^6$, and $E_t \simeq 0$.

The polymerisation of acrylonitrile in dimethylformamide was also studied by the rotating-sector method with initiation by $\gamma$-rays[74]. The reaction rate depends on the intensity of irradiation to the power 0.60. The Arrhenius relationship is observed in the range 0–60°; the values found were $E_p = 3.88$ kcal mole$^{-1}$ and $E_t = 3.70$ kcal mole$^{-1}$. The results for 60°, $k_p = 660$ and $k_t = 8.65 \times 10^7$, agree with earlier data, within the limits of experimental error.

Comparison of the rates of the elementary stages of the polymerisation of nitrogen-containing monomers and styrene at 25° (Table 3) shows that the influence of the free electron pair of the nitrogen is the same for direct conjugation with the C=C double bond in acrylonitrile and for the transfer of this influence through the system of conjugated aromatic bonds in the vinylpyridines. The difference of one order of magnitude in the rates of chain termination indicate a sharp difference in the properties of the polystyrene radical compared with the polyacrylonitrile and polyvinylpyridine radicals. It is possible that the greater mobility of the polystyrene radical brings about more rapid segmental diffusion, compared with the relatively rigid polyacrylonitrile and polyvinylpyridine radicals.

Methacrylamide. For photopolymerisation in aqueous solution, initiated by $H_2O_2$, at 10–40°, the rotating-sector method[75] gave $k_p = 4 \times 10^5 \exp(-3700/RT)$ and $k_t = 1.3 \times 10^{10} \exp(-4000/RT)$. In the calculation of the rate of initiation, the quantum yield was taken as 0.87, by analogy with the reaction for acrylamide.

Esters of vinylphosphonic acid $CH_2=CH-PO(OR)_2$ were polymerised[76] at 50° with 2 mole% benzoic acid. The kinetic curves were used to calculate the values of $k_p/k_t^{1/2}$ for different esters: methyl 0.23, ethyl 0.14, n-propyl 0.23, isopropyl 0.12, n-butyl 0.36, isobutyl 0.22, and isopentyl 0.34.

TABLE 3.

| | Acrylonitrile | 4-Vinylpyridine | 2-Methyl-5-vinylpyridine | Styrene |
|---|---|---|---|---|
| $k_p$ | 51 | | 47 | 44 |
| $k_t$ | $1.8 \cdot 10^6$ | | $3.5 \cdot 10^6$ | $4.0 \cdot 10^7$ |
| $\frac{k_p}{k_t}$ | $2.8 \cdot 10^{-5}$ | $1.9 \cdot 10^{-5}$ | $1.3 \cdot 10^{-5}$ | $1.1 \cdot 10^{-6}$ |

Ethylene. The kinetics of the radical polymerisation of ethylene under the influence of suitable initiators under pressure in the liquid phase or in solution have been studied only recently. For polymerisation "in bulk" at a pressure of 40 atm under the influence of the photochemical decomposition of dimethyl azoisobutyrate at 0°, the viscosimetric method[77] gave the value $k_p/k_t^{1/2} = 5.2 \times 10^{-4}$. It was assumed that $k_{dis} = 0$. The efficiency of the initiation was found to be only 0.05. For polymerisation in t-butyl alcohol[78] under the influence of diethyl peroxydicarbonate at 60° and ~50 atm, $k_p/k_t^{1/2} = 0.0182$. The initial rate depends on the concentration of initiator to the power 0.5. An independent method gave for the rate constant for the decomposition of the initiator in ethylene $k_{decomp} = 5 \times 10^{17} \exp(-33\,000/RT)$. The number-average molecular weight was determined ebulliometrically: the efficiency of initiation was close to 1.

Laita[79,80] obtained the values $k_p = 470$ and $k_t = 1.05 \times 10^9$ by the rotating-sector method at 83° in benzene solution; termination takes place by disproportionation of the radicals. Monoradical termination at initiator also takes place in the system with a rate constant of 185. The rate of initiation for the photodecomposition of azomethane was determined by the inhibition method and also from the number-average molecular weight of the polymer. The polymerisation at high pressures (750–2500 atm) was studied[81] in propane solution at 129° with di-t-butyl peroxide initiator. The rate of polymerisation is approximately proportional to the pressure and to the square root of the initiator concentration. With the assumption that the rate of decomposition of the initiator is independent of the pressure and that the efficiency of initiation is equal to 1, the values found for $k_p/k_t^{1/2}$ were 0.22 at 750 atm and 0.73 at 2500 atm.

Rabel and Ueberreiter[82] studied the polymerisation of ethylene "in bulk" for the photodecomposition of the same initiator at -20°. With the assumption that chain termination takes place by disproportionation, calculation by the method proposed by Schulz and coworkers[3] from the dependence of the viscosity-average degree of polymerisation on the reaction rate gave the value $k_p/k_t^{1/2} = 8.7 \times 10^{-4}$. The rotating-sector method gave $k_p/k_t = 4.1 \times 10^{-8}$. These values give $k_p = 18.6$ and $k_t = 4.55 \times 10^8$. Marked deviations have been observed[79,80,82] from the power $n = 0.50$ for the dependence on the intensity of initiation (up to $n = 0.76$); corrections were introduced by the method proposed by Burnett and Wright[83].

The data given for the constants for the elementary stages of the polymerisation of ethylene are contradictory. The values of $k_p/k_t^{1/2}$ from different papers do not lie on the Arrhenius straight line. This is apparently due to the low solubility of polyethylene in the monomer and also to the necessity to work under considerable pressures, different for different temperatures, in the determintion

of the constants "in bulk". The value of $k_p/k_t^{1/2}$ shows a marked pressure dependence at 750–2500 atm,[81] and it is not excluded that the dependence on pressure is preserved even at 20–60 atm. The nature of the solvent used in a number of experiments also appears to influence the value obtained for the constants.

Isoprene. The radical polymerisation of isoprene, like that of ethylene[78] (see above), stops at low degrees of conversion $x$ as a result of consumption of the initiator. Treatment of these limiting conversion phenomena ("dead end") gives the equations[84]

$$-\ln(1-x_\infty)=2k_p\left(\frac{f(I)_0}{k_t k_{decomp}}\right)^{1/2}$$

and

$$\frac{\ln(1-x)}{\ln(1-x_\infty)}=1-e^{-\frac{k_{decomp}t}{2}},$$

which can be used to find the rate constant for the decomposition of the initiator $k_{decomp}$ from the polymerisation kinetic curves. If the efficiency of initiation $f$ is found by an independent method, the above equations can be used to determine $k_p/k_t^{1/2}$.

For the polymerisation of isoprene[85] "in bulk" at 60–90°, this method gave $k_p/k_t^{1/2}=1\times10^4\exp(-9800/RT)$. Taken with the value $k_p=1.2\times10^8\exp(-9800/RT)$, determined by emulsion polymerisation[86], this gives $k_t=1.34\times\times10^8$.

2,3-Dimethylbuta-1,3-diene. Emulsion polymerisation in the range 5–60°[87] gave the value $k_p=8.9\times\times10^7\exp(-7000/RT)$.

Maleic anhydride. The rate of free-radical polymerisation[88] "in bulk" at 74.5° with benzoyl peroxide is directly proportional to the square root of the initiator concentrations. The length of the polymer chains gives the value $k_p/k_t^{1/2}=0.0092$.

The reactions of telomerisation and the addition of radicals across the double bond of vinyl compounds are similar to polymerisation reactions. In recent years a number of kinetic studies have been made of the reactions involved in the addition of bromotrichloromethane to certain monomers and various compounds containing a double bond. The method used to determine the rates of the elementary steps in these reactions is basically the same as that used for polymerisation reactions. Photochemical reactions involving $CCl_3Br$ are convenient since no sensitising agent is required. $CCl_3Br$ decomposes to $CCl_3^\cdot$ and $Br_3^\cdot$ radicals under the influence of ultraviolet light.

The photochemical addition of bromotrichloromethane to vinyl compounds (denoted M) with the formation of the 1:1 adduct involves the following elementary steps[89]:

$$CCl_3Br+h\nu\longrightarrow CCl_3^\cdot+Br^\cdot \qquad I \qquad (22)$$

$$CCl_3^\cdot+M\longrightarrow CCl_3M \qquad k_2 \qquad (23)$$

$$CCl_3M^\cdot+BrCCl_3\longrightarrow CCl_3MBr+CCl_3^\cdot \qquad k_3 \qquad (24)$$

$$CCl_3^\cdot+CCl_3^\cdot\longrightarrow C_2Cl_6 \qquad k_4 \qquad (25)$$

$$CCl_3^\cdot+CCl_3M^\cdot\longrightarrow \text{products} \qquad k_5 \qquad (26)$$

$$CCl_3M^\cdot+CCl_3M^\cdot\longrightarrow \text{products} \qquad k_6 \qquad (27)$$

Kinetic analysis of the scheme by the method of quasi-steady states gives the equation

$$V_{st}=-\frac{d[M]}{dt}=\frac{k_2 I^{1/2}[M]}{k_4^{1/2}}\times\frac{1}{\sqrt{1+\frac{k_5}{k_4}\left(\frac{k_2}{k_3}\right)^2\left[\frac{[M]}{[CCl_3Br]}\right]^2+\frac{k_2k_5[M]}{k_3k_4[CCl_3Br]}}}, \qquad (28)$$

which becomes Eqn. (4) with $k_p=k_2$ and $k_t=k_4$, if $\alpha=[M]/[CCl_3Br]$ is sufficiently small. The steady-state rate can also be expressed in terms of the $CCl_3Br$ concentration and then the expression, analogous to (29), becmes Eqn. (4) with $k_p=k_3$ and $k_t=k_6$ if $1/\alpha$ is sufficiently small. Thus the values of $k_2$ and $k_4$ are determined in experiments with an excess of $CCl_3Br$ and $k_3$ and $k_6$ are determined in an excess of M. The applicability of Eqn. (4) here is determined experimetanlly from the linear dependence of the steady-state rate on the concentration of M or $CCl_3Br$ respectively, and also from the dependence of $V_{st}$ on the square root of the intensity of illumination.

The reaction of $CCl_3Br$ with cyclohexene. Melville and coworkers[90] obtained the following values for the constants in a large excess of $CCl_3Br$ at 30–50°: $k_2=4\times10^5\exp(-3400/RT)$, $k_4=1\times10^8$, and $E_4=0$. The ratio $k_2/k_4$ was determined by the rotating-sector method and the rate of initiation was found from the rate of consumption of the inhibitor tetrachloro-*o*-quinone.

These determinations were repeated[24] at 25° from the adiabatic increase in temperature and the value $k_2/k_4=2.1\times10^{-5}$ was obtained. The effective activation energy for the photochemical reaction $E_2-\frac{1}{2}E_4=3.5$ kcal, which agrees with Melville's data. The determination of the rate of initiation by the usual method involving the introduction of an inhibitor into the photoinitiated reaction may lead to errors, since tetrachloro-*o*-quinone absorbs light strongly even at the low concentrations required for measurement of the rate of initiation. The value $k_2/k_4^{1/2}=0.87\times10^{-2}$ was obtained at 60° from the rate of decomposition of inhibitor in the reaction initiated by the thermal decomposition of azoisobutyronitrile, and agreed with the value calculated from the rate of decomposition of the initiator for $f=0.40$. The activation energy can be used to calculate $k_2/k_4^{1/2}$ at other temperatures. The values $k_2=1100$ litre mole$^{-1}$ s$^{-1}$ and $k_4=0.52\times10^8$ litre mole$^{-1}\times\times$ s$^{-1}$ were obtained in this way. That the values of $k_2/k_4^{1/2}$ determined by Melville and coworkers[90] and by Bagdasar'yan and Revzin[24] differ by a factor of six is evidently due to some inaccuracy in the former determination[90] (see our paper[24] for more detail).

It was shown[91] that the reaction of $CCl_3Br$ with cyclohexene involves not only the addition of the $CCl_3^\cdot$ radical across the double bond but also the removal of an $\alpha$-hydrogen atom:

$$CCl_3^\cdot+C_6H_{10}\longrightarrow CHCl_3+C_6H_9^\cdot \qquad k_7 \qquad (29)$$

The ratio $k_2/k_7$ was recently determined[92] for a number of hydrocarbons. For cyclohexene, $k_2/k_7=1.20$ at 78° and 1.85 at 40°. From these two points, $E_2-E_7=-2.5$ kcal$\times\times$ mole$^{-1}$, so that $E_7=6.0$ kcal mole$^{-1}$. Extrapolation to 25° gives $k_2/k_7=2.28$, that is $k_7=483$ litre mole$^{-1}$ s$^{-1}$‡.

‡ Bagdasar'yan and Revzin[24] give slightly different figures for $k_2$ and $k_7$, since the experimentally-determined value of $k_2$ was erroneously taken[24] as the sum of the rate constants for reactions (23) and (29). This point was brought to our attention by A.N. Pravednikov.

For an excess of cyclohexene, Melville and coworkers[93] obtained the values $k_3 = 63.8$, $E_3 = 4.5$ kcal mole$^{-1}$, $k_7 = 4 \times 10^7$, and also $k_5 = 5.7 \times 10^8$. The activation energy for termination $E_6 = E_5 \simeq 0$.

The reaction of $CCl_3Br$ with hept-1-ene was studied[24] at different reagent ratios in the range 15–40°. The rate of initiation in an excess of $CCl_3Br$ was assumed to be the same as in the reaction with cyclohexene, and the rate of initiation in an excess of hept-1-ene was calculated at 60° from the rate of the thermal decomposition of the initiators. The adiabatic increase in temperature gave the values $k_2 = 2.3 \times 10^9 \exp(-7000/RT)$, $k_3 = 2.48 \times 10^8 \exp(-8500/RT)$, $k_4 = 1.38 \times 10^8$, and $k_6 = 1.03 \times 10^6$ litre mole$^{-1}$ s$^{-1}$; $E_4 = E_6 \simeq 0$.

A curious feature is the anomalously low value, which is difficult to explain[95], of the rate constant for addition to cyclohexene shown both by the $CH_3^\bullet$ radical and by the $CCl_3^\bullet$ radical. The rate of removal of hydrogen from cyclohexene, however, is apparently quite "normal": by extrapolating $k_2$ for cyclohexene to 77.8° and making use of the value $k_2/k_7 = 1.20$ for this temperature[92], we obtain for cyclohexene $k_7 = 2200$; similar calculations for hept-1-ene give the value $k_7 = 2400$. Thus the difference in the rates of removal of hydrogen $k_7$ by the $CCl_3^\bullet$ radical from cyclohexene and hept-1-ene is insignificant and confirms the observation, found for other radicals, that the reactivity of secondary hydrogen atoms is approximately the same for all alkenes and cycloalkenes.

For the reaction of $CCl_3Br$ with n-butyl vinyl ether[94], $k_2 = 3.16 \times 10^{10} \exp(-7700/RT)$, and for the reaction of $CCl_3Br$ with phenyl vinyl ether, $k_2 = 2.0 \times 10^4$ at 25° (the value of $k_4$ was taken as $1.0 \times 10^8$).

The value $k_2 = 3240$ litre mole$^{-1}$ s$^{-1}$ has been reported[92] for the addition of $CCl_3^\bullet$ to methylallyl acetate at 30°; the activation energy for this reaction is 7.74 kcal mole$^{-1}$.

For the addition to vinyl acetate the rotating-sector method[93] gave $k_2 = 1120$ at 30° and $E_2 = 6.1$ kcal mole$^{-1}$ in the same laboratory; later, Bengough and Thomson[96] determined the rate of initiation from the rate of consumption of diphenylpicrylhydrazyl or from the duration of the induction period in different solutions at 25° and obtained the value $k_2 = 795$–$2410$, depending on the method used to determine $I$. These small values for vinyl acetate are even more surprising than those for cyclohexene, since the rate of addition of $CCl_3^\bullet$ to other rapidly polymerising monomers (styrene, methyl methacrylate) is greater by approximately one order of magnitude. The telomerisation of bromotrichloromethane with a large excess of vinyl acetate[97] leads to the formation of telomers containing different numbers of monomer units for every $CCl_3$ group. From their data[97], the authors concluded that the value obtained by Melville and coworkers[93] for the rate constant for the removal of the Br atom from $CCl_3Br$ by the $CH_3COOCHCH_2CCl_3^\bullet$ radical at 30°, $k = 2740$, is clearly too low. For other substances with different structure, including active monomers (see below), however, this quantity has values in the range 13–400, that is, the value of $k_3$ for vinyl acetate is greater by one order of magnitude than the values for other substances.

Robb and coworkers studied the mechanism and kinetics of the photochemical telomerisation of bromotrichloromethane with styrene[98,99] and methyl methacrylate[100]. The rate of initiation was determined from the duration of the induction period in the presence of diphenylpicrylhydrazyl, and the lifetime of the free radicals was determined by the rotating-sector method. The reaction rate is proportional to the square root of the intensity of illumination.

The following values were found for the rate constants of the dimeric and trimeric teloradicals at 30°:[99]

| | $k_s$ | $k_p$ | $k_t$ |
|---|---|---|---|
| $[(C_8H_7)_2CCl_3]^\bullet$ | $4.4 \cdot 10^3$ | 56.8 | $5 \cdot 10^8$ |
| $[(C_8H_7)_3CCl_3]^\bullet$ | $4.3 \cdot 10^3$ | 1.56 | $1.6 \cdot 10^8$ |

The symbols for the constants have their usual significance: $k_s$ is the constant for the removal of a bromine radical from $CCl_3Br$, $k_p$ the constant for the addition to a molecule of monomer, and $k_t$ the constant for recombination of the radicals. When the number of monomer units in the telomer chain is greater than or equal to 4, the value of $k_p$ again increases to the usual value for the polymerisation of styrene.

For the reaction of methyl methacrylate with trichlorobromomethane[100], the rate constants for the telomeric radicals $[(MMA)_nCCl_3]^\bullet$ at 30° have the following values:

| $n$ | $k_s$ | $k_p$ |
|---|---|---|
| 3 | 13.3 | 160 |
| 4 | 8.34 | 37.9 |
| 5 | 330 | 281 |

The termination rate constant $k_t = 1.6 \times 10^7$ is independent of the value of $n$.

Thus the systems studied show a minimum reactivity for the trimer for styrene and the tetramer for vinyl acetate (according to the data of Bengough and Thomson[97], examined critically by Robb and Senogles[100]) and methyl methacrylate. The same phenomena were observed in the telomerisation of esters of acrylic acid with lower thiols[101]. The reduced reactivity of the trimers and tetramers was attributed to the fact that, as a result of the steric conditions here, the $CCl_3$ (or SH) group attached to the first unit is in direct proximity to the C atom carrying a free valency, and reacts with it. Moreover, the influence of the $CCl_3$ group on the activity of the radical decreases with increase in the length of the telomeric radical chain. The reactions of telomers show particulary clearly that the rate constants for propagation and termination of the chain, determined in polymerisation, refer, strictly speaking, only to the reactions of sufficiently large polymeric radicals containing more than four units. In polymerisation reactions, the difference in the rates of reaction for 2- and 3-unit or longer polymeric radicals is smaller, however, than that for telomerisation reactions.


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# FEATURES OF THE KINETICS OF CHEMICAL REACTIONS OF HIGH-MOLECULAR-WEIGHT COMPOUNDS

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## I. INTRODUCTION

The study of the kinetics of homogeneous reactions of macromolecules has recently received much attention from several investigators [1-37]. The interest in this problem is due to the search for ways of controlling the chemical changes in polymers and of carrying out directed reactions to obtain chemical derivatives with desired properties.

By comparing the kinetic parameters of reactions of functional groups included in the polymer chain with the analogous parameters of the same groups in low-molecular-weight compounds, it is possible to suggest a series of factors which lower the pre-exponential term of the Arrhenius equation for large molecules [1]. Firstly, from the kinetic theory, with increase in the dimensions (mass) of the molecule the rate of the Brownian movement of the molecules falls. Secondly, the high viscosity of the polymeric solutions decreases the number of collisions of the reacting groups. Thirdly, there is the great steric factor due to the screening of the functional groups by coiling of the polymeric chains.

When there is regular attention of the functional groups in the polymeric chain, the interaction of neighbouring groups (of two which have not reacted or which have reacted with those which have not yet entered into reaction, etc.) can affect the energy of activation.

This review shows the influence of the inclusion of a functional group in a polymeric chain and the interaction of regularly alternating functional groups on the kinetic parameters of reactions of macromolecules.

## II. INFLUENCE OF THE INCLUSION OF A FUNCTIONAL GROUP IN A POLYMERIC CHAIN ON THE KINETIC PARAMETERS FOR THE REACTIONS OF THIS GROUP

There are many experimental results which show that the inclusion of a functional group in a polymeric chain does not significantly change either the activation energy or the pre-exponential term of the Arrhenius equation for reactions of this group with low-molecular-weight agents. Thus, Fuoss and coworkers [2], in studying the formation of quaternary salts of poly(vinylpyridine) and low-molecular pyridine compounds obtained the following constants for reaction rates and activation energies (Table 1).

The reaction was effected in tetramethylene sulphone; the alkyl halide used was n-butyl bromide.

TABLE 1. Kinetic parameters of the Menshutkin reaction for poly(vinylpyridine) and low-molecular-weight pyridines.

| | $10^3 K_2$ | | | $E_a$ |
|---|---|---|---|---|
| | 25° | 50° | 75° | |
| Pyridine $C_5H_5N$ | 0.463 | 3.70 | 23.1 | 16.04 |
| 4-Isopropylpyridine $C_3H_7C_5H_4N$ | 0.904 | 6.95 | 39.7 | 15.6 |
| Poly(vinypyridine) (first stage of reaction) | 0.64 | 5.4 | 29.4 | 15.7 |
| 4-Picoline $CH_3C_5H_4N$ | 0.83 | 6.58 | 40.1 | 15.95 |

Table 1 shows that the inclusion of pyridine in the polymeric chain affects neither the activation energy nor the reaction rate constant. Analogous results were obtained when propylene carbonate [4 methyl-1,2-dioxolan-2-one (Ed. of Translation)] [3], 2,4-dimethylsulpholane [2,4-dimethyltetramethylene sulphone (Ed. of Translation)] [4] or a mixture of propylene carbonate and diphenyl ether [5] was used as solvent.