DETERMINATION OF THE CONCENTRATION OF INTERMEDIARIES AND OF RATE CONSTANTS IN RADICAL REACTIONS

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Received November 24, 1953

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I. INTRODUCTION

A great deal of current work on the mechanism of reactions involving organic molecules has indicated that free radicals play a prominent part in the reaction. The results have aroused enormous interest in radical chemistry in both the liquid and the gas phase. The systematic investigation of the chemistry of such processes has, in many cases, revealed directly the nature of the radical involved. In other cases the inferences are less precise, but the reaction often proceeds in a sufficiently well-defined fashion to permit use of the analytical method of chemical kinetics, so that the kind of reactions that form radicals and remove radicals may be accurately obtained. Further, the nature of the reactions between radicals and molecules may be determined. Measurements of the rate of the overall reaction and the chain length, if the reaction is a chain reaction, will enable the rate of radical production to be determined. If, however, radical reactions are to be completely understood, much more information is needed. The most important quantity is the concentration of the radical or radicals concerned. This information, combined with a knowledge of the rate of production of radicals, enables quantitative knowledge to be gained regarding the rate of disappearance of radicals. The rate of chemical change in the system, which is determined by the rate of radical removal, then gives the rate coefficient for the rate-determining step.

In recent years considerable progress has been made in determining by indirect methods such radical concentrations. Normally, of course, the concentrations are so small that any magnetic method, whether direct measurement of the paramagnetism of a system or, say, the rate of conversion of para-hydrogen in contact with the system, is not nearly sensitive enough even to detect the presence of radicals. Although the principles of the methods are easily set down, the experimental difficulties are numerous and there is plenty of scope for the development of a great variety of methods in order to solve the problem in particular reactions. Ever since the theory of chain reactions was proposed, various attempts have been made to prove the existence of a reaction chain; thus the beginnings of the quantitative study of the behavior of transient entities in chemical reactions were made, even though the workers then did not realize precisely the implications of these early attempts to take the analysis of chain reactions to a further stage. Somewhat surprisingly, the problems encountered in the gas phase have proved more difficult to solve than those in the liquid phase, and it is in the latter phase that progress in quantitative measurements has been most rapid.

The present review attempts to bring together the published results and more particularly the methods, excluding mass spectrometry, by which they have been obtained.

II. SPECTROSCOPIC DETECTION OF FREE RADICALS

Knowledge of the structure of free radicals, and of other short-lived species of similar type, has been gained from the emission spectra of flames and electrical discharges. While such methods have led to the recognition of about one hundred different radicals, their application is by no means general, since the spectra of many radicals which have been postulated are unknown. Chemical methods are not adaptable to high-speed manipulation, and physical methods such as electron diffraction are not applicable. Absorption spectroscopy is especially suitable for investigations of this kind; in particular, it can be used to obtain spectra which cannot be observed in emission and has the further advantage that concentration is relatively easy to determine. As more complex radicals are examined it will be necessary for spectral regions other than the ultraviolet to be brought into use.

The main difficulties in the utilization of absorption spectrometry are largely experimental. If kinetics are to be studied the exposure time must be reduced to a minimum (10^{-4} sec. or less). With continuous-discharge sources this is not possible, but there are three main methods which allow the necessary time condition to be fulfilled. Phototubes can have a response time of as low as 10^{-8} sec., but for high-speed scanning a limit is set by the random fluctuations in the tube itself. This will lead to a reduction in the resolving power of the system, so that only if such a reduction in resolution can be tolerated, or if the scanning rate can be reduced, is the method applicable. A system of photographic integration has been successfully applied in certain cases. For this method, it is necessary to use large numbers of exposures either by successive experiments (125) or by the use of a rotating mirror so that the decay of the radical is recorded in the same time (97). The most powerful method yet reported is that of flash spectrometry (128, 129). The very high energy which can be dissipated in a single flash (up to 10,000 joules) and the short duration and easy synchronization of the flash, together with the very good continuous spectrum, make this an ideal method.

Using flash spectrometry Porter has proved the existence of the ClO radical in the reaction mixture for the photolysis of chlorine in the presence of oxygen (128); the radical has a half-life of several milliseconds. The photolysis of hydrogen sulfide to its elements probably proceeds through the primary dissociation to hydrogen atoms and SH radicals (78, 88). Porter has identified the spectrum of the SH radical from the photolysis of hydrogen sulfide and in the same way the SD radical has been found. The absorption bands of the $^2\Sigma$–$^2\Pi$ systems in OH and OD have been obtained by the interaction of hydrogen or deuterium atoms, prepared by the photolysis of small quantities of chlorine or bromine in the presence of hydrogen or deuterium, with oxygen (128).

As was mentioned earlier, the nature of a free radical and its complexity may determine to some degree the methods to be adopted in its detection. Thus, although OH and OD radicals have been identified by the method of flash spectrometry, OH radicals have also been detected from the microwave spectrum (136). This method, in view of its high resolving power, presents an extremely promising tool with which the study of structure, in particular, may be attempted.

Potentially the most powerful method of determining the concentration of free radicals is by the use of the magnetic resonance characteristics of the radical.

Development of such techniques to the sensitivity required for the accurate determination of the low concentrations normally encountered in free-radical reactions would render obsolete many of the indirect methods described in this review.

III. Methods Applicable to Gas-Phase Reactions

A. TEMPORAL INTERFERENCE METHOD FOR NH_2 AND PH_2 RADICALS

NH_2 and PH_2 radicals play an important part in the mechanism of the photochemical and perhaps the thermal (homogeneous or heterogeneous) decomposition of ammonia and phosphine. Probably the most convincing evidence is that in this decomposition atomic hydrogen can be detected by means of the para-hydrogen conversion. Furthermore, if, say, atomic deuterium is produced simultaneously with the decomposition of the hydride, then deuterium enters the hydride by its combining in the back reaction $NH_2 + D \rightarrow NH_2D$. The principle involved in carrying out this kind of reaction involves the use of multiple light sources one of which, S_1, is a zinc spark which decomposes the hydride directly while the other, S_2, produces atomic hydrogen by mercury sensitization (37). A first exposure to S_1 gives the rate of decomposition of the hydride; a second exposure to S_2 produces no measurable result, since essentially only hydrogen is atomized and simply recombines; a third exposure with S_1 and S_2 operating simultaneously gives a much reduced decomposition rate of the hydride, owing to the excess of atomic hydrogen reacting with the NH_2 radicals which would normally decompose to nitrogen and hydrogen either on the walls of the vessel or, probably, in the gas phase. Suppose now the reaction vessel is

TABLE 1

Data illustrating the method of temporal interference for the decomposition of ammonia (37)

SLOT INTERVAL	PRESSURE					$\frac{S}{SA - A}$*
	NH_3	H_2	$N_2 + H_2$			
			A	*S*	*SA*	
	mm. Hg	*mm.* Hg	*mm.* Hg	*mm* Hg	*mm.* Hg	
1.6	4.6	0.296	0.001	0.019	0.014	1.46
3.8	5.5	0.273	0.003	0.028	0.025	1.27
4.5	3.8	0.234	0.006	0.040	0.036	1.48
5.0	3.1	0.307	0.003	0.015	0.011	1.89
7.5	4.0	0.386	0.006	0.031	0.023	1.82
10.0	3.9	0.240	0.006	0.086	0.110	1.02
15	4.0	0.240	0.005	0.024	0.017	2.00
20	4.0	0.240	0.004	0.034	0.037	1.03
30	4.0	0.275	0.007	0.025	0.022	1.66
50	3.9	0.240	0.005	0.024	0.017	1.67
75	4.0	0.240	0.005	0.032	0.027	1.41

* A = the increase in pressure due to irradiation by a mercury lamp.

S = the increase in pressure due to irradiation by a zinc spark.

AS = the increase in pressure due to irradiation by both sources.

$S/(SA - A)$ is the measure of retardation of ammonia decomposition by hydrogen atoms.

cylindrical and that it is surrounded by a cylindrical tube in which a large vertical slot is cut and which may be rotated. When the cylinder is rotated the reaction system will be illuminated successively by S_1 and S_2. If the cylinder is rotated very slowly the decomposition of ammonia will occur when the slot is opposite S_1. As the cylinder moves around, the reaction will soon cease as the atoms and radicals undergo their respective reactions. When the slot comes opposite S_2, atomic hydrogen is produced and no detectable change will occur. If the cylinder is rotated more rapidly, however, when the slot comes opposite S_2 the NH_2 radical concentration will be finite and the hydrogen atoms will catch the NH_2 radicals before they have time to decompose, with the result that ammonia will be re-formed and the net rate of decomposition will be cut down. When this retardation becomes marked, the time interval between the exposures to S_1 and S_2 gives the lifetime of the NH_2 radicals under the specified conditions. The kind of result is shown in table 1, a lifetime of the order of seconds being obtained at the pressures prevailing in the system when the NH_2 radicals must diffuse to the walls and interaction with hydrogen atoms must take place. At higher pressures gas-phase decomposition will occur. Since the rate of radical production is known, the velocity constant for the gas-phase reaction can be computed.

B. SPATIAL COMPETITIVE METHOD

1. Theoretical considerations

As will be evident from the above discussions, probably the most important general problem in quantitative radical chemistry is the determination of the manner and speed of disappearance of radicals. Until these facts are established, calculations of radical concentrations are impossible. There is, however, another method of approach especially applicable to the gas phase. This consists in so arranging matters that the rate of removal is accurately known. The principle of the method is as follows: Consider a flat cylindrical reaction vessel in which the depth is much less than the diameter. If radicals or atoms are produced in such a box photochemically and there is no possibility of these reacting with any molecule present, then these radicals will combine either in the gas phase or at the walls. If the velocity of either of these processes is known and also the extinction coefficient of the molecule from which the radicals are produced photochemically, the spatial distribution of the concentration of the radicals can be accurately computed. But radical–radical interaction coefficients are largely unknown, and wall recombination is incalculable, since reflection coefficients are unknown, as is also the speed of interaction of radicals on any surface. On the other hand, if, on the lower face of the vessel, there is a surface which absorbs at every collision a radical which strikes it, and if the pressure of the radicals is so low that gas-phase recombination can be neglected, then the spatial distribution of radical concentration is given by the equation:

$$-D[\mathrm{d}^2n/\mathrm{d}x^2] + kcI_0 \exp\{-kx\} = 0$$

where D is the diffusion coefficient of the radicals through the gas mixtures, n is the number of radicals per cubic centimeter, I_0 is the incident number of quanta per second, c is the number of radicals produced per absorbed quantum, k is the extinction coefficient of the radical-producing molecule, and x is the distance measured perpendicular to the radical-absorbing surface. The rate of radical production can be measured by observing the rate at which the radical-producing molecule disappears from the gas phase. If, now, molecules are added to the reaction vessel which react with the radicals at a rate gn when $g = K(\mathrm{X})$, K being the appropriate bimolecular rate coefficient and (X) the concentration of the addendum, then:

$$kcI_0 \exp\{-kx\} - D[\mathrm{d}^2n/\mathrm{d}x^2] - gn = 0 \qquad (1)$$

Relationships of this kind can be set up for all kinds of conditions (112, 142), but the difficulty has been that integration is not possible because the boundary conditions are not known. By considering diffusion in only one dimension and putting the boundary condition that $n = 0$ at $x = d/2$ in a reaction vessel of thickness d, and measuring from a plane through the middle of the vessel perpendicular to the axis, equation 1 may be integrated to give:

$$n = \frac{kcI_0}{D(k^2 - b^2)}\left[\frac{\cosh bx}{\cosh (bd/2)} \exp\{-\tfrac{1}{2}kd\} + \frac{\sinh b(\tfrac{1}{2}d - x)}{\cosh (bd/2)} - \exp\{-kx\}\right] \qquad (2)$$

where $b^2 = g/D$. The diffusion coefficient is defined by

$$N = -D(\mathrm{d}n/\mathrm{d}x)_x$$

where N is the number of atoms diffusing at a distance x from the plane of incidence of radiation. If equation 2 is differentiated with respect to x, then:

$$-N = \frac{kcI_0}{(k^2 - b^2)}\left[\frac{b \sinh bx}{\cosh(bd/2)} \exp\{-kd/2\} - \frac{k \cosh b(d/2 - x)}{\cosh (bd/2)} + k \exp\{-kx\}\right] \qquad (3)$$

If R is then defined as the ratio of the number of atoms reacting at the absorbing surface to the total number produced photochemically, then, utilizing equation 3:

$$R = \frac{k}{(b^2 - k^2)(1 - \exp\{-kd/2\})}\left[\frac{b[\exp\{-kd/2\}] \sinh (bd/2)}{\cosh (bd/2)} - \frac{k}{\cosh (bd/2)} + k \exp\{-kd/2\}\right]$$

If, therefore, this value can be determined by analytical means, then the values of b may be found. On account of the non-explicit nature of the expression it is convenient to calculate R as a function of b for various values of $d/2$.

2. Determination of R

The value of R may be determined by gas analysis of the mixture first by performing the experiment with pure hydrogen, when the rate of disappearance of molecular hydrogen will at once give the rate of atom production. The rate of removal of the molecules which react with hydrogen gives the second item of information. It is desirable to maintain *b* constant, and therefore the amount of olefin removed must be a minimum. A more convenient method consists in using the fact that molybdenum trioxide becomes blue in contact with hydrogen atoms. The reaction system is shown in figure 1 (112). The tray, E, containing molybdenum trioxide can be raised or lowered so that the competition factor may readily be altered. Since the time of diffusion is proportional to the square of the distance, a variation in depth of 1:30, which is practicable, gives a variation in competition ratio of about 1:1000. The photoelectric colorimeter consists of a filament lamp to illuminate the surface and a rectifier cell to measure the intensity of the reflected light. By suitable arrangement of the circuits fed by the photocell it is possible to obtain a linear relationship between a simple function of the current through the cell and the number of hydrogen atoms taken up by the oxide. The slope of such a line is then a direct measure of the rate at which atomic hydrogen is taken up on the surface. One further complication occurs. The radicals produced by the addition of atomic hydrogen to olefins are also absorbed by the molybdenum trioxide and turn it blue; hence a suitable correction must be applied to the results. The ratio of blueing rates in the absence and presence of olefin depends not only on the reactivity of the olefin but also on the "blueing coefficient" of the derived radical. By working at another separation $d'/2$, owing to the non-explicit character of equation 3, another relationship is obtained which gives two simultaneous equations containing two unknowns. In some cases the radicals turn molybdenum trioxide blue at the same rate as hydrogen atoms do. Here tungsten oxide becomes useful, for the "blueing coefficient" is different for this oxide.

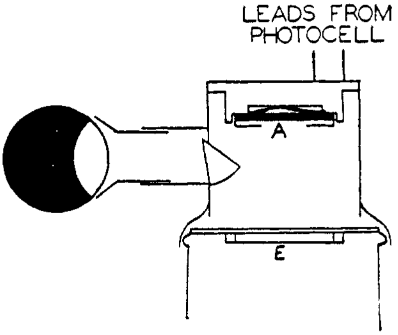


FIG. 1. Photoelectric colorimeter used in experiments with molybdenum trioxide (112)

Using a separation of the order of 1 mm. and a pressure of olefin of a few tenths of a millimeter, collision efficiencies of 1 in 10^3 can be conveniently measured. Lower efficiencies may be measured by increasing the separation and by working at higher pressures, and higher efficiencies may be measured by working at lower pressures. The method covers, however, a range of efficiencies which are not accessible by any other technique.

The original work on the molybdenum trioxide technique (112–116) led to the conclusion that the removal of hydrogen atoms was absolutely efficient on the oxide surface and that reflection of these atoms from the silica walls of the reaction vessel was likewise very efficient. This enabled the necessary boundary conditions to be set up so that the diffusion equation could be solved to give the spatial distribution of hydrogen atoms within the system. No method was then known of checking this distribution, but recently it has become possible to do so (119).

The method of exploring the distribution is to use a fine platinum filament (*ca.* 0.01 mm. in diameter) which can be moved mechanically throughout the reaction space. The combination of atoms on this filament raises the temperature by about 0.01°C.; hence by arranging the filament in a balanced Wheatstone bridge circuit, the out-of-balance signal, which after amplification by a D.C. amplifier is displayed on a pen recorder, gives a measure of the change in resistance and consequently of the rise in temperature. The rise in temperature can be used to calculate the relative concentration of hydrogen atoms in the vicinity of the probe. The ideal system for investigating would be that used in the molybdenum trioxide technique, but here a difficulty arises. The heat evolved by the interaction of hydrogen atoms with the oxide is not conducted away from the surface on account of the poor thermal conductivity of the powdered oxide, but is dissipated throughout the gas phase, setting up thermal gradients which completely interfere with the measurement of atom concentrations in the vicinity of the surface. For this reason the surface of a platinum-plated copper block was used to define the removing surface of the system in place of the oxide layer. This block of low heat capacity effectively "absorbs" the heat of recombination of atoms on its surface. The hydrogen-atom distribution in a vessel having a

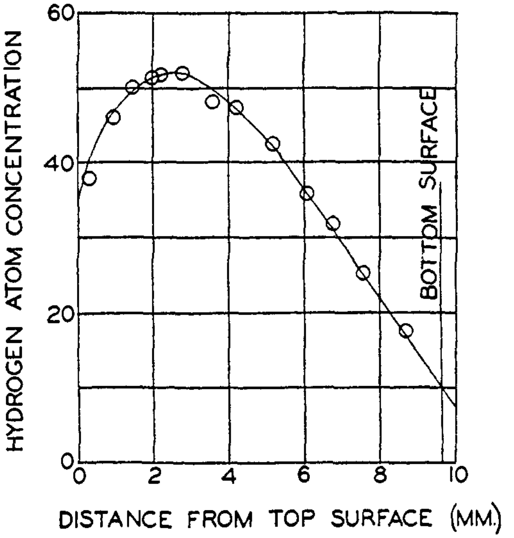


FIG. 2. Distribution of hydrogen atoms (concentration in arbitrary units) as measured by wire technique (119).

spacing of about 1 cm. between the top silica surface and the removing surface is shown in figure 2. This curve is in exact accord with that which may be calculated by taking into account imperfect reflection at the silica surfaces and imperfect removal of hydrogen atoms at the platinum surface. From the diffusion gradients and the intercepts at the surfaces the coefficient for the removal of the atoms at these surfaces can be calculated. In a particular case, for silica the chance of removal at one collision is 0.83 per cent or 1 in 121, and for platinum it is 1.1 per cent or 1 in 89.

Since the block surface and the probe surface are both of bright platinum, it is then possible to apply the value calculated for the coefficient of removal of atoms on the block to the filament and so to measure absolutely the stationary atom concentrations. This approach gives values in reasonable accord with those which can be calculated from a knowledge of the quantum input to the vessel and the diffusion conditions operating therein.

This experimental demonstration of the lack of absolute efficiency of reflection on the silica surface makes it possible to alter the stationary-state diffusion equations in the molybdenum trioxide system (112). The collision efficiencies of a number of hydrogen atom–olefin reactions are given in table 2.

C. SPATIAL INTERFERENCE

In principle the method of obtaining both the velocity coefficient and the relative blueing coefficient for the alkyl radical is as follows. Suppose the blueing

TABLE 2

Collision efficiencies in hydrogen atom–olefin reactions

OLEFIN	BLUEING COEFFICIENT RELATIVE TO HYDROGEN ATOMS (MoO_3)	COLLISION EFFICIENCY × 10^4	REFERENCES
Ethylene	0.38 (0.37)*	11.4 (8.5)*	(3, 115)
Propylene	0.30 (0.34)	1.9 (1.4)	(3, 115)
2-Butene (*trans*)	2.27 (2.26)	5.5 (5.0)	(3, 116)
2-Butene (*cis*)	2.05 (2.05)	8.9 (6.9)	(3, 116)
2-Methylpropene	1.66 (1.60)	6.3 (4.7)	(3, 115)
2-Pentene (*cis*)	0.73 (0.72)	4.6 (2.8)	(3, 115)
Trimethylethylene	2.65 (2.55)	6.4 (5.0)	(3, 116)
Tetramethylethylene	1.98 (1.95)	4.2 (3.6)	(3, 116)
2,2,3-Trimethyl-1-butene	1.2 (1.2)	6.0 (5.2)	(3, 115)
Cyclohexene	2.16 (2.16)	7.9 (5.7)	(3, 116)
Tetrafluoroethylene	0.50	0.3	(3)
Tetrachloroethylene	—	Probably small	(3)
Methyl methacrylate	Small	1.9	(3)
Styrene	—	Probably small	(3)
Benzene	1.36	1.3	(3)
Toluene	8.3	0.2	(3)
p-Xylene	—	Probably small	(3)
Isopropylbenzene	—	Probably small	(3)

* Figures in parentheses are those found on the assumption that the silica surface is a perfect reflector of hydrogen atoms; the higher reference numbers refer to those results.

effect of each hydrogen atom is k_H and that of the alkyl radical is $k_H k_R$. If N' hydrogen atoms are generated per second the blueing rate, R_H, is given by:

$$R_H = k_H N'$$

If the olefin is present, only a fraction N'_H/N' of the hydrogen atoms will reach the oxide and the blueing rate due to these atoms is:

$$R'_H = k_H N'_H$$

The blueing rate due to the alkyl radicals is then:

$$R'_R = k_R k_H (N' - N'_H)$$

The rate observed by the colorimeter is:

$$\begin{aligned} R' &= R'_H + R'_R \\ &= k_H N'_H [1 + k_R (N'/N'_H - 1)] \end{aligned}$$

Experimentally the value of $R'/R_H = A'$ can be measured. Therefore,

$$A' = N'_H (1 - k_R)/N' + k_R$$

or

$$N'_H/N' = (A' - k_R)/(1 - k_R)$$

N'_H is dependent on the rate coefficient for the interaction of hydrogen atoms and on the geometry of the vessel, in particular its depth d, according to equation 3. If, therefore, another experiment is carried out with another depth a similar equation is obtained, namely:

$$N''_H/N' = (A'' - k_R)/(1 - k_R)$$

where A'' is experimentally observable. In order that these simultaneous equations can be solved, there is a unique value of b and k_H which may be computed from the two experiments. These values may be obtained by trial and error, but it is convenient to use a mechanical calculator to solve the equations quickly (112).

D. SPATIAL DIFFUSION METHODS

In gas-phase reactions exploration of the distribution of concentration of radicals can be used to determine the mean lifetime of the radicals no matter how the radicals disappear, i.e., by first- or second-order processes. Again suppose that the reaction is photochemical and suppose that a reaction system is constructed so that two narrow pencils of radiation may be projected into it and that one of the pencils may be moved relative to the other (92). Using such a system it is possible to obtain some measure of the lifetime of the radicals without the use of a probe for direct measurement of the radical concentration. If the rate of reaction is proportional to the square root of the intensity, then the following phenomena will be observed. From each pencil of radiation radicals will diffuse which will in time reduce reaction. Finally they will disappear by interaction. Surrounding each pencil there will be a zone of reaction whose width will be determined by the lifetime of the radicals and their diffusion coefficients through the reaction mixture. If the beams are far enough apart, each zone will be independent; if, however, the beams can be brought close together, radicals from one zone can react with those from another. When the two beams are superimposed the total rate of reaction will only be $1/2^{1/2}$ of that when the beams are far apart. Figure 3 shows the kind of result obtained in the polymerization of methyl acrylate vapor, where it is seen that the predicted diminution in rate occurs when the beams are brought close together.

The next problem is to calculate the mean lifetime of the radicals under some specified conditions such as those obtaining when only one beam of radiation is being used. From figure 3 it will be seen that 50 per cent of interference between the two zones occurs when the separation is 2–4 cm. Under these circumstances the radicals will have diffused a distance of 1.2 cm., and the time required for such diffusion is a measure of the average lifetime. This time may be calculated from the usual diffusion equation $x^2 = 2D\tau$, where x is the diffusion distance, D is the diffusion constant of the radicals through the gas mixture, and τ is the time. In order to get a precise numerical correlation between the midpoint of the interference curve and the lifetime of the radical the calculations have been done for atomic hydrogen, where the mean lifetime can be computed from the rate of production of hydrogen atoms and the combination coefficient. The calculations have to be made by a graphical method of integration, and the result obtained is that the lifetime of the hydrogen atom in one zone is given by the time required to diffuse a distance equal to one-half of the separation at which there is 50 per cent interference between the zones.

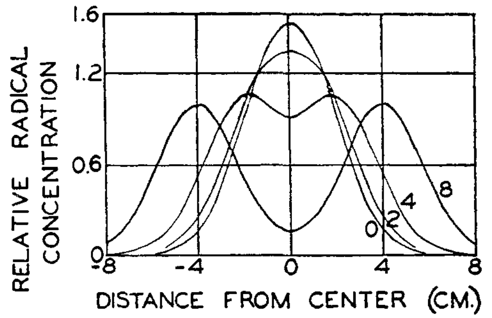


FIG. 3. Distribution of radicals as a function of beam separation using two light sources (92).

The practical precautions which have to be observed in order to get accurate results are mainly two in number. The width of the beam must be small compared with the width of the diffusion zone, and it is important to work under such conditions that the radicals move only by diffusion and not by convection.

It is not absolutely necessary that the two beams should have the same intensity, for the interference curve is easily calculated in this case. It is, however, important that all the radicals disappear two at a time; otherwise the calculations become extremely involved.

This interference technique has another important application in liquid-phase reactions. Here one of the problems is to ensure that the radical concentration as far as possible is uniform throughout the reaction vessel. Normally it is difficult in photochemical reactions to use monochromatic radiation and to calculate the distribution of the radical concentration. If polychromatic radiation is used, calculation can be made only if the intensity of all lines is known and also the primary quantum efficiency at each wave length. A simple method of establishing whether or not there is uniformity consists in using sources of radiation on either side of a plane-sided reaction vessel (52). Three experiments are carried out. The rate of reaction, R_1, due to source 1 is measured, then that due to source 2, R_2, and finally that due to both sources acting simultaneously. If radical production is confined to layers close to the point at which radiation enters the vessel, then the rate observed with both sources in operation is $(R_1 + R_2)$. On the other hand, if radical production is substantially uniform throughout the vessel, the rate should be $(R_1^2 + R_2^2)^{1/2}$.

The quantitative theory of the method may be derived in the following way. If I_0 is the intensity of the sources (assumed to be equal), then the total intensity at a point x from the plane of entry of radiation is:

$$I_t = I_0[\exp\{-kx\} + \exp\{-k(d - x)\}]$$

where d is the thickness of the vessel.

On this basis and assuming that radicals disappear two at a time the radical concentration for one lamp $(P)_1$ is:

$$(P)_1 = KI_0^{1/2} \int_0^d \exp\{-kx/2\}\mathrm{d}x$$

where K is a constant. For the two sources:

$$(P)_2 = KI_0^{1/2} \int_0^d [\exp\{-kx\} + \exp\{-k(d - x)\}]^{1/2}\,\mathrm{d}x$$

It is assumed that the radicals do not diffuse away from their points of production and that there is no convection. Both effects would tend to equalize concentrations and may be important if the radicals are small or the reactions are strongly exothermic. The results are shown in figure 4 for a value of $k = 1$, where it will be seen that for reaction vessels of moderate sizes localized production of radicals can easily be obtained. It is necessary to calculate the percentage (Z) of interference that will occur under these conditions. If the sources are equally intense, this is given by:

$$Z = \frac{2R_1 - R_3}{0.414R_3} \times 100\%$$

Figure 5 shows the results of the calculations and is a practical guide in selecting the reaction conditions such that localized absorption may be avoided. Further,

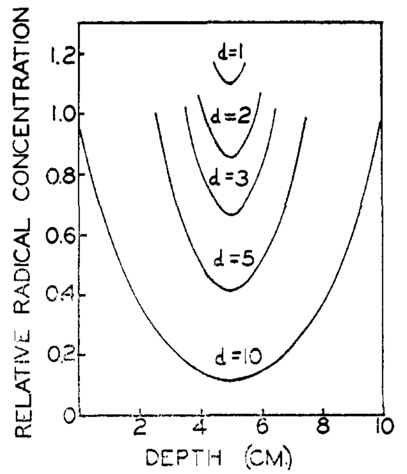


FIG. 4

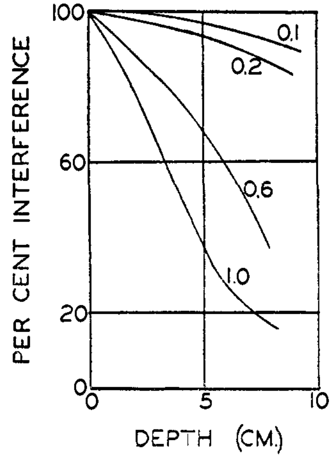


FIG. 5

FIG. 4. Distribution of radicals in two-lamp problem for $k = 1$ and various values of d (52).

FIG. 5. Relationship between interference and path length for various values of k in two-lamp problem (52).

by utilizing figure 5 it is practical to construct a curve showing the relation between the value of Z measured experimentally by this method and the effective volume of the liquid in which the reaction occurs. Hence if ideal conditions cannot be obtained for one reason or another, this curve provides a means of making the necessary correction to results so that "true" radical concentrations can be computed.

E. DEPOSIT METHOD

All the above methods suffer from the restriction that the radicals must disappear two at a time. There are some reactions in which this does not hold and the radicals interact with a molecule in such a way as to give rise to an inactive radical. This happens in the case of the mercury-sensitized polymerization of acetylene in the gas phase, and the following method was devised to deal with this difficulty (110). The acetylene polymer deposited on the walls of the reaction vessel can readily be made visible by charring on heating to a sufficiently high temperature. A cylindrical reaction vessel is used which is uniformly illuminated with the resonance line of mercury in a parallel beam; the mercury pressure is kept below 10^{-4} mm. so that absorption is not strong and there is a negligible diffusion of resonance radiation. A thin foil band is placed round the vessel to act as a radiation shield. If the polymerization is carried out at high pressures and the deposit is carbonized, a sharp shadow is obtained. As the pressure of acetylene is reduced the sharpness of the shadow gradually decreases, and at the lowest pressures—0.1 mm.—the shadow has practically disappeared. While this method cannot be very accurate, it is estimated that at 1 mm. pressure the growing polymer diffuses a few millimeters. Since the chain length of the polymer is known, its diffusion coefficient can be calculated and therefore the time to diffuse a given distance. This then gives the lifetime of the active radical.

IV. Methods Applicable to Gas- and Liquid-Phase Reactions

A. GENERAL PRINCIPLES

The most general type of chain reaction may be described by the following reaction scheme:

$$
\begin{array}{lll}
\left.\begin{array}{l}\mathrm{A} \rightarrow \mathrm{A}\text{—} \\ \mathrm{B} \rightarrow \mathrm{B}\text{—}\end{array}\right. & \text{initiation} & \text{rate} = R_i \\
\left.\begin{array}{l}\mathrm{A}\text{—} + \mathrm{B} \rightarrow \mathrm{X} + \mathrm{B}\text{—} \\ \mathrm{B}\text{—} + \mathrm{A} \rightarrow \mathrm{Y} + \mathrm{A}\text{—}\end{array}\right. & \text{propagation} & \begin{array}{l}\text{rate} = k_p(\mathrm{A}\text{—})(\mathrm{B}) \\ \text{rate} = k'_p(\mathrm{B}\text{—})(\mathrm{A})\end{array} \\
\left.\begin{array}{r}2\mathrm{A}\text{—} \\ 2\mathrm{B}\text{—} \\ \mathrm{A}\text{—} + \mathrm{B}\text{—}\end{array}\right\} \rightarrow \begin{array}{l}\text{inactive} \\ \text{products}\end{array} & \text{termination} & \begin{array}{l}\text{rate} = k_t(\mathrm{A}\text{—})^2 \\ \text{rate} = k'_t(\mathrm{B}\text{—})^2 \\ \text{rate} = k''_t(\mathrm{A}\text{—})(\mathrm{B}\text{—})\end{array}
\end{array}
$$

Kinetic analysis of such a reaction scheme shows that

$$
\begin{aligned}
-\mathrm{d}(\mathrm{A})/\mathrm{d}t &= -\mathrm{d}(\mathrm{B})/\mathrm{d}t \\
&= k'_p(\mathrm{A})R_i^{1/2}\{k_t[k'_p(\mathrm{A})/k_p(\mathrm{B})]^2 + 2k''_t[k'_p(\mathrm{A})/k_p(\mathrm{B})] + k'_t\}^{-1/2}
\end{aligned}
$$

Under certain experimental conditions the only termination step of significance will be that involving the mutual destruction of the chain carriers derived from the A type molecules, i.e.,

$$k'_p(\mathrm{A}) \gg k_p(\mathrm{B})$$

when

$$-\mathrm{d}(\mathrm{A})/\mathrm{d}t = k_p(\mathrm{B})(R_i/k_t)^{1/2}$$

Thus if the rate of initiation of chains can be determined, the ratio $k_p/k_t^{1/2}$ can be calculated, but it is not possible by any conventional methods to separate these constants and the general equation can afford no help in this matter.

Since the determination of the concentration of active chains cannot, in general, be carried out directly in view of the transient nature of the carriers and their exceedingly low concentration, recourse has to be made to other techniques. The simplest way of achieving a separation of the constants is to investigate the lifetime of the kinetic chain which is defined by:

$$
\begin{aligned}
\tau &= \frac{\text{number of chain carriers disappearing per unit volume}}{\text{number of chain carriers present per unit volume per second}} \\
&= (k_t R_i)^{-1/2} = [k_t(C)]^{-1}
\end{aligned}
$$

where (C) is the concentration of chain carriers under steady-state conditions.

B. INTERMITTENT ILLUMINATION

It is a corollary to the nature of chain reactions that the stationary concentration of free radicals is not achieved immediately but is built up gradually according to a well-defined law, the time required being dependent on the lifetime of the chain carrier. In the same way, the reaction rate will not immediately fall to zero when initiation is stopped. Hence, an investigation of the rate of reaction over the first stages of the reaction and during the decay period after initiation has ceased yields information regarding the lifetime of the chain. Such experimental methods are dealt with in Section VII. Using a photochemical means of initiating the reaction, the initiation process can be brought under control. The technique of intermittent illumination whereby the exciting radiation is interrupted in a steady manner to give definite periods of light and dark enables the effect of the build-up and decay of the reaction to be integrated over periods of time, thereby making measurements considerably simpler. This method, instigated by Berthoud and Bellenot (29), has been developed by many authors (29, 48, 51, 57, 62, 70) and is now the most widely used method for the determination of rate constants in chain reactions. As well as the simple case in which the rate of reaction is proportional to the square root of the light intensity, the more complex cases when there is an appreciable dark reaction (20, 51, 102) and when the overall rate is proportional to some power of the light intensity less than unity but greater than 0.5 have also been worked out (51, 54, 131). When various experimental conditions are obeyed, this method can give quite precise results. Although the method is applicable in theory to any chain reaction for which the light intensity law is obeyed, the main applications which have given rise to fruitful results have been in the fields of polymerization and oxidation processes.

Historically, the method was first used (29) to demonstrate that a reaction chain had a definite existence in time. The method was developed in order to enable the lifetime of the chain to be measured with some precision; later developments have been confined to refinements in experimental technique and in apparatus. Melville (111) made an attempt to derive the constants involved in the gas-phase polymerization of methyl methacrylate, but it is only since 1945 that the method has been used as a general tool for the investigation of chain reactions.

In essence the method depends on the variation of the rate of reaction with the duration of the light pulse. It is easily seen that, in the case of mutual termination with no complicating side reactions, if the interruption of the light is very rapid so that the duration of a light flash is short compared to the lifetime of the chain, the rate of reaction is:

$$R_f \propto [I/(r + 1)]^{1/2}$$

where r is the ratio of the dark to light periods. Again, if the rate of flashing is such that the duration of the light flash is greater than the lifetime of the chain, then the rate of reaction is

$$R_s \propto I^{1/2}/(r+1)$$

so that

$$R_f/R_s = (r+1)^{1/2}$$

The detailed analysis of the system shows that the ratio of the rates of reaction under intermittent and steady illumination can be most simply related to a dimensionless parameter, defined by the ratio of the duration of the light flash to the lifetime of the chain. Figure 6 shows curves demonstrating the required relationship for a number of values of r; the curves are normalized to be asymptotic to unity in each case.

Now a determination of the ratio of the rates of reaction under intermittent and steady illumination will give, under favorable circumstances, a measure of m, the ratio of the duration of the light flash to the lifetime of the chain, and since the former is known the latter can be calculated. By definition of the lifetime, $(R_ik_t)^{-1/2}$, it follows that if the rate of initiation can be found, the rate constant can be calculated, and hence k_p from the previous ratio $k_p/k_t^{1/2}$. Alternatively the lifetime can be defined as:

$$\tau = k_p(\mathrm{A})/k_tR$$

where R is the rate of reaction under steady illumination. Plotting τ against R^{-1} gives a straight line with a slope $k_p(\mathrm{A})/k_t$; thus a second ratio involving the two rate constants can be found and consequently the constants can be separated.

As far as the main reactions for which authoritative data are available are concerned, oxidation processes follow on the lines of the reaction scheme set out in Section IV,A. Polymerization reactions, on the other hand, are considerably simpler, since only one chain carrier is concerned in the reaction; this carrier alters only in size as the reaction proceeds. The reaction steps are then:

$\mathrm{A} \rightarrow \mathrm{A}\text{—}$	initiation	rate $= R_i$
$\mathrm{A}_{\overline{n}}\text{—} + \mathrm{A} \rightarrow \mathrm{A}_{\overline{n+1}}$	propagation	rate $= k_p(\mathrm{A}\text{—})(\mathrm{A})$
$\mathrm{A}_{\overline{n}}\text{—} + \mathrm{A}_{\overline{n}}\text{—} \rightarrow\ ?$	termination	rate $= k_t(\mathrm{A}\text{—})^2$

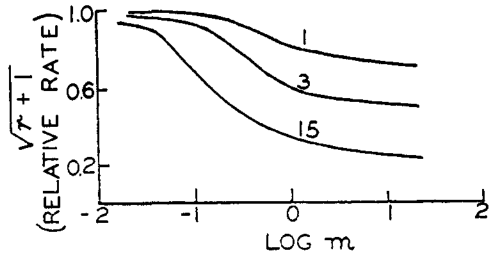


Fig. 6. Rates of reaction for intermittent illumination; m is ratio of duration of flash to lifetime (48).

There may be some complicating reactions such as transfer, but these rarely have any effect on the rate of reaction and can be ignored. For the simultaneous polymerization of two monomers there can be a maximum of three methods of initiation, four of propagation, and three of termination.

In the case of unit polymerization (homopolymerization) the fact that the kinetic chain is represented in the final product as a molecular entity, or by a number of molecules, can be used as a method of determining the ratio $k_p/k_t^{1/2}$ without the necessity of determining the absolute value of the rate of chain starting. If k_f is the rate constant for the transfer reaction, then

$$\begin{aligned}\bar{P}^{-1} &= k_f/k_p + (k_t R_i)^{1/2}/k_p(\mathrm{A}) \\ &= k_f/k_p + k_t R/k_p^2(\mathrm{A})^2\end{aligned}$$

so that a plot of the reciprocal degree of polymerization, $\bar{P}$, against the rate of reaction should give a straight line from which $k_p/k_t^{1/2}$ can be computed. It was shown above that lifetime measurements can be made to yield the ratio k_p/k_t, so that, utilizing this method, the rate constants k_p, k_t, and k_f are all obtainable.

The equation relating the degree of polymerization to the rate of reaction involves the tacit assumption that the termination reaction involves the formation of two molecules of polymer, i.e., the removal of the free radicals is achieved by the abstraction of a hydrogen (or other) atom from one by the other so that a saturated molecule and a monene result. The alternative mechanism whereby the two radicals couple to give only one polymer molecule will produce a polymer whose degree of polymerization is at most twice that of the disproportionation case. It means, therefore, that the slope measured from the method just described will give one-half the ratio mentioned above. Before this method can be successfully applied, it is necessary to ensure that no side reactions involving the polymer itself are of significance and, further, that the initiator (or photosensitizer) plays no part in the reaction other than starting chains (106).

V. Measurement of the Rate of Chain Initiation

A. TERMINATION IN RADICAL POLYMERIZATION

The measurement of the rate of initiation has proved to be one of the most difficult operations in the determination of the rate constants for chain reactions. Allied to this difficulty there is the fact that only in a very few cases has any conclusive proof been offered as to the precise nature of the termination reaction. In the study of polymerization reactions this information is of vital significance. In photochemical reactions the measurement of the intensity of the absorbed radiation cannot offer a way out, since it is known that the absorption of a quantum of energy does not necessarily mean that a chain will be started. The primary quantum efficiency, i.e., the ratio of the number of quanta effective to the number absorbed, is often low, so that probable errors involved in the use of this method must be high. It is essential that methods be evolved to solve this problem. Until recently, however, certain assumptions have always had to be made.

As far as addition radical polymerization is concerned, a rather specialized method of approach can be made. In these reactions the kinetic chain is represented in the final analysis by either a single molecule or a number of molecules of relatively high molecular weight. The gross chain may be broken into smaller entities by virtue of the reaction:

$$A_{\overline{n}}\text{—} + \mathrm{A} \rightarrow \mathrm{P}_n + \mathrm{A}\text{—}$$

in which P_n represents an inactive polymer molecule. Thus, although the activity of the chain is retained by the creation of the new radical A—, the growth reaction has suffered a break. Now the degree of polymerization, i.e., the number of monomer units per polymer molecule, can be measured by determination of the osmotic pressure of polymer solutions. As has already been pointed out, this method affords a means of obtaining a relationship between the rate constants for the propagation and termination reactions without the necessity of measuring the rate of initiation directly.

Since it is necessary to make an assumption with regard to the nature of the termination reaction in order to apply the molecular-weight technique, an examination of the evidence with regard to this point will be made here.

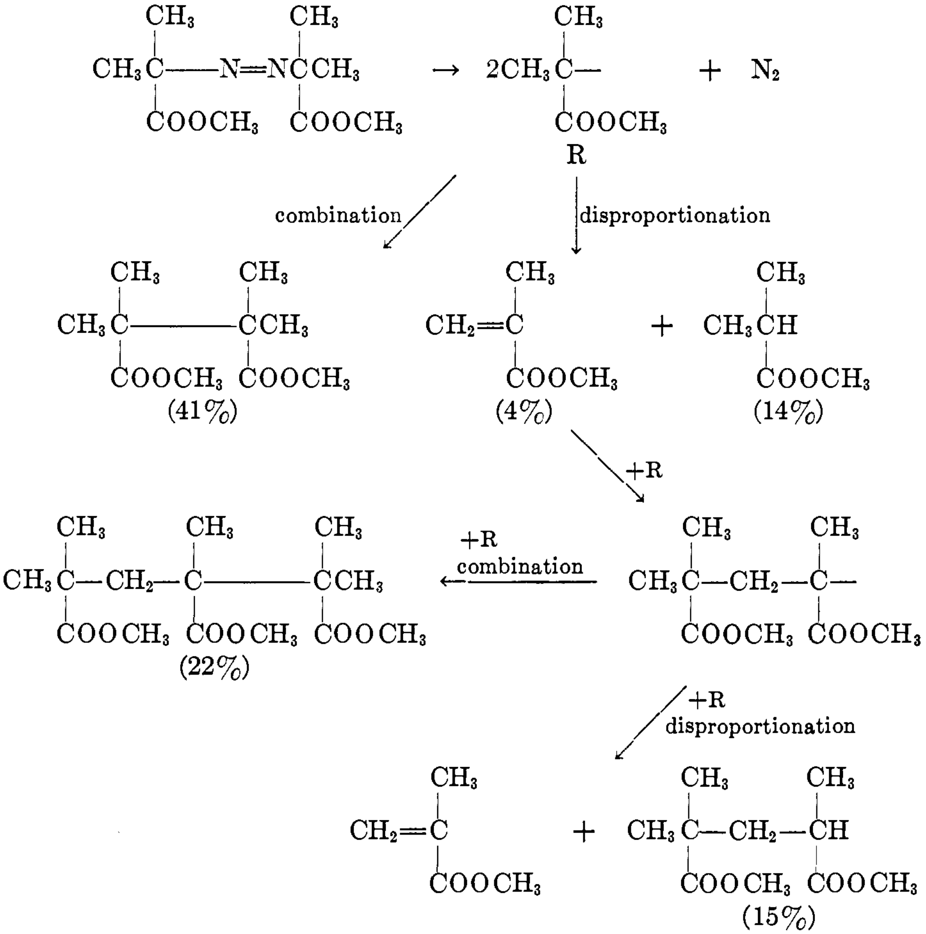
From a purely kinetic standpoint it is not possible to distinguish between the two forms which the termination reaction may take. It is therefore necessary to seek information from less direct observations and, in some cases, from analogy with well-established reactions. For the polymerization of methyl methacrylate in aqueous media, initiated by redox systems in which the active initiating agent is the hydroxyl radical, the resulting polymer was shown to possess two hydroxyl groups per molecule, from which it can be argued that the termination must be by coupling of the growing radicals (26). This argument, however, is based on the assumption that the hydroxyl radicals only initiate the polymerization, although there is no evidence which suggests that the radicals cannot in fact also terminate the chains. Thus what is apparently a clear-cut case is subject to a second construction. The introduction of the second hydroxyl could also arise from a transfer reaction between the growing polymer radical and either water or hydrogen peroxide. The fact that some radical initiators also act as chain terminators has been exemplified by the radicals derived from tetraphenylsuccinodinitrile, which can act as both initiator and terminator of the polymerization of methyl methacrylate (137). By analogy with the fact that radicals of the form $\mathrm{CH_3CH_2\dot{C}(CH_3)COOCH_3}$ combine exclusively, it has been argued that, because of the structural similarity, methyl methacrylate radicals with the end grouping $CH_3CH_2\dot{C}(CH_3)COOCH_3$ ought to do likewise (130).

On the other hand, it has been shown that many larger radicals show a greater tendency to disproportionate than to combine, e.g., *n*-octyl radicals (16). The presence of a permanent dipole moment in many of the polymer radicals with which we are concerned has been taken by Weiss to be a criterion of disproportionation (152).

In the degradation of polymethyl methacrylate at temperatures above 200°C. there is no question that disproportionation must occur, since the number of molecules remains constant (80). Furthermore, the supersonic degradation of the same material gives evidence which points to the fact that disproportionation is the main chain-breaking mechanism even at temperatures of the order of 40°C. (124).

Direct experimental evidence on this point is rather scanty, but one or two items are of significance. As will be shown in Section VII,B,5, exact kinetic analysis of polymerization reactions can be made to yield a precise expression correlating the rate of change of viscosity with the rate of chain initiation (11). It is assumed that by opening the double bond of the olefinic monomer two unpaired electrons result, giving a diradical. If the possibility of the self-termination of such diradicals (87) can be neglected, then it can be shown that for mutual termination by disproportionation the rate of change of viscosity will be proportional to $I^{(1-\alpha)/2}$, where I is the intensity of illumination and α is the Houwink viscosity constant. If, however, combination is the termination mechanism, then the proportionality changes to $I^{1/2}$. The photopolymerization of methyl methacrylate showed that the experimental exponent of I was 0.1, in excellent agreement with the value of $\alpha = 0.82$, so that, on the surface at least, the evidence appears to be conclusive. However, this result is based on the assumption that the initial chain carrier is a diradical, but scission of the molecule is also possible, as in the case of methyl vinyl ketone (93), and since this would give a monoradical initiation process the argument would then break down, since the forms of the two expressions would become identical. The obvious method of circumventing this difficulty is to ensure the diradical nature of the initiating agent, which might be possible by the use of diazomethane, giving methylene radicals, or of cyclohexanone, which photochemically appears to produce penta. methylene radicals, effective in the polymerization of vinyl chloride (147).

The thermal decomposition of a number of aliphatic azo compounds has been investigated by Bickel and Waters (34, 35) in an attempt to resolve the problem- Isolation of the products of reaction for dimethyl 2,2′-azoisobutyrate showed that a tetramethylsuccinate, a trimethylglutarate, methyl methacrylate, methyl isobutyrate, and another ester were formed. The primary step in the reaction is supposed to be the formation of the radical $(CH_3)_2CCOOCH_3$. The full reaction scheme proposed is:



Since the polymerization of methyl methacrylate produces radicals with terminal groups similar to the radicals generated in the above reaction, it appears that termination by combination and disproportionation occur to about the same extent. A similar situation is reported in the decomposition of ω,ω′-azotoluene, $C_6H_5CH_2N{=}NCH_2C_6H_5$, the products of reaction indicating both combination and disproportionation in the ratio of about 2:1. On the other hand, the thermal decomposition of 2,2′-azoisobutyronitrile, $(CH_3)_2C(CN)N{=}NC(CN)(CH_3)_2$, which gives rise to radicals similar to those encountered in the polymerization of methacrylonitrile, gives reaction products which indicate that almost all the interaction of radicals takes place by combination.

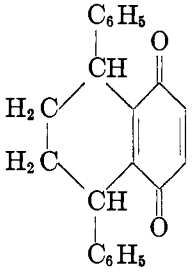
It can be shown that the ratio of the weight to the number-average molecular weights depends on the chemical nature of the termination step. Since the methods of measurement of both these quantities are well developed, tests along these lines might provide an answer to the problem. The ratio is 2 in the case of disproportionation and 1.5 for combination, so that there is the possibility of discrimination provided the reaction is carried out at a sufficiently high overall rate so that transfer does not play a significant part in the reaction. In their investigation of the kinetic constants of the polymerization of vinyl acetate Bartlett, Smith, and Kwart (18) measured the molecular weight of the polymer by both light scattering (weight average) and osmometry (number average) and obtained a ratio of 1.65. This might indicate a preference for combination, but in view of the fact that transfer cannot have been negligible, the evidence is again not conclusive. In a similar series of experiments on polystyrene Breitenbach and Duch (44) concluded that the predominant termination reaction was disproportionation. Again this work takes no account of transfer. In a more exhaustive series of measurements of the same type Billmeyer and Stockmayer (36) showed that the ratio of weight to number-average molecular weight depends to a large extent on the history of the sample; values of the order of 10 were found in some cases. The validity of the results is therefore open to considerable doubt.

A more important technique whose applicability is very wide is the use of radioactive tracer methods. If polymerization is initiated by free radicals obtained from the decomposition of a suitable peroxide or azo compound, it is most likely that the radical will add on to the double bond of the monomer in the initiation step. Generally it is not possible to analyze for end groups, but if they are labelled with C^{14} (radiocarbon), then the number of end groups is relatively easily determined. The molecular weight can be found osmotically, and so the number of end groups per polymer molecule can be calculated. The application of this technique demands that the following conditions should be fulfilled. The initiator fragments must add to the double bond, and the initiator itself must not be susceptible to free-radical attack with subsequent decomposition. The effect of transfer must be negligible and branching must not occur. Arnett and Petersen (6) made an investigation of the polymerization of methyl methacrylate, using 2,2′-azoisobutyronitrile labelled on the methyl group with C^{14} as initiator. The result of this investigation showed that methyl methacrylate radicals combine almost exclusively. This result is in direct contrast to the conclusions of Bevington, Melville, and Taylor (31), who assert that about 80 per cent of the chains terminate by disproportionation. On the other hand, the latter workers find that styrene radicals combine exclusively, as do the radicals involved in the copolymerization of styrene and methyl methacrylate over a wide range of reaction mixtures (32).

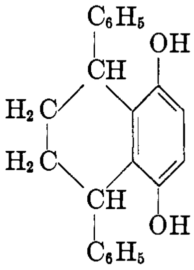
B. RETARDATION AND INHIBITION

The addition of small quantities of foreign material to systems in which reaction proceeds by means of a free-radical mechanism can give rise to a variety of effects. The interaction of the radical with a molecule of the addendum will result in the saturation of the radical and the formation of a new radical from the addendum. This radical may perform one of several roles. It is possible that the radical is capable of starting a new reaction chain and so the addendum acts as a transfer agent, merely bringing about a decrease in the molecular weight of the polymer but having no effect on the rate of reaction. On the other hand, the new radical may be incapable of propagating a new chain and may disappear by interaction either with another of its kind or with a carrier radical. In either of these cases the effect will be to reduce the velocity of reaction. Here it is convenient to differentiate between two phenomena: inhibition will be taken as implying that the chain process is completely suppressed by the foreign substance, while in the case of retardation the rate is merely reduced. The distinction between the two types may in some cases be a matter of degree, although sometimes the nature of the carrier radical has to be taken into consideration (17).

One of the most useful inhibitors has proved to be *p*-benzoquinone. The thermal polymerization of styrene is suppressed over a considerable period of time by the addition of quinone (75, 94, 108, 150). Both Melville and Watson (150) and Kern and Feuerstein (94) isolated a compound which corresponds to the union of two molecules of styrene and one of quinone, having, according to Melville and Watson, the structure:



By analogy with the Diels–Alder reaction they show that the addition of a further two molecules of styrene is unlikely on energetic grounds. While it is true that the inhibition is complete over long periods, the uninhibited rate of polymerization is not set up immediately the quinone is used up. This indicates that the addition compound must also be capable of retarding the reaction. This can be explained if it is assumed that the above compound can rearrange to the phenolic structure:



and it is well known that substances of this type are retarders of polymerization.

If the reaction is completely suppressed by the inhibitor, then it is necessary that all chain carriers react with it. Hence the consumption of a given amount

TABLE 3

Inhibition of the polymerization of vinyl acetate by p-benzoquinone (48)

WEIGHT OF QUINONE (W)	INHIBITION PERIOD (T)	T/W	R_i
grams	*min.*		*radicals per sec.* $\times 10^{-14}$
0.13	112	861	1.085
0.29	250	864	1.082
0.75	670	891	1.050

of inhibitor is a measure of the number of chains stopped in the time and therefore the rate of initiation can be computed, provided the inhibitor has no effect on the production of radicals and that one chain is stopped by each inhibitor molecule. A few illustrative results are shown in table 3.

Since it is assumed in the work in question that the quinone effectively reacted with diradicals, it follows that the rate of radical formation is 2.15×10^{14} per second.

In some cases it is convenient to make use of a retarder rather than an inhibitor. Here the reaction velocity increases with time until eventually the unretarded rate is reached. The approximate kinetic analysis of this type of reaction reveals that the rate of initiation can readily be obtained from experimental data. The only assumption is that the retarder molecules react with all the kinetic chains, so that no mutual termination takes place. On the basis of this, therefore, the only termination step is

$$\text{A—} + \text{X} \rightarrow \text{unreactive product}$$

for which the velocity constant is k_x. Then in the stationary state:

$$\mathrm{d}(\text{A—})/\mathrm{d}t = R_i - k_x(\text{A—})(\text{X}) = 0$$

Further, since each chain reacts with a retarder molecule:

$$-\mathrm{d}(\text{X})/\mathrm{d}t = R_i$$

so that

$$(\text{X}) = (\text{X})_0 - R_i t$$

where $(\text{X})_0$ is the concentration of the retarder initially present. Now the rate of reaction, r, is given by

$$r = k_p(\text{A—})(\text{A}) = k_p(\text{A})R_i/k_x(\text{X})$$

or, on substitution for (X):

$$r^{-1} = k_x(\text{X})_0/k_p(\text{A})R_i - k_x t/k_p(\text{A})$$

Hence the ratio of the slope to the intercept of the resulting straight line is $R_i/(\text{X})_0$.

This method has been used in the measurement of the rate of chain starting in the oxidation of n-decaldehyde (65). In general, the correlation between theory and practice is good except at the very beginning of the run, but this is understandable in this case because the measurement of oxygen uptake becomes more difficult at very low rates. Table 4 gives data on the retarded reaction which demonstrate the efficacy of the method.

Sometimes it is possible to measure directly the rate of disappearance of the retarder or inhibitor. This was done spectrophotometrically in the photopolymerization of vinylidene chloride retarded by *p*-benzoquinone (56).

Although much is now known regarding inhibition and retardation, the selection of a suitable compound with which to make a determination is still largely a matter of trial and error, since much depends on the type of reaction and also on the difficulty of the measurements. The results of an extensive investigation of the effects of phenols as retarders of oxidation reactions are given in table 5.

From this table it will be seen that there is a trend in the retarder efficiency as a function of oxidation–reduction potential, but this is not a clear relationship.

A similar series of measurements has been carried out to investigate the effect of a number of hydroquinones on the polymerization of methyl methacrylate, using benzoin as a photosensitizer. As table 6 shows, there is a trend between the effective retarding efficiency and the redox potential, as before (63). In this case the correlation between log k and E_0 is very good except in the case of 1,4-naphthohydroquinone, the discrepancy being ascribed to the very great

TABLE 4

Rate of initiation in the photoöxidation of n-decaldehyde (65)

QUINOL CONCENTRATION	INITIAL RATE	$\frac{\text{SLOPE}}{\text{INTERCEPT}} \times 10^5$	R_i	CHAIN LENGTH
moles/l. × *10*⁵	*moles/l./sec.* × *10*⁶		*moles /l./sec.* × *10*⁹	
3.16	7.40	14.80	4.7	1350
5.43	4.95	9.74	5.3	900
7.40	3.50	7.86	5.8	720
42.80	0.82	1.71	7.3	150

TABLE 5

Efficiency of phenols as retarders in oxidation reactions (41)

RETARDER	RELATIVE EFFICIENCY	REDOX POTENTIAL
		volts
Resorcinol	0.016	1.179
β-Naphthol	0.077	1.153
p-Methoxyphenol	0.170	0.984
α-Naphthol	0.56	0.933
Pyrogallol	3.0	0.876
Catechol	0.63	0.810
Quinol	1.00	0.715
Toluhydroquinone	1.5	0.653
Trimethylhydroquinone	5.7	0.528
1,4-Naphthohydroquinone	4.0	0.482

TABLE 6

Retardation of the photosensitized polymerization of methyl methacrylate (63)

RETARDER	RETARDATION CONSTANT, k	LOG k	REDOX POTENTIAL
Pyrocatechol	9.99	0.999	0.810
Toluhydroquinone	16.88	1.277	0.653
Trimethylhydroquinone	38.5	1.586	0.528
1,4-Naphthohydroquinone	10.836	4.035	0.482

ease of oxidation to the corresponding quinone, which makes the preparation of a pure sample of the hydroquinone almost impossible.

Although there is little doubt as to the efficacy of the retardation technique, some complications do arise in certain instances. Some reactions are very difficult to retard; for example, the polymerization of butyl acrylate. Here the radical diphenylnitrogen, $(C_6H_5)_2N$—, from the dissociation of tetraphenylhydrazine, is almost the only effective retarder (33). In other cases also it is necessary to use free radicals in order to effect inhibition, e.g., diphenylcyanomethyl in the radical photodegradation of polymethyl methacrylate (68).

Schulz (138) made a careful study of the effect of a number of inhibitors and retarders on the polymerization of styrene. On the basis of his work there appear to be four distinct classes:

(i) Termination inhibitors which increase the rate of chain termination only;
(ii) Initiation inhibitors which decrease the rate of initiation;
(iii) Initiation-termination inhibitors;
(iv) Compensation inhibitors whose action results in an increase in the velocity of the initiation reaction; however, the rate of reaction is reduced by a diminution in the chain length as the result of an increase in the termination rate.

Using Schulz's notation, if q_v and q_p are defined by

$$q_v = v_0/v_i \text{ and } q_p = P_0/P_i$$

where v_0 and v_i are the rates of the unretarded and retarded reactions, respectively, and P_0 and P_i are the corresponding degrees of polymerization, the efficiency of a compound as a retarder is given by

$$k = [(q_v q_p)^{1/2} - 1]/c$$

where c is the concentration. Table 7 gives a list of the retarders which were tested, along with the classes to which they belong.

Despite the fact that inhibition and retardation experiments have been widely used to determine the rate of chain initiation, until recently no examination of the kinetics of the possible chemical process involved had been carried out. Frequently even in the case of a good inhibitor (in the sense defined above) there is not a complete suppression of the reaction, so that a plot of the extent of reaction against time shows a definite "ankle" to the curve. Under these circum-

TABLE 7

Retarders for styrene polymerization (138)

RETARDER	k	EFFECT ON INITIATION	CLASS*
Tetraphenylhexatriene	42	Retarded	iii
Tetraphenyloctatetraene	230	Retarded	iii
Tetraphenyldecapentaene	420	Retarded	iii
Diphenylethylene	42	Accelerated	iv
Phenylnitroethylene	3000	Accelerated slightly	iv
Benzaldehyde	0.7		
Benzoic acid	0		
Hydroquinone	0		
p-Benzoquinone	2×10^4	Accelerated	iv
Anthraquinone	0		
Phenanthraquinone	340	Retarded	iii
Hydrazobenzene	325	Retarded	iii
Azobenzene	0		
Azoxybenzene	25		
Nitrobenzene	19	Retarded	iii
Dinitrobenzene	190	Retarded	iii
Trinitrobenzene	1510	Retarded	iii
1,8-Dinitronaphthalene	245	Retarded	iii
1,5-Dinitronaphthalene	500	Retarded	iii
Tetranitromethane	850	Accelerated slightly	iv
Nitrophenol (*o*, *m*, *p*)	*ca.* 10^4		
Nitrosobenzene	*ca.* 10^4		
Sulfur	*ca.* 10^4	Retarded	iii
Iodine	2500	Retarded	iii

* See classification on page 249.

stances, it is common practice to extrapolate the steady-rate portion of the curve to the time axis and assume that the intercept on that axis gives the time for complete removal of the retarder. Burnett and Cowley (46) have concluded, from a kinetic analysis of the problem, that such a procedure is valid if the ratio of the rate constant for the interaction of radicals and retarder and the propagation constants is much in excess of 100. Further, the plot of the reciprocal rate against time leads to a value of the rate of initiation which is much more precise than that obtained by the more usual extrapolation procedure.

C. DIRECT MEASUREMENT OF INITIATION IN RADICAL POLYMERIZATION

Provided the initiator does not react with the chain-propagating radical, in principle, the application of radioactive tracer techniques provides a very sensitive method of obtaining the rate of chain initiation in polymerization reactions. From the radioactivity assay of a polymer sample it is possible to compute the number of monomer molecules which are associated with each catalyst fragment which effectively initiates a chain, i.e., to find the kinetic chain length. The rate of chain starting is then the ratio of the overall rate of reaction to the kinetic chain length. This method is quite independent of any assumption regarding the nature of the termination reaction and also the effect (if any) of transfer and branching. The main difficulties are on the experimental side, since the removal of residual unreacted initiator from the polymer is difficult, especially since loss of low-molecular-weight material must be avoided.

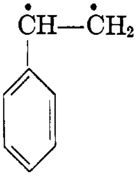
An additional result which follows immediately from this technique is the measurement of the efficiency of the initiator if the rate of decomposition is known. In all cases so far examined the efficiency is very near 0.5 for 2,2′-azoisobutyronitrile (30).

D. MONORADICAL AND DIRADICAL INITIATION

In most radical reactions the initiation process consists in the fission of a molecule into two monoradicals. The kinetic analysis given in this article is therefore directly applicable to such reactions. In certain cases, particularly polymerization, there is the possibility of the initial production of diradicals. The first problem is to devise a means of discriminating between mono- and diradicals. Diradicals in polymerization have been postulated to occur in both thermal and photochemical reactions. In the former the initiation process involves two monomer molecules, which on collision are said to give a dimeric diradical. In photochemical initiation the monomer may initially be electronically excited and if a collision with another monomer occurs before deactivation, a diradical is produced which can grow at both ends.

A discrimination appears to be made in the photopolymerization of vinyl acetate. If benzoquinone is added to the monomer, an induction period occurs, at the expiration of which the reaction rate suddenly becomes equal to that of polymerization of the pure monomer (48). If the same amount of quinone is added to the system in which polymerization is initiated by the photodecomposition of benzoyl peroxide, then only retardation results and polymerization occurs from the start of the reaction. In the gas-phase polymerization of vinyl acetate the reaction can also be induced photochemically and there are two distinct and unique characteristics (146); the reaction is retarded by the addition of inert gases like helium and argon, but this retarded rate is still proportional to the square root of the light intensity, showing that the retardation is concerned with the initiation process. If the pressure of vinyl acetate vapor is reduced, the rate of reaction falls off very rapidly; below a pressure of about 12 mm. at room temperature it is hardly measurable. At higher temperatures this effect of pressure disappears. Because of the existence of these very low rates of reaction it is possible to study the polymerization induced by hydrogen atoms or methyl radicals. There is no question that this is a monoradical process. Here, however, the pressure dependence is normal and the presence of inert gases has no effect. The observations in the direct reaction can be most satisfactorily explained on the assumption that the vinyl acetate molecule is initially excited. If an effective collision with monomer occurs polymerization starts, but the excited molecule can spontaneously lose its energy of excitation or, alternatively, it may be deactivated as in a collision of the second kind with chemically inert molecules.

A kinetic analysis of polymerization in which initiation is by diradicals shows that the dependence of the molecular weight on the rate of polymer production depends on the nature of the termination step. Using a classical type of analysis it can be shown that if termination is by coupling of radicals the molecular weight is independent of the rate, while for disproportionation there is linear dependence of the reciprocal molecular weight on the rate. Johnson and Tobolsky (91) and Baysal and Tobolsky (27) have investigated the variation of molecular weight with rate in the polymerization of styrene and methyl methacrylate, for both radical and photochemical initiation. In both cases there is a linear relationship between reciprocal molecular weight and rate, and the curves for the two modes of initiation are coincident. From the data it is deduced that in both instances the termination step involves coupling and the initiation is by monoradicals. While the former conclusion may be in some doubt, since it assumes the efficiency of the initiator to be nearly unity, the latter is unlikely to be in error. The question as to how the monoradicals arise is rather complicated. While in the cases of esters, ketones, etc. a normal photolysis can take place, styrene poses a more difficult problem. Johnson and Tobolsky (91) suggest the initial formation of an excited diradical:



The stability of the two radical ends depends on the proximity to the phenyl group. It is argued that the more reactive CH_2 end is more likely to abstract a hydrogen atom from a monomer molecule than to add to it. Consequently, virtually in the first step of the reaction the chain involving the diradical ceases to exist and is replaced by two monoradical chains.

In the previous paragraph it was stated that the kinetic expressions derived for diradical initiation depend on a classical analysis, i.e., the basic assumption is that all radicals are equally accessible to one another. If diradicals exist, then it is evident that this assumption cannot be valid, since the radical concentration in the vicinity of one end of a diradical is determined by the separation between the two ends. Working on this basis Haward (87) has shown that this would result in a very high rate of self-termination. A more refined analysis by Zimm (154) has given the same result. This type of reaction can introduce other complications, which again depend on the nature of the termination step. If termination takes place by coupling and the diradicals are able to increase their size to some extent before terminating, large-ring systems will result. These must interlace to some extent to cause the formation of an insoluble gel (153), but such a situation has never been reported even in the case of the purely thermal polymerization of styrene, in which the initial formation of diradicals is still to some extent supported (27, 91).

TABLE 8

Rate constants for polymerization using intermittent illumination

TEMPERATURE	LIFETIME AT 1 PER CENT PER HOUR	$k_p/k_t \times 10^6$	$k_p/k_t^{1/2} \times 10^4$	k_p	$k_t \times 10^{-7}$	REFERENCES
			Styrene			
°C.	*seconds*					
30	1.3	4.94	2.56	50.8	10.1	(104)
10	0.18			27.5	1.05	(120)
			Methyl methacrylate			
24	1.71	4.75	13.7	288	6.07	(97)
25	3.9	10.8	11.2	262	2.3	(102)
25	4.0	11.1	30.3	512		(64)
30	3.41	10.9	27.0	273	4.66	(121)
			n-Propyl methacrylate			
30				467	4.5	(47)
			Butyl methacrylate			
30				369	1.02	(47)
			Methyl acrylate			
25	6.2	10.7		1580	5.5	(133)
30	1.2	3.4		1730	0.94	(103)
			Vinyl acetate			
15	0.52	1.92		750	39	(48, 52)
15	3.0	11		880	8.0	(19)
25	3.9	14		825	5.88	(104)
15	4.0	16.6		980	5.88	(18)
			Vinylidene chloride			
15				2.3	0.0023	(56)
25				8.6	0.0175	(56)
35				36.8	0.18	(56)
			Butyl acrylate			
25		720	970	13	0.0018	(33)
25		1250	1920	22.5	0.0018	(33)
			Vinyl chloride			
25				6200	110	(55)

VI. Rate Constants in Chain Reactions

A. POLYMERIZATION

The data obtained by the use of the rotating sector technique are presented in table 8. From this table it will be seen that for those cases for which more than one set of results is available the agreement is not, at first sight, as good as might be expected. On the whole, however, considering the great experimental difficulties, accord in most cases can be said to be satisfactory. The discrepancies in the measured values of the lifetimes of the kinetic chains appear to be the main sources of error. This is not difficult to understand, since much depends on the purity of the monomer in question. It is evident that the presence of even minute amounts of inhibitory material may bring about significant reductions in both the rate of reaction and the lifetime of the chain. Thus it appears that the main difficulties lie, not in the theory, but in the chemistry which precedes the actual experiments.

An idea of the reproducibility of results obtained in a series of measurements made by the same investigators can be obtained from table 9 (103, 104).

Therefore, although it is assumed that the sector experiments are free from gross errors, the spread of the results of individual investigators is too great to support this contention. As table 9 shows, the measured lifetimes which have been normalized to a rate of 1 per cent per hour seem to have an uncertainty factor of about 2.5 even in the most favorable cases. The lifetime is essentially a measure of $k_t^{1/2}$, so that any error in the determination of the lifetime will be at least doubled in calculating the velocity constant, and to this error must be added that involved in the estimation of the rate of chain initiation.

B. OXIDATION

As was pointed out earlier, use of the rotating sector was made to demonstrate the finite existence in time of reaction chains in the gas phase. More recently the problem of completely resolving the kinetics of reactions involving the oxidation of hydrocarbons and aldehydes by gaseous oxygen has received considerable attention.

For this type of reaction the scheme is:

$$\begin{array}{lll}
\text{Initiation:} & \text{production of radicals} & R_i \\[6pt]
\text{Propagation:} & \text{R—} + \text{O}_2 \rightarrow \text{RO}_2\text{—} & k_2 \\
 & \text{RO}_2\text{—} + \text{RH} \rightarrow \text{RO}_2\text{H} + \text{R—} & k_3 \\[6pt]
\text{Termination:} & \left.\begin{array}{r} 2\text{R—} \\ \text{RO}_2\text{—} + \text{R—} \\ 2\text{RO}_2\text{—} \end{array}\right\} \rightarrow \text{inactive products} & \begin{array}{l} k_4 \\ k_5 \\ k_6 \end{array}
\end{array}$$

Under conditions of high oxygen pressure it has been found that the method of intermittent illumination can be applied to this reaction (15, 20, 66). In this set of circumstances the only termination step of importance is that involving the RO_2 radicals only, so that if the rate of initiation can be measured the

TABLE 9

Lifetimes derived from individual experiments

MONOMER	LIFETIME	MEAN	ERROR OF MEAN
	seconds	*seconds*	
Methyl methacrylate............	0.85; 1.10; 1.00	0.906	0.04
	0.90; 0.95; 0.72		
Vinyl acetate....................	2.98; 6.51; 2.89		

TABLE 10

Rate constants in oxidation using intermittent illumination

COMPOUND	TEMPERATURE	k_3	$k_6 \times 10^{-6}$	E_3	E_6
	°*C.*	*l./mole/sec.*	*l./mole/sec.*	*kcal./mole*	*kcal./mole*
Tetralin (15)..........................	25	13.30	21.5	4.5	0.4
	45	20.87	22.4	4.5	0.4
Cyclohexene (24)......................	15	0.65	0.95	9.5	2
1-Methylcyclohexene (24)..............	15	1.1	0.50	8.5	2
Dihydromyrcene (21)..................	15	0.40	0.65	9.0	2
Ethylene linoleate (21)................	15	5.7	0.50	7.0	2
n-Decaldehyde (66)...................	5	1100*	7.5	4.2	1
	5	2700†	34	4.2	1
Benzaldehyde (90)....................	5	1910	210	1.8	1

* Pure aldehyde.

† 30 per cent solution of aldehyde in *n*-decane.

constants k_3 and k_6 can be found. Under conditions of low oxygen pressure, a non-stationary technique must be used in order to evaluate k_2, k_4, and k_5, since it is not possible to use oxygen pressures sufficiently low to exclude completely the crossed termination step. The results obtained by the rotating sector method are presented in table 10, while those from non-stationary state experiments will be deferred until Section VII,C.

It will be seen from table 10 that the values of k_6 do not vary so much as might be expected from the differences in structure of the radicals. All those which are essentially hydrocarbons, with the exception of tetralin, give results of approximately the same order of magnitude and in each case the activation energy for this termination process is low. The major variation lies in the values of the propagation constants when the structure of the compound appears to exert a greater effect on the reactivity.

C. REACTIONS OF TRICHLOROMETHYL RADICALS

A further radical reaction which has been studied quantitatively is that of the addition of trichloromethyl radicals to olefins. The principal steps in such a reaction are:

$$CCl_3Br + h\nu \rightarrow CCl_3\text{—} + Br \qquad R_i$$

$$CCl_3\text{—} + CH_2{=}CHR \rightarrow CCl_3CH_2CHR\text{—} \qquad k_2$$

$$CCl_3CH_2CHR\text{—} + CCl_3Br \rightarrow CCl_3CH_2CHRBr + CCl_3\text{—} \qquad k_3$$

TABLE 11

Rate constants for interaction of bromotrichloromethane with unsaturated molecules at 30°C.

CONSTANT	METHALLYL ACETATE (107)	ALLYL CHLORIDE (118)	CYCLOHEXENE (117)	VINYL ACETATE (118)	STYRENE (118)	α-METHYLSTYRENE (118)
l./mole/sec.						
k_2	3240		256	1120		
k_3		16	63.8	2740	20	8
$2k_4 \times 10^{-7}$	6.6		10	10		
$2k_5 \times 10^{-7}$			57	380		
$2k_6 \times 10^{-7}$		0.8	4 6.4	5.76 35.3	1.3	0.67
E_2 (kcal.)	7.74		3.1	6.1		
E_3 (kcal.)		5.8	4.5	7.5	10	5
E_4 (kcal.)	5.7	Low	Low	Low		
E_5 (kcal.)		Low	Low	Low		

The possible termination reactions in which the radicals are removed in pairs are:

$$2CCl_3— \rightarrow C_2Cl_6 \qquad k_4$$

$$CCl_3CH_2CHR— + CCl_3— \rightarrow CCl_3CH_2CHRCCl_3 \qquad k_5$$

$$2CCl_3CH_2CHR— \rightarrow (CCl_3CH_2CHR)_2 \qquad k_6$$

When the olefin is in excess the last of these three reactions will predominate, while in the presence of excess bromotrichloromethane the first will be of the greatest significance. Thus sector experiments carried out under these two extreme conditions can be used to determine the rate constants for the interaction of the like radicals. By using intermediate mixtures the rate constant for the interaction of the unlike radicals can be computed. As a result of the measurement of the lifetime of the chains and of the rate of initiation, the rate constants for the propagation reactions can also be found. The interaction of bromotrichloromethane with a number of olefinic substances has been studied by Matheson and Halter (107) and by Melville, Robb, and Tutton (117, 118) with the results shown in table 11.

As in the case of copolymerization and of oxidation, the rate constant for the interaction of unlike radicals is much greater than the geometric mean of the constants for the like radical reactions. The main point of difference between the results of the workers is the value of the activation energy for the combination of the trichloromethyl radicals; whereas Matheson gives 5.7 kcal. per mole, Melville, Robb, and Tutton state that there is no perceptible variation in k_4 with temperature.

D. INTERACTION OF METHYL RADICALS

Methyl radicals can be produced in many simple photolysis reactions. Since, in all cases, the overall reaction rate is proportional to the square root of the light intensity, sector methods can be used to obtain the rate constant for the recombination of methyl radicals.

The photochemical decomposition of acetaldehyde is stated by Dodd (73) to follow the mechanism:

$$\begin{aligned} CH_3CHO + h\nu &\rightarrow CH_4 + CO \\ CH_3CHO + h\nu &\rightarrow CH_3\text{—} + CHO\text{—} \\ CH_3CHO + CH_3\text{—} &\rightarrow CH_4 + CO + CH_3\text{—} \\ 2CH_3\text{—} &\rightarrow C_2H_6 \\ CH_3\text{—} + CHO\text{—} &\rightarrow CH_4 + CO \\ CH_3\text{—}\ (+\ \text{wall}) &\rightarrow \text{inactive products} \end{aligned}$$

This scheme is based on well-established data of various authors (1, 79, 96, 122, 132).

A peculiarity of the kinetics is that the dependence of the rate on the light intensity deviates markedly from the square-root law when the intensity is very low (131). Using a standard rotating sector technique at relatively high light intensities, Dodd gives the value of the kinetic constant for the formation of ethane as:

$$6.3 \times 10^{10}\ T^{1/2} \exp\{(-800 \pm 800)/RT\}\ \text{l. mole}^{-1}\ \text{sec.}^{-1}$$

and the constant for the interaction of methyl radicals and acetaldehyde as:

$$6.3 \times 10^{10}\ T^{1/2} \exp\{(-10{,}700 \pm 500)/RT\}\ \text{l. mole}^{-1}\ \text{sec.}^{-1}$$

The value of the ratio of these two quantities agrees well with the results previously obtained by Hadden and Rice (131) but construed by them as involving the interaction of formyl radicals.

Gomer and Kistiakowsky (77), using similar methods, have studied the photochemical decomposition of acetone and mercury dimethyl. By using the Polanyi flame technique Allen and Bawn (2) were able to estimate that the upper limit of the collision efficiency of the interaction of two methyl radicals was about 0.1 or slightly less. By comparison of the rate of addition of nitric oxide to methyl radicals with the rate of formation of ethane Marcus and Steacie (101) arrived at a factor of 5×10^{-3} for the steric factor for the recombination of methyl radicals. Since this result is derived from the steric factor of 1.4×10^{-5} for the nitric oxide reaction derived by Forsyth (76) from mirror-removal experiments, the validity of Steacie's value is doubtful. Using the rotating sector method Gomer and Kistiakowsky obtained the results of table 12.

TABLE 12

Rate constants for some reactions of methyl radicals (77)

REACTION	RATE CONSTANT	ACTIVATION ENERGY	STERIC FACTOR*
	l./mole/sec.	*kcal./mole*	
$2CH_3\text{—}$	$2.1 \times 10^9\ T^{1/2}$	0	1.00
$CH_3\text{—} + (CH_3)_2CO$	$1.8 \times 10^7\ T^{1/2}$	9.5	1.7×10^{-3}
$CH_3\text{—} + (CH_3)_2Hg$	$4.1 \times 10^6\ T^{1/2}$	9.0	2.9×10^{-3}
$CH_3\text{—} + (CH_2)_2O$	$1.4 \times 10^6\ T^{1/2}$	9.0	1.7×10^{-4}
$CH_3\text{—} + C_4H_{10}$	$3.6 \times 10^6\ T^{1/2}$	8.2	4.9×10^{-4}

The agreement between the rate constants for the interaction of methyl radicals derived by Dodd and by Gomer and Kistiakowsky is not very good, although the error quoted by Dodd leads to a lower limit of about $2 \times 10^{10}\ T^{1/2}$. However, the complexity of the aldehyde case coupled with the increased difficulty in experimentation with sectors in the gas phase makes closer agreement unlikely.

E. RECOMBINATION OF IODINE ATOMS

When a solution of iodine in a non-polar solvent such as hexane is irradiated with visible light of suitable wave length dissociation of the iodine molecules occurs:

$$I_2 \rightarrow 2I \qquad \text{rate} = 2\phi q$$

$$I + I \rightarrow I_2 \qquad \text{rate} = 2k(I)^2$$

where q is the number of quanta absorbed and ϕ is the primary quantum efficiency. The value of ϕ has been determined by Zimmerman and Noyes (155) to be 0.59, using light of wave length 4360 Å. Using the rotating sector technique the value of the rate constant for the recombination of iodine atoms is 1.15×10^{10} l. mole^{-1} sec.$^{-1}$ at 25°C. In the gas phase the rate constant for the collision between iodine atoms on the basis of a van der Waals diameter of 4.3 Å. is 5.7×10^{10} l. mole^{-1} sec.$^{-1}$ (126).

The technique adopted in this investigation was to obtain the ratio of the concentration of iodine atoms under steady and intermittent illumination by utilizing the exchange reaction between radioiodine and *trans*-diiodoethylene. The rate of this exchange is known to be of first order with respect to iodine atoms (125). The rate constant for the exchange reaction between iodine atoms and molecules is about 8×10^7 l. mole^{-1} sec.$^{-1}$ at 25°C. in hexane solution; the activation energy for the exchange reaction is probably about 2–3 kcal. per mole.

F. REACTIONS INVOLVING CHLORINE ATOMS

According to Bodenstein (38, 39) the photochemical formation of phosgene proceeds according to the mechanism:

$$\begin{aligned} Cl_2 + h\nu &\rightarrow 2Cl && k_1 \\ Cl + CO &\rightarrow COCl && k_2 \\ COCl &\rightarrow Cl + CO && k_3 \\ COCl + Cl_2 &\rightarrow COCl_2 + Cl && k_4 \\ COCl + Cl &\rightarrow COCl_2 && k_5 \end{aligned}$$

Bodenstein published the values of the equilibrium constant $K = k_2/k_3$ and the values for the rate constants k_4 and k_5 from a combination of data derived from the photochemical and thermal reactions. However, these values may not be valid in view of the assumptions involved. Previously Bodenstein, Brenschede, and Schumaker (40) had carried out some sector experiments but did not make any evaluation of the constants using the data of this method. Burns and Dainton (58) have reëxamined the reaction and confirmed the Bodenstein mechanism.

Using the rotating sector method corrected for the excessive absorption of light (57), they find the following results:

$$K = 6.8 \times 10^{10} \exp\{-6310/RT\} \text{ mole l.}^{-1}$$
$$k_4 = 2.5 \times 10^{9} \exp\{-2960/RT\} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$
$$k_5 = 4.0 \times 10^{11} \exp\{-830/RT\} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

Nitrosyl chloride is an efficient retarder of the photochemical formation of phosgene. The reaction scheme is as above with the additional reactions (59, 69):

$$\mathrm{Cl + NOCl \rightarrow NO + Cl_2} \qquad k_6$$
$$\mathrm{COCl + NOCl \rightarrow NO + CO + Cl_2} \qquad k_7$$

Providing the equilibrium $\mathrm{CO + Cl \rightleftharpoons COCl}$ is maintained and the chains are not too short:

$$d[\mathrm{COCl_2}]/dt = \frac{2k_1k_4(\mathrm{CO})(\mathrm{Cl_2})I_0}{(\mathrm{NOCl})[k_7(\mathrm{CO}) + k_6K]}$$

From this expression and using the values of the individual constants found from the normal reaction, the two remaining constants can be calculated:

$$k_6 = 1.1 \times 10^{10} \exp\{-1060/RT\}$$
$$k_7 = 4.8 \times 10^{10} \exp\{-1140/RT\}$$

VII. The Non-Stationary State of Chain Reactions

A. GENERAL PRINCIPLES

It is a natural consequence of the nature of chain reactions that a finite time should elapse between the commencement of initiation and the attainment of the maximum (steady state) rate of reaction. Under normal conditions it is not possible to detect the small natural induction periods involved because of the inability to obtain the necessary resolution in time or sufficient sensitivity with the apparatus used. Hence, in order to be able to follow with some precision the natural induction period, apparatus of high sensitivity and high resolution in time is required.

Weigert and Kellermann (151) demonstrated, using spark discharges of varying duration, that the steady-state rate in the hydrogen–chlorine reaction was not attained until between 0.01 and 0.025 sec. after the commencement of the initiation. Although this experiment afforded a qualitative demonstration of the predicted time lag, the sensitivity of the measurements did not enable quantitative results to be obtained. The earliest analysis of a formal type was due to Semenoff (142) and was used by Kowalsky (95). More recently the method of approach has been further developed and extended (15, 22, 23, 24, 45, 143). Essentially similar methods have been applied to the polymerization of a number of ethylenic compounds, utilizing the change in viscosity of the system as the reaction proceeds (7, 10, 11, 13, 14, 71).

Although much of the succeeding discussion will be concerned with the problem of polymerization reactions, the underlying principles may be applied to any chain process and have been used in the case of oxidation at low oxygen pressures (15, 22, 23, 24).

In order to obtain a clearer picture of the general principles involved in the experimental techniques, a brief summary of the formal analysis is necessary. In the first instance assume that the chain termination is by the mutual interaction of two radicals, so that if (A—) is the concentration of the chain carriers and k_t is the termination velocity constant:

$$\mathrm{d(A—)/d}t = R_i - k_t(\mathrm{A—})^2$$

from which

$$(\mathrm{A—}) = (\mathrm{A—})_s \tanh (t/\tau)$$

where $(\mathrm{A—})_s = (R_i/k_t)^{1/2}$ is the concentration of the carriers in the stationary state and $\tau = (R_i k_t)^{-1/2}$ is the lifetime of the active chain. For small amounts of change the fraction, F, of conversion is:

$$F = (k_p/k_t) \ln \cosh (t/\tau)$$

where k_p is the velocity constant for the propagation step. If $t \gg \tau$, then

$$F = (k_p/k_t)(t/\tau - \ln 2) \qquad (4)$$

which gives a linear plot of F against t, whose intercept on the time axis is $(\tau \ln 2)$ so that both the lifetime and the value of the ratio $k_p k_t^{-1}$ are readily accessible. As was explained earlier, the value of the sector technique diminishes as the amount of first-order termination increases, either by wall termination or by the presence of some chain-destroying agent. A similar analysis to that given above can be carried out when the only termination reaction is:

$$\mathrm{A—} + \mathrm{X} \rightarrow \text{inactive products} \qquad k'_t$$

This gives:

$$F = [(k_p R_i/k'_t(\mathrm{X}))t - k_p R_i/k'^2_t(\mathrm{X})^2][1 - \exp\{-k'_t(\mathrm{X})t\}]$$

A similar type of analysis applied to the decay period, after the source of initiation has been removed, shows that for second-order termination:

$$r_t^{-1} - r_s^{-1} = (k_p/k_t(\mathrm{A}))t \qquad (5)$$

where r_s and r_t denote the rates of reaction under the steady state and at time t after initiation has ceased. In the same way for first-order termination:

$$\ln r_t = \ln K - k'_t(\mathrm{X})t \qquad (6)$$

where $K = k_p(\mathrm{A})/k'_t$. Hence by this method of following the decay $k_p k_t^{-1}$ can be found so that, as before, if either the rate of chain starting or the further relationship between the constants can be determined, the individual values of the constants can be computed. In the case of second-order termination it should be noted that the rate will fall to one-half of its original value during one lifetime during the decay period.

B. EXPERIMENTAL METHODS IN POLYMERIZATION

1. Dilatometry

In the foregoing section stress was laid on the need for measurements of very high precision and for high resolution in time. The factor of paramount importance is the achievement of high sensitivity as, in general, the lifetime of the chain can be altered to accord with the experimental limitations in the matter of resolution in time. Thus, unless the investigation of the precise form of the induction period is essential, the time factor is not so deeply concerned as might be at first thought. Dilatometry has been used for a considerable time as a method of following polymerization reactions. Normally the monomer itself acts as the dilatometer recording liquid, but to achieve the highest sensitivity it is necessary to use very fine capillaries in which the natural increase in the viscosity of the mixture would lead to spurious results. For the investigation in question (45) an adaptation of a dilatometer due to Schulz and Harborth (139, 140) was used, in which the movement of a mercury level records the volume changes of the system. The design of the dilatometer is shown in figure 7. A measured volume of monomer, thoroughly purified and freed from dissolved air, was introduced under vacuum into the main reaction bulb, A, in which the mercury was standing at level a. The apparatus was sealed off at b and transferred to a thermostat; after equilibrium had been reached, mercury from a reservoir attached to C was allowed to enter the reaction vessel until the monomer was pressed to the seal and stood at a convenient height in the capillary D. The tap close to C was closed and that at E opened before the readings were taken. It was found that in this way the best and most uniform movement of the mercury thread was obtained.

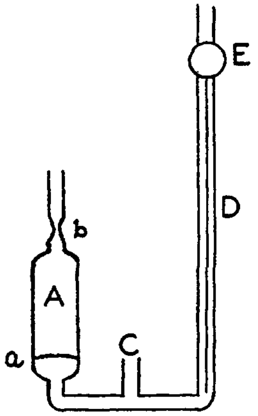


FIG. 7. Mercury recording dilatometer for use in vacuum (45)

By using very slight light absorption the chain initiation was kept so low that the lifetime of the chains was great enough to allow direct reading to be used. The reaction was shown to be sensibly isothermal by analogy with the work of

Schulz and Harborth (140). With the rates observed in the reaction the temperature rise should not have been greater than 2×10^{-4}°C.

The exact conditions of the experiment required the use of 40 ml. of styrene, which was irradiated by light from a mercury arc filtered through soft glass so that only radiation of $\lambda > 3500$ Å. reached the reaction system. The capillary had a bore of 0.2 mm., so that the total movement of the mercury meniscus for 100 per cent conversion was 1.78×10^4 cm.; this gives an ultimate sensitivity corresponding to the formation of about 1 part of polymer in 10^7.

It was considered that for all work of this kind which involves extrapolation the most precise analysis is obtained by the method of least squares. Using this technique at 15° and 25°C. the values of k_p/k_t were obtained; the ancillary data available from molecular-weight measurements allowed the computation of the values of the individual constants. These were found to be:

$$k_p = 1.44 \times 10^6 \exp\{-6300/RT\}$$

$$k_t = 1.43 \times 10^8 \exp\{-1900/RT\}$$

By careful measurement of the purely thermal rate of polymerization, the rate constant for the initiation reaction could be calculated on the assumption that the process was bimolecular. The constant was found to be:

$$k_i = 4.15 \times 10^{11} \exp\{-36{,}400/RT\}$$

These results were based on the assumption that the termination reaction resulted in the formation of two molecules of polymer, so that these figures have an uncertainty factor of at least 2 and possibly 3 when various other errors are taken into consideration.

2. Interferometry (81)

Allied to the change in density of the system there must be a change in refractive index and in dielectric constant. In making use of either of these changes, the nature of the apparatus makes it necessary to tackle the problem from a different standpoint. In both cases, the reaction was carried out under adiabatic conditions, the change in temperature being very small and too minute to affect the rate of reaction to a measurable extent. The most sensitive method of determining the change in refractive index is by making use of the movement of interference fringes. According to the theory of interferometry the change in refractive index, $\Delta\mu$, is related to the number of fringes, n, crossing the field by:

$$n = l\Delta\mu/\lambda$$

where l is the length of the light path and λ is the wave length of the light. Since the order of change in the refractive index for complete conversion of monomer to polymer is about 0.05, this corresponds to 2.3×10^4 fringes for a light path of 25 cm. using light of wave length $\lambda = 5460$ A. On the other hand, if the reaction is carried out adiabatically the rise in temperature produces a much greater change in refractive index in the opposite direction, owing to the increase in temperature. For example, if the polymerization of methyl methacrylate could be carried to completion adiabatically, then the rise in temperature would be 400°C., corresponding to a reduction in refractive index of 0.2. Hence, allowing for the increase in refractive index due to the formation of polymer the total decrease would cause the passage of 7×10^4 fringes. This implies that, providing the shift can be measured with an accuracy of 0.03 fringe, the method can be applied to the study of the non-stationary state.

A standard Jamin-type interferometer was used by Grassie and Melville (80) to determine the change in refractive index. The movement of the fringes was followed either by direct observation or, in the case of high reaction rates, by the use of a cinematograph camera. Figure 8 shows a typical curve obtained in the polymerization of methyl methacrylate, this curve being uncorrected for any heat losses due to the slight non-adiabaticity of the system. Hence it is necessary to make corrections for both loss of heat and formation of polymer.

In the experiments one of the tubes of the interferometer was filled with monomer which had been roughly purified and the other with pure monomer. Only the latter tube was illuminated, but even in the absence of illumination a steady drift was sometimes observed owing to a purely thermal reaction; this drift had also to be allowed for in the final calculation. Figure 9 shows the fully corrected curve for the polymerization of styrene at 15°C. The theory is evidently obeyed to within very close limits, and again the lifetime and the ratio of the velocity constants can be determined. It is of interest to note that none of the anomalies reported by Bamford and Dewar (13, 14) in the polymerization of methyl methacrylate were observed in these experiments. At the same time it was found that when a dilatometer technique was used, the reproducibility of results for methyl methacrylate appeared to vary from day to day.

The results of the investigations with the interferometer are set out in table 13. Comparison with data obtained by other methods can be made by reference to tables 15 and 16.

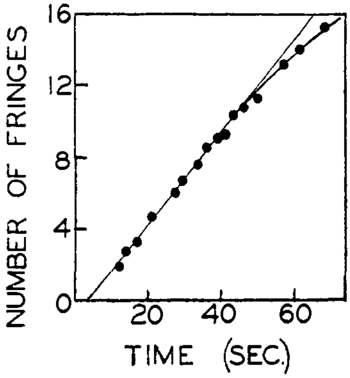


FIG. 8

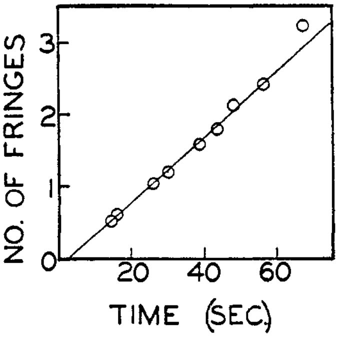


FIG. 9

FIG. 8. Initial stages of photopolymerization of methyl acrylate determined by the interferometric method (uncorrected) (81).

FIG. 9. Initial stages of photopolymerization of styrene determined by the interferometric method (corrected) (81).

TABLE 13

Rate constants of vinyl polymerizations determined by use of the interferometric technique at 15°C.

MONOMER	SENSITIZER	LIFETIME AT 1 PER CENT PER HOUR CONVERSION RATE	$k_p/k_t \times 10^6$
		seconds	
Styrene	Benzoyl peroxide	0.71	2.0
Methyl acrylate	None	5.30	15
Methyl methacrylate	None	2.30	6.75
Vinyl acetate	2,2′-Azoisobutyronitrile	7.32	20

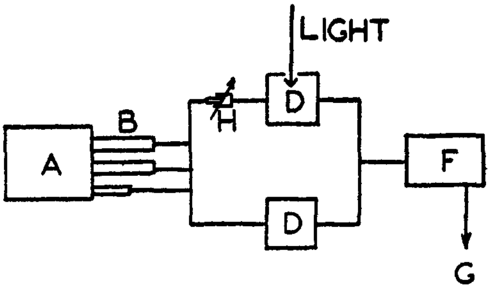


FIG. 10. Block diagram of apparatus used in measuring the dielectric constant (60)

3. *Dielectric-constant method* (*60, 99, 100*)

Analogous to the increase of refractive index on polymerization there is an increase in dielectric constant. Utilization of this change in the physical property of the system gives probably the most adaptable method with which to analyze the induction period, since, owing to the advancement in electronic methods, the sensitivity of measurement is of a very high order and the resolution in time may be made very high by the use of electronic devices.

As in the case of interferometry the reaction is followed by recording the change in dielectric constant arising from the increase in temperature due to the exothermic reaction. In view of the electronic equipment used, the experimental technique will be described in detail.

Figure 10 shows a block diagram of the circuit employed. A 50 Mc/sec. signal generator (A) feeds, *via* piston attenuators (B), the two arms of a bridge formed by tuned circuits (D) of the usual inductance-capacity type. In each of these circuits the monomer, contained in a small parallel-sided vessel, forms the dielectric of the condenser. The output from each resonant circuit is fed simultaneously to a receiver (F) which amplifies the signal before passing to a suitable recorder (G). Before starting a run the bridge is balanced as to both phase and output by adjusting the attenuators and the phase shifter (H). On allowing the light to fall on one of the cells a change, ΔK, is produced in the dielectric constant in one of the resonant circuits. This produces a change, ΔC, in the capacity of the condenser with an alteration in the resonant frequency of the circuit and a phase shift, $\Delta\phi$, given by

$$\Delta\phi = Q(\Delta C/C)$$

where Q has its usual significance. Where the arms of the bridge are no longer in opposition with regard to phase, an out-of-balance signal results which is given by:

$$e = E\Delta\phi$$

and hence

$$\Delta C/C = e/QE$$

where E is the voltage of each circuit. E, e, and Q are measurable quantities, so that $\Delta C/C$ can be computed. It remains to relate this change to the amount of polymerization. The ultimate sensitivity of the apparatus is very high, since when a signal frequency of 50 Mc/sec. is used, a capacity change of 1 part in 10^8 could be detected within the response time of the apparatus, 10^{-4} sec. In terms of the various variables which can be measured, the maximum sensitivity of the apparatus is shown in table 14.

The values quoted for the temperature, heat, and polymerization in table 14 will vary to some extent with the monomer, since they will depend on the heat of polymerization, the specific heat, and the variation of dielectric constant with temperature.

TABLE 14

Sensitivity of bridge for measurement of dielectric constant

CHANGE IN	SMALLEST DETECTABLE CHANGE
Capacity	1 part in 10^8
Dielectric constant	2 parts in 10^8
Temperature	10^{-6}°C.
Heat	3×10^{-5} cal.
Polymerization	1 part in 10^7

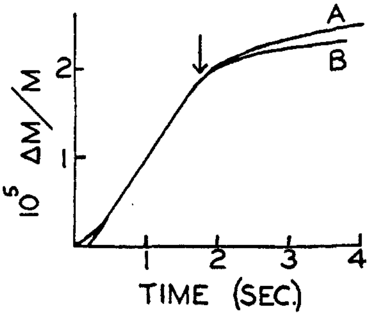


FIG. 11

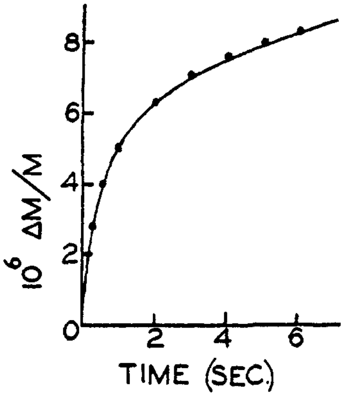


FIG. 12

FIG. 11. Build-up and decay in the photopolymerization of vinyl acetate as measured by the dielectric-constant method; A, theoretical curve for second-order termination; B, experimental curve (100).

FIG. 12. Decay in the photopolymerization of vinyl acetate as measured by the dielectric-constant method with flash initiation (100).

TABLE 15

Rate constants for vinyl polymerization as measured by the dielectric-constant technique at 15°C.

MONOMER	SENSITIZER	METHOD	LIFETIME AT 1 PER CENT PER HOUR CONVERSION RATE	$k_p/k_t \times 10^5$
			seconds	
Styrene*	2,2′-Azoisobutyronitrile	Continuous illumination	0.25	0.68
Methyl acrylate*		Continuous illumination	4.54	11
Vinyl acetate	2,2′-Azoisobutyronitrile	Continuous illumination	1.25	3.5
	2,2′-Azoisobutyronitrile	Flash	0.65	1.8

* No apparent reaction with flash discharge.

As with the interferometer a number of corrections have to be applied to the experimentally determined curves, but, as figure 11 shows, the final curve is again much in accord with theory. As an alternative to the technique of following the entire course of the induction period, a few experiments were carried out in which a short flash of illumination of very high intensity was used. Since the duration of the flash is very much shorter than the lifetime of the chains, the subsequent course of the reaction ought to follow the decay curve (Section VII,A). Figure 12 shows the corrected curve derived from the oscilloscope trace for the polymerization of vinyl acetate initiated in this way; the theoretical points on the assumption of second-order termination show excellent agreement with the practical results. All the results obtained by the dielectric-constant technique are given in table 15.

The application of this method to other problems may be foreseen. Reactions for which the overall rate is proportional to the rate of chain starting cannot be readily analyzed by any conventional means, but the analysis of this type of reaction is theoretically easy, and the methods outlined may give some indication of the values of the kinetic constants under these conditions. The rate of polymerization of vinyl benzoate has been found to be proportional to the intensity of the absorbed radiation (53), but experiments to study the non-stationary state with either continuous or flash illumination were unsuccessful. This may in part be due to the extremely high extinction coefficient of the monomer for light of wave length as high as 3500 Å. The application of the method to the study of the first few steps in the reaction chain might be possible with even greater resolution in time. This might be expected to reveal delays in the reaction of the initiator fragments with the monomer or any anomalous behavior in the reactivity of monomeric, dimeric, and trimeric radicals such as found by Mayo for the interaction of short-chain styrene polymer radicals with carbon tetrachloride (108).

4. Thermal method

Both the dielectric and the interferometric methods of following the non-stationary period of the reaction depend on the measurement of small changes in temperature brought about by the heat of reaction. The applicability of the methods have some limitations, since it is not possible, for example, to thermostat the dielectric-constant apparatus and in neither case can a total conversion exceeding 10 per cent be contemplated. By using the change of resistance of a wire or by means of thermal junctions both of these objections may be overcome, the latter because of the simplicity and cheapness of the apparatus, which becomes expendable. Using a tungsten wire as a resistance thermometer, Ross and Melville (134) were able to plot the non-stationary part of the reaction curve for the photopolymerization of methyl acrylate. The wire formed one arm of a standard bridge circuit and the out-of-balance signal resulting from a change in temperature of the wire after amplification was displayed by means of a pen recorder. Bengough (28) has replaced the resistance thermometer by a pair of thermojunctions. One junction is mounted at the center of the reaction vessel, while the other is sealed in a side arm and is maintained at the temperature of the thermostat bath. The potential developed between the two is amplified by means of a high-gain D.C. amplifier and displayed by a pen recorder. Higher sensitivity with a high signal-to-noise ratio can be obtained by feeding the potential to a short-period galvanometer and photographing the movement of the galvanometer spot on a drum camera. The limit of sensitivity, which is the noise level of the amplifier, corresponds to 1/8000°C., while the limit in time, which is governed by the chopping arrangement in the amplifier, is about 0.04 sec. With the galvanometer arrangement the response time is reduced to 0.026 sec. and the reproducibility of the time measurements is about 0.1 sec. The results given in table 16 show the versatility of the apparatus in dealing with polymerization reactions up to very high degrees of conversion.

5. Viscosity method

It is well known that during the course of polymerization the viscosity of the reaction medium increases, owing to the formation of high-molecular-weight material. Although some use of this property had previously been made as a method of following polymerization, the full significance of the procedure had not been noted until the evolution of the viscosity technique for the determination of the velocity constants for polymerization by Bamford and Dewar (10,

TABLE 16

Rate constants for vinyl polymerization using the viscosity method

MONOMER	TEMPERATURE	$k_i \times 10^{13}$	k_p	$k_f \times 10^5$	$k_t \times 10^{-6}$
	°C.		l. mole^{-1} sec.$^{-1}$		
Styrene	0	4.51	6.91	7.47	1.83
	25	1320	18.7	66.8	2.79
Methyl methacrylate	0	6820	41.6	61.3	2.69
p-Methoxystyrene	0	594	2.92	5.78	1.06
Vinyl acetate	0	0	2830	14000	220
	−15	0	2000	7300	220

11, 13). To explain this method more fully the theoretical implications must be studied. The reaction scheme adopted is:

$$\begin{array}{rll}
2\mathrm{M} \rightarrow 2\mathrm{X} \text{ or } \mathrm{D}_2 & k_i & \textit{initiation} \\
\mathrm{X} + \mathrm{M} \rightarrow \mathrm{X} & k_p & \textit{propagation} \\
\mathrm{D}_2 + \mathrm{M} \rightarrow \mathrm{D}_1 + \mathrm{R} & 2k_f & \\
\mathrm{D}_1 + \mathrm{M} \rightarrow \mathrm{P}_2 + \mathrm{R} & k_f & \textit{transfer} \\
\mathrm{R} + \mathrm{M} \rightarrow \mathrm{P}_1 + \mathrm{R} & k_f & \\
\mathrm{D}_2 + \mathrm{X} \rightarrow \mathrm{D}_1 + \mathrm{Q} & 2k_t & \\
\mathrm{D}_1 + \mathrm{X} \rightarrow \mathrm{P}_2 + \mathrm{Q} & k_t & \textit{termination} \\
\mathrm{R} + \mathrm{X} \rightarrow \mathrm{P}_1 + \mathrm{Q} & k_t & \\
2\mathrm{X} \rightarrow 2\mathrm{Q} & k_t &
\end{array}$$

in which X represents any active center, Q any dead center, D_2 the initial polymer growing at both ends, D_1 the polymer derived from D_2 now growing at only one end, R the growing transfer polymer radical, and P_1 and P_2 the dead transfer and initial polymer molecules, respectively. From stationary-state considerations:

$$(\mathrm{X}) = k_i^{1/2}k_t^{-1/2}(\mathrm{M}); \quad (\mathrm{D}_2) = k_i(\mathrm{M})/4[k_f + (k_ik_t)^{1/2}]; \quad (\mathrm{D}_1) = 2(\mathrm{D}_2)$$

$$(\mathrm{R}) = 4(\mathrm{D}_2)(k_ik_t)^{-1/2}k_f; \quad \bar{P}_1 = k_p/[k_f + (k_ik_t)^{1/2}]; \quad \bar{P}_2 = 2\bar{P}_1$$

$$\mathrm{d}(\mathrm{P}_1)/\mathrm{d}t = k_f(k_i/k_t)^{1/2}(\mathrm{M})^2; \quad \mathrm{d}(\mathrm{P}_2)/\mathrm{d}t = \tfrac{1}{2}k_i(\mathrm{M})^2 \tag{7}$$

where $\bar{P}_1$ and $\bar{P}_2$ are the mean degrees of polymerization of the transfer and the initial polymer, respectively. Now the relationship between the intrinsic viscosity and the degree of polymerization, $\bar{P}$, for a homogeneous system is:

$$[\eta] = K(M_0\bar{P})^{\alpha}$$

where M_0 is the monomer molecular weight. For heterogeneous polymers formed by the growth of mono- and diradicals:

$$[\eta] = K'(M_0\bar{P})^{\alpha} \text{ and } [\eta] = K''(M_0\bar{P})^{\alpha}$$

where $K' = K\Gamma(2 + \alpha)$ and $K'' = K\Gamma(3 + \alpha)/2^{1+\alpha}$. Now the ideal specific viscosity is expressed as

$$\eta = c[\eta] = KM_0^{\alpha}\bar{P}^{\,1+\alpha}(P)$$

since $c = \bar{P}(P)$; hence the rate of change of viscosity is

$$\mathrm{d}\eta/\mathrm{d}t = K'M_0^{\alpha}\{\bar{P}_1^{1+\alpha}\mathrm{d}(\mathrm{P}_1)/\mathrm{d}t + [\Gamma(3+\alpha)/2^{1+\alpha}\Gamma(2+\alpha)]\bar{P}_2^{1+\alpha}\mathrm{d}(\mathrm{P}_2)/\mathrm{d}t\} \tag{8}$$

for purely thermal polymerization.

On substitution for the variables on the right-hand side of equation 8:

$$\mathrm{d}\eta/\mathrm{d}t = K'M_0^{\alpha}(\mathrm{M})^2(k_p^2/k_t)^{(1+\alpha)/2}k_i^{(1-\alpha)/2}[(\beta + 2^{\alpha}\omega)/(\beta + 1)^{1+\alpha}]$$

where

$$\beta = k_f(k_ik_t)^{-1/2} \text{ and } \omega = \Gamma(3 + \alpha)/2^{1+\alpha}\Gamma(2 + \alpha) = (2 + \alpha)/2^{1+\alpha}$$

In the case of simultaneous photochemical and thermal initiation it can be assumed that the rate of initiation is $k_i(1 + AI)(\mathrm{M})^2$, where A is constant and I is the light intensity in arbitrary units. Then:

$$\mathrm{d}\eta/\mathrm{d}t = K'M_0^\alpha(\mathrm{M})^2(k_p^2/k_t)^{(1+\alpha)/2}k_i^{(1-\alpha)/2}\xi(\beta + 2^\alpha\omega\xi)/(\beta + \xi)^{1+\alpha} \tag{9}$$

where $\xi = (1 + AI)^{1/2}$. Measurement of the rate of change of viscosity over a wide range of light intensities gives two relationships between the rate constants, yielding the value of β and $(k_p^2/k_t)^{(1+\alpha)/2}k_i^{(1-\alpha)/2}$. A third relationship is supplied by the fact that the mean degree of polymerization of the purely thermal polymer is:

$$\bar{P}_n = 2k_p(k_ik_t)^{-1/2}/(2\beta + 1) \tag{10}$$

The necessary fourth relationship between the constants is derived from a consideration of the after-effect, this being defined as the difference between the observed specific viscosity at a time t after the light is removed and that calculated on the assumption that the rate falls to the thermal rate when the light is interrupted. The solution of the general equation is not possible unless α can be expressed as m/n, where m and n are integers; this approximation holds in most experimental cases. If this substitution is carried out, then:

$$\Delta\eta_I^t = \frac{nK'M_0^\alpha(\mathrm{M})^{1+\alpha}k_p^{1+\alpha}}{2k_t^{1+\alpha}\theta^\alpha}\left[\int_{x_I^0}^{x_I^t}\left\{\frac{(2^\alpha\omega + \beta)(\lambda^m - x^m)x^{n-m-1}}{(\lambda^n - x^n)\lambda^{m+n}} + \frac{(2^\alpha\omega - \beta)x^{n-m-1}}{\nu^n(x^n - \nu^n)}\right.\right.$$
$$\left.\left. - \frac{(2^\alpha\omega + \beta)x^{n-1}}{\lambda^{m+n}(x^n - \nu^n)}\right\}\mathrm{d}x + \frac{2\beta^2(2^\alpha\omega - 1)}{m\lambda^n\nu^n}\left\{(x_I^t)^{-m} - (x_I^0)^{-m}\right\}\right] \tag{11}$$

where $\theta = (\mathrm{M})k_i^{1/2}k_t^{1/2}$; $\lambda^n = \beta + 1$; $\nu^n = \beta - 1$; and

$$x^n = \left\{\beta + \frac{\xi + 1 + (\xi - 1)\exp\{-2(\mathrm{M})(k_i k_t)^{1/2}t\}}{\xi + 1 - (\xi - 1)\exp\{-2(\mathrm{M})(k_i k_t)^{1/2}t\}}\right\}^{1/2}$$

and for $\alpha = 2/3$:

$$\Delta\eta_I^t = -\tfrac{1}{2}K'M_0^{2/3}(\mathrm{M})k_i^{-1/3}k_p^{5/3}k_t^{-4/3}\left[\frac{(\beta + 4/3)}{\lambda^5}\left\{\frac{1}{2}\ln\frac{(\xi - 1)^3(x^3 - \nu^3)^2}{(\xi + 1)^2(x^2 + \lambda x + \lambda^2)^3}\right.\right.$$
$$\left.\frac{1}{(\psi - \lambda)^3} - \sqrt{3}\tan^{-1}\left\{\frac{2x + \lambda}{\sqrt{3}\lambda}\right\} + \sqrt{3}\tan^{-1}\left\{\frac{2\psi + \lambda}{\sqrt{3}\lambda}\right\}\right\}$$
$$+ \frac{\beta - 4/3}{\nu^5}\left\{\frac{1}{2}\ln\frac{(x - \nu)^3(\xi + 1)}{(x^3 - \nu^3)(\psi - \nu)^3} + \sqrt{3}\tan^{-1}\left\{\frac{2x + \nu}{\sqrt{3}\nu}\right\}\right.$$
$$\left.\left. + \sqrt{3}\tan^{-1}\left\{\frac{2\psi + \nu}{\sqrt{3}\nu}\right\}\right\} - \frac{\beta^2}{\lambda^3\nu^3}\left\{\frac{1}{x^2} - \frac{1}{\psi^2}\right\}\right] \tag{12}$$

where $\psi = (\beta + \xi)^{1/3}$.

Since the basis of the theory is the Houwink law, all the measured specific viscosities have to be converted to the corresponding intrinsic viscosities, which can be done by means of the Schulz and Sing relationship (141):

$$\eta_c = (\eta_{\mathrm{sp}})_c/[1 + 0.28(\eta_{\mathrm{sp}})_c] \tag{13}$$

Although the kinetic expressions are necessarily complex, the experimental technique is relatively simple. By measuring the rate of change of viscosity at various light intensities, making a small correction for the after-effect occurring during measurement, the results can be fitted by trial and error to equation 9, giving values for A and $(k_p^2/k_t)^{5/6}k_i^{1/6}$ in the case of $\alpha = 2/3$ (styrene). Substitution in equation 10 allows the determination of the ratios k_p^2/k_t and k_f^2/k_t along with k_i.

Since the after-effect is a difference measurement, the following procedure is convenient. The monomer is irradiated for t_1 sec., and measurement of the viscosity is made after a further t_2 sec. from the time the light is removed. If the total change in viscosity is $\delta\eta$, then:

$$\delta\eta = at_1 + bt_2 + \Delta\eta_I^{t_1} - \Delta'\eta_I^{t_2}$$

where a and b are the photo and thermal rates, $\Delta\eta_I^{t_2}$ is the after-effect, and $\Delta'\eta_I^{t_1}$ is the pre-effect. For high light intensities the pre-effect is only a small fraction of the after-effect. Now, plotting the value of $(\delta\eta - bt_2)$ against t_1 gives the value of a and of $[\Delta\eta_I^{t_2} - \Delta'\eta_I^{t_1}]$. Since t_1 is always made long enough for the stationary state to be attained, $\Delta'\eta_I^{t_1}$ may be replaced by:

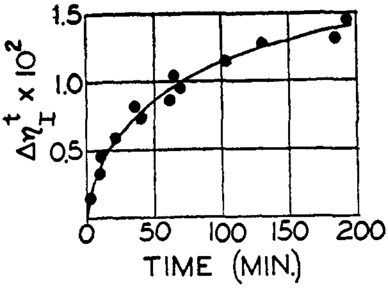


FIG. 13. After-effect in styrene polymerization determined by use of the viscosity method. Zero time when light was switched off (11).

$$\Delta'\eta_I^{\infty} = -\tfrac{1}{2}K'M_0(M)k_i^{-1/3}k_p^{5/3}k_t^{-4/3}\left[\frac{\beta + 4/3}{\psi^5}\left\{\frac{1}{2}\ln\frac{4\xi^2(\xi - 1)^3}{27\psi^6(\xi + 1)^2(\psi - \lambda)^3}\right.\right.$$
$$\left.- \sqrt{3}\tan^{-1}\sqrt{3} + \sqrt{3}\tan^{-1}\frac{2\lambda + \psi}{\sqrt{3}\psi}\right\} + \frac{\beta - 4/3}{\chi^5}\left\{\frac{1}{2}\ln\frac{(\xi + 1)(\psi - \chi)^3}{2\xi(\lambda - \chi)^3}\right.$$
$$\left.\left.- \sqrt{3}\tan^{-1}\frac{2\psi + \chi}{\sqrt{3}\chi} + \sqrt{3}\tan^{-1}\frac{2\lambda + \chi}{\sqrt{3}\chi}\right\} + \frac{\beta^2}{\psi^3\chi^3}\{\chi^{-2} - \psi^{-2}\}\right] \quad (14)$$

where $\chi = (\beta - \xi).^{1/3}$

Figure 13 shows the after-effect in the case of the photopolymerization of styrene at 0°C.

The technique depends on the same principles which have been described in connection with the wider application of non-stationary-state methods. The main assumption in this theory is the formation of a diradical as the first step in both the thermal and the photochemical reaction and disproportionation as the chain-breaking step. As mentioned in Section V,A, if it can be established that the initiation mechanism does involve the formation of a diradical, disproportionation will give a rate of viscosity change proportional to $I^{(1-\alpha)/2}$ for high light intensities, as can be seen from equation 9. If under the same conditions the chain termination occurs by a coupling of the radicals, then it can be shown by a similar analysis that the rate of viscosity change becomes proportional to $I^{1/2}$. In the case of the polymerization of methyl methacrylate the proportionality was found to be $I^{0.1}$, which is in good agreement with the values of α. The main advantages of the method lie in the simplicity of the experimental technique whereby all four velocity constants are found. The measurements are all made at very low conversion, so that there is no possibility of a gel effect. The main disadvantage lies in the necessity of the establishment of a relationship between the intrinsic viscosity and the mean degree of polymerization, but, although this is normally a tedious task, a simpler method has been devised which makes it less time-consuming (12). The results obtained by the viscosity method, which has been applied to the polymerization of styrene, methyl methacrylate, vinyl acetate, and *p*-methoxystyrene, are set out in tables 17 and 18. The technique has to be modified to some extent in the case of vinyl acetate, since there is no thermal polymerization (71).

C. METHODS APPLICABLE TO HETEROGENEOUS OXIDATION

The reaction scheme for the oxidation of non-conjugated olefins, aldehydes, and hydrocarbons is set out in Section VI,B. The kinetic analysis of the general scheme gives:

$$\mathrm{d(RO_2H)/d}t = k_3(\mathrm{RH})\mathrm{R}_i^{1/2}\,\{k_2^{-2}k_3^2k_4(\mathrm{RH})^2(\mathrm{O_2})^{-2} + 2k_2^{-1}k_3k_5(\mathrm{RH})(\mathrm{O_2})^{-1} + k_6\}^{-1/2}$$

At high oxygen pressures the above expression reduces to:

$$\mathrm{d(RO_2H)/d}t = k_3k_6^{-1}(\mathrm{RH})\mathrm{R}_i^{1/2} = r \tag{15}$$

while at low oxygen pressures the rate will tend to:

$$\mathrm{d(RO_2H)/d}t = k_2k_4^{-1}(\mathrm{O_2})\mathrm{R}_i^{1/2} \tag{16}$$

TABLE 17

Frequency factors and energies of activation

MONOMER	INITIATION	PROPAGATION	TRANSFER	TERMINATION
Styrene A	1.23×10^{12}	1.06×10^{6}	1.50×10^{7}	3.07×10^{8}
Styrene E	37.0	6.5	14.2	2.8
Vinyl acetate A		9.8×10^{5}	9.9×10^{3}	2.2×10^{3}
Vinyl acetate E		3.2	6.1	0

TABLE 18

*Rate constants for oxidation at 25°C. (**22**, **23**)*

OLEFIN	k_4/k_3	$k_2 \times 10^{-8}$	k_3	$k_4 \times 10^{-6}$	$k_6 \times 10^{-6}$
			l. mole⁻¹ sec.⁻¹	*l. mole⁻¹ sec.⁻¹*	*l. mole⁻¹ sec.⁻¹*
Digeranyl	18	15	0.5	260	0.3
Ethyl linoleate	3	5	7.0	15	0.3

The results from sector experiments in the high-pressure oxygen region are set out in table 10. Although, in theory, the rate constants for the other reactions ought to be obtainable at low oxygen pressures, this has not been found possible by normal methods.

The "low-pressure" region has been investigated by non-stationary-state methods (15, 22, 23). The work of Bamford and Dewar (15) follows on their investigations of polymerization and the kinetic treatment is similar in general outline. The analysis used by Bateman and Gee (22) is considerably simpler and will be discussed here. As in the case of polymerization, when photoinitiation is stopped, the reaction continues at a diminishing rate, which can be measured in terms of the oxygen absorbed. The photochemical after-effect is defined by:

$$I_d = \int_0^\infty (r - r_D)\,dt \qquad (17)$$

where r_D is the steady dark rate. Now, if the thermal rate of initiation is r_T, then by adaptation of equation 15:

$$r_D = k_3k_6^{-1/2}(\mathrm{RH})r_T^{1/2}$$

The overall rate at any instant is:

$$r = k_3(\mathrm{RH})(\mathrm{RO_2}\text{—})$$

Since (RH) is sensibly constant:

$$dr/dt = r_T - k_6(\mathrm{RO_2}\text{—})^2$$

Combining these equations:

$$dr/dt = k_3^{-1}k_6(\mathrm{RH})^{-1}(r^2 - r_D^2)$$

whence, by definition:

$$I_d = \int_{r_L}^{r_D} [(r - r_D)/(dr/dt)]dr = k_3k_6^{-1}(\mathrm{RH}) \ln [(r_L + r_D)/2r_D] \qquad (18)$$

so that the measurement of r_L, r_D, and I_d immediately gives k_3/k_6. Similarly the growth intercept can be found as:

$$I_g = k_3k_6^{-1}(\mathrm{RH}) \ln [2r_L/(r_L + r_D)] \qquad (19)$$

It is found that two main factors influence the measurement of the intercepts to a greater or less extent. Since the rate of disappearance of oxygen from the gas phase is the measure of the rate of reaction, it is evident that this will represent the true reaction rate only if the oxygen concentration in solution remains constant. In general the concentration of oxygen in solution (c) will be less than that associated with a stationary system saturated with oxygen at a given pressure (c_0). If Δc is a measure of this discrepancy and if the solution obeys Henry's law, the rate of solution will be $k_s(c_0)$, where k_s depends on the shaking. Oxygen is lost from the solution partly by its consumption due to oxidation and partly by evaporation (rate = k_sc), so that the net rate of solution is:

$$k_s(c_0 - c) = r = k_s\Delta c \qquad (20)$$

During the non-stationary state the oxygen concentration in solution will change, and it is clear from equation 20 that during the change from dark to light reaction the concentration will decrease by $(r_L - r_D)/k_s$. Hence, if I'_d and I'_g are the measured intercepts, the errors involved will be diminished to some extent by using the difference between the intercepts:

$$I'_d - I'_g = k_3k_6^{-1}(\mathrm{RH}) \ln [(r_L + r_D)^2/4r_Lr_D] \tag{21}$$

Similarly it can be shown that delayed manometer response gives the same effect, and the result is that the measured intercept is related to the true intercept by

$$I'_d - I_d = (r_L - r_D)(k_s^{-1} + k_m^{-1})$$

where k_m is a constant associated with the manometer response, which is normally negligible compared with k_s.

At low oxygen pressure the rate of the dark reaction is

$$r_D = k_2k_4^{-1/2}(\mathrm{O_2})R_i^{1/2} \tag{22}$$

and the overall rate at any instant is

$$r = k_2(\mathrm{R—})(\mathrm{O_2})$$

Since in the non-stationary state both (R—) and $(\mathrm{O_2})$ are changing, it is convenient to write:

$$x = r/(\mathrm{O_2}) = k_2(\mathrm{R—})$$

from which

$$\mathrm{d}x/\mathrm{d}t = k_4k_2^{-1}(x^2 - x_D^2)$$

To obtain the variation of oxygen pressure with time it can be shown that:

$$\mathrm{d(O_2)/d}t = k_sc_0 - (\mathrm{O_2})(k_s + x)$$

These equations represent the necessary relationships for the computation of I_d, which again appears as only part of the measured intercept. Proceeding as before, the necessary relationship for the growth reaction is:

$$\mathrm{d}x/\mathrm{d}t = k_4k_2^{-1}(r_L^2 - x^2)$$

The equation is not in a form which can be readily handled, so that a method of summation has to be devised whereby k_4/k_2 is expressible as a function of

$$(I_d - I_g)$$

Experiments carried out along these lines gave the results in table 19.

Using a method which is the same in outline as that discussed, Bamford and Dewar (15) have investigated the autoöxidation of tetralin over a range of temperatures, from which they have been able to compute the energies of activation and the frequency factors of the individual steps. The results are shown in table 20.

The results of tables 19 and 20 bring out some points of interest. In the first

TABLE 19

Rate constants, energies of activation, and frequency factors for oxidation of tetralin (15)

RATE CONSTANT AT 15°C.		ENERGY OF ACTIVATION	FREQUENCY FACTOR
	l. mole^{-1} sec.$^{-1}$		
Propagation, k_2	6.67×10^7	0	6.7×10^7
Propagation, k_3	13.3	4.5	2.5×10^4
Termination, k_4	7.1×10^6	2.6	5.5×10^8
Termination, k_6	2.1×10^7	0.4	4.2×10^7

TABLE 20

Composite rate constants in oxidation at 25°C. (24)

OLEFIN	$k_3k_6^{1/2}$	$k_2k_4^{1/2}$	$k_3/k_2 \times 10^6$	k_2/k_4	ϕ
	mole$^{1/2}$ l.$^{-1/2}$	*sec.$^{-1/2}$*			
Ethyl linoleate......	1.21×10^{-2}	2.3×10^3	2.3 ± 0.5	0.6 ± 0.3	2.5
Digeranyl...........	1.07×10^{-3}	1.3×10^3	0.36 ± 0.5	1.4 ± 0.3	3.1

place, the rate constant for the interaction of the radical and the oxygen molecule, k_2, is of the same order of magnitude as those for the interaction of two radicals. Furthermore, the nature of the grouping in the RO_2— radical does not appear to have any pronounced effect on the value of the rate constant, but the reactions involving R type radicals seem to be more sensitive to the structure. It will also be seen that there is a certain "reciprocity" between the two steps of the propagation reaction: the more reactive the radical RO_2—, the less reactive radical the R—.

A more general form of the oxidation equation describing the reaction rate is:

$$r = r_\infty[1 + 2\phi A^{-1}B(\mathrm{RH})(\mathrm{O_2})^{-1} + A^{-2}B^2(\mathrm{RH})^2(\mathrm{O_2})^{-2}]^{-1/2} \qquad (23)$$

where

$$r_\infty = B(\mathrm{RH})R_i^{1/2}$$

and

$$A = k_2k_4^{-1/2}; \quad B = k_3k_6^{-1/2}; \quad \phi = k_4^{-1/2}k_5k_6^{-1/2}$$

A plot of r^{-1} against $(\mathrm{O_2})^{-1}$ therefore gives a curve which will be concave to the $(\mathrm{O_2})^{-1}$ axis if $\phi < 1$ and convex, if $\phi > 1$. It has been assumed previously that $\phi = 1$, in which case equation 23 reduces to:

$$r = r_\infty[1 + A^{-1}B(\mathrm{RH})(\mathrm{O_2})^{-1}]^{-1}$$

Provided the solubility of oxygen can be measured, one can plot either the curves mentioned above or, more conveniently, equation 23 can be written in the form:

$$[(r_\infty/r^2 - 1](\mathrm{O_2}) = 2\phi A^{-1}B(\mathrm{RH}) + A^{-2}B^2(\mathrm{RH})^2(\mathrm{O_2})$$

The left-hand side can be plotted as a function of $(\mathrm{O_2})^{-1}$, giving a linear relationship from which $\phi A^{-1}B$ and $A^{-2}B^2$ can be found and by measurement of r_∞, B may be computed and so ϕ, A, and B are accessible.

This scheme has been adopted by Bateman, Gee, Morris, and Watson (24) when it was found that ϕ differs appreciably from unity, as is found in most cases of copolymerization (4, 5, 42, 43, 121, 148, 149). To find all the constants uniquely it is necessary to extend the investigations to the non-stationary state. Extending the treatment already given it can be shown that:

$$I_d - I_g = a \ln [r_L + r_D)^2/4r_L r_D] \tag{24}$$

where

$$a = \frac{D(\text{RH}) + A^{-2}B^2C(\text{RH})^2(\text{O}_2)^{-1}}{1 + 2A^{-1}B(\text{RH})(\text{O}_2)^{-1} + A^{-2}B^2(\text{O}_2)^{-2}(\text{RH})^2} \tag{25}$$

The plot of the product of a and the denominator of the fraction against $(\text{O}_2)^{-1}$ gives the values of C and D, which are $C = k_2k_4^{-1}$ and $D = k_3k_6^{-1}$. Again the effect of shaking is the most disturbing factor, since it is evident that if the term $(r_L - r_D)k_s^{-1}$ is comparable with or larger than I_d and I_g, accurate determination of these quantities or their difference is very difficult. From direct measurement it was found that the shaking term may amount to as much as 75 per cent of the intercept. Tables 21 and 22 list the composite rate constants and the individual values obtained by the methods outlined.

The main conclusions already reached are substantiated by the newer methods, i.e., increased oxidizability requires an increase in k_3, and k_6 is largely independent of the nature of the hydrocarbon portion, although some slight differences of doubtful significance are now noticeable. The most surprising feature

TABLE 21

Velocity constants for oxidation at 25°C. (24)

OLEFIN	10^6k_2	k_3	10^6k_4	10^6k_5	10^6k_6
Ethyl linoleate	9	10	20	50	30
Digeranyl	1	3	0.9	9	9

TABLE 22

Propagation constants from emulsion measurements

MONOMER	CATALYST	ACTIVATION ENERGY	FREQUENCY FACTOR	k_p AT 60°C.
		kcal./mole		*l./mole/sec.*
Butadiene (135)	Peroxamine	9.3	1.2×10^8	100
Styrene (135)	Persulfate	7.4	4.1×10^7	277
Styrene (144)	Persulfate	11.7	3.5×10^{10}	390*
Styrene (135)	CHP-TETA†	8.4	3.3×10^7	221
Isoprene (135)	DIBHP-TEPA	9.8	1.2×10^6	50

* At 50°C.

† CHP = cumene hydroperoxide,
DIBHP = diisopropylbenzene monohydroperoxide,
TETA = triethylenetetramine, and
TEPA = tetraethylenepentamine.

of the data of table 22 is the higher value of k_t for ethyl linoleate, since energetically the reactivity of R— should be the inverse of that of RH. However, other factors have to be taken into account, in that the activation energy for radical processes is low, so that steric factors can very rapidly play a dominant role in the reaction and therefore confer an apparent stability on the radical from digeranyl.

VIII. Emulsion Polymerization

A. KINETIC ANALYSIS

It is possible from a study of emulsion polymerization to determine values of the rate constants (more particularly for propagation) (144, 145). The main differences between bulk and emulsion reactions lie in the fact that the emulsion reaction takes place in discrete loci so that the treatment of the kinetics of the process must make use of this fact. To understand the method of interpretation of the experimental results it is necessary to study first the theory of the reaction.

The description of the system which is adopted is that due to Harkins (83, 84, 85), in which it is assumed that there are four phases each of which plays a part in the reaction. The water phase containing the chain initiator forms the external phase in which the radicals capable of generating polymerization chains are formed. In this water phase are dispersed droplets of monomer whose function is to keep the other phases supplied with monomer. The third phase is formed by soap micelles, which serve to generate polymer particles on which the soap is adsorbed at the interface until it is all used up. Immediately polymerization starts the micelles begin to disappear on being adsorbed and in their place will appear polymer particles swollen with monomer; it is in these polymer particles that polymerization takes place.

If in 1 ml. of the external phase there are N isolated reaction loci (polymer particles), each having a volume v and an interfacial area a, and if the rate of entry of radicals generated externally into these loci is ρ', the rate of entry into one locus is:

$$\mathrm{d}N/\mathrm{d}t = \rho'/N$$

The radical having entered into a locus will continue to grow until its activity is destroyed either by physical transference from the reaction site or by chemical reaction. The rate of transference is given by

$$\mathrm{d}n/\mathrm{d}t = -k_0a(n/v)$$

where k_0 is a constant and n/v is the concentration of radicals within the particle. The rate of removal by chemical means is:

$$\mathrm{d}n/\mathrm{d}t = 2k_tn[(n - 1)/v]$$

If these conditions are true, then the N_0, N_1, N_2, $\cdots N_n$ loci containing 0, 1, 2, $\cdots n$ radicals are related by the recursion formula:

$$N_{n-1}(\rho'/N) + N_{n+1}k_0a(n + 1)/v + N_{n+2}(n + 2)(n + 1)/v = \\ N_n[\rho'/N + k_0an/v + 2k_tn(n - 1)/v] \quad (26)$$

It is not possible to analyze the problem completely, so that Smith and Ewart (145) consider three possible cases. In the first it is assumed that the rate of transference is so great that the number of radicals per particle becomes very much less than unity. In the second case the number of radicals per particle is about 0.5, and in the third case the number of radicals per particle becomes greater than unity. The last of these cases is more that of pearl polymerization than emulsion polymerization and has been analyzed by Haward (86). Of the other two possible cases the only one of real importance is the second, which is the operative one in all cases studied. Before the appearance of the Smith–Ewart treatment, analyses of the kinetics of emulsion reactions were published by Corrin (67) and Montroll (122), but in neither case were the results obtained amenable to experimental verification.

For the second case cited above it is required that a radical having once entered a polymer particle is incapable of leaving it and termination of chain growth is brought about only by chemical action following the entry of another radical. Under these conditions, the time between successive entries of radicals to a single particle is long compared with the time of coexistence of two radicals within the particle. The mathematical formulation of this is that:

$$k_0 a/v \ll \rho'/N < k_t/v$$

so that the recursion formula (expression 26) reduces to:

$$N_{n-1}(\rho'/N) + N_{n+2}k_t(n + 2)(n + 1)/v = N_n[(\rho'/N) + k_t n(n - 1)/v] \quad (27)$$

Under the condition that $\beta = k_t N/v\rho' > 1$,

$$n_T = (N/2)(1 + 1/\beta - 1/3\beta^2 \cdots) \quad (28)$$

where n_T is the total number of particles containing radicals. From equation 28 if $\beta \gg 1$, then

$$n_T \rightarrow N/2$$

and the rate of reaction is:

$$-\mathrm{d}(\mathrm{M})/\mathrm{d}t = k_p(\mathrm{M})(N/2) \quad (29)$$

Experimentally it can be shown that almost every radical enters a polymer particle, i.e., $\rho = \rho'$, where ρ is the rate of generation of radicals in the external phase. Consequently the lifetime of the radical is:

$$\tau_p = N/2\rho' = N/2\rho \quad (30)$$

In this case therefore the rate of reaction and the lifetime of the radical are both dependent only on the number of particles present. Thus the higher the number of particles the higher the rate of reaction and the longer the lifetime so that, at least, qualitatively, the very high rates and molecular weights found experimentally are accounted for.

Examination of equation 29 reveals that measurement of the rate of reaction, the number of particles present, and the concentration of monomer at the site of reaction will lead to a determination of the rate constant for the propagation step.

It is possible to obtain an approximate expression for the number of polymer particles present when the reaction has reached the steady state. Originally most of the soap is present in the form of micelles containing some dissolved monomer. When a radical enters a micelle from the water, polymerization commences and monomer will diffuse into the micelle, which will finally eject the polymer radical and its attendant monomer to give a polymer particle which is surrounded by a layer of soap. As this ejected particle grows the layer of soap surrounding it is kept intact by drawing more soap from the micelles, until eventually all the micelles have disappeared so that no fresh polymer particles can be formed.

If the total weight of soap is S, it will, at any instant, be present either in the form of micelles or as adsorbed soap, so that:

$$S = S_m + S_p \tag{31}$$

Further, it will be assumed that 1 g. of soap has the same interfacial area, a_s, independent of whether it is present as micelles or in adsorbed form:

$$A/S = A_p/S_p = A_m/S_m = a_s$$

When the ordinary laws of diffusion are applied to the problem, the difficulties are insurmountable. However, approaching the problem by means of two idealized cases, an approximation to the number of polymer particles can be found.

The result of the analysis is that:

$$N = k(\rho/\mu)^{2/5}(a_s S)^{3/5} \tag{32}$$

in which μ is the rate of growth of the particle and k is a constant whose value depends on the assumption made. When it is taken that all the radicals generated enter micelles, k is 0.53, while if it is assumed that the effectiveness of the interfacial soap in collecting radicals is independent of the size of the particle on which it is situated, k is 0.37. The first assumption leads to a result which is much too high, while the second will be too low, so that the correct number lies between the two values given by the analysis.

B. EXPERIMENTAL RESULTS

Many of the assumptions of the foregoing analysis can be made the subject of experimental check. According to the Harkins theories the number of polymer particles should not alter appreciably after the micellar soap has been consumed. This can readily be proved by adding to a latex of polystyrene further monomer and initiator when there is no soap left in the system. Examination of the latex before and after the subsequent polymerization shows no substantial change in the number of particles. Alterations in the number of polymer particles and in the concentration of the initiator give the predicted results according to the second case, i.e., the rate of reaction is proportional to the number of particles and independent of the concentration of initiator.

Emulsion polymerization gives rise to products of very high molecular weight at high rates. The reason for this may be seen as the result of the following simple calculations. The mutual termination reaction can be assumed to give rise to one polymer molecule, the rate constant for the process being k_t. If z chains are growing simultaneously in a particle, then the rate of production of polymer is given by:

$$\mathrm{d}p/\mathrm{d}t = k_t z(z - 1)/v$$

In the case of emulsion reactions we have the case in which a particle already tenanted by a radical is penetrated by a second radical, in which case $z = 2$ and approximately

$$\Delta p/\Delta t \simeq 2k_t/v$$

and since the change in the number of polymer molecules is 1,

$$\Delta t = v/2k_t$$

The average diameter of a polystyrene latex particle is about 600 Å. and the value of k_t is about 7×10^6 l. mole^{-1} sec.$^{-1}$, so that Δt is of the order of 0.005 sec. Thus the two radicals coexist for only a very short time, after which the growth within the particle ceases until the appearance of another radical.

The rate of growth per particle is given by $k_p(\mathrm{M})$ and for styrene k_p is 6×10^{-18} ml. min.$^{-1}$ per radical. The mean value of the monomer concentration in the particle is about 0.5 g. per ml., so that:

$$-\mathrm{d}(\mathrm{M})/\mathrm{d}t = 3 \times 10^{-18} \text{ g./min. or } 1.8 \times 10^4 \text{ molecules/min.}$$

Thus the second radical entering a polymer particle will scarcely have time to react with two styrene molecules before it is destroyed by interaction.

In order to arrive at some idea of the magnitude of the molecular weight to be expected it is necessary to consider the time which elapses between the appearance of successive radicals in the same particle. At 40°C. the rate of production of radicals from persulfate is 12×10^{16} per gram per minute. The number of latex particles of diameter 600 Å. derived from a charge of 50 g. styrene is 4.2×10^{17}, so that on the average the interval between successive penetrations is 3.5 min. In this interval about 63,000 styrene molecules will add to the radical. If no transfer reaction occurs, the molecular weight of the polymer produced should be about 7 million. As the result of the transfer step the limiting molecular weight at 40°C. is about 2.5 million. It is usual, however, especially at higher temperatures, that the limiting molecular weight is exceeded. Thus Ewart has quoted a figure of 3.6 million for styrene at 60°C., which is more than twice the limiting value. This leads to the belief that it is likely that there is some degree of branching in the polymer, but such a conclusion has not yet been verified.

From the Smith–Ewart analysis the rate constant for the propagation reaction can be found by measurement of the number of particles, the rate of reaction, and the concentration of the monomer at the site of reaction. Investiga-

TABLE 23

Rate constants for radical reactions

A. Radical–molecule addition reactions

RADICAL FROM	MOLECULE	TEMPERATURE	CONSTANT	ACTIVATION ENERGY	REFERENCE
		°C.	*l./mole/sec.*	*kcal./mole*	
Styrene	Styrene	30	110		(104)
		25	18.7	6.5	(11)
		30	51.9		(120)
		25	39.5	6.3	(45)
	Butyl acrylate	25	83		
	Methyl methacrylate	25	77		
	Methyl vinyl ketone	25	138		
	Methacrylonitrile	25	133		
	Acrylonitrile	25	100		
	β-Chloroethyl acrylate	25	74		
	Methyl acrylate	25	53.4		
	Vinylidene chloride	25	21.8		
	Methallyl chloride	25	1.8		
	Methallyl acetate	25	0.55		
	Vinyl chloride	25	2.3		
	Vinyl acetate	25	0.71		
	Vinyl ethyl ether	25	0.45		
	Butyl methacrylate	25	42		
Methyl methacrylate	Methyl methacrylate	0	41.6		(14)
		24	310	4.4	(97)
		30	286	6.3	(102)
		25	273		(147)
		22	128		(45a)
		30	273		(121)
		25	512		(64)
	Styrene	25	585		
	Methacrylonitrile	25	403		
	Acrylonitrile	25	200		
	Vinylidene chloride	25	110		
	Methallyl chloride	25	36		
	Vinyl chloride	25	20.6		
	Vinyl acetate	25	13.5		
Vinyl acetate	Vinyl acetate	15	750	4.4	(48)
		25	1100		(19)
		25	1012	7.3	(103)
		25	977		(18)
		0	2800	3.2	(71)
	Styrene	25	1.7×10^5		
	Methyl methacrylate	25	1.1×10^5		
	Acrylonitrile	25	2.8×10^4		
	Vinyl chloride	25	4.2×10^4		
	Methallyl chloride	25	1.3×10^4		

TABLE 23—*Continued*

RADICAL FROM	MOLECULE	TEMPERATURE	CONSTANT	ACTIVATION ENERGY	REFERENCE
		°C.	*l./mole/sec.*	*kcal./mole*	
p-Methoxystyrene	*p*-Methoxystyrene	0	2.92		(7)
	Styrene	25	3.54		
Propyl methacrylate	Propyl methacrylate	25	467		(47)
n-Butyl methacrylate	*n*-Butyl methacrylate	30	369	4.5	(47)
	Styrene	25	550		
Butyl acrylate	Butyl acrylate	30	13	2.1	(33)
	Styrene	25	78		
Vinyl chloride	Vinyl chloride	25	6200	3.7	(55)
	Styrene	25	3×10^5		
	Acrylonitrile	25	3×10^6		
	Vinyl acetate	25	3000		
	Methyl acrylate	25	7.5×10^4		
	Vinylidene chloride	25	3×10^4		
Methyl acrylate	Methyl acrylate	25	1580		(133)
		30	1730	7.1	(105)
			720	7.1	(105)
Trichloromethyl	Cyclohexene	30	256	3.4	(117)
	Methallyl acetate	30	3240	7.7	(107)
	Vinyl acetate	30	1120	6.1	(118)
Methyl	Acetone	30	43	9	
Tetralin	Oxygen	25	6.7×10^7	0	(15)
Ethyl linoleate	Oxygen	25	9×10^6		(23)
Digeranyl	Oxygen	25	1×10^6		(23)

B. Radical-abstraction reactions (transfer)

RADICAL FROM	MOLECULE	TEMPERATURE	CONSTANT × 10^4	ACTIVATION ENERGY	REFERENCE
		°C.	*l./mole/sec.*	*kcal./mole*	
Styrene	Benzene	60	1.76	21.0	(81a)
		60	2.66	19.1	(13a)
	Cyclohexane	60	2.35	19.6	(81a)
	tert-Butylbenzene	60	5.87	19.9	(81a)
	Toluene	60	12.3	16.3	(81a)
		60	9.3	18.2	(13a)
	Isopropylbenzene	60	80.4	11.7	(81a)
	Ethylbenzene	60	66.6	11.7	(81a)
		60	32	18.2	(13a)
	Diphenylmethane	60	225	9.9	(81a)
	Triphenylmethane	60	343	11.3	(81a)
	Fluorene	60	7350	9.3	(81a)
	Pentaphenylethane	60	196×10^4		(81a)
	Decalin	60	39.2		(81a)
	n-Heptane	60	41.2	11.2	(81a)
		80	389		(13a)

TABLE 23—*Continued*

RADICAL FROM	MOLECULE	TEMPERATURE	CONSTANT × 10^4	ACTIVATION ENERGY	REFERENCE
		°C.	*l./mole/sec.*	*kcal./mole*	
	Carbon tetrachloride	60	8700	11.0	(81a)
	Carbon tetrabromide	60	8040	10.7	(13a)
	sym-Dichloroethane	60	19.0	21.2	(13a)
	sym-Dibromoethane	60	325	16.2	(13a)
	Carbon tetrabromide	60	159 × 10^4	6.7	(13a)
Vinyl acetate	Toluene	60	32 × 10^4		(126a)
Tetralin(O_2)	Tetralin	25	13.3 × 10^4	4.5	(15)
Cyclohexene(O_2)	Cyclohexene	15	0.65 × 10^4	9.5	(21)
1-Methylcyclohexene (O_2)	1-Methylcyclohexene	15	1.1 × 10^4	8.5	(21)
Dihydromyrcene(O_2)	Dihydromyrcene	15	0.4 × 10^4	9.0	(21)
Ethyl linoleate(O_2)	Ethyl linoleate	15	5.7 × 10^4	7.0	(21)
n-Decaldehyde(O_2)	*n*-Decaldehyde	5	1.10 × 10^7	4.2	(66)
		5	2.70 × 10^7	4.2	(66)
	Benzaldehyde	5	3.10 × 10^6		(90)
Benzaldehyde(O_2)	Benzaldehyde	5	1.91 × 10^7	1.8	(90)
	n-Decaldehyde	5	9.50 × 10^7		(90)
Methyl	Acetone	30	43 × 10^4	9.5	(77)
	Dimethylmercury	30	22 × 10^4	9.0	(77)
	Ethylene oxide	30	7.5 × 10^4	9.0	(77)
	n-Butane	30	68 × 10^4	8.2	(77)
	Acetaldehyde	30	2.2 × 10^4	10.7	(73)
Iodine atom	Iodine molecule	25	8 × 10^{11}	2–3	(126)
COCl	Chlorine	25	1.7 × 10^7	2.9	(58)
	Nitrosyl chloride	25	7 × 10^9	1.1	(59)
Cl	Nitrosyl chloride	25	1.8 × 10^9	1.1	(59)

C. Radical–radical reactions

REACTION	TEMPERATURE	CONSTANT × 10^{-6}	ACTIVATION ENERGY	REFERENCE
	°C.	*l./mole/sec.*	*kcal./mole*	
Styrene + styrene	30	101	2.4	(104)
	30	10.5		(120)
	25	2.79	2.4	(11)
	25	6.0	1.9	(45)
Styrene + *p*-methoxystyrene	25	4.3		(42)
Styrene + methyl methacrylate	25	350		(121)
Styrene + methyl acrylate	25	1100		(42)
Styrene + butyl acrylate	25	40		(4)
Styrene + butyl methacrylate	25	160		(47)

TABLE 23—*Continued*

REACTION	TEMPERATURE	CONSTANT $\times 10^{-6}$	ACTIVATION ENERGY	REFERENCE
	°C.	*l./mole/sec.*	*kcal./mole*	
Methyl methacrylate + methyl methacrylate	24	68	1	(97)
	30	24.4	2.8	(103)
	0	2.7		(14)
	22	8.4		(45a)
	25	46.6		(64)
Methyl methacrylate + *p*-methoxystyrene	25	120		(42)
Methyl acrylate + methyl acrylate	25	55		(133)
	30	4.3	5.3	(105)
	30	9.4	5.3	(105)
Butyl acrylate + butyl acrylate	25	0.018	0	(33)
Butyl methacrylate + butyl methacrylate	25	10		(47)
Propyl methacrylate + propyl methacrylate	25	45		(47)
p-Methoxystyrene + *p*-methoxystyrene	0	1.06		(7)
Vinyl chloride + vinyl chloride	25	1100		(55)
Vinyl acetate + vinyl acetate	16	390	0	(48)
	25	80		(19)
	25	58.8	5.2	(103)
	25	58.8		(18)
	0	220	0	(71)
Tetralin(O_2) + tetralin(O_2)	25	21.5	0.4	(15)
Cyclohexene(O_2) + cyclohexene(O_2)	15	0.95	2	(21)
1-Methylcyclohexene(O_2) + 1-methylcyclohexene(O_2)	15	0.5	2	(21)
Dihydromyrcene(O_2) + dihydromyrcene(O_2)	15	0.65	2	(21)
Ethyl linoleate(O_2) + ethyl linoleate(O_2)	15	0.5	2	(21)
n-Decaldehyde(O_2) + *n*-decaldehyde(O_2)	5	7.5	1	(66)
Benzaldehyde(O_2) + benzaldehyde(O_2)	5	210	1	(90)
Benzaldehyde(O_2) + *n*-decaldehyde(O_2)	5	85		(90)
Digeranyl(O_2) + digeranyl(O_2)	25	0.3		(24)
Ethyl linoleate(O_2) + ethyl linoleate	25	50		(24)
Digeranyl(O_2) + digeranyl	25	9		(24)
Tetralin(O_2) + tetralin	25	7.1		(15)
Digeranyl + digeranyl	25	0.9		(24)
Ethyl linoleate + ethyl linoleate	25	20		(24)
Tetralin + tetralin	25	7.1	0.4	(15)
CCl_3 + CCl_3	30	66	5.7	(107)
	30	100	Low	(117)
$CCl_3C_6H_{10}$ + $CCl_3C_6H_{10}$	30	40	Low	(117)
$CCl_3C_6H_{10}$ + CCl_3	30	570		(117)
CCl_3(vinyl acetate) + CCl_3(vinyl acetate)	30	57.6		(118)
CCl_3 + CCl_3(vinyl acetate)	30	3800		(118)
CCl_3(styrene) + CCl_3(styrene)	30	13		(118)

TABLE 23—*Concluded*

REACTION	TEMPERATURE	CONSTANT × 10^{-6}	ACTIVATION ENERGY	REFERENCE
	°*C.*	*l./mole/sec.*	*kcal./mole*	
CCl_3(α-methylstyrene) + CCl_3(α-methylstyrene)	30	6.7		(118)
CCl_3(allyl chloride) + CCl_3(allyl chloride)	30	8		(118)
Methyl + methyl	25	2 × 10^4	0.8	(73)
	25	3.6 × 10^4	0	(77)
Iodine atoms + iodine atoms	25	1.15 × 10^4		(126)
COCl + Cl	25	10^5	0.8	(58)

tions along those lines have been carried out by Smith (144) and by Salatiello, Morton, and Landfield (135). The former confined his attention to the polymerization of styrene, while the latter studied the polymerization of butadiene and isoprene as well as styrene. The results of the investigations are set out in table 23, in which also comparison with the bulk reaction has been made. It is of some interest that the emulsion polymerization of butadiene does not follow the case analyzed when use is made of the mutual recipe.

It will be noted from the data of table 23 that in the case of styrene where comparison can be made the three sets of results in emulsion do not agree particularly well but, on the other hand, there is relatively good agreement between Morton's results and the bulk reaction data due to Matheson (104).

IX. Table of Rate Constants for Radical Reactions

The purpose of table 23 is to draw together all the results of the determination of rate constants for reactions involving free radicals. Most of the values quoted are to be found in the individual tables throughout this review, but to these have been added many values which are obtained by using copolymerization data and the results from transfer reactions. The monomer reactivity ratios used are the means of those given by Mayo and Walling (109a).

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