$$CO_2^- + O_2 \rightleftarrows O_2CO_2^- \qquad (E1)$$

$$O_2CO_2^- + Mn^{++} + 2H^+ \longrightarrow Mn(III) + H_2O_2 + CO_2 \qquad (E2)$$

Our data do not seem to indicate whether it is desirable to add the reaction proposed by Weiss[20]

$$CO_2^- + H_2O_2 \longrightarrow CO_2 + OH + OH^- \qquad (E3)$$

A thorough study of the induced oxidation might provide more definite information about these steps and also about the ionization constant of the radical ion and the nature of step (B2).

Summary

If atmospheric oxygen is absent, the following mechanism appears to be consistent with the voluminous information available on the homogeneous reaction between permanganate and oxalate. The equations as presented do not include the many rapid equilibria in the system that involve hydrogen and oxalate ions.

The reaction is initiated by the step

$$MnO_4^- + MnC_2O_4 \longrightarrow MnO_4^{=} + MnC_2O_4^+ \qquad (A1, C1)$$

If manganous ion is present in significant concentration, the subsequent steps are

$$Mn(VI) + Mn(II) \longrightarrow 2Mn(IV) \qquad (A2)$$

$$Mn(IV) + Mn(II) \longrightarrow 2Mn(III) \qquad (A3)$$

If manganous ion is not available, the less favored steps are

$$Mn(VI) + C_2O_4^{=} \longrightarrow Mn(IV) + 2CO_2 \qquad (C2)$$

$$2Mn(IV) + C_2O_4^{=} \longrightarrow 2Mn(III) + 2CO_2 \qquad (C3)$$

These steps involve oxidation of oxalate in two electron transfers and do not produce Mn(II) as an intermediate in (C3).

The Mn(III) subsequently reacts according to the sequence

$$Mn(C_2O_4)_n^{3-2n} \longrightarrow Mn^{++} + (n - 1)C_2O_4^{=} + CO_2 + CO_2^- \qquad (B1)$$

$$Mn(C_2O_4)_n^{3-2n} + CO_2^- \longrightarrow Mn^{++} + nC_2O_4^{=} + CO_2 \qquad (B2)$$

where n may be 1, 2 or 3 and step (B1) is rate determining. The rate and equilibrium constants associated with (B1) have been evaluated by Taube[8] and less completely by us.

At very low concentrations of oxalate, permanganate can also react by the step

$$MnO_4^- + MnC_2O_4^+ \longrightarrow MnO_4^{=} + Mn(IV) \qquad (D)$$

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[20] J. Weiss, *Discs. Faraday Soc.*, No. 2, 188 (1947).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Kinetics of Competitive Processes when Reactive Fragments are Produced in Pairs

BY RICHARD M. NOYES

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If a molecule is dissociated into two radicals in liquid phase, the radicals may undergo primary recombination in the "cage" in which they are formed, may undergo diffusive secondary recombination, or may combine with radicals from other dissociations. A scavenger that can react with radicals may compete with the combination process even at low concentrations, and conventional kinetic expressions are developed to describe the competition. These expressions depend on whether the product of reaction with scavenger is a reactive radical itself or is inert. Only a very reactive scavenger can compete with the secondary recombination of original partners from a dissociation. If such competition does occur, the amount of additional reaction varies approximately as the square root of the concentration of scavenger. Primary recombination occurs too rapidly for competition except in a medium that consists almost entirely of very reactive scavenger. The term "geminate recombination" is proposed for the total of primary and secondary recombination of original partners; this total is usually lumped together in references to "cage" effects.

Introduction

Vinyl polymerization and many other chemical reactions are initiated by the radical fragments produced in pairs by thermal or photochemical dissociation reactions. When it is possible to measure the absolute rate of dissociation, it is usually found that not all of the fragments initiate the reaction of interest and that it is not possible to eliminate competition from reactions between fragments. The purpose of this paper is to develop the kinetics for the competition between these radical–radical reactions and the desired reaction of a radical with some other species (herein referred to as a scavenger). Even in a system containing only one type of radicals and one other chemical species capable of reacting with them three kinetically distinct radical–radical processes may contribute to reduce the efficiency of initiation.

(1) The fragments from a dissociation may undergo "primary recombination" in the "cage" in which they are formed. If this happens, the fragments never attain a separation of as much as a molecular diameter, and recombination takes place in a period that may be of the order of a vibration (10^{-13} sec.) and is certainly less than the time between diffusive displacements (10^{-11} sec.). It is conceivable that molecules in the wall of the "cage" could compete with primary recombination, but they can only do so when the mole fraction of scavenger is near unity and when the scavenger is extremely efficient. In the rest of this paper, we shall neglect primary recombination and consider only those systems in which the dissociating fragments attain separations of at least a molecular diameter.

(2) If the fragments escape the "cage," they undergo random diffusive displacements of the or-

der of a molecular diameter and with a frequency of the order of 10^{11} sec.$^{-1}$ in liquids of ordinary viscosity. During this random diffusion, the fragments from a specific dissociation may re-encounter each other and undergo "secondary recombination." If secondary recombination does not take place within about 10^{-9} second, the fragments will almost certainly have diffused so far apart that there is negligible chance they will ever re-encounter each other; a scavenger can compete only if it is in sufficient concentration that it can usually catch a radical in this short time. Secondary recombination cannot be treated with a conventional rate constant. If many isolated pairs of radicals are produced at time zero and have lived for more than a few diffusive displacements, the rate of recombination of pairs is proportional to $t^{-3/2}$ where t is the time since formation.

Since both primary and secondary recombination involve the fragments from a specific dissociation, and since both take place in times that are frequently short compared to the lifetimes of radicals undergoing other reactions, the recombination of original partners has often been lumped together and referred to as a "cage" effect. Since secondary recombination involves freely diffusing particles that are behaving independently of each other until they recombine, we do not like to use a term that implies the particles are constrained to remain near each other. At the suggestion of Prof. W. H. Hamill, we propose the term "geminate recombination" to designate all forms of recombination of original partners.

(3) If the radical fragments escape both primary and secondary recombination, they still may fail to function as initiators because they combine with fragments from other dissociations. The scavenger competes with this combination reaction by conventional kinetic processes that are discussed briefly below.

Formulation of Problem

If we consider only those fragments that escape primary recombination, three specific reactions must be considered even if only one type of radical and one type of scavenger are in the system. These reactions are

$$R_0\cdot + R_0\cdot \longrightarrow R_2 \qquad (1)$$

$$R_0\cdot + S \longrightarrow P \qquad (2)$$

$$R_0\cdot + R\cdot \longrightarrow R_2 \qquad (3)$$

The subscript 0 refers to a radical from a specific dissociation. Reaction (1) is secondary recombination and reaction (3) is combination with a radical from another dissociation; both of these reactions reduce the efficiency with which dissociation initiates reaction (2) with scavenger S. The scavenger may be a stable radical or a species like a polymerizable monomer that can react with a radical initiator. If P can also react with radicals or with scavenger or both, additional kinetic complications are introduced, but the additional reactions are similar to (2) and (3) above and add no new principles. The object of this paper is to treat the competition of reaction (2) with reactions (1) and (3).

Competition at Low Scavenger Concentrations

If a single pair of radicals is produced in an infinite volume of solution containing no scavenger, let β' be the probability the pair will undergo secondary recombination. Our previous studies[1] have suggested that β' is of the order of 0.53 if the radicals react at every encounter, but this result should be regarded only as a tentative estimate. If the concentration of scavenger is low, reaction (2) may be able to compete with reaction (3) but it cannot compete significantly with reaction (1). This situation will certainly hold when the scavenger is less than 0.01 mole/liter, and it might apply at higher concentrations. In such a solution, the fraction of radicals reacting by process (1) is β', the fraction reacting by process (2) (efficiency of initiation) is[2] $(1 - \beta')k_2[S]/(k_2[S] + k_3[R\cdot])$, and the fraction reacting by process (3) is $(1 - \beta')k_3[R\cdot]/(k_2[S] + k_3[R\cdot])$.

If the rate of dissociation is constant, the efficiency of initiation will be proportional to concentration of scavenger at very low concentrations but will approach a constant value of $1 - \beta'$ in the upper part of this concentration range.

The exact efficiency at intermediate concentrations depends on the subsequent behavior of the product P.

We have considered two limiting situations and have plotted the results in Fig. 1. In the first situation, let P be inert to further reaction with radicals, as is the product in the bleaching of diphenylpicrylhydrazyl. If r_d is the rate of dissociation to produce radical pairs escaping primary recombination, the steady-state assumption requires that

$$2(1 - \beta')r_d = k_2[S][R\cdot] + 2k_3[R\cdot]^2 \qquad (4)$$

Solution leads to

$$\frac{k_2[S]}{k_3[R\cdot]} = \frac{4}{-1 + \sqrt{1 + 16/c^2[S]^2}} \qquad (5)$$

where

$$c = k_2/\sqrt{(1 - \beta')k_3 r_d} \qquad (6)$$

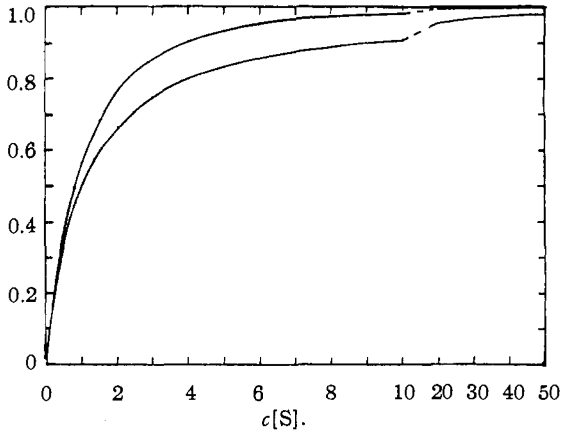

Fig. 1.—Efficiency of competition of scavenger with combination (reaction 3): lower curve is $c[S]/(1 + c[S])$; upper curve is $4/(3 + \sqrt{1 + 16/c^2[S]^2})$.

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(1) R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1954).

(2) Strictly speaking, the treatment should use "long-time" rather than "true" rate constants. The distinction is discussed below and in reference 1. The constants intended in this section are those given by conventional calculations on experimental measurements.

The efficiency of initiation of scavenger reaction at constant r_d and varying [S] is given by

$$\frac{4(1 - \beta')}{3 + \sqrt{1 + 16/c^2[\mathrm{S}]^2}} \qquad (7)$$

and is plotted against c[S] in Fig. 1.

As a second limiting situation, let P be a radical product capable of reacting with R· as efficiently as R· itself can. Then the total concentration of radicals competing with reaction (2) is independent of the concentration of scavenger, and at constant r_d the efficiency of scavenger reaction is given by

$$\frac{(1 - \beta')c[\mathrm{S}]}{1 + c[\mathrm{S}]} \qquad (8)$$

This relation is also plotted against c[S] in Fig. 1.

Competition with Secondary Recombination

The types of competition shown in Fig. 1 have been treated with conventional kinetic expressions. Since the concentration of radicals in a system is usually very low, it is possible to make $k_2[\mathrm{S}] >> k_3[\mathrm{R}\cdot]$ even if reaction (2) has an activation energy of a few kcal./mole. Hence it is possible to attain the limiting initiation efficiency of $1 - \beta'$ even with a scavenger that is rather unreactive compared to radical–radical reactions. If the efficiency is to be increased beyond this value, the scavenger must be so reactive that it can compete with secondary recombination. This competition cannot be handled by conventional kinetic expressions because neither reaction (1) nor (2) can be described by a simple rate constant. This type of competition has recently been treated by Roy, Williams and Hamill[3]; we present here an alternative somewhat simpler treatment that involves comparable assumptions.

To treat the kinetic behavior of reaction (1), consider a pair of radicals that are produced at time zero in an infinite volume of solvent containing no scavenger and that escape primary recombination. Let $h(t)\,\mathrm{d}t$ be the probability that they will undergo secondary recombination between t and $t + \mathrm{d}t$. From the definition of β', we can write

$$\int_0^\infty h(t)\,\mathrm{d}t = \beta' \qquad (9)$$

After sufficient time for a very few diffusive displacements (less than 10^{-10} sec.), $h(t)$ varies[4] inversely as $t^{3/2}$; at times approaching zero, $h(t)$ does not diverge but goes through a maximum and falls toward zero for times less than one diffusive displacement. We have not yet developed a complete expression for $h(t)$ at very short times, but the exact behavior is usually unimportant kinetically because reaction (2) cannot compete significantly with reaction (1) in the time necessary to establish the limiting form of $h(t)$. We shall arbitrarily use the discontinuous function

$$\begin{aligned} h(t) &= 0, && 0 < t < 4a^2/\beta'^2 \\ h(t) &= a/t^{3/2}, && 4a^2/\beta'^2 \leqslant t < \infty \qquad (10) \end{aligned}$$

The parameter a will probably never be greater than about 10^{-6} sec.$^{1/2}$; its dependence on other parameters is discussed below.

Reaction (2) is not completely amenable to conventional treatments either. If a radical is produced at random in a solution containing scavenger, the probability that it will react with scavenger in a given time interval is a function of the time since formation of the radical.[1] We shall ignore this effect and assume that reaction (2) can be described by the "long-time" rate constant k_2'. This constant is strictly applicable only to radicals that have lived about 10^{-9} second—long enough that there is negligible secondary recombination to compete with. The larger "true" rate constant, applicable at very short times, is nearly identical with the "long-time" rate constant unless the scavenger is extremely reactive, and probably it is never different by more than a factor of 2. The use of an unchanging rate constant is satisfactory unless a very reactive scavenger is present in such high concentration that the approximation in equation 10 is also causing errors.

If a single radical were produced in solution, the chance that it would have reacted with scavenger by time t is $1 - e^{-k_2'[\mathrm{S}]t}$. If two radicals are produced and do not undergo secondary recombination by time t, the chance that one or both of them will have reacted with scavenger is $1 - e^{-k_2'[\mathrm{S}]t}$. If many radical pairs are produced in solution, we are interested in the fraction reacting with scavenger that would otherwise have undergone secondary recombination. This fraction is the integral over all times of the probability an isolated pair would undergo secondary recombination at that time multiplied by the probability that at least one of the members of the pair has already reacted with scavenger before that time. Thus, the increased efficiency of scavenger action due to competition with secondary recombination is given by

$$\int_0^\infty h(t)(1 - e^{-2k_2'[\mathrm{S}]t})\,\mathrm{d}t = 2a\sqrt{2\pi k_2'[\mathrm{S}]} - 8k_2'a^2[\mathrm{S}]/\beta' + \ldots \qquad (11)$$

Since the maximum possible values of a and k_2' are about 10^{-6} sec.$^{1/2}$ and 10^{10} liter/mole sec., respectively, we cannot expect significant competition with secondary recombination unless S is present at 0.01 mole/liter or greater. Since [S] can never be greater than about 20 mole/liter (55 for water), k_2' must be at least 10^7 liter/mole sec. if there is to be any chance of competing significantly with secondary recombination; very few reactions have such large rate constants.

The value of the parameter a depends upon the frequency of diffusive displacements in the medium. If other quantities remain the same, a will vary as $\nu^{-1/2}$. For a given value of ν, a will vary almost proportionately to β'. The proportion is not exact, but it is close enough for the present discussion. We can describe β' (the probability a pair will undergo secondary recombination) in terms of three parameters. These are α (the probability two radicals will react with each other during an encounter), β_0 (the probability two radicals formed in a dissociation reaction will ever encounter each other), and β (the probability two radicals separating from a non-

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[3] J. C. Roy, R. R. Williams, Jr., and W. H. Hamill, THIS JOURNAL, **76**, 3274 (1954).

[4] If a particle starts at the origin and is allowed to undergo random displacement in one dimension only, the probability distribution at subsequent times is a Gaussian centered on the origin. In this distribution, the average net displacement varies as $t^{1/2}$ and the probability of being at the origin varies as $t^{-1/2}$. If a particle is free to move independently in three dimensions, the probability of returning to the origin varies as $t^{-3/2}$.

reactive encounter will ever encounter each other again). Roy, Williams and Hamill[3] also required three independent parameters and chose the probability of reaction during an encounter (our α), the initial separation before free diffusion starts, and the ratio of encounter diameter to root-mean-square displacement distance. These parameters can be related to ours as shown below, but we do not see how to describe the system with less than three independent quantities.

We have previously let $\beta = \beta_0$, but the radicals may be produced with kinetic energies in excess of normal thermal values and may attain a larger initial separation before they begin to diffuse at random. In terms of our parameters

$$\beta' = \alpha\beta_0 + \alpha(1 - \alpha)\beta_0\beta + \alpha(1 - \alpha)^2\beta_0\beta^2 + \alpha(1 - \alpha)^3\beta_0\beta^3 + \ldots = \alpha\beta_0/(1 - \beta + \alpha\beta) \quad (12)$$

Equation 12 indicates the dependence of a on our parameters. We have previously shown that β is 0.53 when the encounter diameter and displacement distances are equal, and p.1354 of reference 1 shows the relation between β and the ratio of these distances. If the initial separation of the radicals is greater than that for molecules separating from a non-reactive encounter, β_0 will be less than β. Wijsman[5] indicates that β_0 will vary inversely as the initial separation.

If diffusive displacements of R· radicals take place at a frequency of 2×10^{11} sec.$^{-1}$ and for a distance equal to the encounter diameter for recombination, if the initial separation of radicals that have escaped primary recombination is the same as for molecules that have separated from a non-reactive encounter ($\beta = \beta_0$), and if recombination takes place at every encounter ($\alpha = 1$), then $\beta' = 0.53$ and $a = 1.6 \times 10^{-6}$ sec.$^{1/2}$. This magnitude is a good estimate for a at large values of α, and at values of α less than about 0.1 there is no significant secondary recombination for the scavenger to compete with.

It is easy to compute additional terms in the series expansion of equation 11, but they are less important than errors introduced by the approximation of equation 10 and the assumption that k_2' is independent of time. A more exact theoretical treatment does not seem justified until there is more information on very reactive scavengers.

Summary

If scavenger is present in very low concentration, most of the radicals combine with other radicals and the efficiency with which dissociation leads to scavenger reaction is proportional to scavenger concentration. At higher scavenger concentrations, the efficiency reaches a limiting value in which the scavenger is catching all radicals that escape primary and secondary recombination. This limiting efficiency cannot be increased even with pure scavenger solvent unless k_2 is greater than about 10^7 liter/mole sec., but very reactive scavengers can compete with secondary recombination at concentrations above 0.01 mole/liter. To a first approximation, the increased efficiency of initiation varies as the square root of the concentration of scavenger. If the scavenger reacts with a radical at almost every encounter, then a medium of pure scavenger might begin to compete with primary recombination.

In Fig. 2, we illustrate the variation of initiation efficiency with concentration of a very reactive scavenger. In making the calculations, we have assumed a photochemical initiation of 10^{14} quanta/ml. sec. with each quantum causing dissociation but with 20% primary recombination. We have also taken $\beta' = 0.53$, $a = 1.6 \times 10^{-6}$ sec.$^{1/2}$ and $k_2' = k_3' = 10^{10}$ liter/mole sec. The molar volume of S was taken as 50 ml., and series expansion terms up to $[S]^4$ in equation 11 were used to calculate points for $\log [S] \leqslant 0.4$. The curve at higher concentrations is a subjective estimate.

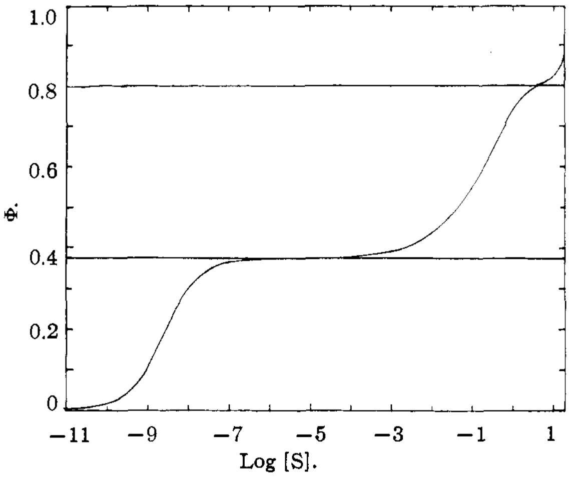

Fig. 2.—Dependence of quantun yield on concentration of very reactive scavenger. Top region represents primary recombination. Middle region represents competition of scavenger with secondary recombination. Bottom region represents competition with combination reaction.

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[5] R. A. Wijsman, *Bull. Math. Biophys.*, **14**, 121 (1952).