

differences between the alcohols and the effect which these exert on the bimolecular step.

The enol acetylation reactions are more difficult to deal with. As the referees of an earlier form of this manuscript have pointed out, a variety of mechanisms for the enol acetylations can be written. These may involve the ketone, its enol, and the various conjugate acids of isopropenyl acetate, as well as both cyclic or noncyclic transition states and intermediates. If one evokes the criterion of simplicity, then it would seem to us that the most reasonable mechanism would be analogous to the ester interchange reaction in which the enol attacks the conjugate acid of isopropenyl acetate. While the data do not allow a clear-cut decision among the various possibilities, the following comments seem in order.

During the early stages of the reaction, before the reverse reaction has assumed importance, the observed rates follow second-order kinetics. The rate constants given in Table III are really "apparent" or "pseudo" second-order constants for they vary with the ratios of the starting materials as well as with the catalyst concentration.

Combining rate data and product analyses for the iodination and bromination of a series of ketones, Cardwell and Kilner¹¹ have concluded that in aqueous acid the relative rates of enolization fall in the order acetone > methyl isobutyl ketone > methyl isopropyl ketone > methyl *t*-butyl ketone. Furthermore, when alternative pathways for enolization exist, the internal enol is formed more rapidly than the external.

(11) H. M. E. Cardwell and A. E. H. Kilner, *J. Chem. Soc.*, 2430 (1951).

Extrapolation of results in aqueous acid to results obtained in the milieu of the enol acetylations is subject to some question. However, the rate values in Table III do show the same order of reactivity, *i.e.*, acetone > methyl isobutyl ketone > methyl isopropyl ketone > methyl *t*-butyl ketone. Regardless of whether the ketone reacts in the keto or enol form, there must, at some point, be a bimolecular collision, and this presumably would be subject to steric considerations which suggest the above order of reactivity. These expectations are, of course, substantiated by the alcohol acetylations.

The initial rapid formation of the terminal olefin is also reasonable. If the enol is the attacking species, then the hydroxyl group is less sterically hindered for the terminal enols as opposed to the internal enols. If the ketone takes part in the bimolecular step, then a proton must be removed from a position α to the carbonyl group in forming the ultimate enol acetate product. Following the considerations of House and Kramar,⁵ it is reasonable that a terminal methyl hydrogen would be more accessible to the base than a more highly substituted internal position.

In summary, it is evident that in situations where more than one enol acetate may be formed both kinetic and thermodynamic control influence the course of the reaction and determine the product composition at a given time. In preparative reactions, the use of an excess of isopropenyl acetate does not greatly enhance the yield but is probably advisable to offset the side reaction which destroys some of the isopropenyl acetate. An increase in the amount of catalyst materially shortens the reaction time without decreasing the yield of product.

Thermal Decomposition of β -Allyloxypropionyl Peroxide. Cyclization of the β -Allyloxyethyl Radical¹

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Results of kinetics runs are reported for decompositions of β -allyloxypropionyl peroxide in toluene and *p*-xylene. The kinetics of decomposition in toluene are approximately first order, although very slight curvatures of first-order plots indicate a small amount of induced decomposition. β -Allyloxypropionyl peroxide decomposes somewhat more rapidly in *p*-xylene than in toluene, and the kinetic behavior is such as to suggest that there is more radical-induced decomposition in the former. Product studies are reported for decompositions of the β -allyloxypropionyl peroxide in *p*-xylene and in the same solvent containing excess galvinoxyl. The main product formed from the β -allyloxyethyl radical is 3-methyltetrahydrofuran, which indicates that this radical, like the 5-hexenyl radical, undergoes cyclization to give a five-membered ring.

It has been found recently that the 5-hexenyl radical cyclizes in solution to give the cyclopentylmethyl radical, whether the 5-hexenyl radical is generated by decomposition of 6-heptenyl peroxide,³ by reaction of 6-mercapto-1-hexene with triethyl phosphite,⁴ or by the Kolbe electrolysis of 6-heptenoic acid.⁵

It is also known that 1-substituted derivatives of the 5-hexenyl radical undergo cyclization to give five-membered ring compounds as the only cyclic products. Thus, Brace has shown that the only cyclic products which are formed in the free-radical addition of 1-iodoperfluoropropane to 1,6-heptadiene have structures I and II.⁶

At the same time, it has been shown by Cadogan that free-radical additions to ethyl diallylacetate result in the formation of both the five- and six-membered

(1) This work was supported by the U. S. Air Force Office of Scientific Research (AF-AFOSR-62-53) and by the National Science Foundation (NSF-G-24910).

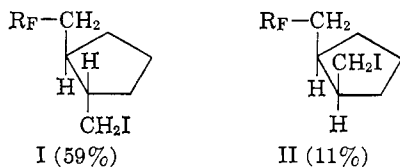
(2) To whom correspondence should be addressed: Head, Department of Chemistry, Augusta College, Augusta, Ga.

(3) R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963).

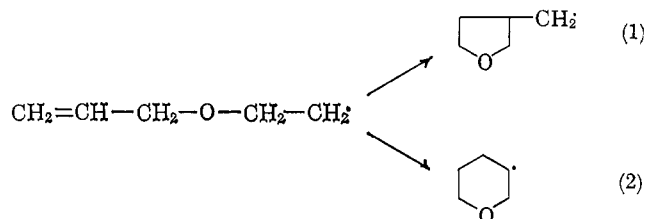
(4) C. Walling and M. S. Pearson, *ibid.*, **86**, 2262 (1964).

(5) R. G. Garwood, C. J. Scott, and B. C. L. Weedon, *Chem. Commun. (London)*, **1**, 14 (1965).

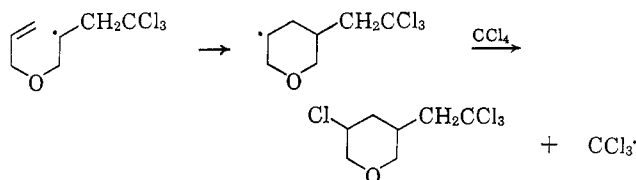
(6) N. O. Brace, *J. Am. Chem. Soc.*, **86**, 523 (1964).



ring products.⁷ In the additions of several compounds containing sulfhydryl groups, as well as diethyl phosphonate, to this ester the yields of cyclohexane derivatives exceed the yields of methylcyclopentane derivatives by ratios near 3:1. The present problem was undertaken to determine whether the presence of the heteroatom would cause the β -allyloxyethyl radical to cyclize in a fashion different from the 5-hexenyl radical. In this connection, it has been reported that



the addition of carbon tetrachloride to diallyl ether results in the formation of a tetrahydropyran derivative.⁸ At the same time, Brace⁶ stated, without giving



experimental evidence, that 1-iodoperfluoropropane adds to diallyl ether to give a product mixture analogous to that given by 1,6-heptadiene, implying that the cyclization proceeds to give a five-membered ring product. While these two reports are not necessarily at variance with each other, it is obvious that further work is needed on the cyclizations of α -substituted β -allyloxyethyl radicals.

Results and Discussion

Although there is a paucity of information on β -alkoxy-substituted aliphatic diacyl peroxides in the literature, there does not seem to be any particular difficulty involved in their synthesis. Thus Fichter and Schnider have reported the synthesis of β -isoamoxypropionyl peroxide by standard methods.⁹ The thermal decomposition of the latter gave products which are most easily explained in terms of the usual expected homolysis of the peroxide.

β -Allyloxypropionic acid was converted to its acid chloride with phosphorus pentachloride; the acid chloride was converted to the peroxide with sodium peroxide. The infrared spectrum of the resulting peroxide showed bands at 1814 (w) and 1785 (s) cm^{-1} . The various samples were found to be 96–98% pure as determined by iodometric titration of weighed portions.

(7) J. I. G. Cadogan, *Chem. Ind.* (London), 753 (1964).

(8) W. S. Friedlander, Abstracts, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April 1958, p. 18N; cf. C. Walling and E. S. Huyser, *Org. Reactions*, **13**, 105 (1963).

(9) F. Fichter and A. Schnider, *Helv. Chim. Acta*, **14**, 857 (1931).

Kinetics of the decompositions of β -allyloxypropionyl peroxide in toluene and *p*-xylene were determined by iodometric titration. The results are presented in Table I. Some of the products in xylene were determined by g.l.c. and infrared analysis. The results of the product studies are given in Table II.

TABLE I
KINETICS OF THE DECOMPOSITION OF β -ALLYLOXYPROPIONYL PEROXIDE IN SOLUTION^a

Run no.	Solvent	P_0, M	$t_{1/2}, \text{min.}$	$T, ^\circ\text{C.}$
1	Toluene	0.093	575	70
2	Toluene	0.093	134	80
3	Toluene	0.093	45.6	90
4	<i>p</i> -Xylene	0.136	450	70
5	<i>p</i> -Xylene	0.136	39.2	90
6	<i>p</i> -Xylene	0.109	498	70
7	<i>p</i> -Xylene	0.109	130	80
8 ^b	<i>p</i> -Xylene	0.09	136	80

^a Runs 1–7 determined iodometrically. Run 8 determined by measuring the disappearance of the 1785- cm^{-1} band by infrared analysis. ^b Solution contained galvinoxyl at an initial concentration of 0.11 *M*. Some galvinoxyl remained after all the peroxide had decomposed.

TABLE II
PRODUCTS OF DECOMPOSITION OF β -ALLYLOXYPROPIONYL PEROXIDE IN *p*-XYLENE

Products	Temp., $^\circ\text{C.}$		
	80	80	150
	—(Peroxide) ₀ , <i>M</i> —		
	0.11	0.11	0.11
	—(Galvinoxyl) ₀ , <i>M</i> —		
	0	0.13	0
	—Yield ^{a, b} —		
Allyl ethyl ether and allyl vinyl ether	0.03	0.03	0.03
3-Methyltetrahydrofuran	0.60	0.01	0.63
1,4-Diallyloxybutane	0.25	0.27	0.28
β -Allyloxyethyl β -allyloxypropionate	0.30	0.30	0.25
β -Allyloxypropionic acid	Trace	Trace	Trace

^a Yields reported in mole per mole of peroxide decomposed.

^b Trace equals less than 0.01 mole/mole of peroxide decomposed.

The kinetics were found to deviate slightly from the first-order law. In particular, the rates were found to decrease slightly at high peroxide conversions.

This behavior is probably due to radical-induced decomposition of a type which leads to first- plus higher order kinetics. The decompositions in toluene obey the first-order law more ideally than those in *p*-xylene. In addition, the three rates obtained in toluene give a somewhat better plot of $\log k_d/T$ vs. $1/T$. The activation parameters obtained from the decomposition rates in toluene from this plot are as follows: $\Delta H^* = 30.7$ kcal.; $\Delta S^* = +9.3$ e.u. The activation enthalpy for the decomposition in *p*-xylene, calculated from the data obtained on the 0.136 *M* solution, is 29.4 kcal.; $\Delta S^* = +5.3$ e.u. Inasmuch as β -allyloxypropionyl peroxide decomposes to a certain extent by radical-induced decomposition as well as homolysis, these estimates of the activation enthalpies calculated from k_{obsd} are somewhat low.

Since the products of the decomposition which we have identified do not indicate the precise nature of the induced decomposition, we have not attempted to adjust statistically our data to first- plus higher order rate laws. Furthermore, although the rate is somewhat dependent of P_0 in *p*-xylene, there are three indica-

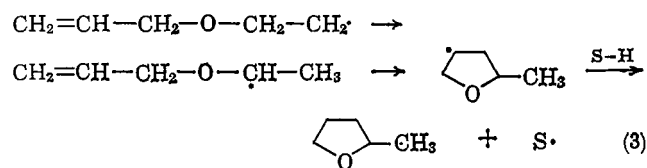
tions that, whatever its nature, the radical-induced decomposition does not constitute a very significant pathway of decomposition of the peroxide in *p*-xylene solutions near 0.1 *M*. Firstly, the rate measured in pure *p*-xylene differs by less than 5% from the rate in the presence of the free-radical scavenger, galvinoxyl.¹⁰ The second point comes from the product studies; the yields of both ester (β -allyloxyethyl β -allyloxypropionate) and dimer (1,4-diallyloxybutane) are almost completely insensitive to galvinoxyl. This result requires that these substances be products either of direct rearrangements of the peroxide, or of radical cage recombination reactions. In either case, if a significant fraction of the peroxide were destroyed by induced decomposition in pure *p*-xylene, then in the presence of galvinoxyl, in a medium in which induced decomposition does not occur, the yields of ester and dimer should increase significantly. Finally, the rates in toluene are only roughly half the rates of decomposition of propionyl,¹¹ heptanoyl,³ and 6-heptenoyl³ peroxides.

The fact that β -allyloxypropionyl peroxide decomposes more slowly than do peroxides which have similar structural features makes it unlikely that there is a neighboring-group participation by the double bond in the homolysis.¹²

3-Methyltetrahydrofuran was found to be one of the major products of decomposition of β -allyloxypropionyl peroxide in *p*-xylene at 80 and 150°. This is clearly a free-radical product, for it is the only product whose yield is significantly different in pure *p*-xylene and in the same solvent containing excess galvinoxyl. Since it was found that the retention times of this product were not greatly different from those of tetrahydropyran on several g.l.c. columns, the $C_5H_{10}O$ g.l.c. fraction was collected, and its n.m.r. spectrum was determined in deuteriochloroform.¹³ The n.m.r. spectrum of this fraction was identical with that of an authentic sample of 3-methyltetrahydrofuran, and quite different from that of tetrahydropyran.¹⁴ The $C_5H_{10}O$ fraction apparently contained only 3-methyltetrahydrofuran. Therefore, the β -allyloxyethyl radical must cyclize exclusively to the five-membered ring (reaction 1, above).

There is also no evidence for the presence of 2-methyltetrahydrofuran, whose g.l.c. retention times and n.m.r. spectrum¹⁵ are both significantly different

from those of 3-methyltetrahydrofuran and tetrahydropyran. Therefore, none of the $C_5H_{10}O$ fraction was formed as a result of reaction sequence 3.



Apparently the β -allyloxy radical does not decompose to ethylene and allyloxy radicals to a significant extent under the conditions used. Although traces of materials (less than 0.01 mole/mole of peroxide decomposed) whose g.l.c. retention times were identical with those of allyl alcohol and acrolein were formed in the decomposition, the fact that their yields were the same at 150° as they were at 80° makes it unlikely that these substances were formed by cleavage of the β -allyloxy radical.

The other products which we have identified are either products of free-radical cage reactions or of direct rearrangement of the peroxide. While our data cannot distinguish between these two possible modes of formation, no direct evidence could be obtained that a rearrangement to an inversion product, such as has been described recently by Greene, Stein, Chu, and Vane, occurs in the decomposition of β -allyloxypropionyl peroxide.¹⁶

Experimental¹⁷

3-Methyltetrahydrofuran,¹⁸ tetrahydropyran,¹⁸ and 2-methyltetrahydrofuran¹⁹ were obtained commercially.

β -Allyloxypropionic acid was obtained commercially, and it was also synthesized by the following procedure.²⁰ β -Propiolactone (144 g., 2 moles) was mixed with allyl alcohol (170 g., 2.9 moles) in a three-necked flask, equipped with mechanical stirrer and reflux condenser. The mixture was heated (pot temperature, 68°) for 24 hr. The mixture was twice distilled under vacuum, b.p. 82.5° (0.45 mm.). The yield of this fraction was 200 g., or 78% of theory.

β -Allyloxypropionyl peroxide was prepared by treatment of the acid chloride (obtained from the acid and phosphorus pentachloride, b.p. 60° (1.5 mm.)), with sodium peroxide in ether. The method used was analogous to that described for the preparation of cyclohexaneformyl peroxide.^{10a} The infrared spectrum showed bands at 1814 (w) and 1785 (s) cm^{-1} indicative of a symmetrically substituted diacyl peroxide; bands were also present at 1648, 927, and 995 cm^{-1} which were taken as evidence for terminal double bonds. Iodometric titration of weighed samples of this liquid peroxide indicated purities between 96 and 98%.

β -Allyloxyethyl β -allyloxypropionate was obtained by reacting the acid chloride and commercial 2-allyloxyethanol in the presence of pyridine. The procedure used was analogous to that reported for the preparation of 5-hexenyl 6-heptenoate.³

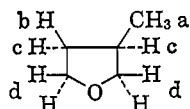
1,4-Diallyloxybutane.—Sodium (48 g., 2.1 g.-atoms) was dissolved in 200 ml. of allyl alcohol. While stirring, 1,4-dibromobutane (216 g., 1 mole) was added over a 30-min. period. The mixture was refluxed for 3 hr. The mixture was taken up in ether;

(10) (a) G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 501 (1957); (b) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957); (c) P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962); (d) F. D. Greene, W. Adam, and J. E. Cantrill, *ibid.*, **83**, 3461 (1961); (e) R. C. Lamb and J. G. Pacifici, *ibid.*, **86**, 914 (1964).

(11) J. Smid, A. Rembaum, and M. Szwarc, *ibid.*, **78**, 3315 (1956).

(12) (a) R. C. Lamb, F. F. Rogers, Jr., G. C. Dean, Jr., and F. W. Voigt, Jr., *ibid.*, **84**, 2635 (1962); (b) T. W. Koenig and J. C. Martin, *J. Org. Chem.*, **29**, 1520 (1964).

(13) Assignments of n.m.r. bands can be made as follows: a, doublet,



τ 8.94, $J = 6.2$ c.p.s. (3 protons); b, multiplet, τ 8.50 (1 proton); c, multiplet, τ 7.81 (2 protons); and d, complex pattern, 6.30 (4 protons). Although this last pattern extends from τ 5.90 to 6.83, there is no absorption at τ 6.45, where tetrahydropyran absorbs strongly. We are indebted to Dr. Y. Shimizu for the interpretation of this spectrum.

(14) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p. 55.

(15) K. Nukada, *Bull. Soc. Chem. Japan*, **33**, 1606 (1960).

(16) F. D. Greene, H. P. Stein, C.-C. Chu, and F. M. Vane, *J. Am. Chem. Soc.*, **86**, 2080 (1964).

(17) A Perkin-Elmer Model 421 infrared spectrophotometer was used in kinetics runs determined by infrared analysis and for quantitative estimation of ester. A Beckman GC-2 gas chromatograph was used in the products study. A Varian A-60 n.m.r. spectrometer was used to record the n.m.r. spectra; tetramethylsilane was the internal standard. Boiling points are uncorrected.

(18) Aldrich Chemical Co., Milwaukee, Wis.

(19) Distillation Products Industries, Eastman Organic Chemicals, Rochester, N. Y.

(20) H. E. Zaugg, *Org. Reactions*, **3**, 305 (1954).

the ether layer was washed with water. The ether was removed, the residue was dried over anhydrous sodium sulfate, and the residue was twice distilled under vacuum, b.p. 54° (1 mm.). The infrared spectrum of this product is in agreement with the assigned structure.

Product Analyses.—All the products except ester and acid have been determined by g.l.c. methods which have been described.³ The previously described column A³ and column F, a 12 ft. × 0.25 in. column packed with 30% diethylene glycol succinate on C-22 firebrick, were used in this work. 1,4-Di-

allyloxybutane was estimated quantitatively, using column F; column A was used for all other products. The ester yields were determined by infrared analysis using the carbonyl band at 1739 cm.⁻¹. Infrared spectra of decomposition mixtures revealed that only a trace β -allyloxypropionic acid was formed in the decomposition.

Kinetics Runs.—Iodometric^{12a} and infrared²¹ kinetics runs were performed by methods which have been described.

(21) D. F. DeTar and R. C. Lamb, *J. Am. Chem. Soc.*, **81**, 122 (1959).

Kinetics in Some Systems in Which Stable Radicals Function as Scavengers of Reactive Radicals. The Decomposition of *trans*- γ -Benzylidenebutyryl Peroxide in Benzonitrile Containing α,γ -Bisdiphenylene- β -phenylallyl¹

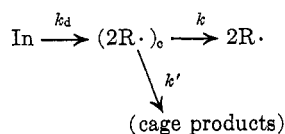
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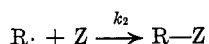
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Several kinetic equations which have potential use in radical scavenger experiments are presented and discussed. Experimental data for the decomposition of *trans*- γ -benzylidenebutyryl peroxide in benzonitrile containing excess³ α,γ -bisdiphenylene- β -phenylallyl are presented, and treated kinetically. This is an example of a system in which there is a slow decomposition of the scavenger α,γ -bisdiphenylene- β -phenylallyl in the solvent even in the absence of initiator. The slow decomposition is treated here as a pseudo-first-order process.

It was pointed out recently that, in solutions in which reactive free radicals are generated at a specific rate $2k_d f$ from an initiator according to the mechanism



[where $(2R\cdot)_0$ = a radical pair in the solvent cage and $f = k/(k + k') =$ free-radical efficiency] under the condition that an excess of a stable radical Z is used as a scavenger for reactive free radicals formed in the decomposition of the initiator (shown as follows),



both k_d and f can be obtained in the same simple experiment if side reactions do not interfere.^{4,5} The above reactions lead to the differential rate expression (eq. 1)

$$-d(Z)/dt = 2k_d f(\text{In}) = 2k_d f(\text{In})_0 \exp(-k_d t) \quad (1)$$

which upon integration gives eq. 2 and 3.

$$\ln(Z - Z_\infty)/(Z_0 - Z_\infty) = -k_d t \quad (2)$$

$$f = (Z_0 - Z_\infty)/2(\text{In})_0 \quad (3)$$

It should also be mentioned that the type of kinetics observed is independent of the mechanism by which radicals are wasted by the initiator system,⁶ although the constants obtained assume a slightly different meaning in case the initiator decomposes by two discreet first-order reactions, only one of which is a homolysis.

(1) This work was supported by the U. S. Air Force Office of Scientific Research, AF-AFOSR-62-53. The experimental data were taken from the dissertation of L. P. Spadafino, presented in partial fulfillment of the Ph.D. degree, Aug. 1963.

(2) Department of Chemistry, Augusta College, Augusta, Ga.

(3) The word *excess* as used here means that some BDPA remained after all the peroxide had decomposed.

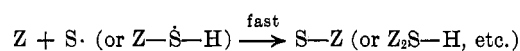
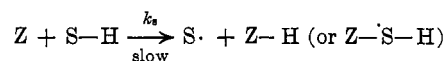
(4) R. C. Lamb, F. F. Rogers, Jr., G. C. Dean, Jr., and F. W. Voigt, Jr., *J. Am. Chem. Soc.*, **84**, 2635 (1962).

(5) R. C. Lamb and J. G. Pacifici, *ibid.*, **86**, 914 (1964).

(6) (a) T. W. Koenig and J. C. Martin, *J. Org. Chem.*, **29**, 1520 (1964);

(b) T. W. Koenig and W. Brewer, *J. Am. Chem. Soc.*, **86**, 2728 (1964).

A problem which is sometimes encountered in scavenger experiments of this type, particularly at higher temperatures, is that the stable radical may undergo a slow spontaneous fading in the absence of initiator.^{5,6a} Thus, if the stable radical undergoes a slow, pseudo-first-order reaction with the solvent (shown below)



then the following differential rate expression applies where $k_s' = k_s(S-H)$.

$$d(Z)/dt + 2k_s'(Z) = -2k_d f(\text{In}) = -2k_d f(\text{In})_0 \exp(-k_d t) \quad (4)$$

After integration [using the integrating factor $\exp(-2k_s' t)$], rearrangement, and insertion of the proper boundary conditions, one obtains eq. 5 and 6. If $k_d >$

$$\ln(Z - \alpha e^{-k_d t}) = -2k_s' t + \ln(Z_0 - \alpha) \quad (5)$$

$$\alpha = 2k_d f(\text{In})_0 / (k_d - 2k_s') \quad (6)$$

$2k_s'$, then at long times (t') such that $\exp(-k_d t') \approx 0$ (no initiator left), eq. 5 reduces to a first-order equation of slope $-2k_s'$ and intercept $\ln(Z_0 - \alpha)$. In other words, a plot of $\ln(Z)$ vs. t falls off rapidly so long as initiator is present. As the initiator is destroyed, the decay of stable radical approaches the slower, pseudo-first-order rate. The slope and the extrapolated intercept of the $\ln(Z)$ line after all initiator (but not all Z) is gone yields k_s' and α . After obtaining k_s' and α , it is best to rearrange eq. 5 into the form of eq. 7 so that k_d may be

$$\ln[Z - (Z_0 - \alpha)e^{-2k_s' t}] = -k_d t + \ln \alpha \quad (7)$$

obtained as a slope. When k_d , k_s' , and α are known, f may be calculated from eq. 6.

The decomposition of γ -benzylidenebutyryl peroxide^{1,4} in benzonitrile containing α,γ -bisdiphenylene-