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 A[3] 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 infrared[21] 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).

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# 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-phenylallyl[1]

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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 excess[3] 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

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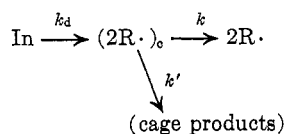
[where $(2\text{R}\cdot)_c$ = a radical pair in the solvent cage and $f = k/(k + k')$ = free-radical efficiency] under the condition that an excess of a stable radical Z is used as a scavenger for reactive free radicals formed in the decomposition of the initiator (shown as follows),

$$\text{R}\cdot + \text{Z} \xrightarrow{k_2} \text{R—Z}$$
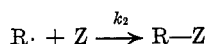
both $k_d$ and $f$ can be obtained in the same simple experiment if side reactions do not interfere.[4,5] The above reactions lead to the differential rate expression (eq. 1)

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

which upon integration gives eq. 2 and 3.

$$\ln (\text{Z} - \text{Z}_\infty)/(\text{Z}_0 - \text{Z}_\infty) = -k_d t \quad (2)$$

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

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.

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)

$$\text{Z} + \text{S—H} \xrightarrow[\text{slow}]{k_s} \text{S}\cdot + \text{Z—H (or Z—}\dot{\text{S}}\text{—H)}$$

$$\text{Z} + \text{S}\cdot \text{ (or Z—}\dot{\text{S}}\text{—H)} \xrightarrow{\text{fast}} \text{S—Z (or Z}_2\text{S—H, etc.)}$$

then the following differential rate expression applies where $k_s' = k_s(\text{S–H})$.

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

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 $k_d >$

$$\ln (\text{Z} - \alpha e^{-k_d t}) = -2k_s' t + \ln (\text{Z}_0 - \alpha) \quad (5)$$

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

$2k_s'$, 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 $\ln (\text{Z}_0 - \alpha)$. In other words, a plot of $\ln (\text{Z})$ 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 $\ln (\text{Z})$ line after all initiator (but not all Z) is gone yields $k_s'$ and $\alpha$. After obtaining $k_s'$ and $\alpha$, it is best to rearrange eq. 5 into the form of eq. 7 so that $k_d$ may be

$$\ln [\text{Z} - (\text{Z}_0 - \alpha)e^{-2k_s' t}] = -k_d t + \ln \alpha \quad (7)$$

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

The decomposition of γ-benzylidenebutyryl peroxide[1,4] in benzonitrile containing α,γ-bisdiphenylene-

(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.

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(3) The word *excess* as used here means that some BDPA remained after all the peroxide had decomposed.
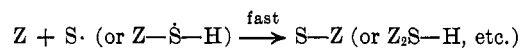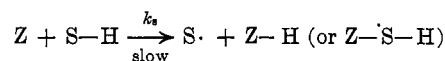
(4) R. C. Lamb, F. F. Rogers, Jr., G. C. Dean, Jr., and F. W. Voigt, Jr., *J. Am. Chem. Soc.*, **84**, 2635 (1962).

(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).

Table I

Decomposition of γ-Benzylidenebutyryl Peroxide in Benzonitrile in the Presence of Excess BDPA at 60°

| Time, min. | (Control)[a] | $D_{60}$[b] (1) | (2) | $10^5[Z - (Z_0 - \alpha)\varepsilon^{-2k_s't}]$[c] (1) | (2) |
|---|---|---|---|---|---|
| 0 | ... | 0.957 | 0.937 | 2.276 | 1.124 |
| 15 | ... | 0.867 | .898 | 1.913 | 0.971 |
| 30 | 0.926 | 0.793 | 0.842 | 1.615 | 0.748 |
| 45 | 0.928 | 0.732 | 0.820 | 1.371 | 0.665 |
| 60 | 0.923 | 0.679 | 0.788 | 1.159 | 0.540 |
| 75 | 0.922 | 0.634 | 0.762 | 0.980 | 0.439 |
| 105 | 0.915 | 0.564 | 0.728 | 0.704 | 0.313 |
| 135 | 0.909 | 0.513 | 0.698 | 0.505 | 0.203 |
| 150 | 0.903 | 0.498 | 0.691 | 0.449 | 0.180 |
| 195 | 0.893 | 0.449 | 0.661 | 0.263 | 0.104 |
| 225 | 0.891 | 0.434 | 0.662 | 0.211 | 0.092 |
| 450 | 0.848 | 0.369 | 0.619 | ... | ... |
| 555 | 0.838 | 0.354 | 0.609 | ... | ... |

[a] $(P)_0$ in control $= 0$; $(P)_0$ in (1) $= 3.48 \times 10^{-5} M$; $(P)_0$ in (2) $= 1.74 \times 10^{-5} M$, based on a peroxide purity of 96.5% determined by iodometric titration. [b] $D$ = absorbance at 490 mµ, the $\lambda_{max}$ of BDPA. $(BDPA)_0 = 3.88 \times 10^{-5} M$ in all vials. [c] See eq. 7 and Figure 2.

β-phenylallyl (BDPA)[7] lends itself to this treatment in an admirable fashion. The data are presented in Table I and are plotted in Figures 1 and 2.

Thus, three vials were used which contained benzonitrile solutions of BDPA [$(BDPA)_0 = (Z)_0 = 3.88 \times 10^{-5} M$ in all three vials]. One vial contained no peroxide (control); in the other two vials $10^5(P)_0 = 3.48$ (1) and 1.74 (2). In Figure 1, ln (Z) is plotted for the three vials. For the two samples containing peroxide, the slope (and hence $k_s'$) of the linear portion of the curve was calculated from the 450- and 555-min. points, then the intercept ln $(Z_0 - \alpha)$ was calculated by extrapolation of a pseudo-first-order equation back to zero time.

With the values of $\alpha$ and $k_s'$ thus obtained, the data could be plotted according to eq. 7 (Figure 2). The resulting values of $\alpha$, $k_s'$, $k_d$, and $f$ are given in Table II.

Table II

Decomposition of γ-Benzylidenebutyryl Peroxide. Adjustment of Rate Data to Eq. 5, 6, and 7

| | (1)[a] $A$[c] | $B$[d] | (2)[b] $A$[c] | $B$[d] |
|---|---|---|---|---|
| $10^5k_s'$, min.$^{-1}$ | 10.35 | 10.18 | 7.74 | 10.18 |
| $10^5\alpha$, mole/l. | 2.28 | 2.27 | 1.12 | 1.10 |
| $10^3k_d$, min.$^{-1}$ | 10.8 | 10.8 | 10.7 | 11.4 |
| $f$ | 0.32 | 0.32 | 0.32 | 0.31 |

[a] $(P)_0 = 3.48 \times 10^{-5} M$. [b] $(P)_0 = 1.74 \times 10^{-5} M$. [c] In columns A, $k_s'$ was calculated from the data at 450 and 555 min. for the kinetic samples. [d] In columns B, $k_s'$ was calculated by least-squares adjustment of the data obtained on the control sample to eq. 8.

A rather minor problem encountered with these particular data arose because we had not formulated this kinetic analysis at the time the data were obtained. It would have been better if more absorbance readings had been taken at long times on the vials containing peroxide, so that the estimates of $k_s'$ and $\alpha$ would have been more accurate. Actually, $k_s'$ should be the same for all three vials; two of the values are very similar,

(7) (a) C. F. Koelsch, J. Am. Chem. Soc., 79, 4439 (1957); 54, 4744 (1932); (b) S. L. Solar and R. M. Lindquist, ibid., 82, 4285 (1960); (c) S. L. Solar, J. Org. Chem., 28, 2911 (1963); (d) R. Kuhn and F. A. Neugebauer, Monatsh., 95, 3 (1964).
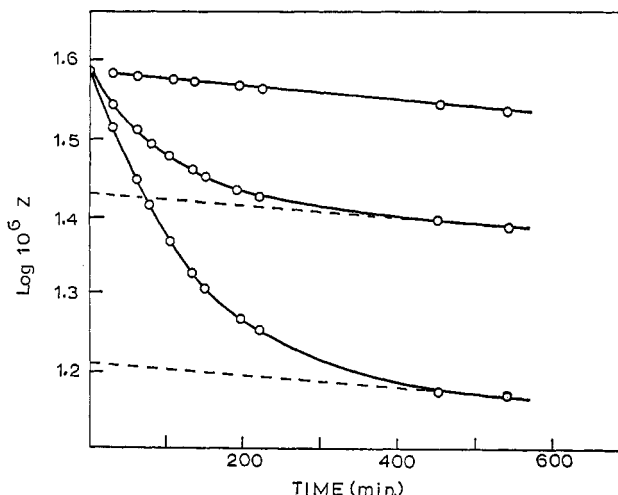


Figure 1.—Plot of ln (Z) vs. time for the decomposition of γ-benzylidenebutyryl peroxide in benzonitrile (eq. 5 and 8).
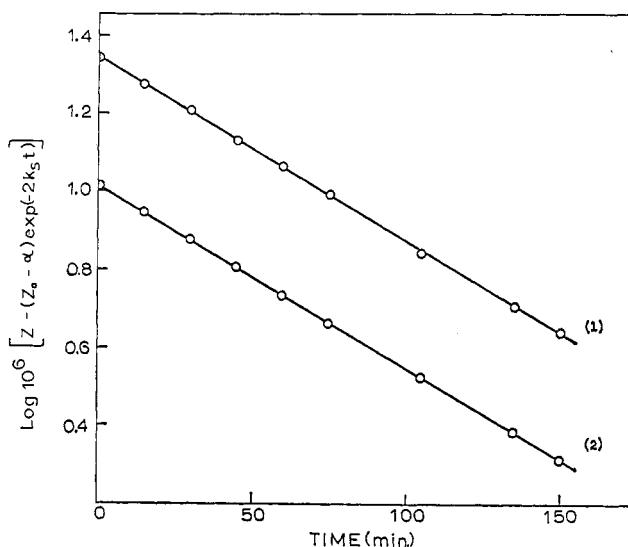


Figure 2.—Plot of eq. 7. Decomposition of γ-benzylidenebutyryl peroxide in benzonitrile at 60°.

while the other differs considerably (Table II). The most certain value of $k_s'$ can be obtained by adjustment of the data for the control sample to the pseudo-first-order expression (eq. 8).

$$\ln (Z) = -2k_s't + \ln (Z)_0 \qquad (8)$$

Using this value of $k_s'$, the line was extrapolated back from the 450-min. point to obtain new values of $\alpha$; these values of $k_s'$ and $\alpha$ were then used for statistical adjustment to eq. 7. Data so obtained are listed for comparison in Table II. It is apparent that a rather large difference in $k_s'$ results in only small differences in $k_d$ and $f$.

The results presented here are generally in agreement with earlier experiments on this peroxide,[4] which led to the proposal that it decomposes homolytically and heterolytically by processes which involve neighboring group participation by the double bond.[6a] Thus, the rate in the polar solvent, benzonitrile, is greater by a factor of 4, and the efficiency is less (0.32 vs. 0.43) than in carbon tetrachloride.

In the remainder of this paper, we wish to present a few additional kinetic functions which may be applied

to initiator–scavenger systems. First, we will consider the case in which free radicals are formed in a second-order reaction according to the mechanism shown

$$A + B \xrightarrow{k_2} (2R\cdot)_c \begin{array}{c} \xrightarrow{k} 2R\cdot \\ \xrightarrow{k'} \text{cage products} \end{array}$$
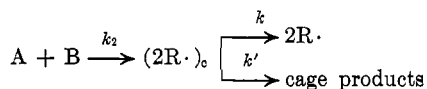
and the reactive free radicals so formed are scavenged by a stable radical, and if initial conditions are chosen such that $(A)_0 = (B)_0$, then $(A) = (B)$, and the pertinent differential rate expressions become eq. 9 and 10. Division of eq. 9 by eq. 10 followed by integration leads to eq. 11. Now if the solution for $(A_0 - A)$

$$-d(Z)/dt = 2k_2 f(A)^2 \tag{9}$$

$$-d(A)/dt = k_2(A)^2 \tag{10}$$

$$(Z_0 - Z)/2(A_0 - A) = (Z_0 - Z_\infty)/2(A)_0 = f \tag{11}$$

and $(A)$ from eq. 11 are substituted into the *reciprocal* of the integral of eq. 10, i.e., into eq. 12, and the

$$\frac{A}{A_0 - A} = \frac{1}{k_2(A)_0 t} \tag{12}$$

result is rearranged, eq. 13 results. Therefore, a plot

$$1/(Z_0 - Z) = {}^1\!/_2 f(A)_0^2 t + {}^1\!/_2 f(A)_0 \tag{13}$$

of $(Z_0 - Z)^{-1}$ vs. $t^{-1}$ should be linear, and the slope and intercept give two simultaneous equations which allow the determination of $k_2$ and $f$. This equation is superior to two others which can be derived from it, but which have a more recognizable form. Thus it is obvious that as $t \to \infty$, $(Z_0 - Z_\infty)^{-1} \to [2f(A)_0]^{-1}$, which is another way of expressing eq. 11. If this particular solution for $f$ is then inserted into eq. 13, and the equation rearranged, it becomes eq. 14 which has the usual second-order form.

$$(Z_0 - Z_\infty)/(Z - Z_\infty) = k_2(A)_0 t + 1 \tag{14}$$

However, eq. 13 is to be preferred for the following reason. Let us suppose that the time required for 8 half-lives is taken as "infinity time." For a first-order decomposition, the duration of 8 half-lives is eight times the first half-life. For a second-order reaction in which $(A)_0 = (B)_0$, the duration of 8 half-lives is 255 times the first half-life! Therefore, an extrapolation procedure is suggested, hence eq. 13.

Finally, in case $(B)_0 > (A)_0$, the differential rate expressions become eq. 15 and 16. Division of eq. 15 by

$$-d(Z)/dt = 2k_2 f(A)(B) \tag{15}$$

$$-d(A)/dt = k_2(A) \tag{16}$$

eq. 16 followed by integration leads again to eq. 11. When the solution for $(A)$ in terms of $(Z)$ and $f$, taken from eq. 11, is substituted into the integral of (1), the rearranged equation becomes eq. 17.
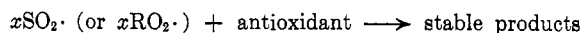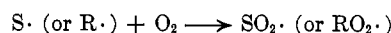
$$\ln \frac{[Z - Z_0 + 2f(B)_0]}{[Z - Z_0 + 2f(A)_0]} = k_2(B_0 - A_0)t + \ln \frac{(A)_0}{(B)_0} \tag{17}$$

The value of $f$ can be obtained from the infinity–time boundary condition (see eq. 11), and $k_2$ can then be obtained from eq. 17. It turns out that the problem discussed above concerning the duration of the experiment is not so serious for a second-order reaction in which $(A)_0 \neq (B)_0$. Thus, if $(B)_0 = 2(A)_0$, 99.5% reaction has transpired in 11.3 times the first half-life.

Also, in case $(B)_0 \gg (A)_0$, eq. 17 collapses to eq. 2; i.e., the initiation becomes pseudo first order.

In general, so long as the decomposition of the initiator is first order, it is at least aesthetically, if not practically desirable, to use the scavenger in excess in initiator–scavenger experiments and to follow the entire course of the decomposition of the initiator. This principle should apply no matter what the chemical nature of the scavenger.

Consider for example, the oxygen–autoxidizable hydrocarbon–antioxidant scavenger systems developed by Hammond and co-workers,[8] which are three-phase scavengers whose kinetics are similar to those which apply to the fading of stable radicals. These scavenger systems operate according to the mechanism shown

$$R\cdot + S{-}H \longrightarrow R{-}H + S\cdot$$

$$S\cdot \text{ (or } R\cdot) + O_2 \longrightarrow SO_2\cdot \text{ (or } RO_2\cdot)$$

$$xSO_2\cdot \text{ (or } xRO_2\cdot) + \text{antioxidant} \longrightarrow \text{stable products}$$

where $R\cdot$ is the radical formed in the decomposition of the initiator, S–H represents an easily autoxidized substrate, $S\cdot$ represents the free radical formed from the latter by chain transfer, and $x$ represents the stoichiometric factor.

The differential rate expressions for this system are eq. 18 and 19. Dividing eq. 18 by eq. 19 and integrating

$$-d(O_2)/dt = 2k_d f(In) = 2k_d f(In)_0 \exp(-k_d t) \tag{18}$$

$$-d(In)/dt = k_d(In) \tag{19}$$

between zero and infinity times one obtains eq. 20.

$$f = \frac{(O_2)_0 - (O_2)}{2[(In)_0 - (In)]} = \frac{(O_2)_0 - (O_2)_\infty}{2(In)_0} = \frac{\text{(moles of } O_2 \text{ absorbed)}}{2\text{(moles of initiator used)}} \tag{20}$$

Substitution of this result in the integral of eq. 18 gives eq. 21.

$$\ln \frac{(O_2) - (O_2)_\infty}{(O_2)_0 - (O_2)_\infty} = \ln \frac{(n_{O_2} \text{ absorbed at time } t)}{(n_{O_2} \text{ absorbed at time } t = \infty)} = -k_d t \tag{21}$$

Therefore, the kinetic form obtained from the scavenger systems developed by Hammond and co-workers is similar to that obtained using excess, stable radicals. (This results from the fact that, in either case, the kinetics are first order in initiator and zero order in scavenger.) The obvious advantage of using both the oxygen and antioxidant in excess, and following the reaction to completion, is that the stoichiometric factor $x$ of the reaction of the peroxyalkyl radicals with the antioxidant need not be known. The fate of the peroxyalkyl radicals is not pertinent to the experiment, so long as their destruction does not regenerate oxygen.[9]

It should be noted that Linnell[10] has used a system very similar to this to determine the efficiency of radical production in the decomposition of ABN in chlorobenzene. The difference is that Linnell used a more general definition of $f$ (eq. 22) in his experiments.

$$f = \frac{d(O_2)/dt}{d(In)/dt} = (R)_2/(R)_{N/2} \tag{22}$$

(8) G. S. Hammond and R. C. Neuman, Jr., *J. Am. Chem. Soc.*, **85**, 1501 (1963), and literature cited therein, particularly G. S. Hammond, J. N. Sen, and C. E. Boozer, *ibid.*, **77**, 3244 (1955).

(9) G. A. Russell, *ibid.*, **78**, 1047 (1956); **79**, 3871 (1957).

(10) R. H. Linnell, *J. Org. Chem.*, **29**, 1278 (1964).

In the determination of free-radical efficiencies with such scavengers as stable free radicals oxygen, or iodine, the reaction is (or is assumed to be) zero order with respect to scavenger. The Tobolsky dead-end polymerization technique is an interesting contrast in that excess vinyl monomer is used as the "scavenger," and the rate of polymerization is first order in monomer.[11]

The mechanism of the scavenger action is as follows.

$$R\cdot + M \xrightarrow{k_1} M\cdot$$

$$M\cdot + M \xrightarrow{k_p} M\cdot$$

$$2M\cdot \xrightarrow{k_t} polymer$$
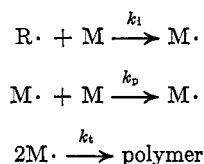
Assuming the initiator decomposes by the first mechanism given and neglecting the volume change due to contraction, the differential rate expression becomes eq. 23 which when integrated becomes eq. 24 and 25.

$$-d(M)/dt = k_p/k_t^{1/2}[k_d f(In)_0 \exp(-k_d t)]^{1/2}(M) \quad (23)$$

$$\ln\left[\frac{\ln (M/M_\infty)}{\ln (M_0/M_\infty)}\right] = -k_d t/2 \quad (24)$$

$$\ln (M)_0/(M)_\infty = 2k_p/k_t^{1/2}[f(In)_0/k_d]^{1/2} \quad (25)$$

Therefore if $k_p/k_t^{1/2}$ is known (and truly constant) for the polymerization used, then both $k_d$ and $f$ may be determined in the same experiment. More complex equations result in case volume contraction due to polymerization is important.[12]

(11) A. V. Tobolsky, J. Am. Chem. Soc., 80, 5927 (1958).

(12) A. V. Tobolsky, C. E. Rogers, and R. D. Brickman, ibid., 82, 1277 (1960).

Finally, we mention the case in which excess stable radical is used when an initiator is decomposed in vinyl monomer. In case concentrations of the initiator and stable radical are both dilute, there is a chance that the free radicals formed in the decomposition of the initiator will add to vinyl monomer before reacting with the stable radical. Should the stable radical subsequently scavenge all the growing polymer radicals, this will not alter the kinetics of disappearance of stable radical, i.e., eq. 1, 2, and 3 still hold. However, this amounts to changing the mechanism of termination of polymerization to

$$M\cdot + Z \xrightarrow{k_t'} M\text{—}Z$$
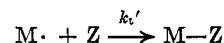
and the rate of disappearance of monomer becomes eq. 26. Dividing eq. 26 by eq. 1 and integrating, one obtains eq. 27. Thus, if one can measure the degree of

$$-d(M)/dt = k_p(M\cdot)(M) = \frac{2k_a f(In)}{k_t'(Z)}k_p(M) \quad (26)$$

$$\ln (M_0/M) = k_p/k_t' \ln (Z_0/Z) \quad (27)$$

polymerization in a stable free radical inhibited polymerization, the selectively $k_p/k_t'$ can be determined.

### Experimental

# A Solvent Effect in the Reaction of Benzaldesoxybenzoin with Phosphorus Pentachloride[1]

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Reaction of benzaldesoxybenzoin (I) with phosphorus pentachloride in methylene chloride led to a mixture of products from which 1-chloro-2,3-diphenylindene (V) was obtained in 30% yield. In a similar reaction in carbon tetrachloride a different mixture of products was obtained from which 3,3-dichloro-1,2,3-triphenylpropene (VII) was isolated in 47% yield. These results are discussed in the light of the fact that phosphorus pentachloride is monomeric in methylene chloride and dimeric in carbon tetrachloride.

In a discussion of possible mechanisms for the reaction of ketones with phosphorus pentachloride, the hypothesis was made that chlorocarbonium ions were involved.[3] As a result of studies on 4-phenyl-2-butanone and 5-phenyl-2-pentanone, the conclusion was reached that chlorocarbonium ions were not involved because no products resulting from cyclization

were obtained.[4] In the present work, the behavior of benzaldesoxybenzoin (I) with phosphorus pentachloride has been studied.

Treatment of I with 1 equiv. of phosphorus pentachloride in methylene chloride at room temperature for 2 hr. (the same result after 20 hr.) yielded about 30% of 1-chloro-2,3-diphenylindene (V). The oily residue contained other products which were not studied in detail because of their instability. However, when a mixture of these products in carbon disulfide was treated with a catalytic amount of aluminum chloride, hydro-

(3) M. S. Newman and L. L. Wood, Jr., J. Am. Chem. Soc., 81, 4300 (1959).

(4) M. S. Newman, G. Fraenkel, and W. N. Kirn, J. Org. Chem., 28, 1851 (1963).