The Viscosity Dependence of Bond Homolysis. A Qualitative and Semiquantitative Test for Cage Return[1,2]

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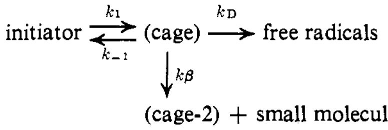
Abstract: The rate constants for decomposition of a wide variety of free-radical initiators have been determined in a series of alkane solvents of varying viscosities. The viscosity dependence of these observed rate constants is proposed as a test to allow initiators to be divided into two classes. One-bond initiators, *i.e.*, those which decompose by the initial scission of only one bond, have observed rate constants that decrease as the solvent viscosity increases. Multibond initiators, *i.e.*, those that decompose by the simultaneous scission of more than one bond, have observed rate constants that are independent of the solvent viscosity. This qualitative test has been applied to azo initiators, peresters, and peroxides, and the results are compared with related data from the literature. An equation has been developed which quantitatively relates the observed rate constant for decomposition of an initiator to the solvent viscosity. This equation is used to estimate k_{obsd}/k_1 for several initiators, where k_1 is the true unimolecular homolysis rate constant. Values of k_{obsd}/k_1 have been reported by Martin and by Koenig using oxygen-18 scrambling techniques, and values derived from our viscosity treatment are compared with these literature values. The quantitative agreement is only fair. However, it appears possible that the viscosity method can be refined and developed further.

In recent years there has been great interest in the effect of viscosity on the rate of bond homolysis.[4-6] We here report attempts to develop a relationship between the viscosity dependence of the observed rate constant for decomposition of a free-radical initiator, k_{obsd}, and the number of bonds which undergo synchronous scission in the decomposition of the initiator.[2,6]

The generalized mechanism for decomposition of an initiator is given in Scheme I. In this scheme, the observed rate constant for decomposition of the initiator is given as

Scheme I



$$k_{obsd} = \frac{k_1(k_D + k_\beta)}{k_{-1} + k_D + k_\beta} \quad (1)$$

where k_1 is the rate constant for bond homolysis; k_{-1} is the rate constant for recombination of the *first pair of* geminate radicals (a step we call cage return); k_D is the rate constant for diffusive separation of the geminate radicals; k_β is the rate constant (or sum of the rate constants) for any β-scission process that competes with diffusion and cage return; (cage) represents the first-formed geminate radical pair; and (cage-2) represents the geminate pair after β-scission has occurred.

The viscosity of a solvent may be written as[7]

$$\eta = A_v \exp(E_v/RT) \quad (2)$$

where the quantity E_v is the energy barrier that must be overcome before the self-diffusive flow process in the solvent can occur. The temperature dependence of the rate constant for diffusion, k_D, also can be expressed in the form of an Arrhenius equation. Here,

$$k_D = A_D \exp(-E_D/RT) \quad (3)$$

E_D is the energy barrier that must be overcome before a diffusive displacement can occur. If we assume that there is a linear relationship between E_D and E_v (eq 4), then the rate constant for diffusion as a function of the solvent viscosity is given by eq 5.

$$E_D = \alpha E_v \quad (4)$$

$$k_D = A_D(A_v/\eta)^\alpha \quad (5)$$

Equation 1 can be rearranged to yield eq 6. If

$$1/k_{obsd} = \frac{k_{-1}}{k_1 k_D}\left[\frac{1}{1 + k_\beta/k_D}\right] + 1/k_1 \quad (6)$$

it is assumed that k_D is the only rate constant in Scheme

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[1] (a) Reactions of Radicals. XXV. (b) This work was partially supported by Grant 11908 from the National Institutes of Health, U. S. Public Health Service.

[2] Preliminary communications: (a) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **89**, 1741 (1967); (b) Abstracts, 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967, Paper O 50; (c) Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Paper P 76 (in this abstract, α should be defined as $\alpha = E_2/E_v$ rather than the inverse); (d) Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Paper ORGN-113.

[3] (a) NASA Trainee 1965–1968; (b) W. K. Smith held a Petroleum Research Fund terminal year predoctoral fellowship (No. 249) for the 1968–1969 academic year; acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Dr. Smith was a postdoctoral fellow on NIH Grant 11908 during the summer of 1969; (c) taken in part from the Ph.D. Dissertation of W. K. Smith, Louisiana State University, 1969.

[4] (a) R. M. Noyes, *Progr. Reaction Kinetics*, **1**, 131 (1961); (b) W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1991 (1962); (c) H. P. Waits and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 1911 (1964); (d) S. Kodama, *Bull. Chem. Soc. Jap.*, **35**, 652 (1962); (e) L. Herk, M. Field, and M. Szwarc, *J. Amer. Chem. Soc.*, **83**, 2998 (1961); (f) S. W. Benson and A. M. North, *ibid.*, **84**, 935 (1962); (g) *ibid.*, **81**, 1339 (1959); (h) A. M. North and G. A. Reed, *Trans. Faraday Soc.*, **57**, 859 (1961); (i) *J. Polym. Sci., Part A*, **1**, 1311 (1963); (j) A. N. Atherton and A. M. North, *Trans. Faraday Soc.*, **58**, 2049 (1962); (k) H. Kiefer and T. G. Traylor, *J. Amer. Chem. Soc.*, **89**, 6667 (1967); (l) J. C. Martin and S. A. Dombchick, *Advan. Chem. Ser.*, No. **75**, 269 (1968); (m) F. E. Herkes, J. Friedman, and P. D. Bartlett, *Int. J. Chem. Kinetics*, **1**, 193 (1969).

[5] (a) T. Koenig and M. Deinzer, *J. Amer. Chem. Soc.*, **90**, 7014 (1968); (b) T. Koenig and R. Cruthoff, *ibid.*, **91**, 2562 (1969); (c) T. Koenig, J. Huntington, and R. Cruthoff, *ibid.*, **92**, 5413 (1970).

[6] W. A. Pryor and K. Smith, *Intra-Sci. Chem. Rep.*, **3**, 255 (1969).

[7] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 484.

I which is sensitive to viscosity, then eq 5 can be substituted in eq 6 to give the viscosity dependence of k_{obsd}. There are two limiting cases:[3c] k_β is either greater than or less than k_{D}. If k_β is greater than k_{D}, the initiator will appear to be in the multibond class by the viscosity test; this case is discussed further below.[8] If k_β is less than k_{D}, then the expression within the brackets in eq 6 can be replaced by a series expansion to give

$$1/k_{\mathrm{obsd}} = \frac{k_{-1}}{k_1 k_{\mathrm{D}}}\left\{1 - \frac{k_\beta}{k_{\mathrm{D}}} + \left(\frac{k_\beta}{k_{\mathrm{D}}}\right)^2 - \left(\frac{k_\beta}{k_{\mathrm{D}}}\right)^3 + \ldots\right\} + 1/k_1 \quad (7)$$

Substitution of eq 5 gives an equation relating the observed rate constant for bond homolysis and the solvent viscosity.

$$1/k_{\mathrm{obsd}} = \frac{k_{-1}}{k_1 A_{\mathrm{D}}}\left(\frac{\eta}{A_{\mathrm{v}}}\right)^\alpha \times \left\{1 - \frac{k_\beta}{A_{\mathrm{D}}}\left(\frac{\eta}{A_{\mathrm{v}}}\right)^\alpha + \left(\frac{k_\beta}{A_{\mathrm{D}}}\right)^2\left(\frac{\eta}{A_{\mathrm{v}}}\right)^{2\alpha} - \ldots\right\} + 1/k_1 \quad (8)$$

In the special case where k_β is zero or when k_β/k_{D} can be neglected relative to unity, then eq 7 becomes

$$1/k_{\mathrm{obsd}} = 1/k_1 + (k_{-1}/k_1 A_{\mathrm{D}})(\eta/A_{\mathrm{v}})^\alpha \quad (9)$$

This equation predicts a linear relationship between $1/k_{\mathrm{obsd}}$ and $(\eta/A_{\mathrm{v}})^\alpha$. We have observed that this linear correlation can be obtained for a wide variety of experimental data if α is set equal to 0.5.[9] However, we do not believe that the same value of α necessarily applies to all initiators. It seems probable that α is dependent upon the solvent series, the temperature, and the size and shape of the geminate radicals. It does not appear worthwhile at this time, in view of the paucity of the data available, to use variable values of α; perhaps in the future it will be desirable to do so.[6]

The Qualitative Viscosity Test. Qualitatively, eq 9 allows initiators to be divided into two classes: multibond initiators that give no cage return and have $k_{-1} = 0$, and one-bond initiators that do give cage return. This separation of initiators into two classes is based on the following postulates. (1) Any molecule that decomposes by the synchronous scission of more than one bond breaks into too many pieces to allow cage return; such molecules will have a rate constant that is independent of the solvent viscosity. (2) Any molecule that decomposes by the scission of only one bond can give cage return in solution by a simple radical recombination. For such a molecule, the observed rate constant for decomposition will decrease as the viscosity of the solvent increases since fewer geminate pairs will separate at higher viscosities and more will undergo cage return.

Several requirements must be met before this test can be applied. First, all the rate constants except k_{D} either must remain invariant as the viscosity of the system is changed, or the changes in them must be small compared to the change in k_{D}. Second, it must be possible to change the solvent viscosity in such a way as to keep the solvating power of the solvent constant. Third, the change in the measured macroscopic viscosity of the solvent must parallel the change in the diffusive barrier experienced by molecular species. Finally, the lifetime of the radicals produced by the initial bond homolysis must be at least of the same order of magnitude as the time required for diffusive separation of the geminate pair. The time required for diffusive separation in solution is about 10^{-10} sec.[4a] Thus the geminate pair must be stable for about 10^2 to 10^3 bond vibrations.

The viscosity test can be expected to become insensitive and unreliable when the amount of cage return becomes small. In such cases, solvent effects on the other rate constants, particularly on k_1, may appear to become more important than viscosity effects on k_{D}.

If a large fraction of the geminate pairs decompose within the primary cage, then it is possible for cage return to occur and k_{obsd} to appear to be independent of the solvent viscosity. This limitation of the viscosity test is best illustrated by the figures shown in Table I. The values of the rate constants in the first two rows were estimated from data on the decomposition of acetyl peroxide at 80°. (A detailed discussion of how these rate constants were obtained is given later.) The values of the ratio k_{obsd}/k_1 shown for acetyl peroxide clearly indicate that the change in viscosity associated with changing the solvent from octane to octadecane, 0.3 to 1.5 cP, will produce a measureable viscosity effect for this initiator. However, the lower half of Table I shows the comparable data for a hypothetical initator which has the same values of k_{-1} and k_{D} but undergoes β-scission with a rate constant tenfold larger than acetyl peroxide. Such an initiator would decompose to produce fragments which were very unstable, and the data in the table show that the viscosity dependence of k_{obsd} would be too small to be observed. This hypothetical initiator, therefore, would appear to be a two-bond initiator by the viscosity test. In fact, however, it decomposes one bond at a time but produces fragments which are not sufficiently stable to diffuse apart.

Table I. The Effect of β-Scission on the Viscosity Dependence of the Observed Rate Constant

Initiator	Solvent	10^9k			
		k_β	k_{-1}	k_{D}	k_{obsd}/k_1[a]
Acetyl peroxide	Octane	3.0	6.0	8.3	0.64
	Octadecane	3.0	6.0	3.2	0.50
Hypothetical "10×" initiator	Octane	30.0	6.0	8.3	0.87
	Octadecane	30.0	6.0	3.2	0.85

[a] It will be shown later than $k_{\mathrm{obsd}}/k_1 = 1 - f_{\mathrm{r}}$, where f_{r} is the fraction of the geminate pairs which undergo cage return.

An example of a system in which β-scission is fast enough to mask the viscosity dependence of k_{obsd} has

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(8) M. T. Nieh, S. G. Mylonkis, and S. Seltzer, *J. Amer. Chem. Soc.*, in press.

(9) (a) The significance of α, from both a theoretical and an empirical viewpoint, is discussed in ref 3c and to a limited extent in ref 6. (b) Koenig[5] has presented a theoretical justification for the specific value of $\alpha = 0.5$ in an equation which is related to our eq 9.

recently been reported by Seltzer, *et al.*[8] From a comparison of the rate of decomposition and the rate of loss of optical activity, they conclude that α-phenylethylazomethane decomposes by one-bond homolysis and that the geminate radicals recombine within the cage; however, the rate of decomposition is viscosity independent. At the high temperature at which these decompositions were carried out it is reasonable to expect the diazenyl radical to undergo β-scission rapidly.

In order to avoid unwanted and unknown solvent effects, it is necessary to choose a solvent system in which the viscosity can be varied over as wide a range as possible without drastically changing any other properties of the solvent. If solvents of various structural types and widely different solvating power are used, there will be no clear relationship between the observed rate constant and viscosity.[10] One way to vary the viscosity of the system is by mixing two solvents, one of very high viscosity and one of very low viscosity. However, there are two dangers in this approach. First, if the solvents differ greatly in their ability to solvate either the substrate or the activated complex, then any change in the rate constant caused by changing the proportions of the two solvents could produce a solvent effect in addition to any effect of viscosity. This may be the explanation for the change in k_{obsd} for the decomposition for AIBN in the solvent system dimethylformamide–glycerol.[11] The second danger is that if the high-viscosity component is a very large molecule, either a polymer or a long chain hydrocarbon, then the bulk viscosity of the system may increase faster than the microviscosity. In order to avoid the difficulties discussed above, the solvent systems chosen for this work were the series of alkanes, pentane to octadecane, and the corresponding 1-olefins.

Results and Discussion

Application of the Viscosity Test to Some Azo Initiators. *p*-Nitrophenylazotriphenylmethane (NAT). Some azo initiators decompose by the synchronous scission of both carbon–nitrogen bonds.[10a] However, the viscosity test indicates that NAT is a one-bond initiator. Table II and the plot of eq 9 in Figure 1 show that k_{obsd} decreases regularly as the solvent is changed from low molecular weight, low-viscosity solvents to high molecular weight, high-viscosity solvents. This is evidence that NAT decomposes by the initial scission of only one carbon–nitrogen bond.

$$\mathrm{ArN{=}NCPh_3} \rightleftarrows (\mathrm{ArN_2\cdot}\ \cdot\mathrm{CPh_3}) \longrightarrow \mathrm{ArN_2\cdot} + \cdot\mathrm{CPh_3}$$

When this conclusion was first published[2a] there was very little evidence to support the existence of aryldiazenyl radicals. The esr spectrum obtained on photolysis of AIBN at −196° in a frozen glass had been interpreted as indicating a diazenyl radical,[12] but this is of questionable relevance to work at room temperature in solution. In addition, the interpretation of the esr spectrum has been questioned.[13] The only other evidence was Kodama's proposal, based on the temperature dependence of the quantum yield, that azomethane decomposes into a methyl and a methyldiazenyl radical when photolyzed.[4d]

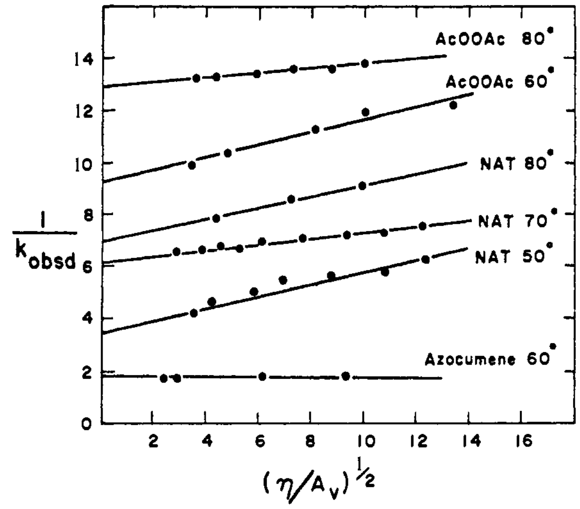

Figure 1. The observed rate constant as a function of the solvent viscosity. $1/k_{obsd}$ is scaled as follows: acetyl peroxide 80° ($\times 10^{-4}$); 60° ($\times 10^{-5} + 9$); NAT 80° ($\times 10^{-2}$); 70° ($\times 10^{-3} + 4$); 50° ($\times 10^{-4} + 0.5$).

Table II. Rate Constants[a] for the Decomposition of NAT in Unbranched Hydrocarbon Solvents[b]

No. of carbon atoms	Solvent *n*-Alkanes 50° $k \times 10^5$	 60° $k \times 10^4$	 70° $k \times 10^4$	 77.5° $k \times 10^3$	 1-Olefins 60° $k \times 10^5$
5	3.600	1.2800			
6	2.750	1.1950			11.43
7	2.716	1.0430	3.900		
8		1.0150	3.650	1.28	11.23
9	2.200	0.9900	3.710		
10	2.017	0.9988	3.350	1.16	10.38
12	1.933	0.9166	3.250		
14	1.866	0.8800	3.116		9.02
16	1.716	0.8133	2.966	1.09	8.25
18		0.7780	2.783		7.58
20					7.60

[a] Rate constant k_{obsd} in sec^{-1}. [b] Rate constants determined by disappearance of initiator (method 1a; see Experimental Section).

Recently, more concrete evidence for the existence of diazenyl radicals has been published. Kooyman[14] has proposed their existence in the decomposition of arenediazothiolates. He reached this conclusion because no Ar–SR is formed as a cage product, but it is a free-solution product. Apparently the $\mathrm{ArN_2\cdot}$ radical is stable for at least the lifetime of the cage. Kosower[15] has explained the chemical properties of

$$\mathrm{ArN{=}NSR} \longrightarrow (\mathrm{ArN_2\cdot} + \cdot\mathrm{SR}) \xrightarrow{\text{diffusion}} \mathrm{ArN_2\cdot} + \mathrm{RS\cdot}$$

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(10) (a) P. D. Bartlett and S. F. Nelsen, *J. Amer. Chem. Soc.*, **88**, 137 (1966); (b) W. R. Ware, *J. Phys. Chem.*, **66**, 455 (1962).

(11) S. R. Rafikov, P. E. Mesderle, G. P. Gladyshev, and I. B. Shafranskaya, *Polym. Lett.*, **5**, 715 (1967).

(12) P. B. Ayscough, B. R. Brooks, and H. E. Evans, *J. Phys. Chem.*, **68**, 3889 (1964).

(13) J. M. McBride, Ph.D. Dissertation, Harvard University, 1966.

(14) H. van Zwet and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **86**, 1143 (1967).

(15) H. C. Huang and E. M. Kosower, *J. Amer. Chem. Soc.*, **90**, 2367 (1968).

phenyldiazene, Ph—N=N—H, using phenyldiazenyl radicals as reactive intermediates.

The very pronounced viscosity dependence of k_{obsd} for NAT and the ease with which it can be prepared and studied led us to use this inititator to probe the relationship between macroscopic viscosity and cage return. The data in the top half of Table III indicate how k_{obsd} varies with viscosity in the alkane solvents. (These data are taken from Table II.) The lower half of the table shows the effect on k_{obsd} of adding either biphenyl or polystyrene to the solvent benzene. The change in viscosity caused by biphenyl produces essentially the same change in k_{obsd} as is observed in the alkanes. However, changing the viscosity of the system with polystyrene does not reduce k_{obsd} to the value expected from the alkane data. Indeed, it appears that the resistance to diffusion experienced by the geminate radicals from NAT is the same in polystyrene-thickened benzene as it is in benzene. We conclude that in solutions thickened with high molecular weight polymers the macroscopic viscosity does not truly reflect the resistance to translational motion experienced by monomeric radicals.

Table III. A Comparison of the Effect of Homogeneous and Mixed Solvents on the Microscopic Viscosity of a System

Solvent	Relative viscosity, 60°	Relative k_{obsd}, NAT, 60°
Hexane	1.0[a]	1.0
Nonane	2.04	0.83
Hexadecane	7.10	0.68
Benzene	1.0[b]	1.0
Benzene + biphenyl	2.1	0.82
Benzene + polystyrene	8.7	1.02

[a] Absolute viscosity 0.222 cP. [b] Absolute viscosity 0.392 cP.

Phenylazotriphenylmethane (PAT). Data on the viscosity dependence of k_{obsd} for this initiator at 60° in the alkanes are listed in ref 3c. The qualitative conclusions from the viscosity test are the same as for NAT; it also is a one-bond initiator.

Azocumene. Data for the decomposition of azocumene are shown in Figure 1. The slope of the graph of eq 9 is zero, indicating that azocumene decomposes by a concerted mechanism. There is other evidence to

$$\mathrm{PhCMe_2N{=}NCMe_2Ph \longrightarrow (Ph\dot{C}Me_2\ N_2 \cdot CMe_2Ph)}$$

support this conclusion. Seltzer has reported[16,17] on the decomposition of azo-α-phenylethane, PhCHMeN=NCHMePh. The kinetic isotope effect, k_H/k_D, for this compound, with one deuterium in both benzylic positions, is 1.27. This value suggests that both carbon-nitrogen bonds are breaking in the transition state. The activation energy required to reach this

$$\mathrm{PhCHMeN{=}NCHMePh \longrightarrow (PhCHMe{-}{-}N{=}N{-}{-}CHMePh)^{\ddagger}}$$

transition state will be lowered, relative to the corresponding transition state involving one-bond scission, by the resonance stabilization energy of the α-phenylethyl radical. Since the cumyl radical has 3 kcal/mol more resonance stabilization energy than does the α-phenylethyl radical, azocumene also must decompose by a concerted mechanism.[18]

Application of the Viscosity Test to a Diacyl Peroxide. Acetyl Peroxide. In 1965, Taylor and Martin[19a] resolved a long-standing polemic[20] by proving conclusively that acetyl peroxide is a one-bond initiator. They showed that acetoxy radicals recombine within the cage by observing the "scrambling" of ^{18}O between the carbonyl and peroxidic oxygens. In the same year, Koenig and Brewer[21a] reported the kinetic isotope effect for the decomposition of acetyl peroxide-d_6 to be 1.02 and concluded that there was little or no methyl radical character in the transition state for the decomposition.

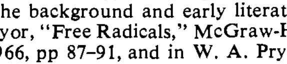
We have determined the rate constant for decomposition of acetyl peroxide in a series of alkanes by following the disappearance of the carbonyl band at 1800 K and the disappearance of an even stronger band at 1157 K. The kinetic data are shown in Table IV, and Figure 1 shows a plot of eq 9 for acetyl peroxide at 60 and 80°. The expected dependence of k_{obsd} on viscosity is evident.[22]

Table IV. Rate Constants for the Decomposition of Acetyl Peroxide in *n*-Alkane Solvents at 80° [a]

	10^5k_{obsd}	
n-Alkane	1800 cm^{-1}	1157 cm^{-1}
Heptane	7.72	7.62
Octane	7.34	7.21
Decane	6.85	6.99
Dodecane	6.15	6.38
Tetradecane	5.90	6.12
Hexadecane	5.39	5.49

[a] Kinetics by disappearance of initiator (method 1b; see Experimental Section).

Application of the Viscosity Test to Some *t*-Butyl Peresters. Bartlett and his group have presented evidence, based on the relative values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the decomposition, that a series of peresters with structures **1** or **2** decompose thermally with concerted rupture of both the O-O and C-C bonds.[23,24] Bartlett and



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$\mathrm{Ph_2CHCO_2\text{-}O\text{-}}t\mathrm{\text{-}Bu}$

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(16) (a) S. Seltzer, *J. Amer. Chem. Soc.*, **83**, 2625 (1961); (b) *ibid.*, **85**, 14 (1963).

(17) (a) S. Seltzer and F. T. Dunne, *ibid.*, **87**, 2628 (1965); (b) S. Seltzer and E. Hamilton, *ibid.*, **88**, 3775 (1966).

(18) Calculated from bond dissociation energies: $D(\mathrm{PhCMe_2\text{-}H})$ = 79 kcal/mol, $D(\mathrm{PhCHMe\text{-}H})$ = 82 kcal/mol. See S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, Inc., New York, N. Y., 1968.

(19) (a) J. W. Taylor and J. C. Martin, *J. Amer. Chem. Soc.*, **87**, 3650 (1965); (b) J. W. Taylor and J. C. Martin, *ibid.*, **89**, 6904 (1967); (c) J. C. Martin, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, ORGN 114.

(20) The background and early literature references are reviewed in W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 87–91, and in W. A. Pryor, "Solutions Manual to Accompany Free Radicals," McGraw-Hill Book Co., New York, N. Y., 1967, p 14.

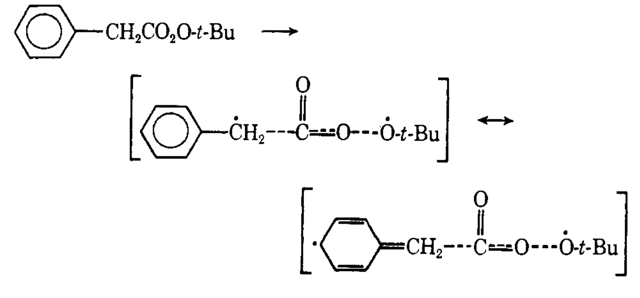
(21) (a) T. Koenig and W. D. Brewer, *Tetrahedron Lett.*, 2773 (1965); (b) T. Koenig and R. Wolf, *J. Amer. Chem. Soc.*, **91**, 2574 (1969).

(22) The data at 60° were obtained by Eirich, *et al.*[4b] The implications of these data with regard to cage recombination were mentioned by the authors, but discounted in deference to some erroneous ^{18}O exchange data of Szwarc.[4e] See also ref 20.

(23) P. D. Bartlett and C. Rüchardt, *J. Amer. Chem. Soc.*, **82**, 1756 (1960).

(24) (a) P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958); (b) P. D. Bartlett, *Experientia Suppl.*, *VII*, 275 (1957); (c) P. D. Bartlett and D. M. Simons, *J. Amer. Chem. Soc.*, **82**, 1753 (1960).

Hiatt[24a] pointed out that the activation enthalpy for concerted decomposition of these peresters would be lower than for nonconcerted decomposition because of electron delocalization into the aromatic ring(s). However, this resonance stabilization of the incipient benzylic radical can occur only if the rotation about the Ph–C bond is restricted. Therefore, Bartlett and Hiatt



suggested that the magnitude of the activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, for such a perester can be used to identify the number of bonds that become rotationally restricted in the transition state.[25] We have examined the viscosity dependence of k_{obsd} for five of these peresters. The data are given in Table V and discussed in the following paragraphs.

Table V. Rate Constants[d] for the Homolysis of RCO_2O-*t*-Bu

R	Solvent	$k_{\text{obsd}} \times 10^6$, sec^{-1}
p-CH_3OPhCH_2[a]	Octane	253.0
p-CH_3OPhCH_2	Decane	252.0
p-CH_3OPhCH_2	Dodecane	265.0
p-CH_3OPhCH_2	Dodecane	254.0
p-CH_3OPhCH_2	Tetradecane	266.0
p-CH_3OPhCH_2	Tetradecane	270.0
p-CH_3PhCH_2[a]	Octane	88.3
p-CH_3PhCH_2	Decane	90.8
p-CH_3PhCH_2	Dodecane	85.7
p-CH_3PhCH_2	Tetradecane	77.5
p-CH_3PhCH_2	Hexadecane	103.2
$PhCH_2$[a]	Octane	31.7
$PhCH_2$	Octane	30.6
$PhCH_2$	Nonane	31.2
$PhCH_2$	Decane	30.0
$PhCH_2$	Dodecane	27.4
$PhCH_2$	Dodecane	27.6
$PhCH_2$	Tetradecane	26.6
$PhCH_2$	Hexadecane	26.0
p-NO_2PhCH_2[b]	Octane	6.42
p-NO_2PhCH_2	Decane	6.30
p-NO_2PhCH_2	Dodecane	5.81
p-NO_2PhCH_2	Tetradecane	5.56
p-NO_2PhCH_2	Hexadecane	5.11
p-NO_2PhCH_2 (100°)[c,d]	Octane	160.0
p-NO_2PhCH_2 (100°)	Dodecane	131.0
Ph_2CH[a]	Octane	1651.0
Ph_2CH	Decane	1660.0
Ph_2CH	Dodecane	1688.0
Ph_2CH	Tetradecane	1627.0
Ph_2CH	Hexadecane	1632.0

[a] Kinetics by limiting initiator (method 2). [b] Kinetics by excess initiator (method 3). [c] Kinetics by disappearance of initiator (method 1b). [d] All rate constants were determined at 77.5°, except where noted.

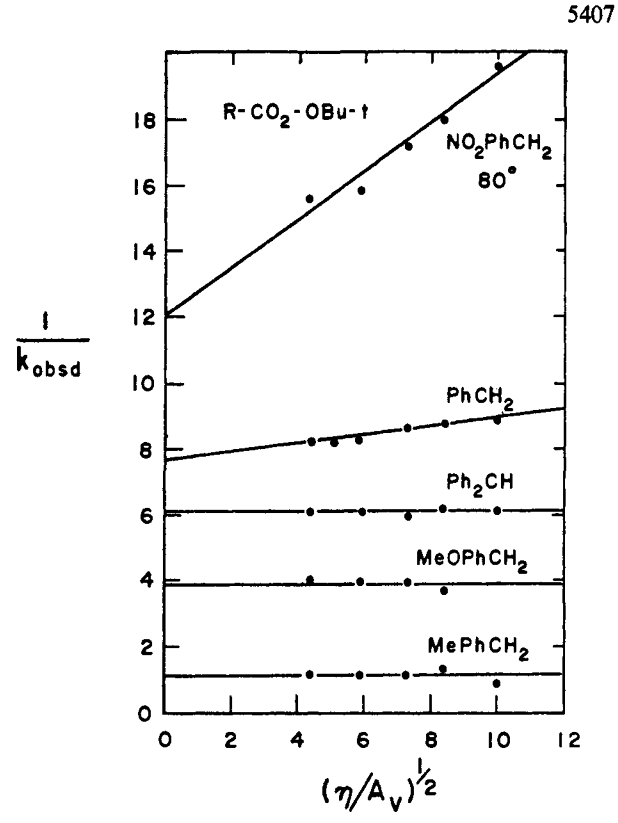


Figure 2. The viscosity plot for several peresters. $1/k_{\text{obsd}}$ is scaled as follows: CH_3, 130° ($\times 10^{-3} + 13$); CH_3, 100° ($\times 10^{-4} + 5$); $PhCH_2$, 80° ($\times 10^{-4} + 5$); Ph_2CH, 80° ($\times 10^{-4} + 3$); *p*-$MeOPhCH_2$, 80° ($\times 10^{-3}$); *p*-CH_3PhCH_2, 80° ($\times 10^{-4}$).

***t*-Butyl Diphenylperacetate, *t*-Butyl *p*-Methoxyphenylperacetate, and *t*-Butyl *p*-Methylphenylperacetate.** The data in Table V and the plots in Figure 2 show that the rate of decomposition of these three peresters is viscosity independent. We conclude that they decompose by a concerted mechanism, in accord with the data of Bartlett[24] and Koenig.[5]

***t*-Butyl Phenylperacetate and *t*-Butyl *p*-Nitrophenylperacetate.** From the data in Table V and the plot in Figure 2 it can be seen that k_{obsd} for these two initiators is viscosity dependent, and, according to the postulates enumerated previously, these initiators decompose by a nonconcerted mechanism. This conclusion raises two questions. First, why do these initiators decompose by a different mechanism than the structurally similar peresters discussed in the previous paragraph; and second, how can we reconcile our result with the conclusions of Bartlett,[24] Koenig,[5] and Neuman,[26] that these initiators decompose by a concerted mechanism? Bartlett's analysis was based on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, Koenig's on isotope effects, and Neuman's on the pressure dependence of the rate constants.

Bartlett has observed[23] that the substituent effect upon the decomposition of *t*-butyl phenylperacetates fits the Hammett equation with the use of σ^+ and with $\rho^+ = -1.09$. This indicates that the homolysis of these peresters involves a substantial amount of charge separation and a transition state like **3a**–**3b**. The electronic effect of a substituent, X, on the rate of scission of the O–O bond in these peresters would be

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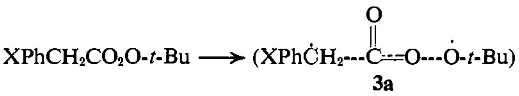
(25) This correlation has mistakenly been extended and used to distinguish between one- and two-bond initiators. This will be discussed in a subsequent paper of ours.

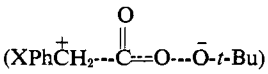
(26) R. C. Neuman and J. V. Behar, *J. Amer. Chem. Soc.*, **91**, 6024 (1969).

expected to be quite small. The rate of O–O bond scission in benzoyl peroxides is rather insensitive to electronic substituent effects,[27a] and the O–O bond in the peresters under consideration here should be even less sensitive to substituents because the reaction site is insulated from the ring by a methylene group. However, the electronic effect of a substituent on the rate of scission of the C–C bond in these peresters should be quite significant and it can be argued that a strong electron donating group such as *p*-methoxy will stabilize canonical form **3b** and facilitate two-bond homolysis. A strong electron withdrawing group such as *p*-nitro could destabilize **3b** and raise the energy of activation of the two-bond homolysis enough to cause the initiator to decompose at least partially by one-bond homolysis. The *p*-nitro perester decomposes more slowly than does the *p*-methoxy and this often indicates a less facile, one-bond (or partially one-bond) homolysis.



$$\mathrm{XPhCH_2CO_2O\text{-}}t\text{-}\mathrm{Bu} \longrightarrow (\mathrm{XPh\dot{C}H_2}\text{---}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\!=\!\mathrm{O}\text{---}\dot{\mathrm{O}}\text{-}t\text{-}\mathrm{Bu})$$

3a



$$(\mathrm{XPh\overset{+}{C}H_2}\text{---}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\!=\!\mathrm{O}\text{---}\overset{-}{\mathrm{O}}\text{-}t\text{-}\mathrm{Bu})$$

3b

An argument can be made from kinetic isotope effect studies that both the phenyl- and the *p*-nitrophenylperacetates decompose at least partially by two-bond scission. Koenig[21] has determined both the α and β isotope effects for the decomposition of PhCH(CH$_3$)CO$_3$-*t*-Bu. The β-isotope effect is the same as for the decomposition of CH$_3$CHPhN=NCHPhCH$_3$,[17] but the α effect is much lower (1.06 *vs.* 1.13). If we assume, as is likely, that this perester decomposes entirely by a two-bond path and that its isotope effect is general for the class, then 1.06 *per deuterium* is the expected α-isotope effect for concerted decomposition of peresters. Koenig's data then suggest that both the phenyl- and the *p*-nitrophenylperacetates decompose by a concerted path. (He finds the α isotope effect for *two* deuteriums to be 1.12 for the former and 1.10 for the latter compound. These values do appear too large to be secondary isotope effects of the second kind.[28a]) However, if the true α isotope effect for concerted decomposition of these two peresters is more nearly 1.13 per deuterium, as would appear from the azo compound series,[16,17] then Koenig's data are less conclusive. Koenig[5b] also has reported some data on the viscosity dependence of the isotope effects which indicate that the phenyl perester decomposes by a concerted pathway.

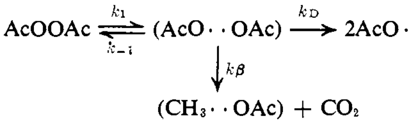
A suggestion which reconciles our data with the isotope effect studies is that the phenyl- and *p*-nitrophenylperacetates decompose simultaneously by both the one-bond and two-bond paths.[28b] If the kinetic isotope effect for two-bond scission is 1.06 per deuterium, it is probable that a perester that decomposed predominantly but not entirely by the two-bond path could not be distinguished from one that went entirely by that mode. That is to say, the isotope effect could distinguish two-bond scission most sensitively, but it may not be particularly sensitive to some simultaneous one-bond scission. On the other hand, the viscosity test can detect the presence of one-bond scission, even if this is not the main mechanistic pathway, but it gives no direct evidence for the existence of two-bond homolysis in the presence of one-bond homolysis.

We must recognize that there is another explanation for the results of the viscosity test on these two peresters. It is entirely possible that what we interpreted as a viscosity effect on k_{obsd} is actually a solvent effect on the rate constant for bond homolysis, k_1. There is evidence to indicate that k_1 is subject to a solvent effect in the alkane solvents in the decomposition of acetyl peroxide[3c] and *t*-butyl peracetate.[5] It is difficult to understand, however, why the phenyl- and *p*-nitrophenylperacetates should show a solvent effect if the *p*-methoxyphenyl- and the *p*-methylphenylperacetates do not. It is impossible to resolve fully these conflicts at the present time and work in this area is continuing.

Quantitative Estimation of Extent of Cage Return Using the Viscosity Equation. Theory. The decomposition of a one-bond initiator produces a pair of radicals which can recombine to re-form the initiator, diffuse apart, or, in some cases, react by some other process. Consider, for example, the decomposition of acetyl peroxide as shown in Scheme II. The observed rate constant is

$$k_{\mathrm{obsd}} = \frac{k_1(k_{\mathrm{D}} + k_\beta)}{k_{-1} + k_{\mathrm{D}} + k_\beta} \tag{10}$$

Scheme II[a]



$$\begin{tikzcd} \mathrm{AcOOAc} \arrow[r, shift left, "k_1"] & (\mathrm{AcO}\cdot\ \cdot\mathrm{OAc}) \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_{\mathrm{D}}"] \arrow[d, "k_\beta"] & 2\mathrm{AcO}\cdot \\ & (\mathrm{CH_3}\cdot\ \cdot\mathrm{OAc}) + \mathrm{CO_2} & \end{tikzcd}$$

[a] Ac is the acetyl group.

If we define f_{D} to be the fraction of the geminate pairs that diffuse apart

$$f_{\mathrm{D}} = \frac{k_{\mathrm{D}}}{k_{-1} + k_{\mathrm{D}} + k_\beta} \tag{11}$$

f_β to be the fraction of the geminate pairs that undergo β-scission

$$f_\beta = \frac{k_\beta}{k_{-1} + k_{\mathrm{D}} + k_\beta} \tag{12}$$

and f_{r} to be the fraction of the geminate pairs that give cage return

$$f_{\mathrm{r}} = \frac{k_{-1}}{k_{-1} + k_{\mathrm{D}} + k_\beta} \tag{13}$$

then the observed rate constant can be written as

$$k_{\mathrm{obsd}} = k_1(f_{\mathrm{D}} + f_\beta) \tag{14}$$

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[27] (a) C. G. Swain, W. H. Stockmayer, and J. T. Clark, *J. Amer. Chem. Soc.*, **72**, 5426 (1950). The ρ value for decomposition of substituted benzoyl peroxides is −0.4. (b) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

[28] (a) E. I. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963); also see W. A. Pryor, R. W. Henderson, R. A. Patsiga, and N. Carroll, *J. Amer. Chem. Soc.*, **88**, 1199 (1966). (b) Professor Koenig has considered and tentatively rejected this possibility. His arguments are complex and are presented in detail in ref 5c.

Since the sum of f_D, f_r, and f_β must be unity, it follows that

$$k_{obsd} = k_1(1 - f_r) \qquad (15)$$

$$f_r = 1 - k_{obsd}/k_1 \qquad (16)$$

The fraction of cage return can be calculated from eq 16 if k_1 is known, and according to eq 9, k_1 can be estimated from the intercept of a plot of $1/k_{obsd}$ *vs.* $(\eta/A_v)^\alpha$. The derivation of eq 9 involved the assumptions that k_β was zero or that k_β/k_D was small compared to unity. The first of these assumptions is not true for any of the initiators in this study, but the latter apparently is a fair approximation in the low viscosity solvents.[29] If k_β/k_D is not small compared to unity, then a plot of eq 9 should not be linear but should be concave downward. The fact that we have seen no indication of this deviation from linearity suggests that eq 9 is not sensitive to the presence of moderate amounts of β-scission over the limited viscosity range that is accessible.

Quantitative Results. We have used eq 9 and 16 to calculate the value of f_r for several initiators, and the results are shown in Table VI. Notice that for NAT, acetyl peroxide, and *t*-butyl peracetate, f_r decreases as the temperature increases. It is possible to use the temperature dependence of f_r to determine the difference between the activation energy for diffusion and for cage recombination or to estimate the importance of β-scission, but as yet our data only allow preliminary calculations.[3c]

Table VI. Cage Return, f_r, as a Function of Solvent and Temperature for Several Initiators

Initiator	Solvent[a]	Temp, °C	f_r
p-NO$_2$PhN=NCPh$_3$ (NAT)	Octane	50	0.25
NAT	Octane	60	0.22
NAT	Octane	70	0.20
NAT	Octane	80	0.13
PhN=N—CPh$_3$	Octane	60	0.29
CH$_3$CO$_2$O-*t*-Bu	Octane	100	0.30
CH$_3$CO$_2$O-*t*-Bu	Nonane	130	0.12
AcOOAc[b]	Octane	60	0.33
AcOOAc	Isooctane	80	0.28

[a] Solvent in which k_{obsd} was measured. [b] Ac is the acetyl group, CH$_3$C=O.

Acetyl Peroxide. Cage return in acetyl peroxide has been studied by measuring the rate constant, k_s, for scrambling of the ^{18}O label between the carbonyl and the peroxidic oxygen.[41] In terms of the mechanism shown in Scheme II, the rate constant for scrambling may be written as

$$k_s = \frac{k_1k_{-1}}{k_{-1} + k_D + k_\beta} \qquad (17)$$

The fraction of cage return can be determined from k_s using either of the following equations

$$f_r = k_s/k_1 \qquad (18)$$

$$f_r = (1 + k_{obsd}/k_s)^{-1} \qquad (19)$$

One consequence of these two equations is that if k_{obsd} and k_s are known, k_1 can be calculated. The values of k_1 in Table VII were calculated from Martin's[41] values of k_s and our values of k_{obsd}. The slight decrease in k_1 from isooctane to octadecane indicates that our assumption that k_1 is constant throughout the series of alkane solvents is not correct for acetyl peroxide. However, the value of k_1 calculated from eq 9 is a good approximation of the average value of k_1 in this series of solvents.

Table VII. Rate Constants in the Decomposition of Acetyl Peroxide at 80°

Solvent	10^5k_s, sec^{-1}	10^5k_{obsd}, sec^{-1}	10^5k_1, sec^{-1}
Isooctane	4.00[a]	7.28[b]	11.3
Dodecane	4.68	6.26[b]	10.9
Octadecane	5.25	5.18[c]	10.5
k_1 calculated from viscosity data[d]			10.11
k_g gas phase rate constant			9.75[e]

[a] Data from J. C. Martin and S. A. Dombchick, *Advan. Chem. Ser.*, **No. 75**, 269 (1968). [b] Our values; Martin has reported k_{obsd} in isooctane of 7.2 × 10^{-5} sec^{-1}. [c] Value extrapolated from a plot of eq 9. [d] Calculated from the plot of k_{obsd} in Figure 1; the data can be found in Table IV. [e] A. Rembaum and M. Szwarc, *J. Amer. Chem. Soc.*, **76**, 5975 (1954).

Equation 19 can be used to calculate a true value of f_r from values of the rate constant for ^{18}O scrambling and k_{obsd}. Table VIII shows these values of f_r calculated using Martin's values of k_s and our values of k_{obsd}. The agreement between the values of f_r that are calculated by the viscosity method and the true values determined by ^{18}O scrambling is quite encouraging. It should be pointed out here that the viscosity method has the advantages of speed and the fact that it can be applied to any type of initiator.

Table VIII. A Comparison of f_r Calculated by ^{18}O Scrambling and the Viscosity Method

Solvent	f_r(^{18}O)[a]	f_r(viscosity)[b]
Isooctane	0.35	0.28
Dodecane	0.43	0.39
Octadecane	0.50	0.49

[a] Calculated from eq 19. [b] Estimated from eq 16 using the value of k_1 calculated from viscosity data.

The viscosity-derived values of f_r given in Table VIII are lower than the scrambling-derived values. It is reasonable that the viscosity method should give values which are lower than the true values in this system. The value of k_1 used to calculate the f_r values was determined from eq 9 which was derived by assuming

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[29] It is probable that these plots could be improved. A computer program could be used to fit viscosity *vs.* k_{obsd} data to one of the nonlinear equations from which eq 9 was derived, but we do not feel that we have sufficient data at the present time to justify such an attempt. Also, it may be possible to measure α from diffusion studies, and use different values of α for each initiator. We are currently attempting such a study; see ref 6.

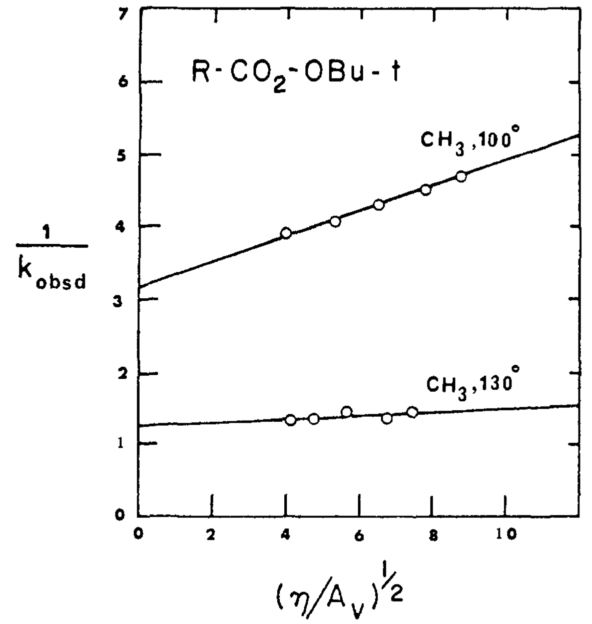

Figure 3. The viscosity plot for *t*-butyl peracetate. Scale factors: 100°, $1/k_{obsd} \times 10^{-4}$; 130°, $1/k_{obsd} \times 10^{-3}$.

that k_β was either zero or negligibly small compared to the rate constant for diffusion, k_D. The rate constant for β-scission of the acetoxy radical, k_β, has been estimated to be 2.9×10^9 sec^{-1} at 80°; the rate constant for diffusion in these solvents is about 10^{10} sec^{-1}. A comparison of eq 8 and 9 shows that if k_β is not zero, then a plot of eq 9 will lead to a calculated value of k_1 that is smaller than the true value, and this, in turn, will lead to a value of f_r that is erroneously low. Thus, in general, values of f_r calculated by the viscosity method must be considered to be minimum values.[30] The trend toward better agreement between the two sets of f_r values in Table VIII is caused by the variation of k_1. The value of k_1 estimated from the viscosity plot is lower than the average value of k_1 throughout the solvent series; but, it is closer to the value of k_1 in octadecane than to the value in isooctane.

We have seen that the viscosity method and the ^{18}O scrambling method can be used to estimate the fraction of acetoxy radicals that recombine during the lifetime of the geminate pair. A combination of these two methods allows us to estimate the fraction of the geminate pairs that diffuse apart and the fraction that decompose by β-scission. The equation defining the rate constant for scrambling, eq 17, can be combined with eq 10 and eq 5 to give

$$k_{obsd}/k_s = k_\beta/k_{-1} + \frac{A_D}{k_{-1}}(A_v/\eta)^\alpha \qquad (20)$$

Data can be plotted in the form of this equation, and the value of k_β/k_{-1} can be obtained from the intercept. Note that k_{-1} is not a second-order rate constant for the reaction of two acetoxy radicals but rather the first-order rate constant for the reaction of a geminate pair to form a molecule of acetyl peroxide. Likewise, k_β is the rate constant for β-scission of the geminate pair; thus, it is twice the value of the rate constant for β-scission of an acetoxy radical. From the intercept of a plot of eq 20 we have determined that k_β/k_{-1} is 0.48. Therefore

$$\frac{k_{\beta\text{-scission acetoxy}}}{k_{\text{cage recombination}}} = 0.24$$

Once k_β/k_{-1} is known, the relative importance of all the primary cage processes for acetyl peroxide can be estimated using eq 11–13. The results are shown in Table IX.

Table IX. Ratios of Cage Processes for Acetyl Peroxide at 80°

Solvent	f_r	f_D	f_β	k_D/k_{-1}	k_β/k_{-1}	k_β/k_D
Isooctane	0.36	0.47	0.17	1.34	0.48	0.36
Dodecane	0.43	0.27	0.21	0.86	0.48	0.56
Octadecane	0.50	0.26	0.24	0.51	0.48	0.95

Some discussion of Table IX is necessary. The values of f_r were calculated as discussed previously using eq 19. The values of k_β/k_{-1} were calculated from a plot of eq 20. The assumptions inherent in eq 20 are that k_{-1} and k_β remain constant throughout the range of the experiment, and that the viscosity dependence of k_D can be represented by eq 5. The values of f_r and k_β/k_{-1} were then used to calculate the other quantities in the table, using eq 11–13. All the entries for each solvent are thus internally consistent.

We have previously shown (Table VIII) that eq 9 can be used to obtain values of f_r that are in good agreement with the values obtained from ^{18}O scrambling data. However, this equation was derived by assuming that k_β/k_D was small relative to unity. The data in the last column of Table IX show that for the decomposition of acetyl peroxide this is not a valid assumption. It is therefore quite surprising that the values of f_r calculated using eq 9 agree so well with the values from the ^{18}O scrambling studies. This good agreement could be due to a variation in k_1 which compensates for the error introduced into eq 9 by the assumption that k_β/k_D is small.[29]

***t*-Butyl Peracetate.** The decomposition of *t*-butyl peracetate has been studied at two temperatures. A plot of the data according to eq 9 is shown in Figure 3. Koenig[5a] has measured the rate of oxygen-18 scrambling for this initiator and has calculated f_r using eq 19. His data give a less ambiguous measure of f_r and we therefore would like to compare our estimates with his. We cannot make a direct comparison between our results and the ^{18}O results because Koenig used paraffin oil (Nujol) as his solvent. The values of the energy of activation for viscous flow and the Arrhenius preexponential shown in Table X indicate that Nujol may not be compatible with the alkanes. The relationship that we have derived between k_{obsd} and viscosity, eq 9, does not correlate data in Nujol and in the alkanes on the same graph for some initiators we have examined.[31] The lack of correlation between data in the

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(30) This analysis of the expected error in f_r is based on the assumption that k_1, k_{-1}, and k_β do not change as the solvent viscosity is changed, and that the true value of α has been used in eq 9.

(31) Koenig has derived a relationship between k_{obsd} and viscosity that correlates both alkane and Nujol data. See ref 5a.

Table X. Arrhenius Parameters for Viscous Flow of Some Hydrocarbon Solvents[a]

	$A_v \times 10^{+2}$, cP	E_v, kcal/mol
n-Pentane	2.275	1.358
n-Hexane	1.910	1.612
n-Heptane	1.726	1.855
n-Octane	1.592	2.060
n-Nonane	1.422	2.272
n-Decane	1.294	2.486
n-Dodecane	1.219	2.781
n-Tetradecane	1.146	3.046
n-Hexadecane	1.169	3.219
n-Octadecane	1.169	3.387
Nujol (paraffin oil)	0.00186	9.28
Isooctane	1.303	2.05

[a] Values obtained by a least squares analysis of the equation: $\eta = A_v\exp(E_v/RT)$.

alkanes and in Nujol may be an indication that the same value of α is not valid for both of these solvents. Also the high energy of activation for viscous flow of Nujol may not reflect the barrier to diffusion experienced by small molecular species. Another indication that Nujol is significantly different from the alkanes for at least some initiators is the observation of Kiefer and Traylor[4k] that the rate of decomposition of di-*t*-butyl hyponitrite (DBH) is 25% faster in Nujol than in isooctane. They explain this in terms of a solvent stabilization of DBH by isooctane in excess of that provided by Nujol.[32]

Table XI. Comparison of the Values of f_r for *t*-Butyl Peracetate in Nujol Obtained from Oxygen-18 Scrambling Data and Viscosity Data[a]

Method	f_r	
	100°	130°
Oxygen-18	0.42	0.30
Viscosity	0.67	0.47

[a] The Nujol used was a sample of the "paraffin oil" which Professor Koenig's group had used for their studies, and we wish to thank Professor Koenig for his kindness in sending us this material. We find the infrared spectrum and viscosity of this material to be identical to the Nujol we had been using.

We have determined k_{obsd} for *t*-butyl peracetate in paraffin oil and used the value of k_1 in the alkanes to estimate f_r. Table XI shows the comparison between our results and Koenig's, and the agreement is poor. Because of the high temperature at which this perester was decomposed, it is likely that a considerable fraction of the geminate radicals are being destroyed by β-scission. We have calculated the rate constant for β-scission of the acetoxy radical from the Arrhenius parameters reported by Eirich.[4b] At 80, 100, and 130° the values are 2.9, 4.8, and 9.4 $\times$ 10^9 sec^{-1}, respectively. The uncertainty in these values should be considered to be about a factor of 10 because Eirich's estimation of the Arrhenius parameters required that he choose approximate values for the collision diameter of the methyl radical, the radius of the methyl and the acetoxy radical.[33] The rate constant for diffusion from the cage is about 10^{10} sec^{-1} in octane. The values of k_β indicate that it is about half of k_D at 100° and nearly identical with it at 130°. We have already seen that the presence of β-scission will cause the viscosity test to predict a value of f_r that is smaller than the true value. Table XI shows that the discrepancy we observe for *t*-butyl peracetate is in the opposite direction. This discrepancy can be explained by postulating that k_1 is much smaller in Nujol than in the alkanes. This seems reasonable in view of the decrease in k_1 for acetyl peroxide that is evident in Table VII. At the present time, it is impossible to tell how much of the discrepancy between Koenig's values for f_r and ours is due to the importance of β-scission and how much is due to some peculiarity of Nujol in our treatment.

Conclusions. The viscosity test usually appears to be reliable for dividing initiators into one-bond and multibond scission classes. The operational definition in this test is that a multibond initiator is one in which the "second" bond undergoes β-scission before the intermediate species has an opportunity to diffuse from the cage. The test also requires that k_1 *not* vary either from viscosity or a general solvent effect as the viscosity of the solvent is changed. For the alkane solvents, this is only approximately true for some initiators. The quantitative calculation of the fraction of the geminate pairs which return, f_r, from viscosity data gives fair agreement with oxygen-18 scrambling studies at present. There are several possible ways to improve this agreement,[29] including varying α, determining α experimentally,[6] using one of the nonlinear equations from which eq 9 was derived, and using solvents other than alkanes. Work along these lines is continuing.

Experimental Section

Hydrocarbons. *n*-Alkanes from Phillips Petroleum Co., pure grade, were stirred for several hours with concentrated sulfuric acid, washed with 10% sodium bicarbonate and distilled water, and distilled through a 24-in. Vigreux column.

Peresters. All peresters were prepared and purified by the method of Bartlett and Rüchardt[23] except *t*-butyl peracetate, which was purchased from Lucidol and purified by distillation.

***p*-Nitrophenylazotriphenylmethane (NAT).** The hydrazo precusor to NAT was prepared by the method of Cohen and Wang[34] and recrystallized from benzene, mp 186–188°. This material can be oxidized by refluxing for 1 hr in ether with a twofold excess of isoamyl nitrite. The crude NAT is best recrystallized from a mixture of petroleum ether (30–40°) and methylene chloride, 2:1, by dissolving the NAT in a minimum of CH_2Cl_2 at room temperature, adding the petroleum ether, and allowing the solution to stand in the refrigerator overnight.

Phenylazotriphenylmethane (PAT). This material was purchased from Eastman Chemical Co. and recrystallized from benzene–petroleum ether.

Azocumene. This was prepared by the method of Bartlett and Nelsen.[10a]

Acetyl Peroxide. Acetyl peroxide was prepared as described by Shine[35] except that pentane was used as the solvent.

Procedure in Kinetic Runs. In order to study a number of initiators at the same temperature, we found it necessary to obtain rate constants by three methods: either the disappearance of the initiator, or the first-order disappearance of scavenger, or the zero-order

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[32] DBH is presumed to decompose by a concerted mechanism so its rate constant for decomposition should not be influenced by the change in viscosity from isooctane to Nujol.

[33] Szwarc[4e] has estimated E_a for decarboxylation of the acetate radical to be 5.0 kcal/mol, and Martin[19c] has estimated it to be 8.0 kcal/mol.

[34] S. J. Cohen and C. H. Wang, *J. Amer. Chem. Soc.*, **75**, 5504 (1953).

[35] J. R. Slagle and H. J. Shine, *J. Org. Chem.*, **24**, 107 (1959).

disappearance of scavenger was followed. In all cases, the raw data were treated by a computer program to obtain a least squares fit of the data to the applicable rate law.

Method 1. Disappearance of Initiator. (a) Ultraviolet. The rate constants for decomposition of the NAT, PAT, and azocumene were obtained by following the disappearance of the azo absorption band. A solution of the azo compound was placed in a standard cuvette, sealed with a rubber septum, and placed in the thermostated cell compartment of a Beckman DK-1 ultraviolet spectrophotometer. The decrease in absorption was monitored continuously. Experiments have shown that identical rate constants are obtained regardless of whether or not the samples were degassed.

(b) Infrared. A solution of the initiator, approximately 0.03 *M*, was distributed into a series of 1-ml ampoules which were sealed at atmospheric pressure without degassing. The entire lot was placed in a constant-temperature bath. Samples were removed at preselected times, quenched at −77°, and placed in cold storage. After all the samples had been removed, including two time–infinity samples at ten half-lives, the optical density was determined on a Beckman IR-7 using a cell thickness of 0.5 mm.

The transmittance *vs.* time data for both method 1a and 1b were fitted to the equation

$$\ln (A_t - A_\infty) = k_{\text{obsd}}t - \ln (A_0 - A_\infty)$$

where A_t is the absorbance at time t and A_∞ is the experimentally determined value of the absorbance after the initiator has decomposed for ten half-lives.

Method 2. Limiting Initiator (First-Order Disappearance of Scavenger. A solution containing approximately 1×10^{-3} mol of galvinoxyl[36] and 4×10^{-4} mol of initiator was prepared as follows. Approximately 4 mg of initiator was dissolved in a selected solvent and diluted to 10 ml. A 2-ml aliquot of this solution was added to an accurately weighed sample (about 4.0 mg) of galvinoxyl and the resulting solution diluted to 10 ml. The resulting solutions were degassed by bubbling N_2 through them at room temperature and sealing them with a rubber septum in a glove bag. The solutions were allowed to decompose in the thermostated cell compartment of a Beckman DK-1, and the disappearance of the galvinoxyl was followed at 5600 Å. The data were analyzed as in method 1.

Method 3. Excess Initiator (Zero-Order Disappearance of Scavenger). A solution containing 1×10^{-3} mol of galvinoxyl and 19×10^{-3} mol of perester was prepared by weighing the materials on a Cahn electrobalance and diluting to 10 ml. The solution was placed in cuvettes which were degassed and sealed under vacuum.

If the scavenger is the only species absorbing at the wavelength used, then eq 21 can be used to obtain the rate constant. A is the

$$A = -2k_dI_0\epsilon_st + A_0 \qquad (21)$$

absorbance at time t, A_0 is the absorbance at time zero, k_d is the rate constant for decomposition of the initiator, ϵ_s is the extinction coefficient of the scavenger, I_0 is the initial concentration of initiator, and S_0 is the initial concentration of scavenger. If the scavenger is not the only species absorbing at the wavelength used, the total absorbance can be regarded as a sum of the absorbance due to the scavenger, the cell, and the products.

$$A = A_s + A_c + A_p \qquad (22)$$

$$A = \epsilon_s(S) + \epsilon_p(P) + A_c \qquad (23)$$

From the stoichiometry of the reaction $S + R\cdot \rightarrow$ products, we can derive the relationship

$$A = \epsilon_s(S) + \epsilon_p(S_0 - S) + A_c \qquad (24)$$

Equation 24 can be solved for (S) after noting that $S_0 = P_\infty$ and $\epsilon_pS_0 = \epsilon_pP = A_\infty'$. The resulting equation can be substituted into eq 21 to give

$$\frac{A_t - A_c - A_\infty'}{A_0 - A_c - A_\infty} = 2k_d(I_0/S_0)t + 1.0 \qquad (25)$$

Note that A_∞' is the calculated infinity point, but $(A_c + A_\infty')$ is the experimental A_∞. A computer program was developed which

$$\frac{A_t - A_\infty}{A_0 - A_\infty} = 2k_d(I_0/S_0)t + 1.0 \qquad (26)$$

would accept values of transmittance *vs.* time, plot absorbance *vs.* time, and calculate the best value of A_0 by a least-squares fit of the data to eq 21. The resulting value of A_0 was used in eq 26, and k_d was calculated.

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[36] 2,6-Di-*t*-butyl-α-(3,5-di-*t*-butyl-4-oxo-2,5-cyclohexadiene-1-ylidine)-*p*-tolyloxy; the galvinoxyl used in these experiments was prepared by H. T. Bickley.