Homolysis of Some Radical Initiators. Viscosity Dependence and Cage Return[1]

WILLIAM A. PRYOR,*[2] EVA H. MORKVED,[3] AND H. T. BICKLEY[4]

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

Received September 8, 1971

Our previously derived viscosity test for distinguishing one-bond from multi-bond initiators has been applied to the homolysis of nine peroxy compounds in alkane solvents (Table I). The results are consistent with findings by other authors (Table II), and the viscosity test appears to offer a fast and convenient method for initial screening of all types of initiators. The amounts of cage return for acetyl peroxide (Ac_2O_2), propionyl peroxide (PPO), and benzoyl peroxide (Bz_2O_2) are compared with those of the corresponding *tert*-butyl peroxy esters (Table VII). In each pair, the diacyl or diaroyl peroxide undergoes the smaller amount of cage return. This can be explained for the Ac_2O_2/*tert*-butyl peroxyacetate and PPO/*tert*-butyl peroxypropionate pairs by the higher stability of the *tert*-butoxy radical of the peroxy ester compared to the acyloxy radical of the diacyl peroxide (Table VI). However, for the Bz_2O_2/*tert*-butyl peroxybenzoate pair both the *t*-BuO· and the $PhCO_2\cdot$ radicals undergo β scission too slowly to compete with diffusion from the cage (Table VI); the small amount of cage return for Bz_2O_2 appears to be an anomaly. Some CO_2 trapping experiments for the *tert*-butyl peroxy esters RCO_2OBu-*t*, where R is methyl, ethyl, or *tert*-butyl, support the kinetic data (Table II). These experiments also indicate that *tert*-butyl peroxyisobutyrate (R = isopropyl) is a two-bond initiator. However, the viscosity test shows a small amount of cage return (~1%). Therefore, we conclude that this compound either decomposes by both mechanisms (but mainly two-bond) or undergoes only a small amount of cage return due to the high instability of the $C_3H_7CO_2\cdot$ radical. *tert*-Butoxy radicals from the decomposition of di-*tert*-butyl peroxide (TOOT) undergo negligible amounts of β scission or disproportionation in the cage. The viscosity dependence of k_{obsd} for TOOT can be used to calculate the fraction of cage return, f_r, from eq 2 and 3, and the values are compared with those of Kiefer and Traylor.

The effect of solvent viscosity on the observed rate constant for homolysis of radical initiators can be used to determine the number of bonds which break at the transition state.[5] There are two possibilities: homolysis may involve the cleavage of only one bond, or several bonds may undergo simultaneous cleavage. To further test these ideas, we have studied the viscosity dependence of the rates of decomposition of the peroxy compounds which are listed in Table I. (The abbreviations given there for the names of the compounds will be used throughout this article.)

TABLE I

PEROXY COMPOUNDS WHICH HAVE BEEN STUDIED

Formula[a]	Name	Abbreviations for peroxy compounds
$[PhC(O)O-]_2$	Benzoyl peroxide	Bz_2O_2
$[EtC(O)O-]_2$	Propionyl peroxide	PPO
MeC(O)OOBu-*t*	*tert*-Butyl peroxyacetate	TAc
EtC(O)OOBu-*t*	*tert*-Butyl peroxypropionate	TPr
$Me_2CHC(O)OOBu$-*t*	*tert*-Butyl peroxyisobutyrate	TiBu
$Me_3CC(O)OOBu$-*t*	*tert*-Butyl peroxypivalate	TPiv
PhC(O)OOBu-*t*	*tert*-Butyl peroxybenzoate	TBz
$[t\text{-BuOOC(O)}]_2$	Di-*tert*-butyl peroxyoxalate	TOx
$(t\text{-BuO}-)_2$	*tert*-Butyl peroxide	TOOT
$(n\text{-BuO}-)_2$	*n*-Butyl peroxide	NOON
$[EtCH(Me)O-]_2$	*sec*-Butyl peroxide	SOOS

[a] The following abbreviations are used: Ph, C_6H_5; Et, C_2H_5; Me, CH_3; Bu, C_4H_9.

For a one-bond initiator, the generalized mechanism for homolysis is shown in Scheme I, where [cage] represents the geminate pair of radicals produced by the scission of one bond, and [cage′] is the pair of radicals produced by some β-scission process. In terms of this mechanism, the observed rate constant k_{obsd} is given by eq 1, where k_1 is the rate constant for bond homolysis, k_{-1} is the rate constant for cage return, k_D is the rate constant for diffusive separation of the geminate radicals, and k_β is the rate constant for β scission. The fraction of geminate radicals which combine to reform the initiator is defined in eq 2.

SCHEME I

$$\begin{tikzcd}
\text{Initiator} \arrow[r, shift left, "k_1"] & \text{[cage]} \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_D"] \arrow[d, "k_\beta"] & \text{free radicals} \\
& \text{[cage}'\text{]} + \text{small molecule} &
\end{tikzcd}$$

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

$$f_r = k_{-1}/(k_{-1} + k_D + k_\beta) \tag{2}$$

For a multi-bond initiator the decomposition involves the simultaneous cleavage of two or more bonds, and we assume that the three or more species formed cannot combine to re-form the initiator. Therefore, the observed rate constant would be expected to be independent of the cage lifetime and, consequently, of the solvent viscosity.

We have derived an equation (eq 3) which relates k_{obsd} to solvent viscosity.[5] For a one-bond initiator,

$$1/k_{obsd} = 1/k_1 + [k_{-1}/A_D k_1][\eta/A_v]^\alpha \tag{3}$$

a fraction, f_r, of the geminate radicals recombines to reform the initiator, and f_r is viscosity dependent. For a multi-bond initiator, $k_{-1} = 0$ and the value of $1/k_{obsd}$ in eq 3 will be independent of viscosity and equal to $1/k_1$. The derivation of eq 3 is based on the assumptions that k_D is the only rate constant in Scheme I

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[1] This work was partially supported by Grant GP-3820 from the National Science Foundation.

[2] Address all correspondence to this author. John Simon Guggenheim Fellow, 1970–1971; NIH Special Postdoctoral Fellow, summer 1971.

[3] E. Morkved was a Postdoctoral Fellow on NSF Grant GP-3820 from June 1969 to December 1969 and from June 1970 to February 1971.

[4] H. T. Bickley was a Predoctoral Fellow on NSF Grant GP-3820 from January 1966 to May 1969 and on NIH Grant GM 11908 from May 1969 to December 1970.

[5] (a) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **89**, 1741 (1967); (b) *ibid.*, **92**, 5403 (1970); (c) *Intra-Sci. Chem. Rep.*, **3**, 255 (1969).

which is viscosity sensitive, that $k_\beta < k_D$, that $k_D = A_D \exp(-E_D/RT)$, that $\eta = A_v \exp(E_v/RT)$, and that $E_D = \alpha E_v$ where α is a proportionality constant. Equation 3 predicts a linear relationship between $1/k_{obsd}$ and $(\eta/A_v)^\alpha$, and k_1 can be determined from the intercept if the value of α is known. We suggested an α value of 0.5 as a convenient value for initial work,[5b] and this choice has been justified by theoretical arguments by Koenig.[6] However, recent diffusion experiments in these laboratories[7] gave an α value of 0.72 when benzene was used as a model for caged radical fragments, and an analysis of literature data gave α values of 0.74 for toluene and 0.76 for iodine. We were surprised to find that all three of these solutes had such similar α values; we previously had suggested[5b] that α might vary for each initiator. It is not clear at present whether all initiators have α values near 0.7, or whether the similarities in the data now available result from the fact that the solutes studied to date (benzene, toluene, and iodine) all have similar size and polarity. Our present position is that it is a worthwhile working hypothesis to assume that the α value for all initiators will be near 0.7 and to calculate cage return data for initiators using this value. However, until α values are known with more confidence, we also will continue to calculate the amount of cage return for $\alpha = 0.5$.

We also have applied the technique of Shine, *et al.*,[8a,b] to distinguish one-bond from multi-bond initiators. This technique involves the use of cyclohexene as a solvent to scavenge acyloxy radicals before they decarboxylate. Shine[8b] has shown, for example, that acetyl peroxide gives a larger yield of CO_2 in benzene as a solvent than in cyclohexene, indicating that the $CH_3CO_2\cdot$ radical can be scavenged, and that acetyl peroxide is a one-bond initiator.[9] We applied this method to the series of peroxy esters RCO_2OBu-*t*, where R = methyl, ethyl, isopropyl, or *tert*-butyl.

Results and Discussion

We will discuss separately each of the three classes of peroxy compounds which we have studied: the diaroyl peroxide, the *tert*-butyl peroxy esters, and the dialkyl peroxides. For convenience, we have summarized all of our results in Table II. This table shows the comparison between the mode of decomposition for each compound as concluded from the viscosity test, the CO_2 trapping experiments, and that suggested by other workers using different methods.

TABLE II

MODE OF DECOMPOSITION FOR SOME PEROXY COMPOUNDS

Compd[a]	Mode of decomposition[b]		
	Viscosity test	CO_2 Trapping	Other work
Diaroyl Peroxide			
Bz_2O_2	1		1[c]
Diacyl Peroxide			
PPO[d]	*d*		1[e]
Peroxy Esters			
TAc	1	1	1[f]
TPr	1	1	1[g]
TiBu	1[h]	2	
TPiv	2	2	2[i]
TBz	1		1[j]
TOx	multi		multi[k]
Dialkyl Peroxides			
TOOT	1		1[l]
NOON	1		

[a] For explanation of abbreviations, see Table I. [b] The number of bonds which initially are broken are referred to as follows: 1 for one bond, 2 for two bonds, and "multi" if there is a possibility for homolysis of more than two bonds. [c] G. S. Hammond and L. M. Soffer, *J. Amer. Chem. Soc.*, **72**, 4711 (1950); A. E. Nicholson and R. G. W. Norrish, *Discuss. Faraday Soc.*, **22**, 97 (1956); C. Walling and J. Pellon, *J. Amer. Chem. Soc.*, **79**, 4786 (1957), J. K. Kochi, *ibid.*, **84**, 1572 (1962); H. J. Shine, J. A. Waters, and D. M. Hoffman, *ibid.*, **85**, 3613 (1963); J. C. Martin and J. H. Hargis, *ibid.*, **91**, 5399 (1969). [d] See footnote 10 for a discussion of our incomplete studies of propionyl peroxide. [e] J. C. Martin and J. H. Hargis, submitted for publication. [f] P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958); T. Koenig and M. Deinzer, *ibid.*, **90**, 7014 (1968); T. Koenig, J. Huntington, and R. Cruthoff, submitted for publication. [g] No α-D secondary isotope effect was found in the decomposition of TPr: J. P. Stanley, Louisiana State University, private communication, 1968. [h] The viscosity test indicates a small amount (1%) of cage return for TiBu. However, both mechanisms (one-bond and two-bond scission) might occur simultaneously for this compound. See footnote 20c. [i] P. D. Bartlett and D. M. Simons, *J. Amer. Chem. Soc.*, **82**, 1753 (1960); T. Koenig and R. Wolf, *ibid.*, **89**, 2948 (1967). [j] P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958); R. C. Neuman and J. V. Behar, *ibid.*, **91**, 6024 (1969); T. Koenig, M. Deinzer, and J. A. Hoobler, *ibid.*, **93**, 938 (1971). [k] P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *ibid.*, **82**, 1762 (1960); R. Hiatt and T. G. Traylor, *ibid.*, **87**, 3766 (1965); H. Kiefer and T. G. Traylor, *ibid.*, **89**, 6667 (1967). [l] C. Walling and G. Metzger, *ibid.*, **81**, 5365 (1959); C. Walling and H. P. Waits, *J. Phys. Chem.*, **71**, 2361 (1967); H. Kiefer and T. G. Traylor, *J. Amer. Chem. Soc.*, **89**, 6667 (1967); E. S. Huyser and R. M. VanScoy, *J. Org. Chem.*, **33**, 3524 (1968).

Benzoyl Peroxide (Bz_2O_2).[10,11]—This compound is known to be a one-bond initiator.[12-14] Firstly, an almost quantitative yield of benzoic acid is obtained from the decomposition of Bz_2O_2 in wet carbon tetra-

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(6) T. Koenig, *J. Amer. Chem. Soc.*, **91**, 2558 (1969).

(7) (a) The diaphragm cell technique was used to measure the diffusion coefficients D at 32° for 0.02–0.03 M solutions of benzene in the alkanes with carbon numbers 6, 7, 8, 10, 12, 14, and 16. (The method and equations are given in ref 5c.) The D values are correlated by the equation $\log D = A - \alpha \log \eta$ (where A and α are disposable parameters) with a correlation coefficient of −0.9992. Using our new data for benzene and literature data for toluene and iodine, values of A and α are as follows: benzene, −6.13, 0.72; toluene,[7b] −6.22, 0.74; iodine,[7b,c] −6.29, 0.76. (b) P. Chang and C. R. Wilke, *J. Phys. Chem.*, **59**, 592 (1955). (c) R. H. Stokes, P. J. Dunlop, and J. R. Hall, *Trans. Faraday Soc.*, **49**, 866 (1953).

(8) (a) H. J. Shine and J. R. Slagle, *J. Amer. Chem. Soc.*, **81**, 6309 (1959). (b) H. J. Shine, J. A. Waters, and D. M. Hoffman, *ibid.*, **85**, 3613 (1963). (c) Instead of cyclohexene, used by Shine and coworkers,[8a,b] we used 4MC because of its higher boiling point.

(9) J. C. Martin, J. W. Taylor, and E. H. Drew, *J. Amer. Chem. Soc.*, **89**, 129 (1967), have argued that the unusually fast reaction between acetoxy radicals and cyclohexene (rate constant of the order 10^8 l. mol^{-1} sec^{-1}) is explained by the initial formation of a π complex in the cage. The π complex would subsequently react with a cage partner, or diffuse out of the cage and thereafter abstract a hydrogen atom from the solvent. The π complex would decarboxylate less readily than the acetoxy radical itself, explaining the lower CO_2 yields.

(10) We also have studied[11] the viscosity dependence of k_{obsd} for the two diacyl peroxides, propionyl peroxide and lauroyl peroxide. Our studies indicate that the values of k_{obsd} for both are independent of viscosity. However, it is difficult to distinguish a small, finite slope in eq 3 from no slope, and we have collected an insufficient amount of data for these two compounds to distinguish between the two possibilities. Propionyl peroxide previously was shown to undergo 9% cage return at 80° in isooctane.[12]

(11) H. T. Bickley, Ph.D. Dissertation, Louisiana State University, 1971.

(12) J. C. Martin and J. H. Hargis, submitted for publication.

(13) (a) A. E. Nicholson and R. G. W. Norrish, *Discuss. Faraday Soc.*, **22**, 97 (1956); (b) C. Walling and J. Pellon, *J. Amer. Chem. Soc.*, **79**, 4786 (1957); (c) R. C. Neuman and J. V. Behar, *ibid.*, **91**, 6024 (1969).

(14) (a) G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950); (b) J. K. Kochi, *ibid.*, **84**, 1572 (1962); (c) J. C. Martin and J. H. Hargis, *ibid.*, **91**, 5399 (1969).

chloride in the presence of iodine.[14a] Secondly, a 94% yield of *sec*-butyl benzoate is obtained when Bz_2O_2 and *cis*-butene-2 are heated in benzene.[14b] Thirdly, Martin and Hargis find that some ^{18}O scrambling has occurred in Bz_2O_2 recovered after partial decomposition;[14c] surprisingly, however, the amount of scrambling is anomalously small. Fourthly, high-pressure studies[13a,b] of Bz_2O_2 have been summarized by Neuman and Behar,[13c] and they conclude that the large activation volumes for Bz_2O_2 indicate initial scission of one bond.

Table III indicates some decrease in k_{obsd} for Bz_2O_2 with increasing solvent viscosity in the solvents hexane through hexadecane.[15] Analysis of these data using eq 3 (with $\alpha = 0.7$) gives a slope of 139 sec with a confidence level of 97.8%. Similar calculations for the known two-bond initiator TPiv (this compound will be discussed in detail later) give a slope of 3.6 sec with a confidence level of 64%. Since pure chance could yield a positive slope with a confidence level of 50%, the difference between Bz_2O_2 and TPiv is significant. From the magnitude and confidence level of the slope for Bz_2O_2, we conclude that Bz_2O_2 is a one-bond initiator.[16]

TABLE III

DECOMPOSITION OF BENZOYL PEROXIDE, Bz_2O_2, AT 80° IN ALKANE SOLVENTS[a]

Carbon no. of alkane	$10^5 k_{obsd}$, sec^{-1}		
6	2.85	2.85^b	
7	2.57	2.71^b	2.98^c
7	2.75		
7	2.80		
iso-8	2.79	2.79^b	
10	2.53	2.53^b	
14	2.64	2.64^b	
14	2.64		
14	2.63		
16	2.51	2.51^b	2.70^c

[a] Disappearance of initiator measured by the disappearance of its infrared carbonyl absorption. Concentration of initiator was 2×10^{-2} *M*. We also have measured $k_{obsd} = 2.94 \times 10^{-5}$ sec^{-1} in Nujol. This value has been disregarded, since induced decomposition might occur in this highly viscous solvent: J. C. Martin and J. H. Hargis, *J. Amer. Chem. Soc.*, **91**, 5399 (1969). [b] Average k_{obsd} values in each solvent. [c] 0.2 *M* styrene added.

The amount of cage return for Bz_2O_2 in isooctane can be calculated from these data, and 0.4% return is obtained. This value certainly cannot be very accurate, but it is in qualitative agreement with the finding of Martin that only a small fraction (4%) of the benzoyloxy radicals give cage return. It is puzzling that 35% of the acetoxy radicals from acetyl peroxide recombine in the cage under the same conditions where only about 4% of the benzoyloxy radicals from Bz_2O_2 do so.[17] Recent studies by Martin and Hargis[12] rule out the possibility that Bz_2O_2 undergoes significant amounts of return without scrambling of its oxygens. These authors also considered the possibility that the low value of f_r is due to electrostatic repulsive forces between the benzoyloxy radicals. To probe this, they carried out ^{18}O scrambling studies for three symmetrically substituted benzoyl peroxides, and their results indicate that there is no correlation between f_r and polar substitutent effects. The possibility that a larger activation barrier exists for the combination of the benzoyloxy radicals than for the acetoxy radicals has not been ruled out, but the reason why such a barrier might exist is not clear at present.[18]

***tert*-Butyl Peroxy Esters.**—We have studied the decomposition of six peroxy esters in alkane solvents. Three of the peroxy esters, *tert*-butyl peroxyacetate (TAc), *tert*-butyl peroxypropionate (TPr), and *tert*-butyl peroxybenzoate (TBz), show decreasing values of k_{obsd} with increasing solvent viscosity; therefore, these peroxy esters are one-bond initiators (Table IV). This is in agreement with work by other authors.[13c,19a,b,c,g] The two peroxy esters, *tert*-butyl peroxypivalate (TPiv) and di-*tert*-butyl peroxyoxalate (TOx), show values of k_{obsd} that are independent of solvent viscosity and, therefore, behave as multi-bond initiators. The last compound, *tert*-butyl peroxyisobutyrate (TiBu), shows a small and somewhat irregular decrease in k_{obsd} with increasing solvent viscosity. When the data for TiBu are analyzed using eq 3 ($\alpha = 0.7$), a slope of 26 sec is found (confidence level 91%) and the amount of cage return is calculated to be about 1% in isooctane.

We also applied the acyloxy trapping technique[8a,b] to the alkyl series of peroxy esters, RCO_2OBu-*t*, where R varies from methyl (TAc) to ethyl (TPr) to isopropyl (TiBu) to *tert*-butyl (TPiv). The CO_2 yields from the decompositions of these peroxy esters in 4-methyl-1-cyclohexene (4MC)[8c] were measured gravimetrically, and these yields are listed in Table V together with the CO_2 yields from decompositions of the peroxy esters in alkane solvents under the same conditions. TAc and TPr give a smaller amount of CO_2 when decom-

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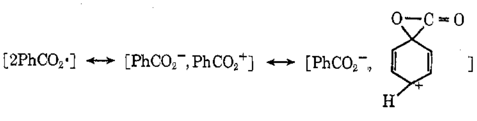
[15] We have disregarded the k_{obsd} value in Nujol (Table III, footnote *a*), since other workers[14c] also have had inconsistent results, probably caused by induced decomposition, in this highly viscous solvent.

[16] Induced decomposition is not affecting the data of Table III importantly since the addition of styrene hardly changes k_{obsd}. We normally measured these rates under 1 atm air; degassing of the reaction mixtures increased k_{obsd} by 40–50% ($k_{obsd} = 3.84 \times 10^{-5}$ sec^{-1} in heptane, 4.14×10^{-5} sec^{-1} in tetradecane), indicating that induced decomposition of Bz_2O_2 occurs in the absence of air. Apparently there is enough oxygen present under atmospheric conditions to scavenge the radicals which cause induced decomposition.

[17] (a) J. W. Taylor and J. C. Martin, *J. Amer. Chem. Soc.*, **88**, 3650 (1966). (b) *ibid.*, **89**, 6904 (1967). (c) Martin and Taylor's data[17a,b] have been critized recently by M. J. Goldstein and H. A. Judson, *ibid.*, **92**, 4119 (1970). However, J. C. Martin has reevaluated Goldstein's data using very high ^{18}O levels and has obtained results in good agreement with his own previously published data. Private communication from J. C. Martin to W. A. Pryor, Jan 1971.

[18] One possibility which has not been suggested is that a complex between a carboxylate group of one fragment and the aromatic ring of another keeps the alignment of the two caged fragments such that they are poorly disposed to recombine. The Hammett correlation of the decomposition of benzoyl peroxides as well as Walling's recent mechanism for the induced decomposition provide some evidence for this: C. Walling and Ž. Čekovič, *J. Amer. Chem. Soc.*, **89**, 6681 (1967). Resonance structures involving charge transfer can be written for the geminate pair.



[19] (a) P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958). (b) T. Koenig, J. Huntington, and R. Cruthoff, submitted for publication. (c) No α-D secondary isotope effect was found in the decomposition of TPr: J. P. Stanley, Louisiana State University, private communication, 1968. (d) P. D. Bartlett and L. B. Gortler, *J. Amer. Chem. Soc.*, **85**, 1864 (1963). (e) P. D. Bartlett and D. M. Simons, *ibid.*, **82**, 1753 (1960). (f) T. Koenig and R. Wolf, *ibid.*, **89**, 2948 (1967). (g) T. Koenig, M. Deinzer, and J. A. Hoobler, *ibid.*, **93**, 938 (1971). (h) T. Koenig and M. Deinzer, *ibid.*, **90**, 7014 (1968).

TABLE IV

RATE CONSTANTS, $10^5 k_{obsd}$, SEC^{-1}, FOR HOMOLYSIS OF PEROXY ESTERS, RCO_2O-*t*-Bu, IN ALKANE SOLVENTS[a]

Carbon no. of alkane	R Temp, °C	CH_3[b] (TAc) 100	CH_3CH_2 (TPr) 100	$(CH_3)_2CH$ (TiBu) 100	$(CH_3)_3C$ (TPiv) 80	$(CH_3)_3C$[c] (TPiv) 80	C_6H_5 (TBz) 115	$(CH_3)_3COOC(O)$ (TOx) 41
7						23.3	7.21	
8		2.07	2.03	15.9	23.4	23.4	7.06	17.9
10		1.95	1.82	14.6	23.8	21.8	6.77	17.5
12		1.78	1.78	15.6	20.0	23.8	6.44	18.1
14		1.67	1.68	15.2	21.6	22.7	6.03	17.1
16		1.55	1.58	14.7	24.4	23.9	5.97	

[a] All rate constants were obtained by directly observing the disappearance of peroxy ester except for di-*tert*-butyl peroxyoxalate (TOx), where the excess scavenger technique was used and with galvinoxyl as the scavenger. Most rate constants are the average of at least three separate runs. [b] Rate constants from Ph.D. Dissertation of K. W. Smith, Louisiana State University, 1969. [c] 74% peroxy ester in mineral spirits as purchased from Lucidol. The purities of the peroxy esters TPr, TiBu, and TPiv were determined by iodometric titration, using the method by L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958); 95% pure peroxy ester was considered satisfactory.

TABLE V

CO_2 YIELDS FROM DECOMPOSITIONS OF PEROXY ESTERS, RCO_2O-*t*-Bu

R	Solvent	Temp, °C	CO_2, %[a]
CH_3	Isooctane	80	97
	Isooctane	100	103
(TAc)	Decane	130	100, 102
	4MC[b]	80	75, 76, 77
	4MC	100	70, 74, 77, 77, 78, 78, 79
CH_3CH_2	Isooctane	100	92
	Decane	130	95
(TPr)	4MC	80	48, 59
	4MC	100	54, 55, 57, 61, 65
$(CH_3)_2CH$	Isooctane	80	92, 94
	Isooctane	100	100
(TiBu)	4MC	80	98, 101
	4MC	100	104
$(CH_3)_3C$[c]	Isooctane	80	95, 101
(TPiv)	4MC	80	103, 103, 91

[a] Purity of the peroxy esters was determined by iodometric titration, method by L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958). The CO_2 yields were corrected for less than 100% pure peroxy ester; theoretical molar ratio of CO_2 to peroxy ester is 1:1. [b] 4-Methyl-1-cyclohexene. [c] 15% Mineral spirits present in the peroxy ester before dissolving in isooctane or 4MC.

TABLE VI

RATE CONSTANTS FOR β SCISSION OF SOME RADICALS[a]

Reaction	Rate constant, sec^{-1}	Temp, °C
$CH_3CO_2\cdot \longrightarrow CH_3\cdot + CO_2$	1.6×10^9[b]	60
$C_2H_5CO_2\cdot \longrightarrow C_2H_5\cdot + CO_2$	1.6×10^9[c]	60
t-BuO$\cdot \longrightarrow CH_3\cdot + CH_3COCH_3$	2×10^5[d]	80
$C_6H_5CO_2\cdot \longrightarrow C_6H_5\cdot + CO_2$	10^4–10^5[e,f]	80

[a] The rate constant for diffusion of a radical from a solvent cage is of the order of 10^{10} sec^{-1}. [b] W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962). [c] This rate contant is not smaller than that for the acetoxy radical; decarboxylation of the acetoxy and propionyloxy radicals has $\Delta H = -15$ and -17 kcal/mol [S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, pp 178–181; S. W. Benson in "Organic Peroxides," Vol. I, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1970, p 121; G. P. Adams, D. H. Fine, P. Gray, and P. G. Laye, *J. Chem. Soc. B*, 720 (1967)]. [d] Calculated using an *A* factor of $10^{13.4}$ sec^{-1} and $E_a = 13$ kcal/mol (P. Gray, R. Shaw, and J. C. J. Thynne in "Progress in Reaction Kinetics," Vol. 4, G. Porter Ed., Pergamon Press, Oxford, 1967, pp 79, 81, and 97). A rate constant of 10^3 sec^{-1} at 160° was measured for this reaction in the gas phase by F. W. Birss, C. J. Danby, and C. Hinshelwood, *Proc. Roy. Soc., Ser. A*, **239**, 154 (1957). [e] D. F. DeTar, *J. Amer. Chem. Soc.*, **89**, 4058 (1967). [f] J. C. Bevington and J. Toole, *J. Polym. Sci.*, **28**, 413 (1958).

posed in 4MC than in decane or isooctane, whereas TiBu and TPiv give close to theoretical amounts of CO_2 when decomposed in both 4MC and in alkane solvents. Thus, the acyloxy fragments from TAc and TPr can be trapped[20a] and these peroxy esters are one-bond initiators, whereas TiBu and TPiv behave as multi-bond initiators. Literature results for TAc,[19a,b,h] TPr,[19c] and TPiv[19e,f] support these conclusions (Table II). The nonconcerted decomposition of TAc and TPr clearly is due to the fact that $CH_3CO_2\cdot$ and $C_2H_5CO_2\cdot$ are sufficiently stable so that cage return can compete with decarboxylation (Table VI).

The viscosity and the CO_2 scavenging data for TiBu do not agree, and this compound requires more extensive discussion. The rate of decomposition of TiBu is sensitive to solvent viscosity, but the *i*-Pr$CO_2\cdot$ radical from it cannot be scavenged by 4MC. In the series of peroxy esters RCO_2OBu-*t*, where R is Me, Et, *i*-Pr, or *t*-Bu, the first two compounds decompose by a one-bond mechanism, the fourth by a two-bond path, and the third compound is borderline (see Table

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[20] (a) Martin and Dombchik[20b] were unable to find any cyclohexyl propionate from the decomposition of acetyl propionyl peroxide in cyclohexene, and, therefore, the reduced amount of CO_2 from the decomposition of TPr in 4MC is unexpected. We cannot explain the difference in our results and Martin's. We did not isolate any products from the reaction of TPr in 4MC, but infrared analysis of the crude reaction mixture showed that the disappearance of the perester carbonyl absorption at 1787 cm^{-1} coincided with the appearance of an absorption at 1743 cm^{-1}, typical of an ester carbonyl group. We also cannot explain why we observe a greater reduction in CO_2 yields for TPr than for TAc, opposite of what would be expected. However, our results are not due to induced decomposition, since the rate constants for decomposition of both TAc and TPr were the same in the alkane solvents and 4MC. (b) J. C. Martin, private communication. Also see J. C. Martin and S. A. Dombchik, *Advan. Chem. Ser.*, **75**, 269 (1968). (c) It is conceivable that an initiator exists which has relative energies for one- and two-bond scission such that the two processes can occur simultaneously. (Even if the transition state for one has a slightly higher energy than the other, differing trajectories on the region of the reaction surface where the two paths divide would not be improbable for molecules having different kinetic energies.) If this were to describe the behavior of TiBu, then an overall 1% return could result, for example, from the average of 10% return by 10% of the peroxy ester plus 0% return by 90% of the material which undergoes two-bond scission. (d) We have discussed the case of an initiator which decarboxylates ten times faster than does acetyl peroxide but undergoes diffusion and cage recombination at the same rate as Ac_2O_2. Such a compound would appear to be a two-bond initiator by the viscosity test even if it were a one-bond. See ref 5b, Table I. (e) T. W. Koenig and W. D. Brewer, *Tetrahedron Lett.*, **No. 32**, 2773 (1965). (f) The only data in the literature relevant to the mechanism of decomposition of TiBu is the measurement by Bartlett and Gortler[19d] of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values. This allows the application of the isokinetic test to this compound, and the method predicts that the peroxy ester is a two-bond initiator. However, the lack of reliability of this method has recently been discussed, and it is extremely doubtful if the isokinetic plot can be used to decide the number of bonds which initially break in peroxy ester decompositions.[20g] (g) W. A. Pryor and K. Smith, *Int. J. Chem. Kinet.*, **3**, 387 (1971).

TABLE VII

COMPARISON OF AMOUNTS OF CAGE RETURN FOR DIACYL OR DIAROYL AND RELATED PEROXY ESTERS[a]

	Cage return, % (Temp, °C)[b]	
R	RC(=O)OOC(=O)R	RC(=O)OO-*t*-Bu
CH_3	18[b,c] (80)	18[b,d] (100)
C_2H_5	9[e] (80)	15[d] (100)
Ph	4[f] (80)	11[d] (115)

[a] Decomposition of PPO and Bz_2O_2 in isooctane, all the other compounds in octane. [b] All the peroxy esters were decomposed at higher temperatures than the related peroxides. Therefore, since the amount of cage return increases with decreasing temperature, TAc (R = CH_3) would give more than 18% return at 80°. [c] By viscosity test, $\alpha = 0.7$: W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970). [d] By viscosity test, $\alpha = 0.7$. [e] J. C. Martin and J. H. Hargis, submitted for publication. [f] J. C. Martin and J. H. Hargis, *J. Amer. Chem. Soc.*, **91**, 5399 (1969).

IV). The stability of the *i*-$PrCO_2\cdot$ radical is such that its rate of decarboxylation is comparable to its rate of cage recombination; nevertheless, the viscosity test indicates a very small amount of cage return.[20c,d]

The lack of agreement of the scavenging and viscosity data for TiBu is not unexpected, since the viscosity test should be more sensitive than the CO_2 scavenging method. One-bond behavior will be registered by the viscosity test if radical recombination in the cage is able to compete with decarboxylation; the CO_2 scavenging method, however, requires that addition of the acyloxy radical to an olefin compete with decarboxylation. Since radical recombination is much faster than addition of a radical to an olefin, it is not surprising that the more sensitive viscosity test can detect one-bond behavior for a borderline compound such as TiBu, although the intermediate acyloxy radical cannot be trapped by 4MC.

Two further features of the behavior of this peroxy ester are worthy of mention. Firstly, no study has yet been made by more reliable methods to determine whether this is a one- or two-bond initiator. Both the secondary deuterium isotope effect test[20e] and the ^{18}O method[20b] should be applied to TiBu to test the prediction from our viscosity test.[20f] Secondly, the amount of cage return in octane calculated for TiBu from the data in Table IV is 1%. Despite the moderate confidence level for this slope (91%), the data are sufficiently scattered and the total change in k_{obsd} values from octane to hexadecane is so small (*ca.* 8%) that the intercept of a plot of eq 3 predicts the return to be 1 ± 2%. Thus, the conclusions based on the viscosity data, although reasonable, must be taken as tentative.

Comparison of Peroxy Esters and Diacyl or Diaroyl Peroxides.—It is interesting to compare the amount of cage return for some of the peroxy esters and the corresponding diacyl or diaroyl peroxides which we have studied. Table VII lists three peroxides and the related peroxy esters and shows that each peroxy ester undergoes cage return to a larger extent than the corresponding peroxide (see also Table VIII). In the two cases where R is an alkyl group, methyl or ethyl, this can be explained. Table VI gives rate constants for β scission of acetoxy, propionyloxy, *tert*-butoxy, and benzoyloxy radicals; only the first two radicals undergo β scission fast enough to compete with cage return. Therefore, in going from Ac_2O_2 to TAc, one of the unstable acetoxy fragments is replaced with the relatively stable *tert*-butoxy, and the peroxy ester would be expected to undergo a larger amount of cage return. However, for Bz_2O_2 and TBz, both the $PhCO_2\cdot$ and the *t*-$BuO\cdot$ radicals are stable on the time scale of cage processes. Thus, the smaller amount of cage return for Bz_2O_2 relative to TBz can be explained only by assuming that two $PhCO_2\cdot$ radicals combine more slowly than do a $PhCO_2\cdot$ and a *tert*-butoxy. It is not obvious why this should be true,[12] but it may be related to the ambident nature of the benzoyloxy radicals.[18]

TABLE VIII

CAGE RETURN, f_r, OF ONE-BOND INITIATORS DECOMPOSED IN ALKANE SOLVENTS

			f_r[b]		
			By viscosity test using		
Initiator[a]	Carbon no. of alkane	Temp, °C	$\alpha = 0.5$	$\alpha = 0.7$	By ^{18}O
Ac_2O_2	8	80	0.28[c]	0.18	0.35[d]
TAc	8	100	0.30[e]	0.18	
TAc	9	130	0.12[e]	0.09	
TAc	Nujol	100	0.67[e]	0.61	0.38[f]
TAc	Nujol	130	0.47[e]	0.40	
TPr	8	100	0.23	0.15	
Bz_2O_2	iso-8	80	0.02	0.004	0.04[g]
TBz	8	115	0.17	0.11	0.06[h]
NOON	8	80	0.79[i]	0.49[i]	
TOOT	8	80	0.32	0.20	
TOOT	9	80	0.36	0.22	
	9	100	0.33	0.20	
	9	110	0.18	0.07	
	9	120	0.16	0.07	
	9	130	0.11	0.06	

[a] Acetyl peroxide is listed as Ac_2O_2, and for the other abbreviations, see Table I. [b] The value of f_r was calculated from eq 16, footnote c of this table. [c] W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970). [d] Calculated from eq 19, ref 5b, using the k_s value of J. C. Martin and S. A. Dombchik, *Advan. Chem. Ser.*, **75**, 269 (1968). The solvent is isooctane. [e] Data from Ph.D. Dissertation by K. Smith, Louisiana State University, 1969. [f] T. Koenig and M. Deinzer, *J. Amer. Chem. Soc.*, **90**, 7014 (1968). [g] J. C. Martin and J. H. Hargis, *ibid.*, **91**, 5399 (1969). [h] Calculated as in footnote d using data of T. Koenig, M. Deinzer, and J. A. Hoobler, *ibid.*, **93**, 938 (1971); temperature is 130° and solvent is isooctane. [i] These values are too high; see the discussion in the text.

TABLE IX

RATE CONSTANT, $10^7\ k_{obsd}$, SEC^{-1}, FOR HOMOLYSIS OF DIALKYL PEROXIDES, ROOR, IN ALKANE SOLVENTS[a]

Carbon no. of alkane	R	$(CH_3)_3C$[b] (TOOT)	$(CH_3)_3C$[c] (TOOT)	$(CH_3)_3C$[c] (TOOT)	n-C_4H_9[b] (NOON)
	Temp, °C	80	110	130	80
6		0.164	21.7		
7		0.144	21.9		0.204
8		0.148	21.9		0.158
9		0.136	20.1	254 (250)	
10		0.139	20.1	248	0.143
12		0.129	18.7	244 (246)	0.117
14		0.112	18.2	238 (214)	0.096
16		0.107	18.2	233	0.088

[a] Most rate constants are the average from at least three separate runs. We also measured k_{obsd} for TOOT in Nujol: 110°, 12.9 × 10^{-7} sec^{-1}; 130°, 166 × 10^{-7} sec^{-1}. [b] Rate constant by excess initiator method; iodine was used as the scavenger. [c] Disappearance of peroxide measured directly by the disappearance of an infrared absorption peak at 878 cm^{-1}. The numbers in parenthesis are by excess scavenger technique, using iodine as the scavenger.

Dialkyl Peroxides.—*tert*-Butyl peroxide (TOOT) and *n*-butyl peroxide (NOON) were decomposed in alkane solvents, and k_{obsd} for both initiators decreases with increasing solvent viscosity (Table IX). There-

Table X

Decomposition Products from Alkyl Peroxides, ROOR, in Alkane Solvents at 130°

R	Carbon no. of alkane	10^2 [ROOR]$_0$, *M*	% ROH[a]	% Acetone[a]	ROH/Acetone	ROH/MEK[b]
$(CH_3)_3C$	Benzene[c]	10.14	23.3	76.0		
(TOOT)	iso-8	9.44	98.9			
	8	7.82	96.8	2.5	38.7	
	12	9.45	93.0	2.4	38.8	
	14	9.51	95.8	2.0	47.9	
	16	10.66	93.9	2.3	40.8	
$C_2H_5CH(CH_3)$	12	4.65				1.73
(SOOS)	14	4.79				1.60
	Nujol	4.87				1.05

[a] Based on 2 mol of product per mole of peroxide. [b] The decomposition of *sec*-butyl peroxide was carried out to only one half-life, but the ratio ROH/MEK was checked at different times during the decomposition and was found to be constant. [c] The ratio ROH/acetone = 0.3 from this decomposition of TOOT in benzene compares well with the ratio of 0.6 obtained when TOOT was decomposed in *tert*-butyl benzene at 125°: J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, **70,** 1336 (1948).

fore, these peroxides are one-bond initiators, in agreement with chemical intuition and with the results of other workers.[21]

Our studies of the decomposition products from TOOT in alkanes at 130° (Table X) show that *tert*-butyl alcohol is formed in almost quantitative yield. This indicates that essentially no β scission of the *tert*-butoxy radical occurs, and also that no cage disproportionation occurs between two *tert*-butoxy radicals. We found no *tert*-butyl methyl ether[22] in the reaction products; this also implies that β scission of the *tert*-butoxy radicals does not occur. Calculation from our viscosity data of f_r for TOOT at 80° in octane gives 20–32% cage return, depending on the α value used (see Table VIII). Kiefer and Traylor[23] have studied the photolytic decomposition of TOOT at 45° and have concluded that TOOT undergoes 12% cage return in isooctane. This value is fairly close to the range suggested by our studies, but several facts should be kept in mind when our work and Kiefer and Traylor's are compared. Firstly, our choice of α value of either 0.5 or 0.7 is still somewhat arbitrary. We have shown[7] that several small molecules, including benzene and iodine, diffuse with an α value of 0.7, but we have not studied the diffusion of a molecule which was specifically chosen as a model for *tert*-butoxy radicals (*e.g.*, *tert*-butyl alcohol). Secondly, the procedure used by Kiefer and Traylor can be criticized. They measured the amount of TOOT formed as a cage product from the thermal decomposition of di-*tert*-butyl hyponitrile (DBH) and di-*tert*-butyl peroxyoxalate (TOx) in alkanes at 45°. Decreasing amounts of TOOT were formed from these two compounds with decreasing solvent viscosity, and both compounds gave the same yield of TOOT (4%) in pentane. They then *assumed* that this could be taken as the f_r value for TOOT in pentane, and they used this value together with the k_{obsd} value found by photolysis of TOOT to calculate 12% cage return for TOOT in octane. One weakness of this approach is that even though the same yield of TOOT is produced as a cage product when one N_2 molecule separates two t-BuO· radicals (as in DBH) or when two CO_2 molecules do so (as in TOx), it does not necessarily follow that the same yield of TOOT will be produced by cage return when no molecules at all separate the geminate pair. This could be a very different situation and could produce a larger yield of "cage product" from TOOT relative to DBH or TOx. A second weakness of Traylor's approach is that DBH and TOx were thermalized, but, in order to achieve similar rates, TOOT was photolyzed. It is not safe to assume that thermolysis and photolysis of an initiator give the same extent of cage return. Radicals formed by photolysis can be kinetically excited ("hot"), and their diffusion apart may be enhanced relative to their combination.[24a,b] Clearly, therefore, our measured values of f_r for TOOT are not necessarily in conflict with the results of Kiefer and Traylor.

The amount of cage return for di-*n*-butyl peroxide (NOON), as calculated from our viscosity data, is more than twice as large as f_r for TOOT (Table VIII). We could not follow the disappearance of NOON directly, since there is no significant change in its absorption spectra upon decomposition. Therefore, the excess scavenger technique[5b] was employed. When this method is used, disproportionation of the initially formed radicals in the cage could reduce the yield of scavengable radicals and lower the apparent observed rate constant for decomposition. The amount of this cage disproportionation could increase with solvent viscosity, and part of the viscosity dependence of k_{obsd} could be caused by this. Unfortunately, the decomposition of NOON was not studied by any other method. When we attempted to probe whether the *n*-butoxy radicals undergo cage disproportionation, we found one of the expected products, butyraldehyde, to be unstable in the presence of radicals. Therefore, we studied the decomposition of di-*sec*-butyl peroxide (SOOS) under identical conditions and found that there is a significant amount of cage disproportionation of the *sec*-butoxy radicals. Firstly, a significant amount of methyl ethyl ketone (MEK) is formed, and, secondly, the ratio of *sec*-butyl alcohol to MEK decreases with in-

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[21] E. S. Huyser and R. M. VanScoy, *J. Org. Chem.*, **33,** 3524 (1968); C. Walling and G. Metzger, *J. Amer. Chem. Soc.*, **81,** 5365 (1959); C. Walling and H. P. Waits, *J. Phys. Chem.*, **71,** 2361 (1967).

[22] We analyzed the products by glc and an amount of 3×10^{-5} *M* of *tert*-butyl methyl ether could be detected.

[23] H. Kiefer and T. G. Traylor, *J. Amer. Chem. Soc.*, **89,** 6667 (1967).

(24) (a) W. A. Pryor and R. W. Henderson, *ibid.*, **92,** 7234 (1970), have compared the reaction products from *tert*-butyl peroxyformate when the compound was decomposed thermally and photolytically. Photolysis gave more CO_2 and less formic acid than thermolysis. This can be interpreted as implying that the photolysis is a two-bond process whereas thermolysis is one-bond. (b) Kiefer and Traylor show that both photochemical and thermal decomposition of DBH give the same cage yield of TOOT. However, DBH, an azo compound, probably decomposes from an excited singlet state. If TOOT were to decompose *via* a triplet, then the photochemical and thermal cage return yields would be expected to be different. At present, there is no reason to exclude photodecomposition of TOOT from a triplet state.

creasing solvent viscosity (Table X). We conclude from these results that cage disproportionation also occurs during the decomposition of NOON. Therefore, the amount of cage return calculated from our viscosity data on NOON is too high.[25]

Conclusion.—Thus we conclude that the viscosity test gives the "correct" answer for all the compounds which we have studied. However, for peroxides such as Bz_2O_2 which undergo a very small amount of cage return, the viscosity test may not always be capable of distinguishing one-bond from multi-bond scission.

Experimental Section

Hydrocarbons.—Technical grade alkanes from Phillips Petroleum Co. were purified as previously described.[5b]

Radical Scavengers.—Triply sublimed iodine from W. H. Curtin and Co. was used without further purification. Galvinoxyl was synthesized by the procedure of Kharasch and Joshi.[26] 4-Methyl-1-cyclohexene from Aldrich Chemical Co. was used without further purification. Styrene (Aldrich) was washed with 10% sodium hydroxide and water, dried, and distilled three times under reduced pressure.

Diaroyl Peroxide.—Benzoyl peroxide (Bz_2O_2) (Lucidol) was recrystallized several times from CCl_4 and methanol.

***tert*-Butyl Peroxy Esters.**—*tert*-Butyl peroxyacetate (TAc) and *tert*-butyl peroxyisobutyrate (TiBu), Lucidol, were distilled under reduced pressure at 25°. *tert*-Butyl peroxypropionate (TPr) was prepared by the method of Bartlett and Hiatt[19a] for TAc. A 75% solution of *tert*-butyl peroxypivalate (TPiv) in mineral spirits was purchased from Lucidol. The boiling points of the peroxy ester and the solvent were too close to allow separation by distillation. Chromatography, three passages, on Woelm neutral alumina grade 1, and with hexane as eluent, gave about 10% of 91% pure peroxy ester. The mineral spirits were eluted from the column very shortly before the peroxy ester. *tert*-Butyl peroxybenzoate (TBz), 98% pure (Lucidol), was used without further purification. Di-*tert*-butyl peroxyoxalate (TOx) was prepared by the method of Bartlett, Benzing, and Pincock.[27] The compound was recrystallized from pentane at −78°. (This compound is susceptible to detonation.) The peroxy esters TPr, TiBu, and TPiv were analyzed by iodometric titration.[28]

Dialkyl Peroxides.—*tert*-Butyl peroxide (TOOT), Lucidol, was used without further purification. *n*-Butyl peroxide (NOON) was prepared by the method of Mosher, *et al.*[29] *sec*-Butyl peroxide (SOOS) was synthesized by the method of Pryor and coworkers.[30]

Determination of CO_2 from Homolysis of Peroxy Esters.—Round-bottom ampoules (25 ml, Kontes) with two sealed tip side arms, 7 × 100 mm, were used as reaction vessels. The peroxy ester solution and a Teflon stir bar were introduced into the ampoule through its 10 × 70 mm neck, which was connected to a vacuum pump during the degassing procedure and thereafter was sealed off. The sealed ampoules were immersed in a constant-temperature bath and after complete reaction, the CO_2 was measured by absorption on Ascarite, KOH on asbestos (A. H. Thomas Co.) by the method of Shine and coworkers.[8b]

Procedure for Kinetic Runs.—We have used three methods for obtaining rate constants for homolysis of radical initiators: direct observance of initiator disappearance, first-order disappearance of scavenger, or zero-order disappearance of scavenger. These methods have been described previously,[5b] and the raw data were treated by a computer program to obtain a least squares fit of the data to the applicable rate law. Tables III, IV, and IX indicate the method used to find the rate constant for each peroxy compound. Our estimate of the accuracy of the rate constants is ±6% as determined from the probable error in each rate constant and the random variation in k_{obsd} with solvent viscosity for the multi-bond initiators in Table IV.

Registry No.—Benzoyl peroxide, 94-36-0; TAc, 107-71-1; TPr, 14206-05-4; TiBu, 109-13-7; TPiv, 927-07-1; TBz, 614-45-9; TOx, 1876-22-8; Ac_2O_2, 110-22-5; NOON, 3849-34-1; TOOT, 110-05-4; SOOS, 4715-28-0.

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(25) (a) β Scission of the *n*-BuO· radical to formaldehyde and a propyl radical is considered negligible, since no β scission occurs for the *t*-BuO· radical, and both reactions have the same activation energy (13 kcal/mol) and preexponential ($\sim 10^{14}$ sec^{-1}) for β scission.[25b] The other decomposition mode of the *n*-BuO· radical to form a hydrogen atom and butyraldehyde will occur with even less probability.[25b] (b) P. Gray, R. Shaw, and J. C. J. Thynne in "Progress in Reaction Kinetics," Vol. 4, G. Porter, Ed., Pergamon Press, Oxford, 1967, pp 92–93.

(26) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).

(27) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, **82**, 1762 (1960).

(28) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

(29) F. Welch, H. R. Williams, and H. S. Mosher, *J. Amer. Chem. Soc.*, **77**, 551 (1955).

(30) W. A. Pryor, D. M. Huston, T. R. Fiske, T. L. Pickering, and E. Ciuffarin, *ibid.*, **86**, 4237 (1964).

The Synthesis and Properties of Phosgene Phenylhydrazones

M. W. MOON

The Upjohn Company, Kalamazoo, Michigan 49001

Received December 13, 1971

Methods for the synthesis of phosgene phenylhydrazones, a new group of imidoyl chlorides, are described. Chlorination of various 2,3,4-pentanetrione 3-phenylhydrazones gave ring-substituted 1,1-dichloro-1-phenylazo-2-propanones that were readily hydrolyzed to the corresponding phosgene phenylhydrazones. Chlorination of glyoxylic acid 2-[(2,4,6-trichlorophenyl)hydrazone] (**19**) and formaldehyde (*p*-nitrophenyl) hydrazone (**23**) gave phosgene (2,4,6-trichlorophenyl)hydrazone (**10a**) and phosgene (2-chloro-4-nitrophenyl)hydrazone (**26**), respectively. Phosgene phenylhydrazones react relatively slowly with nucleophilic reagents with displacement of both acid chloride substituents; products formed by displacement of only one chlorine atom were not detected.

The chemistry of imidoyl halides has received considerable attention in the past and has recently been reviewed by Ulrich.[1] In the course of studies on the chlorination of phenylhydrazones we have discovered a new group of imidoyl chlorides, the phosgene phenylhydrazones (**2**); the preparation and properties of these compounds are detailed herein.

While synthesis of the carbonyl halide hydrazones **3**[2] and **4**[3] and preparation of a variety of carbonyl halide azines have been described,[2,4] no phosgene phenylhydrazone had been reported prior to our description of phosgene (2,4,6-trichloro-*m*-tolyl)hydrazone, which was prepared by refluxing ethyl dichloro[(2,4,6-tri-

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(1) H. Ulrich, "The Chemistry of Imidoyl Halides," Plenum Press, New York, N. Y., 1968.

(2) J. Thiele, *Justus Liebigs Ann. Chem.*, **303**, 57 (1898).

(3) R. C. Dobbie and H. J. Emeleus, *J. Chem. Soc. A*, 933 (1966).

(4) (a) H. Reimlinger, *Chem. Ber.*, **97**, 3505 (1964); (b) R. A. Mitsch and P. H. Ogden, *J. Org. Chem.*, **31**, 3833 (1966); (c) F. L. Scott and D. A. Cronin, *Chem. Ind. (London)*, 1757 (1964); (d) F. L. Scott, J. Donovan, and J. K. O'Halloran, *Tetrahedron Lett.*, 4079 (1970).