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One-Bond and Two-Bond Homolytic Scission of *tert*-Butyl *p*-Nitrophenylperacetate[1]

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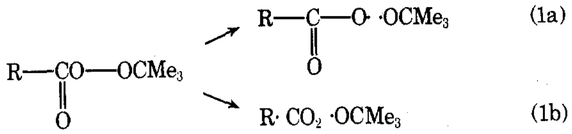
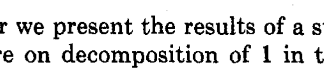
It is accepted that some *tert*-butyl peresters thermally decompose by one-bond scission (eq 1a) while others decompose by simultaneous scission of two bonds (eq 1b) so as to produce carbon dioxide in the primary step.[2–5] However, the proposal that a few peresters decompose simultaneously by both pathways[4,6] remains controversial.[3,5,7]



R groups which can become reasonably stable radicals (R·), such as diphenylmethyl,[2,6] trityl,[8] *tert*-butyl,[2,4,7,9,10] *p*-methoxybenzyl[3,6,11,12] and *p*-methylbenzyl,[6,11,12] lead to decomposition via path 1b, while phenyl,[2,13] vinyl,[14] methyl,[2–4] and ethyl[4] groups promote one-bond scission (eq 1a). One perester which has been proposed to decompose by both routes is *tert*-butyl *p*-nitrophenylperacetate (**1**).[6]

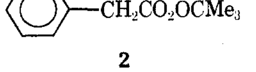


1

In this paper we present the results of a study of the effect of pressure on decomposition of **1** in the solvent cumene. We feel that the data indicate that **1** decomposes only by two-bond scission; however, the results are not unambiguous.

Results and Discussion

The rates of decomposition of **1** (cumene, 85°) at various pressures are given in Table I along with data for unsubstituted *tert*-butyl phenylperacetate (**2**) under the same conditions. The atmospheric pressure data for these two peresters give the solid point in Figure 1.[15] This Hammett plot for decomposition of ring-substituted *tert*-butyl phenylperacetates was drawn using data obtained by Bartlett (chlorobenzene, 90.7°)[11] and by Behar (cumene, 79.6°)[12] and the fit of this solid point provides justification for comparison of these studies of **1** to the earlier data.[11,12] A question had been raised that the apparent positive deviation of Bartlett's point for **1** in chlorobenzene from the best straight line through the other points (Figure 1) might reflect induced decomposition.[11] The congruence of our data point for **1** in cumene with that for **1** in chlorobenzene suggests, however, that induced decomposition is probably not important. It seems unlikely that it would occur to the same extent in these two different solvents.



2

Table I
Rate Constants for Decomposition of *tert*-Butyl *p*-Nitrophenylperacetate (**1**) and *tert*-Butyl Phenylperacetate (**2**) in Cumene at 85°

Perester	P, atm	$k \times 10^5$, sec^{-1}
1	1	3.10 ± 0.06
	1250	2.74 ± 0.04
	2000	2.73 ± 0.07
	3000	2.65 ± 0.04
	4000	2.71 ± 0.06
	6000	2.02 ± 0.07
2	1	13.2
	2000	12.3
	4000	10.6

[a] Ranges reported are derived from least-squares analysis of the kinetic data.

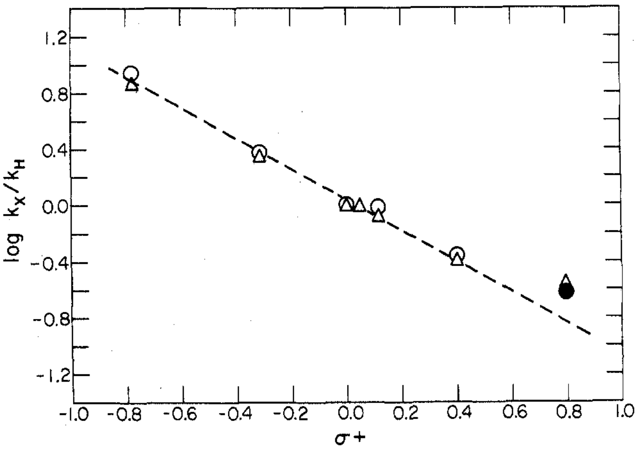


Figure 1. Plot of log (k_X/k_H) vs. σ^+ for thermal decomposition of ring substituted *tert*-butyl phenylperacetates where, from left to right, X = *p*-MeO, *p*-Me, H, *m*-Me, *p*-Cl, *m*-Cl, and *p*-NO_2 in chlorobenzene at 90.7° (△), cumene at 79.6° (○), and cumene at 85° (●).

The data for **2** were determined at 85° not only to provide results for the Hammett plot, but to see if the same pressure dependence obtained in the earlier study[12] was observed. A comparison of the earlier data for **2** at 79.6° with those determined here at 85° (Figure 2) show that this is the case.

The data for **1** are plotted in Figure 2 along with those for *tert*-butyl phenylperacetate, *tert*-butyl trimethylperacetate,[7] *tert*-butyl dimethylperacetate[7] and the cis and trans isomers of *tert*-butyl 2-propyl-2-peroxypentenoate (**3**).[14] These latter two peresters decompose by one-bond

$$EtCH{=}C(CH_2Et)CO_3CMe_3$$

3

scission[14] (path 1a) while the trimethylperacetate is generally accepted to decompose by two-bond scission.[2,4,7,9,10] It seems to us that two families of curves are visible in this figure and that the data for **1** fall within that family with a

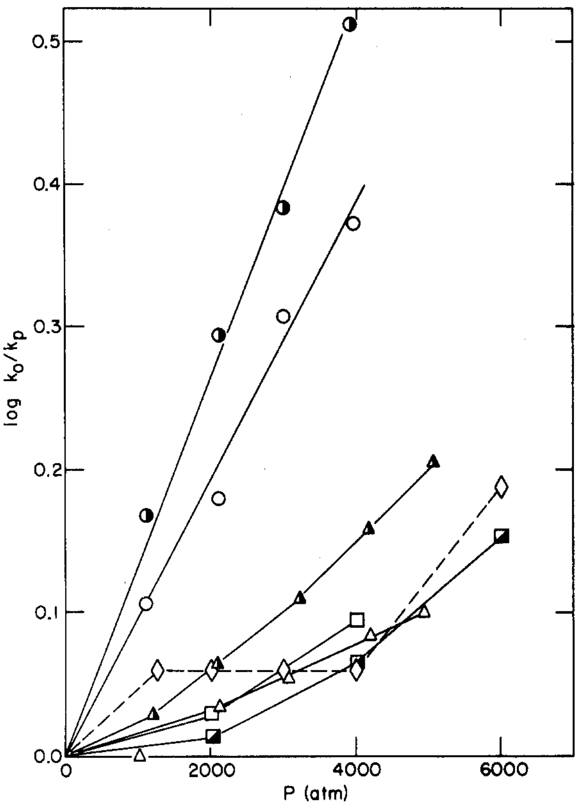


Figure 2. Pressure dependence of the decomposition rates of *cis*- (○) and *trans*- (◑) *tert*-butyl 2-propyl-2-peroxypentenoate, *tert*-butyl phenylperacetate (◪, 79.6°; □, 85°), *tert*-butyl trimethylperacetate (△), *tert*-butyl dimethylperacetate (▲), and *tert*-butyl *p*-nitrophenylperacetate (◇).

small pressure dependence that we have argued[5,7] is characteristic of a two-bond scission decomposition mechanism.[16]

The interpretation that 1 decomposes by two-bond scission would be consistent with kinetic isotope studies reported by Koenig.[3] The basis for proposing that 1 and some other peresters[17] decompose simultaneously by two mechanisms has been derived primarily from the effects of varying medium viscosity on the observed rates of decomposition of these peresters.[4,6] It is assumed that variation in the viscosity of solvents will not affect the rate of decomposition of peresters decomposing by path 1b, but that increasing viscosity will retard decomposition by path 1a because separative diffusion of the first formed radicals (k_d, eq 2)

$$\mathrm{RCO_2OCMe_3} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overline{\mathrm{RCO_2\cdot \cdot OCMe_3}} \begin{matrix} \xrightarrow{k_d} \\ \xrightarrow[k_c]{} \end{matrix} \qquad (2)$$

will be retarded causing the radicals to revert to starting perester (k_{-1}) a greater percentage of the time.

This "viscosity test" has been very useful in probing the decomposition mechanisms of a variety of free-radical initiators. Large rate retardations have been observed for various phenylazotriphenylmethanes, dialkyl peroxides, and diacyl peroxides, clearly demonstrating that one-bond scission occurs with "cage return" of the primary geminate radicals.[4,6] Conversely, a variety of symmetrical azo compounds as well as certain *tert*-butyl phenylperacetates including the *p*-methoxy and *p*-methyl substituted compounds show no rate dependence on viscosity suggesting two-bond scission decomposition mechanisms.[4,6]

However, in the cases of the peresters proposed to decompose by both paths the dependences of decomposition rates on solvent viscosity have been small and irregular. Since perester decompositions seem to involve polar contributions in the homolytic scission transition states,[5,7,11,12] we have suspected that the small effects observed with viscosity variation could be due to a combination of experimental uncertainty and solvation effects. Viscosity variation is accomplished by changing the solvent.[18]

Several years ago we showed that the effect of externally applied pressure on the rates of solution phase initiator decompositions could be used as a diagnostic test for one- *vs.* two-bond scission.[5,19] Pressure increases the viscosity of the solvent causing k_d to decrease, thus leading to a marked retardation of the apparent rate of initiator decomposition when cage return can occur (eq 2). The effect is similar to that of the viscosity test with two important distinctions: (1) the medium is not varied to achieve the viscosity change; and (2) all homolytic scission reactions, whether occurring by one- or two-bond scission, are retarded to some extent by pressure because homolytic scission leads to an expanded transition state.

The first point is an advantage because changes in solvation with medium variation are avoided. The second requires that a baseline be established for the pressure effect on homolytic scission processes uncomplicated by return. Extensive studies of a variety of radical initiators indicate that activation volumes for homolytic scission without return are less than or equal to +5 cm^3/mol, while activation volumes for scission complicated by return are substantially greater. Decomposition of 1 shows an overall pressure dependence less than that corresponding to a ΔV^* of +5 cm^3/mol. Between 1 and 1250 atm the apparent ΔV^* is +3 cm^3/mol, there is no significant effect of pressure on rate between 1250 and 4000 atm, and the ΔV^* between 4000 and 6000 atm is +4 cm^3/mol. Thus, we feel that 1 should be classified as a two-bond scission initiator. It is always possible that one-bond scission (path 1a) could occur without return and our data cannot distinguish this from two-bond scission. However, if the solvent dependence of the decomposition rate of 1 at atmospheric pressure[6] is due to an effect on diffusion which competes with return, we would have expected a much larger ΔV^* value in these pressure studies than that which was observed.

A troubling aspect of our results for 1 is the apparent plateau in the log *k* vs. *P* plot (Figure 2). Outside of experimental error, we have no ready explanation for this other than that it could indicate a mixture of mechanisms. In this case the shape of the curve would suggest a competition between a pressure-retarded process and one that was pressure accelerated. This would not be consistent with competing one- and two-bond scission (eq 1a and 1b) because both of these reactions would be pressure retarded. It could indicate the presence of induced decomposition facilitated by increasing pressure. This would lead to an apparent rate increase offsetting the pressure-induced retardation associated with bond scission. We have argued earlier against induced decomposition based on the comparative results in cumene and chlorobenzene. Also our prejudice is that any induced decomposition process would not overshadow the large ΔV^* value expected for one-bond scission with return. Thus we stand behind our interpretation of two-bond scission with the hope that future studies might clarify the unusual aspects of the data obtained here.

Experimental Section

Materials. All solvents were carefully purified. *tert*-Butyl hydroperoxide (Lucidol) was distilled (bp 34–35°, 18–20 mm) and its purity confirmed by iodimetric titration.

***tert*-Butyl Phenylperacetate.** This perester was synthesized from phenylacetyl chloride and *tert*-butyl hydroperoxide as previously reported:[13] ir 1775 cm^{-1}; NMR δ 7.04, 3.24, 1.06 with respective areas of 5, 2, and 9.

***tert*-Butyl *p*-Nitrophenylperacetate.** This perester was synthesized from *p*-nitrophenylacetyl chloride (mp 45.6–46.6°, ir 1800 cm^{-1}) and *tert*-butyl hydroperoxide by the procedure described by Bartlett and Rüchardt.[11] The compound was a crystalline solid: ir 1775 cm^{-1}; NMR δ 8.10, 7.40, 3.61, 1.20 with respective areas of 2, 2, 2, and 9.

Kinetic Studies. Thermal decomposition of 0.1 *M* solutions of the respective peresters in carefully purified cumene was monitored by infrared spectroscopy as previously described.[13] The high-pressure apparatus and procedures concerning its use in kinetic studies have been described in detail.[12,13]

Registry No.—**1,** 29540-08-7; **2,** 3377-89-7; *cis*-**3,** 33509-65-8; *trans*-**3,** 33509-66-9; *tert*-butyl trimethylperacetate, 927-07-1; *tert*-butyl dimethylperacetate, 109-13-7; *tert*-butyl *p*-methoxyphenylperacetate, 27396-21-0; *tert*-butyl *p*-tolylperacetate, 27396-20-9; *tert*-butyl *m*-tolylperacetate, 56391-29-8; *tert*-butyl *p*-chlorophenylperacetate, 27396-18-5; *tert*-butyl *m*-chlorophenylperacetate, 27396-17-4; *tert*-butyl hydroperoxide, 75-91-2.

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(15) The solid point corresponds to log $k_{p\text{-NO}_2}/k_H$ from Table I.
(16) The only other pressure data available for a one-bond scission perester are limited results for *tert*-butyl perbenzoate (R = phenyl)[13] which give a ΔV^* (and pressure dependence) even greater than those for the vinyl peresters.
(17) Besides *tert*-butyl *p*-nitrophenylperacetate, it had been suggested that *tert*-butyl phenylperacetate and *tert*-butyl dimethylperacetate also might simultaneously decompose by paths 1a and 1b[4,6] but the evidence was weak. In any case, earlier data reported by us seem to rule out this possibility for the latter two systems.[7,12]
(18) (a) Traylor[18b] has seen evidence for solvent effects using homologous saturated hydrocarbon solvents in which to decompose di-*tert*-butyl hyponitrite ($Me_3CON{=}NOCMe_3$), a compound most certainly decomposing via two-bond scission.[18c] (b) H. Kiefer and T. Traylor, *J. Am. Chem. Soc.*, **89,** 6667 (1967). (c) R. C. Neuman, Jr. and R. J. Bussey, *ibid.*, **92,** 2440 (1970).
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Chelation and the Nucleophilicity of α-Ketoaldehyde and α-Diketone Monophenylhydrazones

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Certain properties of hydrazones have been attributed to chelation. Thus, Fieser and Fieser[1] suggested that chelation of saccharide bishydrazones (osazones) was responsible for their stability, and Chapman[2] attributed to chelation the fact that osazone formation did not proceed beyond C-2 to give, for example, tris- or tetrakishydrazones. Further, it was suggested[3–5] that osazones form mono-*N*-acyl derivatives and not diacylated ones, because chelation inhibited the acylation of the imino nitrogen whose proton was involved in hydrogen bonding. By analogy, it was assumed that chelation was the reason why the bishydrazones of benzil and phenylglyoxal could only undergo monoacylation.[6–7]

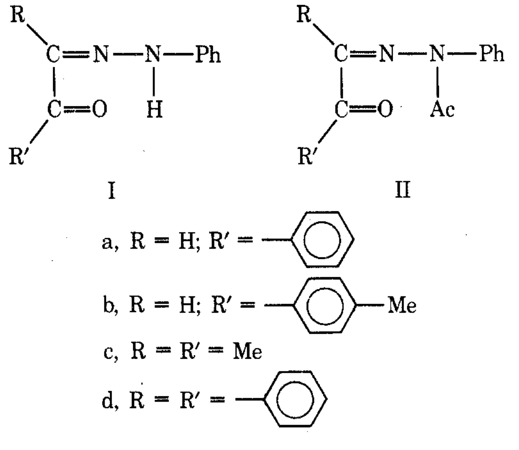
Table I
Summary of ^{1}H NMR Parameters[a]

Compd	Solvent	OH	NH	Aromatic	HC=	$-CH_3$
Ia	*b*	14.66	12.1	6.8–8.4	7.36, 7.91	
Ib	*b*	14.60	12.1	6.8–8.4	7.40, 7.96	2.28
Ic	*d*		8.1	6.9–7.4		2.01, 2 05
Id	*d*		7.9	7.4–8.1		
IIa	*c*			7.0–8.1	7.41	3.55
IIb	*b*			7.1–8.2	7.20	2.28, 2.50

[a] Chemical shift in δ from Me_4Si. [b] Pyridine-d_5. [c] Me_2SO-d_6 [d] $CDCl_3$.

To verify whether involvement of the imino protons of hydrazones in hydrogen bonding inhibited the ability of the imino nitrogen to undergo acylation, we studied the acetylation of substituted α-ketoaldehyde monophenylhydrazones and α-diketone monophenylhydrazones.

It was found that in substituted α-ketoaldehyde monophenylhydrazones of type I (R = H; R′ = Ar), acetylation occurred readily, affording the *N*-acetyl derivatives IIa or IIb. The latter compounds were completely colorless, unlike the starting monophenylhydrazones, which were yellow. On the other hand, substituted α-diketone monophenylhydrazones I (R = R′ = Me or Ph) resisted acetylation even on prolonged boiling with acetic anhydride.



A correlation could be made between the reactivity of α-ketoaldehyde monophenylhydrazones (Ia and Ib) and their existence in chelated tautomeric forms. Their ^{1}H NMR spectra (see Table I) showed two resonances in the downfield region of the spectrum, one at δ 12.1 and one at δ 14.6, which together integrated for one exchangeable proton, suggesting their existence as equilibrium mixtures. The chemical shift of the signal at δ 12.1 was comparable to that of the chelated imino protons of bisarylhydrazones[8–10] and the signal at δ 14.6 was quite close to that of chelated enolic protons in bisaroylhydrazones.[11] Accordingly, the observed resonances at δ 12.1 and 14.6 were assigned to the chelated keto structure A and the enol structure B, respectively. Analogous keto–enol tautomerisms have been observed in bisaroylhydrazones.[11,12] The existence of compounds Ia and Ib in the form of tautomeric mixtures was also appar-