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POLAR SOLVENT EFFECTS ON THE HOMOLYTIC DECOMPOSITION OF A PERESTER

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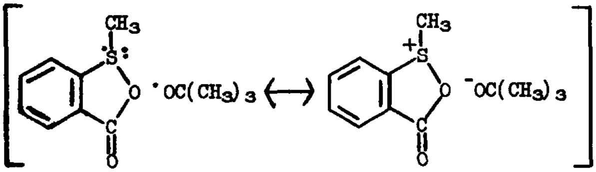
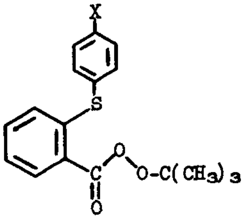
THE enhancement in rate of the radical decompositions of t-butyl perbenzoates containing an <u>ortho</u> sulfide grouping has been attributed to anchimeric[1] acceleration by sulfur. We have postulated[2] that the decomposition of t-butyl <u>o</u>-(methylthio)-perbenzoate proceeds through a singlet transition state represented by canonical forms I and II.



I

II



IIIa X = H
IIIb X = $-OCH_3$
IIIc X = -Cl
IIId X = $-NO_2$

The effects on the rate of thermal decomposition of IIIa resulting from the introduction of substituents into the para position of the phenylthio grouping and the effects of changes in the polarity of the solvent described herein serve to establish an important contribution to the transition state by dipolar structures such as II. The types of products

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[1] S. Winstein, C.R. Lindegren, H. Marshall and L. Ingraham, <u>J. Amer. Chem. Soc.</u> <u>75</u>, 147 (1953).

[2] J.C. Martin and W.G. Bentrude, <u>Chem. & Ind.</u> 192 (1959); W.G. Bentrude and J.C. Martin, <u>J. Amer. Chem. Soc.</u> in press.

isolated and the trapping of intermediates by radical scavengers indicate that the decompositions, for which these substituent and solvent effects are observed, do follow a free-radical pathway.[2]

The rates of the first-order decomposition of IIIa-IIId in chlorobenzene (with 0.2 M added styrene) were measured at three temperatures by observing the disappearance of the perester carbonyl in the infrared. The relative rates at 50.3° are as follows: IIIa, 1.0; IIIb, 1.8; IIIc, 0.32; IIId, 0.092. The rates at this temperature are correlated by σ, not σ^+, in a Hammett treatment with $\rho = -1.4$. The sign and magnitude of ρ indicate that the contribution to the transition state by dipolar structures involving positive charge on sulfur may be quite large.

The rate of the radical decomposition of IIIa is quite sensitive to changes in solvent polarity. We have determined the rate of decomposition as reflected in the zero-order disappearance of the 570 mμ absorption of the radical scavenger galvinoxyl[3] in a system containing a large excess of perester. The first-order decomposition of IIIa was also followed by disappearance of the carbonyl peak in the infrared spectrum. The results at 40° are summarized in Table 1.

The thesis that these changes in rate on variation of solvent reflect the ability of the solvent to stabilize charge dipoles, i.e. that the solvent effect is a polar solvent effect, is supported by the fact that these changing rates may be correlated with two accepted measures of solvent polarity, the Z values of Kosower[4] and the recently proposed[5] measure of solvent polarity based on the rate of ionization of p-methoxyneophyl p-toluenesulfonate. We obtain a linear plot (Fig. 1) of log k for

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[3] P.D. Bartlett and C. Ruchardt, J. Amer. Chem. Soc. **82**, 1756 (1960).

[4] E.M. Kosower, J. Amer. Chem. Soc. **80**, 3253, 3267 (1958).

[5] S.G. Smith, A.H. Fainberg and S. Winstein, J. Amer. Chem. Soc. **83**, 618 (1961).

TABLE 1

Rate of Decomposition of Perester IIIa at 40°

Solvent	$k \times 10^4$ (sec^{-1})		% trap
	I.R.[a]	Scavenger[b]	
Cyclohexane[c]	0.0686	0.024	35
Tetrahydrofuran	0.300		
Chlorobenzene	1.03	0.48	47
Acetone	1.22	0.67	55
90% Dioxane-10% water	2.40		
t-Butanol	3.24		
Acetonitrile	5.44	2.4	44
Dimethylsulfoxide	6.02		
80% Dioxane-20% water	7.19		
2-Propanol	7.25		
Ethanol	16.5	5.9	36
Methanol	47.5	11	23

[a] Rates followed by infrared spectroscopy.

[b] Rates followed by use of the scavenger, galvinoxyl.

[c] I.R. rates extrapolated from plot of ln.k/T vs.1/T. All I.R. rates except those designated by c are from runs including 0.2 M styrene.

the ionization of the tosylate vs. log k for the perester disappearance with a slope of 0.64. A similar correlation with log k for free-radical scavenging is illustrated. This indicates that the radical decomposition of IIIa is about 64% as sensitive to solvent polarity as is this ionization reaction over a wide range of solvent types and solvent polarities.

Linearity in plots of log k/T vs. 1/T for the decomposition of IIIa in cyclohexane and chlorobenzene renders improbable a mechanism for decomposition involving competition between radical and ionic paths.[2] However, it does not rule out a mechanism involving a rate-determining ionization to an intermediate which can react to give products by competing ionic and radical mechanisms. The relative rates of the two path-

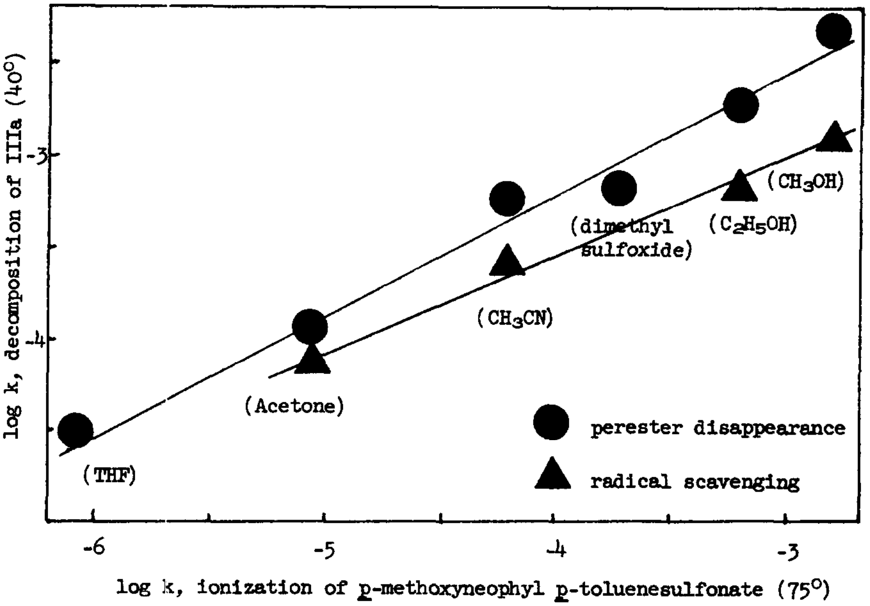
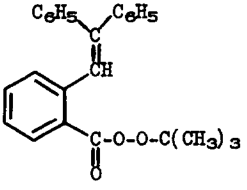


FIG. 1

Solvent dependence of perester decomposition.

ways in such a mechanism would be expected to be sensitive to changes in solvent polarity, and one would expect a drastic reduction of the ionic portion in a non-polar solvent such as cyclohexane. The results in Table 1 show that the fraction of the total rate constant accounted for by use of the scavenger galvinoxyl is lower in cyclohexane than in chlorobenzene. The related observation, from Fig. 1, that the change in the rate of disappearance of perester very closely parallels the rate of radical production with changing solvent seems to rule out any major contribution from an ionic reaction. Decomposition of IIIa in acetic acid yields approximately 15% of acetone (isolated as the 2,4-dinitrophenylhydrazone). This indicates that even in this highly polar solvent the radical reaction is important. We have been unable to formulate any plausible ionic mechanism, consistent with substituent effects described earlier, which will yield acetone.



IV

Honsberg and Leffler[6] have reported rate data, obtained over a smaller range of solvent polarity (benzene-nitrobenzene), which indicate that the rate of decomposition of o-iodo-p'-nitrobenzoyl peroxide is quite sensitive to solvent polarity. The radical decomposition of perester IV, involving anchimeric acceleration by the neighboring double bond, has also been shown[7] to be sensitive to solvent polarity, presumably for reasons similar to those important in the decomposition of IIIa.

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[6] W. Honsberg and J.E. Leffler, J. Org. Chem. **26**, 733 (1961).

[7] Unpublished results of Thomas W. Koenig.