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CAGE EFFECTS AND THE SIGNIFICANCE OF ACTIVATION VOLUMES[1,2]

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Recently, we communicated results which showed that volumes of activation for homolytic scission reactions did not generally reflect the pressure coefficient of the bond scission process.[1] In those systems in which the primary geminate radical products could return to starting material the observed activation volumes included the pressure dependence of the ratio k_{-1}/k_2 leading to

$$\text{A-B} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (\text{A}\cdot\ \text{B}\cdot) \xrightarrow{k_2} \text{A}\cdot + \text{B}\cdot \qquad (1)$$

values significantly greater than the true value of ΔV_1^*. It was pointed out that homolytic scission reactions involving one bond cleavage would generally be expected to follow the general scheme outlined in (1), whereas reactions which involved concerted breaking of two or more bonds in the primary transition state would be unlikely to involve cage return (k_{-1}) and would give values of ΔV^*_{obs} equal to ΔV_1^*. Perester decomposition can occur by both mechanisms[3] and the observed volumes of activation for t-butyl phenylperacetate (I) decomposition (a two-bond process)[4] in cumene and chlorobenzene of +1 to +2 cc/mole were proposed as representative of values of ΔV_1^*.[1] Support for this proposal included the results of product studies at 1 and 4000 atm. indicating no induced decomposition or major mechanism changes at high pressure, and the observation that activation volumes for thermal decomposition of t-butyl perbenzoate (a one-bond scission perester)[3] were in the region of +11 to +13 cc/mole.

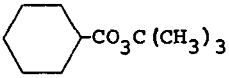
However, it has been proposed that a polar structure such as II contributes

$$\text{R}\overset{\delta+}{--}\text{CO}_2\text{--}\overset{\delta-}{-}\text{OC(CH}_3)_3$$

II

to the transition state for decomposition of I.[4] This suggests that solvent electrostriction[5] may contribute to the measured activation volume for I with the result that it would be somewhat smaller than the true value ΔV_1^*. Additionally, the apparent activation volume for decomposition of azo- bis-isobutyronitrile, mechanistically quite similar to that of I, is about +4 cc/mole.[6]

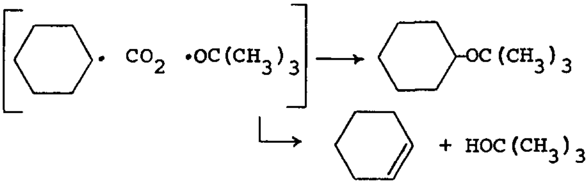
Carbo-t-butylperoxycyclohexane (III)[7] should be a two-bond scission per-



III

ester according to Bartlett's criteria[3] and additionally may be less susceptible to polar effects of the type shown in II based on the relative stabilities of benzyl and cyclohexyl carbonium ions. A study of its thermal decomposition as a function of pressure in cumene (79.55°) gave the kinetic data in Table I and the product data in Table II. The resulting activation volume (+3.9 ± 0.5 cc/mole) suggests to us that those values reported for t-butyl phenylperacetate may be abnormally low due to solvent electrostriction.[8,9]

Detailed product data have not been previously available for decomposition of III.[7] This system is particularly interesting because cage reactions can include both coupling (reaction 2) and disproportionation (reaction 3). The



(2)

(3)

effect of pressure on this competition will give information about the relative activation volumes for these two processes and additionally little is known about the relative importance of these reactions for a t-butoxy-alkyl radical pair. Although an extra-cage source of t-butyl cyclohexyl ether is virtually impossible, cyclohexene could conceivably arise in a disproportionation reaction between free cyclohexyl and cumyl radicals. However, we consider this to be an unlikely event. The diffused cyclohexyl radical most likely abstracts hydrogen from cumene (an energetically favorable reaction) to give cyclohexane (see Table II) and disproportionation of cyclohexyl and cumyl radicals would probably lead mainly to cyclohexane and α-methylstyrene.[10]

Using the combined yields of t-butyl cyclohexyl ether and cyclohexene as a measure of the cage effect, the increase from 30% (1 atm.) to 62% (4000 atm.) corresponds to a value of +11 cc/mole for ΔV^* (diffusion) - ΔV^* (cage reactions) which is very similar to the value +10 cc/mole obtained in our studies of I.[1] The pressure variation of the relative yields of ether and cyclohexene give a

Table I. Carbo-t-butylperoxycyclohexane Kinetic Data at 79.55° in Cumene.[a]

Pressure (atm.)	$k \times 10^{5}$ (sec^{-1})
1	1.86±0.07
2000	1.42
4000	1.15±0.03

a. Reactions followed by infrared spectroscopy.

Table II. Carbo-t-Butylperoxycyclohexane Product Data at 79.55° in Cumene.[a]

	% yield		
Product	1 atm.	2000 atm.	4000 atm.
t-butanol	72.3	60.8	52.6
acetone	tr	tr	tr
cyclohexytl t-butyl ether	17.2	(25)	33.1
total t-butoxy	89.5	(86)	85.7
cyclohexyl t-butyl ether	17.2		33.1
cyclohexene	12.8		28.4
cyclohexane	57.0		29.2
total cyclohexyl	87.0		90.7

a. Determined by glpc.

value of +1 cc/mole for ΔV^*(coupling) - ΔV^*(disproportionation), indicating that the activation volumes for these two types of processes are very similar. The relative yields of ether and cyclohexene at atmospheric pressure further indicate that the coupling and disproportionation reactions between t-butoxy and cyclohexyl radicals are quite competitive.

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(8) The greater endothermicity for decomposition of III compared to I suggests that greater bond breaking has occurred at the transition state for the former. This could also lead to a larger value of ΔV_1^* for III.

(9) The magnitude of ΔV_1^* for decomposition of III supports the two-bond scission mechanism for this compound.

(10) This conclusion is based on steric considerations and the relative stabilities of the possible disproportionation products.