

the solvent-separated fluorenyl ion pair the coordinating ether molecules are very close to the aromatic ring, and the shielding effect due to the aromatic ring current apparently causes the strong upfield shift. These shifts are reminiscent of those found for dimethoxyethane in mixtures of benzene with fluorenyllithium,<sup>5</sup> although it is probable that in this case solvated contact ion pairs are involved.

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(5) J. A. Dixon, P. A. Gwinner, and D. C. Lini, *J. Am. Chem. Soc.*, **87**, 1379 (1965).

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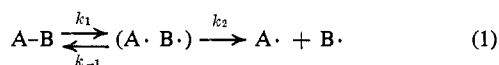
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### Activation Volumes of Homolytic Scission Reactions. *t*-Butyl Phenylperacetate

Sir:

Homolytic scission reactions are characterized by relatively large positive activation volumes.<sup>1-6</sup> With the exception of the *t*-butyl peroxide data in benzene and carbon tetrachloride,<sup>1,6</sup> these have been presumed to reflect the volume difference between ground and transition state for homolytic scission. However, recent work now suggests that none of these data (with the possible exception of that for AIBN) directly measures the pressure dependence of the bond-scission process.

The effective assumption made in identifying  $\Delta V^*$  with this process ( $k_1$ ) is that internal return ( $k_{-1}$ ) does not occur. However, this has now been demonstrated



to be significant in atmospheric pressure solution phase decomposition of acetyl peroxide,<sup>7,8</sup> *p*-nitrophenylazotriphenylmethane (NAT),<sup>8</sup> and *t*-butyl peroxide,<sup>9</sup> suggesting that this feature characterizes the majority of the systems studied as a function of pressure.<sup>1,10</sup> Observed decomposition rate constants are therefore not equal to  $k_1$  but rather to  $k_1/(1 + k_{-1}/k_2)$ , and the activation volumes represent a composite pressure effect. Increasing pressure most certainly decreases  $k_1$ , and other studies of geminate recombination reactions<sup>2,11,12</sup> show that the ratio  $k_{-1}/k_2$  is increased.

(1) Compound, solvent, temperature,  $\Delta V^*$  (cc/mole): AIBN,<sup>2</sup> toluene, 62.5°, +3.8; benzoyl peroxide,<sup>3</sup> CCl<sub>4</sub>, 60°, +9.7; benzoyl peroxide,<sup>4</sup> styrene, 30°, +10; benzoyl peroxide,<sup>9</sup> acetophenone, 80°, +5; *t*-butyl peroxide<sup>6</sup> (DBPO), benzene, 120°, +13; DBPO,<sup>8</sup> CCl<sub>4</sub>, 120°, +13; DBPO,<sup>6</sup> cyclohexene, 120°, +7; DBPO,<sup>6</sup> toluene, 120°, +5; pentaphenylethane,<sup>2</sup> toluene, 70°, +13.

(2) A. H. Ewald, *Discussions Faraday Soc.*, **22**, 138 (1956).

(3) A. E. Nicholson and R. G. W. Norrish, *ibid.*, **22**, 97 (1956).

(4) A. E. Nicholson and R. G. W. Norrish, *ibid.*, **22**, 104 (1956).

(5) C. Walling and J. Pellon, *J. Am. Chem. Soc.*, **79**, 4786 (1957).

(6) C. Walling and G. Metzger, *ibid.*, **81**, 5365 (1959).

(7) J. W. Taylor and J. C. Martin, *ibid.*, **88**, 3650 (1966).

(8) W. A. Pryor and K. Smith, *ibid.*, **89**, 1741 (1967).

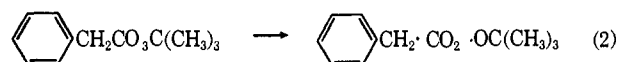
(9) C. Walling and H. P. Waits, *J. Phys. Chem.*, **71**, 2361 (1967).

(10) Internal return in AIBN decomposition will be unlikely if N<sub>2</sub> is a primary decomposition product (*vide infra*).

(11) T. C. Vogt, Jr., and W. H. Hamill, *J. Phys. Chem.*, **67**, 292 (1963).

Thus, the values<sup>1</sup> of  $\Delta V^*$  may be significantly larger than the values of  $\Delta V_1^*$ .<sup>13</sup>

In principle, any system undergoing a homolytic scission of only a *single* chemical bond is subject to internal return. However, volumes of activation for concerted two-bond homolyses in which a stable molecule is produced should reflect the volume changes associated with bond breaking since internal return to starting material will be unlikely. Available data indicate that *t*-butyl phenylperacetate decomposition follows this latter mechanistic path.<sup>14-17</sup>



Kinetic studies of the thermal decomposition (79.55°) of *t*-butyl phenylperacetate (0.10 *M*) in cumene and chlorobenzene have yielded the data in Table I and

Table I. *t*-Butyl Phenylperacetate Kinetic Data at 79.55°

| <i>P</i> , atm | <i>k</i> × 10 <sup>4</sup> , sec <sup>-1</sup> |                            |
|----------------|--|----------------------------|
|                | Cumene <sup>a</sup>                            | Chlorobenzene <sup>a</sup> |
| 1              | 0.66   | 1.07                       |
| 2000           | 0.62   | 0.95                       |
| 4000           | 0.56   | 0.91                       |

<sup>a</sup> Reactions followed by infrared;<sup>18</sup> 1-atm data collected under the same conditions as the high-pressure data.

Figure 1. The resulting activation volumes are +1.0 ± 0.1 cc/mole (cumene) and +1.5 ± 0.3 cc/mole (chlorobenzene).<sup>18</sup> We suggest that these very low values reflect the absence of internal return and are a good approximation of  $\Delta V_1^*$ .<sup>17</sup> In support of this hypothesis, preliminary data at 1 and 4000 atm for the thermal decomposition (79.55°) of *t*-butyl perbenzoate (a one-bond scission process)<sup>14</sup> yield activation volumes of +11 ± 2 cc/mole (cumene) and +13 ± 4 cc/mole (chlorobenzene).

Possible competing induced decomposition and cyclic rearrangements (*e.g.*, the Criegee rearrangement) for *t*-butyl phenylperacetate would be pressure accelerated. However, the activation volumes are virtually identical in cumene and chlorobenzene, although induced decomposition would be more likely in chlorobenzene. Product data at 1 and 4000 atm in both cumene and chlorobenzene (Table II) do not suggest any induced decomposition or unusual mechanism changes at high

(12) R. C. Lamb and J. G. Pacifici, *ibid.*, **70**, 314 (1966).

(13) Walling reasoned that the low values of  $\Delta V^*$  for DBPO in cyclohexene and toluene reflected cage scavenging which prevented internal return.<sup>6</sup> Recently he has concluded that this is unlikely and that internal return probably occurs in these solvents.<sup>9</sup>

(14) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).

(15) P. D. Bartlett and D. M. Simons, *ibid.*, **82**, 1753 (1960).

(16) P. D. Bartlett and C. Richardt, *ibid.*, **82**, 1756 (1960).

(17) In this case,  $\Delta V_1^*$  grossly represents two breaking bonds and a probable decrease in the length of one C-O bond associated with incipient CO<sub>2</sub>.

(18) (a) Compressibility data for cumene<sup>18b</sup> and chlorobenzene<sup>18c</sup> indicate no phase transition over our pressure ranges. Extreme care was taken to correct for nonequilibrium conditions during pressure generation. Volumes of activation, at best, are tenuous numbers; however, the closeness of these values to zero precludes substantial absolute errors. (b) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **77**, 129 (1949); reprinted in "Collected Experimental Papers of P. W. Bridgman," Vol. VI, Harvard University Press, Cambridge, Mass., 1950, pp 3915-3932. (c) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **61**, 57 (1926); reprinted in "Collected Experimental Papers of P. W. Bridgman," Vol. IV, Harvard University Press, Cambridge, Mass., 1960, pp 2043-2086.

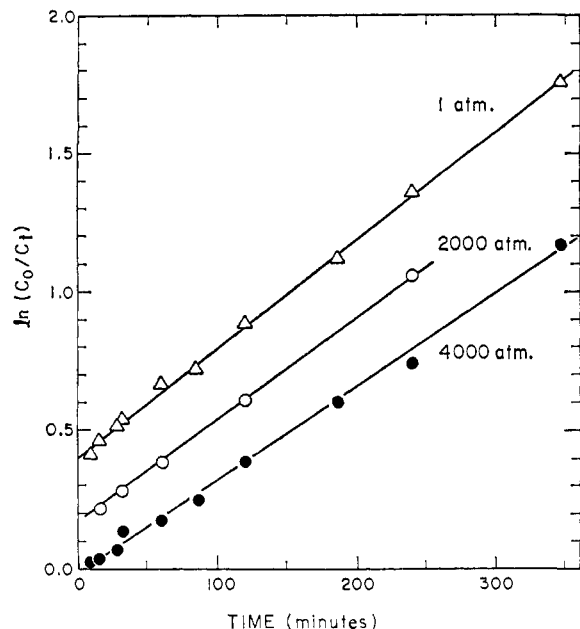


Figure 1. First-order rate plots for *t*-butyl phenylperacetate decomposition in cumene (79.55°). The 2000- and 1-atm data are displaced upward by 0.2 and 0.4 unit, respectively, on the vertical axis.

pressure. No carbonyl absorption was detected in the infrared spectra of infinite time samples in cumene.

Table II. *t*-Butyl Phenylperacetate Product Data at 79.55°<sup>a</sup>

| Product                      | % cumene at |          | % chlorobenzene at |          |
|------------------------------|-------------|----------|--------------------|----------|
|                              | 1 atm       | 4000 atm | 1 atm              | 4000 atm |
| <i>t</i> -Butyl alcohol      | 70          | 50       | 30                 | 44       |
| Acetone                      | Trace       | Trace    | 50                 | 28       |
| Benzyl <i>t</i> -butyl ether | 21.4        | 50.0     | 13                 | 34       |
| Total <i>t</i> -butoxy       | 91.4        | 100.0    | 92                 | 106      |
| Benzyl <i>t</i> -butyl ether | 21.4        | 50.0     | 13                 | 34       |
| Bibenzyl                     | 27.0        | 12.0     | 33                 | 30       |
| Toluene                      | 6.4         | 12.0     | Trace              | Trace    |
| Total benzy <sup>b</sup>     | >54.8       | >74.0    | >46                | >64      |

<sup>a</sup> Determined by glpc. <sup>b</sup> In cumene,  $\alpha,\alpha$ -dimethyldibenzyl and bicumyl were formed in significant yields, but not quantitatively determined. In chlorobenzene, stilbene and benzaldehyde were detected, but not quantitatively determined.

Ether formation in cumene must occur by a cage recombination of the primary radical products since the *t*-butoxy radicals which have diffused from the primary cage should react exclusively with solvent.<sup>19</sup> Studies of the efficiency of radical production from *t*-butyl phenylperacetate have given variable results,<sup>16</sup> but approximately agree with the value 0.79 from our cumene data. The ether data thus offer another example of the effect of pressure on competition between cage reactions and diffusion<sup>2,6,12</sup> and give a value of  $\Delta V^*_2 - \Delta V^*_{-1}$  in both solvents of about +10 cc/mole.

(19) (a) The lower ether yields in chlorobenzene may be due to secondary reactions with *t*-butoxy; the appearance of benzaldehyde (Table II) substantiates this view.<sup>19b</sup> Glpc analyses indicated no significant ether contamination of the unreacted perester. (b) See C. Walling and M. Mintz, *J. Am. Chem. Soc.*, **89**, 1515 (1967).

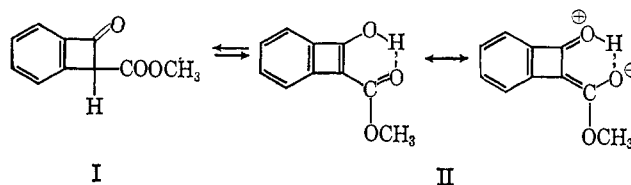
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## 2-Carbomethoxybenzocyclobutenone. Synthesis of a Photochemically Sensitive Small-Ring System by a Pyrolytic Wolff Rearrangement

Sir:

We wish to report a novel synthesis of 2-carbomethoxybenzocyclobutenone (I), the  $\beta$ -keto ester tautomer of a benzocyclobutadiene derivative (II) which might be expected to be stabilized not only by intramolecular hydrogen bonding but also by a "push-pull" resonance effect of the hydroxyl and carbomethoxy substituents.<sup>1,2</sup>



Since benzocyclobutenecarboxylic acid has been synthesized by the photochemical Wolff rearrangement of 2-diazoindan-1-one,<sup>3</sup> it was anticipated that photolysis of the known 2-diazoindan-1,3-dione (III)<sup>4</sup> in methanol solution would constitute a simple synthesis of I. Ultraviolet irradiation<sup>5</sup> of a  $5 \times 10^{-3}$  M solution of III in methanol afforded, however, dimethyl homophthalate (VI) as the major volatile product (30% yield). It seemed likely that the desired ring contraction was taking place, producing I as an intermediate which then underwent photochemical conversion to VI *via* the quinonoid ketene V. This postulate received indirect support by the smooth conversion of benzocyclobutenone (VII)<sup>6</sup> to methyl *o*-toluate (VIII) by irradiation in methanol solution under similar conditions.<sup>7</sup>

The mass spectral cracking pattern of diazo ketone III can best be rationalized as proceeding *via* the desired Wolff rearrangement path.<sup>8</sup> In view of the parallel behavior of certain other organic compounds on electron impact and on pyrolysis,<sup>9</sup> we were encouraged to inves-

(1) So-called "push-pull" stabilization of this type was initially proposed by J. D. Roberts, Special Publication No. 12, The Chemical Society, London, 1958, p 111.

(2) For the attempted synthesis of some "push-pull" stabilized cyclobutadiene derivatives, see R. Breslow, D. Kivelevich, M. J. Mitchell, W. Fabian, and K. Wendel, *J. Am. Chem. Soc.*, **87**, 5132 (1965); for the attempted synthesis of a "push-pull" stabilized benzocyclobutadiene, see A. T. Blomquist and C. G. Bottomley, *ibid.*, **87**, 86 (1965).

(3) M. P. Cava, R. L. Litle, and D. R. Napier, *ibid.*, **80**, 2257 (1958); L. Horner, W. Kirmse, and K. Muth, *Chem. Ber.*, **91**, 430 (1958).

(4) M. Regitz and G. Heck, *ibid.*, **97**, 1482 (1964).

(5) Melting points are uncorrected. Irradiations were carried out using a Model 679A36 Hanovia lamp and a Pyrex filter. Ultraviolet spectra were determined in dioxane; infrared spectra were determined in CHCl<sub>3</sub>; nuclear magnetic resonance spectra were run in CDCl<sub>3</sub>.

(6) M. P. Cava, D. Mangold, and K. Muth, *J. Org. Chem.*, **29**, 2947 (1964).

(7) A related photochemical cleavage of benzocyclobutenedione has been observed: H. A. Staab and J. Ipaktschi, *Tetrahedron Letters*, 583 (1966).

(8) R. Van Fossen, M.S. Thesis, Wayne State University, 1966.

(9) For example, see D. C. DeJongh, R. Y. Van Fossen, and C. F. Bourgeois, *Tetrahedron Letters*, 271 (1967), and references cited therein.