phism is suggested by the shape of the curves in Figs. 1 and 3. As can be seen from the portions of the curves at the right of the eutectics, the initial addition of aliphatic comonomer to the aryl homopolymer did not immediately produce a linear depression of the melting point. This seems to indicate that, within the range of composition covered by the curvilinear portion of the curves, isomorphism could have occurred. To use suberic acid and *p*-benzenediacetic acid as an example, partial isomorphism will signify that, at low molar ratios, suberic acid can enter the crystalline lattice of *p*-benzenediacetic acid. This is not an unreasonable explanation, since it is conceivable to rotate the bonds of a flexible molecule in order to fit the lattice of a rigid one, but not conversely. However, rotating a comonomer molecule out of its most stable configuration will introduce a strain to the lattice, which increases with increased replacement. When the strain surpasses the lattice stability, nonisomorphism and a linear depression of melting point will ensue.

**Acknowledgment.**—The authors are indebted to Drs. J. A. Howsmon and M. R. Lytton for their interest and encouragement in this work. Thanks are due to Dr. J. T. Massengale for organic synthesis, and to Mr. F. F. Morehead for the determination of polymer melting points.

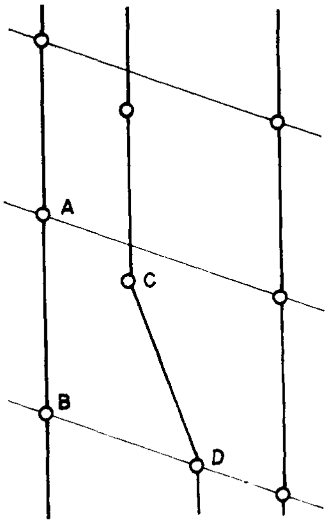

Fig. 9.—Schematic chain alignment of copolyamide of suberic acid and *p*-benzenediacetic acid. AB represents suberic acid and CD *p*-benzenediacetic acid.

MARCUS HOOK, PENNA.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

# Organic Reactions under High Pressure. V. The Decomposition of Di-*t*-butyl Peroxide[1]

BY CHEVES WALLING AND GERSHON METZGER

RECEIVED MARCH 23, 1959

The effect of pressures up to 7300 kg./cm.$^2$ on the decomposition of di-*t*-butyl peroxide at 120° has been studied in four solvents. In all, the rate is depressed by pressure, and values of $\Delta V^{\pm}$ are calculated in cc./mole as 5.4 (toluene), 6.7 (cyclohexene), 12.6 (benzene) and 13.3 ($CCl_4$). The variation has been interpreted as arising from the competition between recombination of *t*-butoxy radicals, attack on solvent (both within the solvent cage) and diffusion out of the cage. $\Delta V^{\pm}$ for diffusion is apparently <8 cc./mole. The ratio of *t*-butyl alcohol to acetone produced in toluene increases with pressure with the difference in $\Delta V^{\pm}$ for the two processes being 8.9 cc./mole. $\Delta V^{\pm}$ for hydrogen abstraction is estimated as −3 to −6 cc./mole. In benzene, toluene has been detected as a reaction product.

Di-*t*-butyl peroxide provides a particularly convenient source of free radicals in the temperature range of 100–150° since it decomposes by a clean unimolecular path at a rate which is almost independent of solvent to yield the highly reactive *t*-butoxy radical.[2] Accordingly, as part of our general program for the investigation of the effect of high pressures on free radical processes, it appeared desirable to study the effect of pressure upon di-*t*-butyl peroxide decomposition as a basis for interpreting pressure effects in radical chain reactions in which it is employed as an initiator.

In general, homolytic dissociation processes might be expected to be retarded by pressure, since the over-all reaction is accompanied by an increase in volume which should be partially achieved in the transition state. Accordingly in the relation

$$d \ln k/dP = -\Delta V^{\pm}/RT \qquad (1)$$

the quantity $\Delta V^{\pm}$ (the difference in volume between transition state and reactants) should be positive. Previous work in this Laboratory has shown such a retardation by pressure in the case of benzoyl peroxide[3] (although, at higher pressures the rate rises presumably due to induced decomposition) and qualitatively similar results have been reported by Nicholson and Norrish,[4] and, for azobisisobutyronitrile, by Ewald.[5]

Measurements reported here on di-*t*-butyl peroxide were made at 120° in four solvents, benzene, toluene, cyclohexene and carbon tetrachloride, at pressures up to 7300 kg./cm.$^2$. In every case the decomposition was retarded by pressure, but values of $\Delta V^{\pm}$ were found to vary markedly with

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[1] Taken from the Ph.D. dissertation of Gershon Metzger, Columbia University, 1958. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

[2] For a review of previous literature, *cf.* C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 469–472.

[3] (a) C. Walling and J. Pellon, THIS JOURNAL, **79**, 4782 (1957); (b) **79**, 4786 (1957).

[4] A. E. Nicholson and R. G. W. Norrish, *Disc. Faraday Soc.*, **22**, 97 (1956).

[5] A. H. Ewald, *ibid.*, **22**, 138 (1956).

solvent. This observation, which we consider the most significant result of the investigation, we believe has considerable bearing on the nature of "cage" phenomena in radical dissociation processes. The products formed in the decomposition were also found to vary significantly with pressure.

## Experimental

**Materials.**—Solvents were reagent grade materials. Their purity was checked usually by gas chromatography, and they were dried over sodium (or $CaCl_2$ in the case of $CCl_4$) and distilled before use. Di-*t*-butyl peroxide was obtained from the Lucidol Division of Wallace and Tiernan Inc. Gas chromatography showed only traces of impurities in most samples, but one contained small amounts of acetone and *t*-butyl alcohol. These had no effect upon decomposition rates, and were corrected for in product analyses.

**Apparatus and Technique.**—The high pressure apparatus was that described previously,[6] the only change being the use of a Teflon o-ring in the Bridgman closure of the reaction vessel. This material proved greatly superior to rubber and could be repeatedly reused at temperatures up to 160°.

The samples under study were contained in vessel B,[3b] a collapsible Teflon vessel of approximately 11-cc. capacity. Reaction mixtures were made up by adding the peroxide (usually 5 cc.) to 100 cc. of solvent, degassing three times, and transfering to the reaction vessel under nitrogen with the aid of a hypodermic syringe. The vessel was then placed in the preheated pressure apparatus, put under pressure for a suitable time and then removed for analysis of its contents. In the case of runs at atmospheric pressure degassed samples in sealed tubes were simply placed in the thermostat surrounding the high pressure apparatus.

**Analysis of Reaction Mixtures.**—All reaction mixtures were analyzed by gas chromatography using a Perkin–Elmer model 154 Vapor Fractometer. A two meter A column (phthalate ester) was used for cyclohexene and carbon tetrachloride systems, and a C column (silicone) for benzene, all at 85° and 25 p.s.i. helium pressure. Toluene systems required A and C columns in series at 100°. Rates of peroxide decomposition were determined by comparison of the peroxide peak height with that of the solvent as an internal standard. Since the solvent was always present in large excess, its concentration was considered constant. Typical data, those for the benzene system, appear in Table I.

Analyses also indicated the composition of the peroxide decomposition products (chiefly acetone and *t*-butyl alcohol), and determinations were made quantitative by comparison of peak heights with those of known mixtures. In benzene some toluene was also detected. In carbon tetrachloride, acetone and an approximately equal amount of methyl chloride were found, but also some *t*-butyl alcohol, amounting to 0.1–0.5 mole/mole of peroxide decomposed. Since the solvent in this case contains no hydrogen, it seemed likely that the alcohol resulted from a small amount of attack of *t*-butoxy radicals upon peroxide as is known to occur in undiluted peroxide at atmospheric pressure.[7] It was accordingly necessary to correct the observed rates for this induced decomposition by taking the amount of peroxide disappearing by first-order decomposition as the difference between initial peroxide and peroxide remaining plus *t*-butyl alcohol formed. Actual data appear in Table II. Data on the remaining solvents are listed in Tables III and IV.

## Results and Discussion

**Effect of Pressure on Decomposition Rates.**—First-order decomposition rates of di-*t*-butyl peroxide from Tables I–IV are plotted on a logarithmic scale against pressure in Fig. 1. Our data at atmospheric pressure are in reasonable agreement with literature values,[8] although rates in the aromatic solvents appear significantly faster than in cyclohexene and $CCl_4$.

TABLE I

EFFECT OF PRESSURE ON THE DECOMPOSITION OF DI-*t*-BUTYL PEROXIDE IN BENZENE AT 120°

($[DTBP]_0$ = 0.26 *M* unless indicated)

| *P*, kg./cm.$^2$ | *t*, min. | $[DTBP]_0$/[DTBP] | [*t*-Butyl alcohol]/[acetone] | *k*, sec.$^1$ × 10$^{-6}$ |
|---|---|---|---|---|
| 1 | .. | ... | 0.370 | ... |
| 1[a] | 207 | 1.186 | .375 | 13.9 |
| 880 | 1315 | 1.879 | .619 | 7.6 |
| 1480[a] | 1457 | 2.140 | .76 | 8.7 |
| 1650 | 1385 | 1.858 | .655 | 7.5 |
| 2810 | 1211 | 1.442 | .795 | 5.0 |
| 3550 | 4328 | 2.626 | 1.032 | 3.7 |
| 4570[a] | 1455 | 1.244 | 0.878 | 2.5 |
| 5620[a] | 1394 | 1.227 | 1.055 | 2.45 |
| 7140[a] | 4295 | 1.853 | 1.772 | 2.4 |

[a] $[DTBP]_0$ = 0.49 *M*.

TABLE II

EFFECT OF PRESSURE ON THE DECOMPOSITION OF 0.36 *M* DI-*t*-BUTYL PEROXIDE IN $CCl_4$ AT 120°

| *P*, kg./cm.$^2$ | *t*, min. | [DTBP] | [*t*-Butyl alcohol] | *k*, sec.$^{-1}$ × 10$^6$ |
|---|---|---|---|---|
| 1 | 1276 | 0.1520 | 0.00553 | 9 |
| 1970 | 1076 | .1428 | .0113 | 2.4 |
| 2950 | 1158 | .2813 | .00265 | 2.3 |
| 4920 | 1186 | .2752 | .00515 | 1.5 |
| 5625 | 4181 | .1934 | .0117 | 0.86 |

TABLE III

EFFECT OF PRESSURE ON THE DECOMPOSITION OF 0.26 *M* DI-*t*-BUTYL PEROXIDE IN TOLUENE AT 120°

| *P*, kg./cm.$^2$ | *k*, sec.$^{-1}$ × 10$^6$ | [*t*-Butyl alcohol]/[acetone] |
|---|---|---|
| 1 | 13.4 | 2.99 |
| 2040 | 9.5 | 4.90 |
| 2900 | 8.0 | 7.57 |
| 4480 | 6.6 | 10.26 |
| 5270 | 5.7 | 11.72 |

TABLE IV

EFFECT OF PRESSURE ON THE DECOMPOSITION OF 0.26 *M* DI-*t*-BUTYL PEROXIDE IN CYCLOHEXENE AT 120°

| *P*, kg./cm.$^2$ | *k*, sec.$^{-1}$ × 10$^6$ | *t*-Butyl alcohol/peroxide consumed |
|---|---|---|
| 1 | 8.30 | 1.0 |
| 1300 | 6.20 | 0.70 |
| 2110 | 5.42 | .55 |
| 2950 | 3.77 | .61 |
| 4570 | 3.15 | .57 |
| 5840 | 2.65 | .30 |

In benzene as solvent, the unimolecular nature of the decomposition is confirmed by the good agreement of rate constants obtained at two initial peroxide concentrations. Similar kinetics are assumed in the other solvents, but the assumption is supported by the linear plots of Fig. 1, since reaction times in different experiments varied considerably in a random manner (*cf.* Tables I and II). Reactions in $CCl_4$ show rather more scatter than other systems, perhaps because of the induced decomposition mentioned above.

In contrast to other systems, data in benzene show an abrupt change in slope at approximately 4600 kg./cm.$^2$ Interpolation of Bridgman's data[9] indicates that benzene should freeze at about this

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(6) C. Walling and J. Pellon, THIS JOURNAL, **79**, 4776 (1957).

(7) E. R. Bell, F. F. Rust and W. E. Vaughan, *ibid.*, **72**, 337 (1950).

(8) J. A. Offenbach and A. V. Tobolsky, *ibid.*, **79**, 278 (1957); *cf.* also ref. 2.

(9) P. W. Bridgman, "Physics of High Pressures," G. Bell and Sons, Ltd., London, 1952, p. 198.

pressure at 120°. We believe the discontinuity is associated with this phase change, although we have no unequivocal explanation as to why the reaction should become pressure independent in the solid state.[10]

From the slopes of the lines in Fig. 1, values of $\Delta V^{\pm}$ for the decomposition of *t*-butyl peroxide in the four solvents may be calculated *via* equation 1. Values are listed in Table V, together with literature values for other homolytic dissociations.

A least squares treatment was used in determining the values from our data, and experimental errors given are the standard deviations indicated by the analysis. In the benzene system all points up to 4600 kg./cm.$^2$ were used except that at 880 kg./cm.$^2$, while in the $CCl_4$ system the best line passing through the point at atmospheric pressure was determined since that measurement required no correction as described above. In the other systems all measurements were included.

The most striking feature of our results is that $\Delta V^{\pm}$ varies significantly with solvent. In fact, $\Delta V^{\pm}$'s fall into two groups, those in benzene and $CCl_4$ being roughly twice those in toluene and cyclohexene. One hypothesis to account for the variation which cannot be excluded is that the large $\Delta V^{\pm}$'s represent essentially true values for the homolytic dissociation, while the smaller ones arise from composite reactions in which there is contribution from some sort of direct bimolecular reaction with solvent, the importance of which increases with pressure. However, we see nothing in the structure of the solvents employed to really suggest such a process, and prefer an interpretation based upon the "cage" nature of homolytic dissociations. Here we believe that the pertinent features of di-*t*-butyl peroxide dissociation in a solvent SH containing abstractable hydrogens are given by the sequence of equations below, where (2RO·) represents a pair of *t*-butoxy radicals still confined within the same solvent cage

$$\text{ROOR} \xrightarrow{k_2} (2\text{RO}\cdot) \quad (2)$$

$$(2\text{RO}\cdot) \xrightarrow{k_3} \text{ROOR} \quad (3)$$

$$(2\text{RO}\cdot) + \text{SH} \xrightarrow{k_4} \text{RO}\cdot + \text{S}\cdot + \text{ROH} \quad (4)$$

$$(2\text{RO}\cdot) \xrightarrow{k_5} 2\text{RO}\cdot \quad (5)$$

$$\text{RO}\cdot + \text{SH} \xrightarrow{k_6} \text{ROH} + \text{S}\cdot \quad (6)$$

$$\text{RO}\cdot \xrightarrow{k_7} \text{CH}_3\text{COCH}_3 + \cdot\text{CH}_3 \quad (7)$$

Although this is essentially a conventional formulation for a "cage" process,[11] certain of the steps deserve special comment. Reaction 3, the reverse of the initial dissociation, has not usually been considered in peroxide decompositions, although there is some evidence for coupling reactions of peroxy radicals.[12] Processes such as (4), *i.e.*, attack on solvent by an initial fragment still in the solvent cage, have been discounted by Flory in polymerization initiation since known rates of alkyl radical additions to olefins are too slow to compete with (5), diffusion of fragments from the initial cage.[11] However, it is now clear that some radical–substrate reactions, for example, chlorine atom attack on hydrocarbons,[13] occur at rates comparable to diffusion processes. It is quite possible that certain hydrogen abstractions by alkoxy radicals fall in this class. The O–H bond dissociation energy of *t*-butyl alcohol has been estimated as 104 kcal. by Gray,[14] so all abstractions should be exothermic. Free radical chain halogenations using *t*-butyl hypochlorite (which appear to involve the *t*-butoxy radical as a chain carrier) occur with great ease, even at −78°,[15] indicating a very low activation energy process. It accordingly seems plausible as well that there should be little peroxide reformation by recombination of alkoxy radicals after their escape from the initial cage. Finally, reaction 7, while of importance in determining products in unreactive solvents, is relatively slow, with an activation energy of approximately 11 kcal.[16]

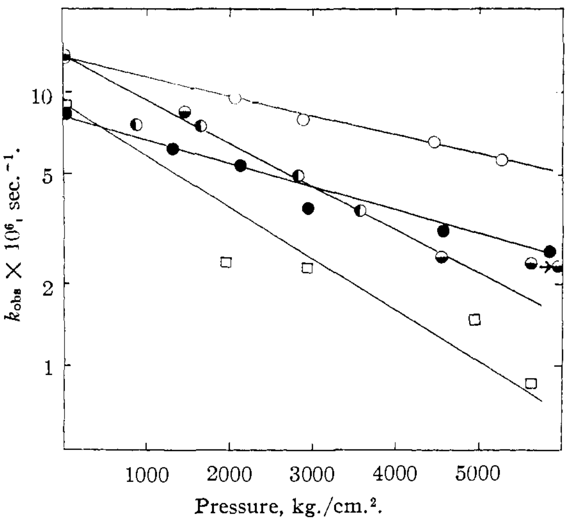

Fig. 1.—Effect of pressure on the rate of decomposition of di-*t*-butyl peroxide at 120° in various solvents: ◐, benzene, 0.26 *M*; ◒, 0.49 *M*; ○, toluene; ●, cyclohexene; □, $CCl_4$.

TABLE V

VALUES OF $\Delta V^{\pm}$ FOR HOMOLYTIC DISSOCIATIONS

| Substance | Solvent | *T*, °C. | $\Delta V^{\pm}$, cc./mole |
|---|---|---|---|
| Di-*t*-butyl peroxide | Toluene | 120 | 5.4 ± 0.6 |
| Di-*t*-butyl peroxide | Cyclohexene | 120 | 6.7 ± 0.3 |
| Di-*t*-butyl peroxide | Benzene | 120 | 12.6 ± 1.3 |
| Di-*t*-butyl peroxide | $CCl_4$ | 120 | 13.3 ± 3 |
| Azobisisobutyronitrile[5] | Toluene | 62.5 | 3.8[a] |
| Azobisisobutyronitrile[5] | Toluene | 62.5 | 9.36[b] |
| Benzoyl peroxide[3] | Acetophenone | 80 | 4.8 |
| Benzoyl peroxide[4] | $CCl_4$ | 60 | 9.65 |
| Benzoyl peroxide[4] | $CCl_4$ | 70 | 8.56 |

[a] Photometric analysis. [b] By $I_2$ scavenger technique.

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[10] H. A. Bent and B. Crawford, Jr., THIS JOURNAL, **79**, 1793 (1957).

[11] For discussion and references *cf.* ref. 2, pp. 73–79.

[12] J. H. Raley, L. M. Porter F. F. Rust and W. E. Vaughan, THIS JOURNAL, **73**, 15 (1951).

[13] H. O. Pritchard, J. B. Pyke and A. F. Trotman-Dickenson, *ibid.*, **77**, 2629 (1955).

[14] P. Gray, *Trans. Faraday Soc.*, **52**, 344 (1956).

[15] C. Walling and B. B. Jacknow, unpublished work.

[16] D. H. Volman and W. M. Graven, THIS JOURNAL, **75**, 3111 (1953).

Accordingly no disproportion of alkoxy radicals would be expected within the solvent cage.

On the basis of the scheme outlined, it is evident that the measured rate constant for peroxide decomposition, $k_{\text{obs}}$ is a composite quantity, specifically

$$k_{\text{obs}} = k_2(k_4 + k_5)/(k_3 + k_4 + k_5) \qquad (8)$$

although, in the case that $k_3 \ll (k_4 + k_5)$, (8) reduces to $k_{\text{obs}} = k_2$ as is usually assumed. Indeed, the observation that, while decomposition rates at atmospheric pressure vary somewhat with solvent there is no simple correlation with hydrogen reactivity, indicates that here either $k_3$ is negligible or $k_4 \ll k_5$. Thus, from our own data, decomposition in cyclohexene (with easily abstracted hydrogens) is slower than in benzene and comparable to that in $CCl_4$. Under pressure $k_3$ and $k_4$ should both increase since transition states should be smaller than reactants, while $k_2$ should diminish as should also $k_5$ which refers to a diffusion process.[17]

Applying the foregoing to our own measurements we suggest that in toluene and cyclohexene, solvents readily attacked by *t*-butoxy radicals, $k_4 > k_3$, so that $k_{\text{obs}} = k_2$. Accordingly $\Delta V^{\pm}$'s measured (5–7 cc./mole) are essentially $\Delta V_2^{\pm}$. On the other hand, in benzene and $CCl_4$, $k_4$ is negligible, and under pressure $k_5 < k_3$, so that

$$k_{\text{obs}} = k_2k_5/(k_3 + k_5) \qquad (9)$$

and $\Delta V_{\text{obs}}^{\pm}$ is a composite quantity. Since the ratio $k_5/(k_3 + k_5)$ decreases with pressure as diffusion out of the cage is retarded the larger values of $\Delta V_{\text{obs}}^{\pm}$ are accounted for. Further, if we assume that $\Delta V_2^{\pm} = 6$ cc./mole, and that the reaction in $CCl_4$ represents the limiting case of $k_{\text{obs}} = k_2/k_5/k_3$,

$$\frac{\mathrm{d}\ln k_{\text{obs}}}{\mathrm{d}P} = \frac{\Delta V_3^{\pm} - \Delta V_2^{\pm} - \Delta V_5^{\pm}}{RT} \qquad (10)$$

Since $\Delta V_3^{\pm}$ is presumably negative, we conclude that $\Delta V_5^{\pm} < 8$ cc./mole.

**Effect of Pressure on Decomposition Products.**—Acetone and *t*-butyl alcohol arising from reactions 7 and 6 or 4, respectively, are the major products of *t*-butyl peroxide decomposition. In our experiments yields correspond closely to peroxide consumed (with the exception of reactions in cyclohexene discussed further below) and the effect of pressure is in good accord with the formulation of the reaction given in the preceding section.

In toluene (Table III) *t*-butyl alcohol is the major product at atmospheric pressure, and the yield of acetone formed decreases continuously with pressure. A plot of log [*t*-butyl alcohol]/[acetone] *vs.* pressure is linear, corresponding to $\Delta V_7^{\pm} - \Delta V_6^{\pm}$ (or $\Delta V_4^{\pm}$, which is presumably the same) = 8.9 cc./mole. Since $\Delta V_7^{\pm}$ is almost certainly positive to the extent of 3–6 cc./mole, $\Delta V_6^{\pm}$ is apparently −3–6 cc./mole. This is smaller than values for radical displacements reported previously in polymerization processes[3,6] and the difference may arise because here we are dealing with a very rapid low-activation energy process in which little van der Waals' compression is required in the transition state.

In cyclohexene (Table IV) essentially no acetone was detected, presumably because the solvent reacts with the *t*-butoxy radicals before they can decompose. However, yields of *t*-butyl alcohol become as low as 30% at 5840 kg./cm.². Although no search was made for any resulting high molecular weight products, we believe that the loss represents *t*-butoxy radical addition to the cyclohexene, favored by the relatively small negative $\Delta V^{\pm}$ for hydrogen abstraction indicated in the toluene system.

Turning next to the unreactive solvents, the small amount of *t*-butyl alcohol noted in $CCl_4$ has been attributed to some induced decomposition of peroxide, and the rate constants corrected accordingly (Table II). Methyl radicals produced *via* reaction 7 in this solvent should yield methyl chloride which was detected in amounts approximately equal to the acetone formed. The other expected product, $C_2Cl_6$, was not investigated.

In benzene (Table I) some *t*-butyl alcohol is also formed, the amount increasing with pressure, although there is considerable scatter in the alcohol/acetone ratios observed. This might arise from direct hydrogen abstraction, induced decomposition or *via* interaction between *t*-butoxy radicals and radical intermediates formed by addition to the aromatic system. The induced decomposition seems unlikely, since there is no dependence of alcohol yield on initial peroxide concentration. However, the correction for any such induced reaction, if it did occur, would yield an even larger value for $\Delta V_{\text{obs}}^{\pm}$ than that reported in Table I. Finally, analysis of our reaction products indicated at all pressures an amount of toluene equal to about 10% of the acetone present. Alkylation of simple aromatic molecules by methyl radicals (presumably by addition followed by some sort of disproportionation of the intermediate radical produced) has frequently been postulated, and recently observed in the decomposition of acetyl peroxide in benzene.[18] Our results are a further confirmation of the reality of this reaction.

**Other Data on Homolytic Dissociations.**—We may now discuss published data on the effect of pressure on other homolytic dissociations (Table V) in the light of our own results. The most interesting data are those of Ewald[5] on azobisisobutyronitrile (AIBN) in which different values of $\Delta V^{\pm}$ were obtained when the reaction was followed photometrically (which determines the actual disappearance of AIBN) and by iodine disappearance (which measures the production of free radicals capable of reacting with iodine). Ewald has suggested that the discrepancy arises from a "cage" effect, and we may interpret it in more detail in the same manner as we have discussed solvent effects previously.

Where again substances in parentheses represent fragments in the solvent cage, the pertinent reactions are

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[17] Viscosities of organic liquids increase markedly with pressure. References and a summary of data are given by S. D. Hamman "Physico-Chemical Effects of Pressure," Academic Press, Inc., New York, N. Y., 1957, pp. 81–84. Theory predicts an inverse relation between viscosity and diffusion, which is obeyed only qualitatively in the self diffusion of $CS_2$, the only organic system for which data are available; R. C. Koeller and H. G. Drickamer, *J. Chem. Phys.*, **21**, 267 (1953).

[18] E. L. Eliel, K. Rabindran and S. H. Wilen, *J. Org. Chem.* **22** 859 (1957).

$$\text{AIBN} \xrightarrow{k_{11}} (2\text{R}\cdot) + \text{N}_2 \quad (11)$$

$$(2\text{R}\cdot) \xrightarrow{k_{12}} \text{R–R} \quad (12)$$

$$(2\text{R}\cdot) \xrightarrow{k_{13}} 2\text{R}\cdot \quad (13)$$

$$\text{R}\cdot + \text{I}_2 \longrightarrow \text{RI} + \text{I}\cdot \quad (14)$$

Here the photometric experiment measures $k_{11}$, hence $\Delta V_{11}^{\pm} = 3.8$ cc./mole. $k_{\text{obs}}$ for the iodine experiment is actually $k_{11}k_{13}/(k_{12} + k_{13})$, or, under pressure where $k_{13} \ll k_{12}$, it approaches $k_{11}k_{13}/k_{12}$ and we obtain

$$\frac{\text{d} \ln k_{\text{obs}}}{\text{d}P} = \frac{\Delta V_{12}^{\pm} - \Delta V_{11}^{\pm} - \Delta V_{13}^{\pm}}{RT} \quad (15)$$

Accordingly $\Delta V_{12}^{\pm} - \Delta V_{13}^{\pm} = 5.56$ cc./mole. Since $\Delta V_{12}^{\pm}$ is presumably negative, $\Delta V_{13}^{\pm} < 5.56$ cc./mole which may be compared with our value of $<8$ cc./mole for the *t*-butoxy radical. Stated qualitatively, pressure favors retention of the radicals in the solvent cage where they can combine, rather than diffusing out into the solution.

Qualitatively, benzoyl peroxide follows the same pattern, showing larger values of $\Delta V^{\pm}$ in $CCl_4$, a solvent necessarily unreactive toward benzoyloxy radicals, than in acetophenone. These results suggest the generalization that, except in the case of initiators yielding fragments sufficiently reactive to attack substrates while in the solvent cage, high pressures will decrease the chain starting-efficiency of initiators which dissociate homolytically to initiate free radical chains.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

# Reaction Rates by Distillation. VIII. The Alkylation of Aromatic Compounds by Benzyl Alcohols and Benzhydrols[1]

BY ERNEST F. PRATT AND HAROLD J. E. SEGRAVE[2]

RECEIVED APRIL 11, 1959

It has been found, contrary to expectation, that in the alkylation of aromatic compounds by phenylcarbinols the yields tend to decrease as the electron-releasing ability of a *para* substituent in the carbinol increases, while, as expected, the yields tend to increase as the electron-releasing ability of the substituent on the compound being alkylated increases (Table I). As the reactivity of the phenylcarbinol increases its selectivity in alkylating either of two aromatic compounds was found to increase, as would be expected if the derived carbonium ion is the attacking particle. It has been shown that the compound being alkylated is involved in the rate-controlling step of the reaction and that selected aromatic compounds are smoothly benzylated upon warming them with benzyl alcohol and anhydrous *p*-toluenesulfonic acid on the steam-bath for 15 minutes. The formation of benzhydryl butyl ether, which proceeds readily in toluene solution at low concentrations of *p*-toluenesulfonic acid, is almost completely suppressed in favor of alkylation of the toluene at high concentrations of the acid (Table II).

In Table I are shown the results of alkylations of anisole, toluene and benzene by a variety of benzyl alcohols and benzhydrols with *p*-toluenesulfonic acid as the catalyst. The procedure was that previously described in which the by-product water is collected as rapidly as formed by distillation into a Dean–Stark trap.[3] The tendency for the yield to increase with an increase in electron-releasing ability of the substituent on the compound being alkylated was expected, but the tendency for the yield to decrease with an increase in electron-releasing ability of the substituent on the alcohol, that is with an increase in reactivity of the alcohol, was somewhat unexpected.

The increasing catalyst concentrations required in the experiments of Table I (see Experimental), as the electron-releasing ability of the substituent on the alcohol was decreased, show, in agreement with previous observations,[3] that the alcohol is involved in the rate-controlling step. Since, however, these experiments were carried out at the widely differing boiling points of the compounds being alkylated, it is not directly evident whether they are also involved in the rate-controlling process. Benzene, toluene and mesitylene were, therefore, benzylated at the reflux temperature of a 3:1 by volume mixture of cyclohexane and nitrobenzene. With a 1:4 molar ratio of benzyl alcohol to compound being benzylated the yields of monobenzylated products were 21, 39 and 62%, respectively, and a 75% yield of water was obtained in 339, 130 and 65 minutes. A 100 ± 2% total yield of water was obtained in all cases, indicating self-benzylation of the alcohol was also occurring. This was confirmed experimentally when it was found that a molecule of water per molecule of benzyl alcohol was readily evolved in the absence of any other alkylatable compound and a resinous product was formed. The tendency for the yield of monobenzylated product to increase among benzene, toluene and mesitylene in that order, which is also the order of increasing reactivity, is well understood on this basis and it is clear that both the compound being alkylated and the alcohol are involved in the rate-controlling process. The closely related trends in yields shown in the horizontal rows of Table I can reasonably be explained on the same basis.

It is apparent (Table I) that the yields for the more reactive benzhydrols are in general lower than those for the corresponding benzyl alcohols. This results chiefly from the tendency of the intermediate symmetrical dibenzhydryl ethers[3] to disproportionate more readily than do the analogous dibenzyl ethers.[4] Thus from the experiments

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[1] For the preceding paper in this series see E. F. Pratt and J. Lasky, THIS JOURNAL, **78**, 4310 (1956).

[2] From the Ph.D. thesis of Harold J. E. Segrave, May, 1952.

[3] E. F. Pratt, R. K. Preston and J. D. Draper, THIS JOURNAL, **72**, 1367 (1950).

[4] J. F. Norris and R. C. Young, *ibid.*, **52**, 753 (1930).