Oxidation of Hindered Phenols. VIII. Kinetics of the Oxidation of 2,4,6-Tri-*t*-butylphenol by Benzoyl Peroxide

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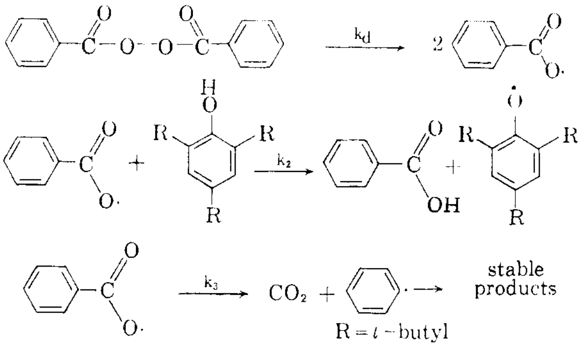
We have previously noted that the reaction of benzoyl peroxide with hindered phenols such as 2,4,6-tri-*t*-butylphenol produces the corresponding phenoxy radicals.[1] This became of particular interest in view of Walling's recent work demonstrating that most phenols (unhindered) interact with benzoyl peroxide by a relatively rapid non-radical process.[2] Walling noted that 2,4,6-tri-*t*-butylphenol was unreactive toward benzoyl peroxide at room temperature and that upon heating the characteristic blue color of 2,4,6-tri-*t*-butylphenoxy developed. He suggested that the process involves attack of benzoyloxy radicals upon the phenol and thus markedly differs from the reaction of unhindered phenols with benzoyl peroxide. Recent kinetic studies in these laboratories confirm this suggestion and provide further details on the process.

We have followed the reaction by spectophotometrically observing the rate of formation of the stable phenoxy radicals. Since these radicals have a sufficiently high molar absorbancy index (400 ± 3),[3] to make it possible to work with rather dilute solutions of the peroxide (0.005 to 0.04*M*), induced decomposition of the peroxide was presumably essentially eliminated.

Under these conditions, we have found that tri-*t*-butylphenol is an inefficient radical trap; to explain the kinetics of formation of tri-*t*-butylphenoxy it is necessary to assume that some of the benzoyloxy radicals are destroyed by a first order process. Since it has been observed that yields of CO_2 increase with increasing temperature,[4] we believe that this first order process is the decarboxylation of benzoyloxy radicals. Thus the process becomes:



The usual steady state kinetics applied to the above scheme (or any similar process involving the first order loss of benzoyloxy radicals) predicts that the rate of production of phenoxy radicals will be given by the expression

$$\frac{p\ (\text{Phenoxy})}{dt} = \frac{2k_dk_2\ (\text{peroxide})\ (\text{phenol})}{k_3 + k_2\ (\text{phenol})} \qquad (1)$$

This may be rearranged to yield, for the initial rate

$$\frac{(\text{phenol})_i\ (\text{peroxide})_i}{\left(\frac{d(\text{phenoxy})}{dt}\right)_i} = \frac{k_3}{2k_2k_d} + \frac{(\text{phenol})i}{2k_d} \qquad (2)$$

Equation 2 predicts that a plot of $\frac{(\text{phenol})_i\ (\text{peroxide})_i}{\left(\frac{d(\text{phenoxy})}{dt}\right)_i}$ *vs.* $(\text{phenol})_i$ should give a straight line, the slope being $^1/_2\ k_d$ and the intercept $k_3/2k_2k_d$. Figure 1 shows that this relationship does in fact provide a linear correlation of the data (summarized in Table I).

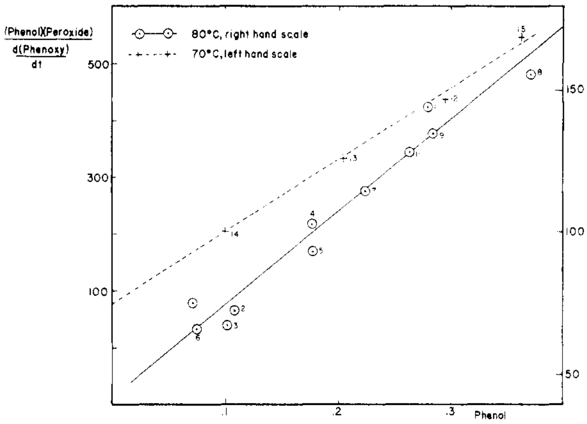


Fig. 1. Relationship of initial rate of 2,4,6-tri-*t*-butylphenoxy formation to phenol concentration in benzene solution. All concentrations in moles/l.; time in seconds

The extinction coefficient of 2,4,6-tri-*t*-butylphenoxy is sufficiently large to permit the measurement of its initial rate of formation before any appreciable consumption of peroxide or phenol has occurred. As a consequence, the value of k_d derived on this basis should agree with values for this constant derived by other measurements. The value obtained was $2.6 \pm 0.1 \times 10^{-5}$ sec.$^{-1}$ at 80°. Values derived for k_d at 80° from data cited in the literature are 2.83×10^{-5} and 2.87×10^{-5} by Hammond,[5] 4.3×10^{-5} by Swain,[6] 3.28×10^{-5} by

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(1) C. D. Cook, D. A. Kuhn, and P. Fianu, *J. Am. Chem. Soc.*, **78**, 2002 (1956).

(2) C. Walling and R. B. Hodgdon, Jr., *J. Am. Chem. Soc.*, **80**, 228 (1958).

(3) C. D. Cook, C. B. Depatie, and E. S. English, unpublished work.

(4) *See Free Radicals in Solution*, C. Walling, John Wiley & Sons, Inc., New York, 1957, p. 476. See also ref. 11.

(5) G. S. Hammond, *J. Am. Chem. Soc.*, **72**, 3737 (1950). The above are Hammond's values extrapolated from 79 to 80°. One value was obtained by a normal decomposition of 0.001*M* peroxide solutions, the other by using iodine as a radical trap.

(6) C. G. Swain, W. Stockmeyer, and T. Clarke, Jr., *J. Am. Chem. Soc.*, **72**, 5426 (1950). This result was obtained using styrene to inhibit induced decomposition.

TABLE I

RUNS 1-11 AT 80°, RUNS 12-15 AT 70°

Run No.	Initial Peroxide Concentration Mole/l.	Peroxide Concn. at Time of Mixing Mole/l.	Initial Rate of Formation of Phenoxy Radical Moles/l./Min.	Initial Phenol Concn. Mole/l.	$\frac{(\text{Phenol})(\text{Peroxide})_i}{(\text{Rate of Formation of Phenoxy Radical})_i}$
1	0.0099	0.0089	8.5×10^{-6}	0.0722	75.4
2	0.0105	0.0098	14.6×10^{-6}	0.108	72.6
3	0.0099	0.0092	13.8×10^{-6}	0.101	67.4
4	0.0101	0.0095	16.4×10^{-6}	0.177	103
5	0.0101	0.0095	18.1×10^{-6}	0.177	93.4
6	0.0202	0.0188	21.0×10^{-6}	0.0738	66.1
7	0.0101	0.0095	18.5×10^{-6}	0.224	115
8	0.0085	0.0080	19.1×10^{-6}	0.371	156
9	0.0098	0.0094	19.8×10^{-6}	0.284	135
10	0.0360	0.0340	69.8×10^{-6}	0.263	128
11	0.00535	0.00490	9.5×10^{-6}	0.280	145
12	0.0200	0.0199	13.4×10^{-6}	0.296	440
13	0.0184	0.0183	11.2×10^{-6}	0.205	334
14	0.0196	0.0195	9.6×10^{-6}	0.100	208
15	0.0150	0.0149	9.9×10^{-6}	0.363	546

Bartlett,[7] 3.32×10^{-5} by Hartman,[8] and 2.01×10^{-5} by Bawn.[9]

Our value would seem to be within the accepted range. It is appreciably lower than the value of 6.5×10^{-5} sec.$^{-1}$ which Walling reports[1] for the value in the presence of 2,4,6-tri-*t*-butylphenol. However, Walling indicates that the temperature was not closely controlled and, due to the inefficiency of tri-*t*-butylphenol as a radical trap, it is likely that considerable induced decomposition occurred in the relatively concentrated solution with which he worked.

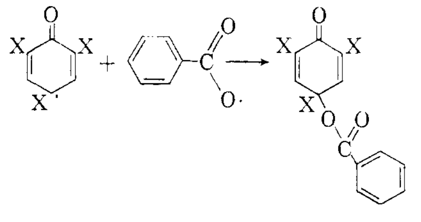
At 70° C., we obtained a value of $6.6 \pm 0.2 \times 10^{-6}$ sec.$^{-1}$ for k_d. This leads to an activation energy of 33 kcal./mole for the primary dissociation process. In view of the narrow temperature range used, we consider this in good agreement with the reported values of 29.9,[8] 29.6,[9] and 33.3.[7]

From the values of the intercepts, the ratios of k_3/k_2 are calculated to be 0.13 at 80° and 0.06 at 70°. This represents a difference in activation energy between reactions 3 and 2 of approximately 18 kcal./mole. Since hydrogen abstractions of this type are expected to have low activation energies,[10] perhaps on the order of 0–5 kcal./mole, this suggests that the activation energy for the decarboxylation of benzoyloxy radicals lies roughly in the range of 18–23 kcal./mole. In view of the uncertainties in evaluating k_3/k_2 it should be realized that no great precision can be attached to this range.

Support for the view that the competitive reaction is indeed decarboxylation comes from the fact that yields of carbon dioxide have been found to increase with increasing temperature and that both Walling[1] and we have noted relatively high yields of benzoic acid when benzoyl peroxide is decomposed in the presence of tri-*t*-butylphenol. Thus, in a typical experiment, when 0.01 mole of benzoyl peroxide in 100 ml. of benzene was heated at 80° for 48 hr., 0.0027 mole of benzoic acid was produced; when 0.01 mole of tri-*t*-butylphenol was added to such a run, 0.0094 mole of benzoic acid was produced.

These results are consistent with the work of Barson and Bevington,[11] who, by use of tracer techniques, have shown that appreciable decarboxylation of benzoyloxy radicals occurs at 60° in benzene even in the presence of such radical traps as styrene, cumene, or diphenylpicrylhydrazyl.

The fact that 2,4,6-tri-*t*-butylphenoxy can be produced in appreciable concentration in the presence of benzoyloxy radicals is in itself of considerable interest. A reaction of the type indicated by



(3)

Equation 3 would seem rather likely. However, the formation of appreciable concentrations of the phenoxy radical shows that this reaction must be relatively slow, if, indeed, it does occur. The de-

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[7] K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946).

[8] P. F. Hartman, H. G. Sellers, and D. Turnbull, *J. Am. Chem. Soc.*, **69**, 2416 (1947). Calculated from data for 0.05*M* peroxide solutions.

[9] C. E. H. Bawn and S. F. Mellish, *Trans. Fara. Soc.*, **47**, 1216 (1951). The above represents Bawn's data extrapolated from 76° to 80°.

[10] See A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 2415 (1957).

[11] C. A. Barson and J. C. Bevington, *J. Polymer Chem.*, **20**, 133 (1956), see also *Tetrahedron*, **4**, 147 (1958).

crease in rate of production of phenoxy radical over the first hour or so can be completely accounted for by the decrease in peroxide concentration, again implying that the above reaction is not important in our work. The fact that most of the radical has disappeared after 24 hr. at 80°, however, does suggest that this reaction, or a similar one, becomes of some importance in later stages of the reaction since disproportionation of tri-*t*-butylphenoxy is rather slow in dilute solution. Unfortunately, the reaction mixture was an intractable, oily mixture which we were unable to resolve into any pure components other than benzoic acid. It should be pointed out that since the rates are extrapolated to zero time, the incursion of the above reaction, (and also disproportionation of the phenoxy radical) should not introduce any appreciable error with the kinetic analysis.

EXPERIMENTAL

Kinetic runs. The rate of production of phenoxy radicals was followed by use of the reaction vessel shown in Fig. 2. An appropriate amount of 2,4,6-tri-*t*-butyl phenol[11] was placed in one bulb and a solution of benzoyl peroxide in benzene introduced into the other. The vessel was then attached to a manifold by means of the ball joint and the benzene solution degassed by alternate freezing and thawing under vacuum. The vessel was sealed off at the constriction and placed in a constant temperature bath. During these operations, extreme care was taken to prevent mixing of the materials in the two bulbs. Approximately 20 min. were allowed for equilibration. The phenol was then mixed with the benzoyl peroxide solution by vigorous shaking and the apparatus placed in a Beckman DK-1 spectrometer equipped with a thermostated cabinet mounted over the cell housing. Simultaneously, the chart drive was started. The absorbancy was followed at 625 $m\mu$ for 15 to 60 min. and the initial slope, as determined with a straight-edge, was taken as $[d(\text{phenoxy})/dt]_i$. The volume was measured by means of the calibrated tube and the concentration of benzoyl peroxide at the time of mixing was calculated from this value and the time of immersion in the bath using Bartlett's equation.[5] It will be noted from Table I that these corrections were not very large.

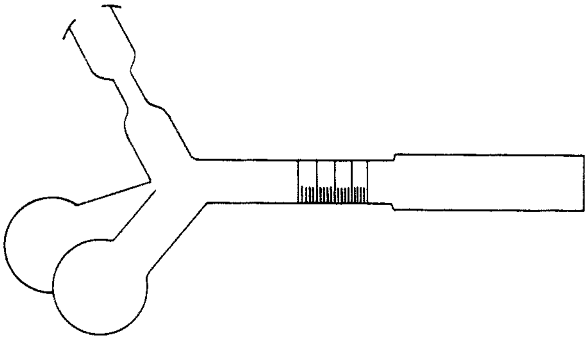

Fig. 2. Reaction vessel for kinetic studies

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[11] C. D. Cook and R. C. Woodworth, *J. Am. Chem. Soc.*, **75**, 6242 (1953).

Styrene-*p*-carboxylic Acid[1]

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Styrene-*p*-carboxylic acid was first prepared by Marvel and Overberger in 1945.[2] Their method involved the dehydration of *p*-(α-hydroxyethyl) benzonitrile followed by base hydrolysis of the nitrile. The carbinol was prepared from *p*-bromoacetophenone, a relatively expensive starting material.[3] The over-all yield for the four-step synthesis was 13%. A second synthesis, starting from *p*-ethylacetophenone, was reported later by Emerson *et al.*[4] It involves five steps and results in 19% over-all yields. The low yield step in each case was a potassium bisulfate dehydration.[5]

We wish to report a four-step synthesis of styrene-*p*-carboxylic acid from readily available ethylbenzene, which affords over-all yields of 24%. *p*-Bromoethylbenzene was prepared in 87% yield by the iodine-catalyzed bromination of ethylbenzene at 0° in the absence of a solvent. Treatment of this material with cuprous cyanide in pyridine afforded a 63% yield of *p*-ethylbenzonitrile, which was again brominated, this time in the α position. Treatment of the *p*-(α-bromoethyl)benzonitrile thus obtained with alcoholic potassium hydroxide resulted in simultaneous hydrolysis and dehydrobromination to yield styrene-*p*-carboxylic acid. The yields on the last two steps were 84 and 52%, respectively.

p-Bromoethylbenzene has been prepared previously by several methods.[6-9] We believe the iodine

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] C. S. Marvel and C. G. Overberger, *J. Am. Chem. Soc.*, **67**, 2250 (1945).

[3] An alternate synthesis from *p*-dibromobenzene resulted in much lower yields.

[4] W. S. Emerson, J. W. Heyd, V. E. Lucas, E. C. Chapin, G. R. Owens, and R. W. Shortridge, *J. Am. Chem. Soc.*, **68**, 674 (1946); British Patent **636,196**.

[5] An alternate to dehydration, pyrolysis of *p*-cyano-α-methyl-benzylacetate, was reported by C. G. Overberger and R. E. Allen, *J. Am. Chem. Soc.*, **68**, 722 (1946). This route affords a five-step synthesis from *p*-bromoacetophenone with over-all yields of 29%.

[6] R. Fittig and J. Konig, *Ann.*, **144**, 277 (1867).

[7] P. Karrer, E. Schlitter, K. Pfaehler, and F. Benz, *Helv. Chim. Acta*, **17**, 1516 (1934).

[8] J. W. Copenhaver, M. F. Roy, and C. S. Marvel, *J. Am. Chem. Soc.*, **57**, 1311 (1935).

[9] P. S. Varma, V. Sahay, and B. R. Subramonium, *J. Indian Chem. Soc.*, **14**, 157 (1937).