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DECOMPOSITION OF BENZOYL PEROXIDE IN BENZENE IN THE PRESENCE OF OXYGEN

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Abstract—Benzoyl peroxide was decomposed in benzene in the presence of O_2 at various temp, and the reaction products were determined. The ratio of phenol to biphenyl formed depends on the reaction temperature and shows that phenyl radicals react with oxygen with a greater activation energy than with benzene. The mechanistic implication of this finding is discussed.

IT HAS been shown that, whereas the decomposition of N-nitrosoacetanilide in dilute benzene solution at room temperature under nitrogen affords more than 91% biphenyl, the presence of oxygen diminishes the yield of biphenyl to only 5–7% with simultaneous production of phenol and phenolic materials in substantial amount (in 70–85%).[1] A similar effect of oxygen has also been observed in the decomposition of phenylazotriphenylmethane in benzene at 50°[2] and in the reaction[3] of aniline and isoamyl nitrite in benzene at 75°.[4] On the other hand, Eberhardt and Eliel reported that decomposition of benzoyl peroxide in dilute benzene solution under reflux, with oxygen being bubbled, gave biphenyl in yields of 1·26–1·51 moles per mole of the peroxide and phenol in 10% yield, whereas in the absence of oxygen the yield of biphenyl was about 0·5 mole.[5] Subsequently Morrison *et al.*, reported similar results.[6] This seemingly contradictory behaviour of oxygen towards several arylating reagents prompted a reinvestigation of the decomposition of benzoyl peroxide in benzene in the presence of oxygen, and the results are reported here.

Benzoyl peroxide was allowed to decompose completely in dilute benzene solution in a rapid stream of oxygen at 60–80°; the results are summarized in the Table. Extraction of the reaction mixture with water gave an aqueous extract containing peroxidic material, which seemed to be hydrogen peroxide, in 1–4 mole% as determined by iodometric titration. 1,4-Dihydrobiphenyl was not detected by gas chromatography.

The reaction in boiling benzene (at 80·1°) gave 108% of biphenyl and 25% of phenol in approximate agreement with Eberhardt and Eliel's finding.[5] However, the decrease of the reaction temperature to 75° resulted in a remarkable reduction of the yield of biphenyl with the corresponding increase of phenol. The effect of further lowering the temperature was not so conspicuous, gradually decreasing the yield of biphenyl on the one hand and increasing that of phenol on the other. Evidently, to the extent that the solubility of oxygen increases with the decrease of the reaction

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[1] R. Ito, T. Migita and O. Simamura, *Abstracts of Papers, the 16th Annual Meeting of the Chemical Society of Japan* p. 223, Tokyo (April, 1963); R. Ito, Thesis, Tokyo University (1963).

[2] M. Harada, R. Ito, T. Migita and O. Simamura, *Abstracts of Papers, the 16th Annual Meeting of the Chemical Society of Japan* p. 223, Tokyo (April, 1963).

[3] J. I. G. Cadogan, *J. Chem. Soc.* 4257 (1962).

[4] R. Ito, M. Kinoshita and O. Simamura, *Abstracts of Papers, the 17th Annual Meeting of the Chemical Society of Japan* p. 116, Tokyo (April, 1964).

[5] M. Eberhardt and E. L. Eliel, *J. Org. Chem.* **27**, 2289 (1962).

[6] R. T. Morrison, J. Cazes, N. Samkoff and C. A. Howe, *J. Amer. Chem. Soc.* **84**, 4152 (1962).

temperature, the yield of phenol increased at the expense of biphenyl. Thus, under the present experimental conditions except for the experiment with boiling benzene the behaviour of oxygen is normal and similar to that observed with other arylating reagents in this laboratory. In boiling benzene, however, the obvious conclusion is that the concentration of oxygen is nil, so that the phenyl radical cannot react with oxygen, ultimately to give phenol, except perhaps on the liquid-vapour interface. But the amount of oxygen available at the surface seems to be sufficient for the efficient production of biphenyl, probably according to the mechanism proposed by Eberhardt and Eliel.[5] The probable presence of hydrogen peroxide in the final reaction mixtures supports this mechanism.

It having been established that the phenyl radical reacts with oxygen and benzene competitively also in the case of benzoyl peroxide, the present experimental data enable a more or less quantitative comparison of these competitive reactions to be made.

$$\mathrm{Ph\cdot} + \mathrm{O_2} \xrightarrow{k_1} (\mathrm{PhO_2\cdot}) \longrightarrow \mathrm{PhOH} \qquad (1)$$

$$\mathrm{Ph\cdot} + \mathrm{C_6H_6} \xrightarrow{k_2} \mathrm{PhC_6H_6\cdot} \longrightarrow \mathrm{Ph_2} \qquad (2)$$

The phenyl radical will initially add to a molecule of oxygen probably to give a phenylperoxy radical, but its subsequent process of decomposition to give phenol as the final product is quite obscure. However, it is reasonable to assume that the yield of phenol represents a measure of addition reaction between the phenyl radical and oxygen. The yield of biphenyl is taken to be a measure of the addition of the phenyl radical to benzene. Thus, the ratio of the rate constants of the competitive reactions is assumed to be given by

$$\frac{k_1}{k_2} = \frac{[\mathrm{C_6H_6}]}{[\mathrm{O_2}]} \cdot \frac{\text{Yield of phenol}}{\text{Yield of biphenyl}}$$

and the observed values for k_1/k_2 are shown in the Table. Apparently the phenyl

TABLE 1. PRODUCTS FROM DECOMPOSITION OF BENZOYL PEROXIDE IN BENZENE IN THE PRESENCE OF OXYGEN AND THE RELATIVE REACTIVITY OF THE PHENYL RADICAL TOWARDS OXYGEN AND BENZENE[a]

Temp. (°C)	Yields of the products (mole % of the peroxide)				$\frac{\mathrm{PhOH}}{\mathrm{Ph_2}}$	$[\mathrm{O_2}]^e$ $\times 10^{+3}$ mol/l.	k_1/k_2 $\times 10^{-3}$
	PhOH[b]	$\mathrm{Ph_2}$[b]	$\mathrm{PhCO_2H}$[c]	$\mathrm{CO_2}$[d]			
80·1	25	108	23		0·23		
75	45	53	38	127	0·85	1·47	6·5
70	53	49	42	139	1·08	2·68	4·5
65	65	47	47	147	1·38	3·71	4·2
60	43	34	42	110	1·26	4·56	3·1

[a] Benzoyl peroxide (2·5 g) in 500 ml benzene (the molar ratio of benzene to the peroxide, 550), and oxygen passed in a rapid stream. [b] Determined by gas chromatography. [c] Isolated and weighed. [d] Determined by absorption in a potash bulb. [e] The concentration of oxygen in the reaction mixture, evaluated from the solubility values of oxygen[7] and the vapour pressures of benzene.[8]

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[7] Landolt-Börnstein, *Zahlenwerte und Funktionen aus Physik, Astronomie, Geophysik und Technik*, Band II, Teil 2b, p. 1–74 (1962).

[8] *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, Vol. III, p. 221. McGraw-Hill, New York (1928).

radical adds to oxygen about 10^3 times as rapidly as to benzene, but the change of k_1/k_2 with temperature shows that the activation energy for the addition to oxygen is higher by 10·4 kcal/mole than for the addition to benzene. The same value of 10·2 kcal/mole is obtained, when the difference between the amounts of the carbon dioxide and biphenyl formed is used as a measure of the amount of phenol produced.

It may be concluded from the following argument that the activation energy for the addition of the phenyl radical to oxygen should be considerably larger than that for the addition of the benzyl type radical to oxygen. It is known that the polystyryl radical reacts with styrene about $5{\cdot}5 \times 10^5$ times as rapidly as with benzene at 60°,[9] the activation energy being lower by 14·8 kcal/mole, and that the β-aralkylperoxystyryl radical adds to oxygen about $2{\cdot}5 \times 10^6$ times as fast as to styrene at 50°.[10] The difference in the activation energy is not known between the latter two reactions of the β-aralkylperoxystyryl radical, but it appears to be a reasonable estimate that the activation energy for the reaction with oxygen will be lower by, at the most, 10 kcal/mole than for the reaction with styrene, since the assumption of the equal frequency factors for these reactions leads to 8 kcal/mole for the difference in activation energy and the variation in the ratio of these frequency factors by a factor of 10^3 causes a variation of 4·5 kcal/mole in the difference in activation energy. These values suggest that k_1/k_2 for the benzyl type radical in the reactions with oxygen and with benzene will be of the order of 10^{11} and that the activation energy for the reaction of the benzyl type radical with oxygen should be lower by about 25 kcal/mole than that of the reaction with benzene. It is reasonable to assume the activation energy for the addition of the phenyl radical to benzene to be definitely lower than that of the addition of the benzyl type radical to benzene, because of the resonance stabilization in the latter type of radical. But the difference between the activation energies will be of the order of 10 kcal/mole since the extra resonance energy in the benzyl radical is estimated at 24·5 kcal/mole.[11] Accordingly, the activation energy of the addition of the phenyl radical to oxygen is thought to be larger by about 25 kcal/mole than that of the corresponding reaction of the benzyl type radical. Although this estimate may be subject to error because of lack of some of the relevant experimental values and the true value may be much lower, it is certain that the former reaction has a considerably larger activation energy.*

In view of the generally accepted electronegativity of oxygen, the cause for the higher activation energy for the phenyl radical established above is undoubtedly attributed to its higher ionization potential. Since the odd electron of the phenyl radical is regarded as occupying an sp^2-hybrid orbital, which is not conjugated with the pi-orbitals in the benzene ring, as is supported by an ESR work,[12] the ionization potential of the phenyl radical is expected to be larger than that of a benzyl type radical or of a simple aliphatic radical. In fact, the ionization potential of the

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* In a report, which became available when this work had nearly been completed, Russell and Bridger (*J. Amer. Chem. Soc.* **85**, 3765 (1963)) argued that the phenyl radical reacted less rapidly with oxygen than the benzyl type radical and pointed out the importance of a polar effect in the transition state, without however giving sufficient consideration to the activation energy.

[9] R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.* **2**, 328 (1947).
[10] A. A. Miller and F. R. Mayo, *J. Amer. Chem. Soc.* **78**, 1017 (1956).
[11] M. Szwarc, *Disc. Faraday Soc.* **2**, 39 (1947).
[12] K. Morokuma, S. Ohnishi, T. Masuda and K. Fukui, *Bull. Chem. Soc. Japan* **36**, 1228 (1963).

phenyl radical is found to be 9·90 eV[13] and that of the benzyl radical, 7·73 eV.[14]

The foregoing argument is put forth in a more explicit form by considering an electron-transfer between a radical R· and a molecule of oxygen contributing more or less to stabilization of the transition state:

$$R\cdot + O_2 \rightarrow [(R\cdot O_2) \leftrightarrow (R^+O_2^-\cdot) \leftrightarrow (RO_2\cdot)] \rightarrow RO_2\cdot$$

A similar electron-transfer has been postulated for attack by radicals on the peroxide linkage.[15] With the phenyl radical with a larger ionization potential this electron-transfer effect will not take place to the same extent as with the benzyl radical; accordingly, the activation energy will be higher.

In interaction with a radical, a molecule of oxygen, owing to its electronegativity, should readily accept an electron from the former in one of the degenerate anti-bonding pi-orbitals vπ, say $\pi_y{}^*2p$,[16] causing the electron-transfer stabilization, and further in the transition state the electron originally present in $\pi_y{}^*2p$ will be localized on one of the oxygen atom to form a bond with the attacking radical and a pair of electrons which occupy the corresponding $\pi_y 2p$ orbital will be forced to become localized as a lone pair on the other oxygen atom.

EXPERIMENTAL

Materials. Benzoyl peroxide was purified by reprecipitation from its solution in dichloromethane by addition of MeOH. Benzene was purified by the usual method and stored over Na metal; it was redistilled before use.

Reaction and analysis of the products. Benzoyl peroxide (2·5 g) was dissolved in 500 ml benzene (the molar ratio of benzene to the peroxide, 550) and allowed to stand, with O_2 being bubbled, at a specified temp until the peroxide had completely decomposed. The CO_2 evolved was determined by absorption in a potash bulb. One half of the reaction mixture was concentrated to 10–15 ml by distillation through a Vigreux column 60 cm in ht, and this concentrate was analysed for phenol and biphenyl with a Perkin-Elmer Vapour Fractometer Model 154 using an Apiezon grease column at 200° with nitrobenzene as an internal standard.

The remaining half of the reaction mixture was shaken with water, and then extracted repeatedly with 5% $NaHCO_3$aq. The aqueous extract was subjected to iodometric titration to estimate any amount of peroxidic material. The $NaHCO_3$ extract was acidified with H_2SO_4 and subjected to steam distillation, and extraction of the distillate with dichloromethane and evaporation of the solvent afforded benzoic acid, m.p. 121°, which was weighed.

Evaluation of the concentration of oxygen in benzene. The concentration of O_2 in benzene was calculated according to the equation: $[O_2] = \alpha\cdot(760 - p)/(760 \times 22\cdot4)$, where α and p denote Bunsen's absorption coefficient of O_2 in benzene[7] and the vapour press of benzene,[8] respectively.

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[13] R. J. Kandel, *J. Chem. Phys.* **22**, 1496 (1954).

[14] E. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.* **22**, 621 (1954).

[15] K. Tokumaru and O. Simamura, *Bull. Chem. Soc. Japan* **36**, 333 (1963).

[16] R. S. Mulliken, *Rev. Mod. Phys.* **4**, 1 (1932).