660. *Polar Influences in Radical Reactions. Part I. The Dehydrogenation of Substituted Dibenzyl Ethers by Free Benzoyloxy- and t-Butoxy-radicals.*

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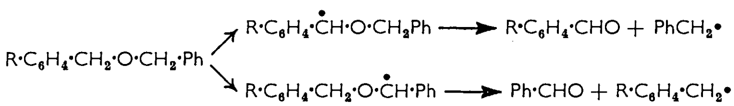
By using substituted dibenzyl ethers as substrate, effects of substituents on the abstraction of benzylic hydrogen atoms by the benzoyloxy-radical have been measured. The rates of reaction follow the Hammett ρσ relationship, showing a polar effect comparable with that for the peroxy-radical. Earlier work on the t-butoxy-radical has been confirmed and extended.

In the study of polar effects in radical reactions, the method of widest applicability has been measurement of the effect of *meta*- and *para*-substituents on the rate of abstraction of benzylic hydrogen atoms from toluenes and related compounds. Radicals which have been studied include atomic bromine[1] and chlorine,[2] and free peroxy,[3] t-butoxy,[4] succinimidyl,[1] and trichloromethyl[1, 5] radicals. Except for the last radical,[5] the rate of reaction in each case has been found to follow the Hammett ρσ relationship. This paper reports a similar study of the benzoyloxy-radical, the substrate used being monosubstituted dibenzyl ethers. Earlier qualitative work[6] on the t-butoxy-radical has been confirmed on a semi-quantitative basis.

Except for the peroxy-radical, the relative rates of hydrogen abstraction have previously been estimated by using intermolecular competitive reactions, in which a radical is generated in an excess of a mixture of two competing substrates. The method now reported differs from this in that it makes use of an intramolecular competitive process between phenyl and substituted phenyl groups in the ether molecule, abstraction occurring as follows:



$$R{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}Ph \begin{cases} \nearrow R{\cdot}C_6H_4{\cdot}\dot{C}H{\cdot}O{\cdot}CH_2Ph \longrightarrow R{\cdot}C_6H_4{\cdot}CHO + PhCH_2{\bullet} \\ \searrow R{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}\dot{C}H{\cdot}Ph \longrightarrow Ph{\cdot}CHO + R{\cdot}C_6H_4{\cdot}CH_2{\bullet} \end{cases}$$

The radicals generated then disproportionate[7] independently to give two aldehydes, which are isolated by chromatography of their 2,4-dinitrophenylhydrazones. One of the sources of error inherent in the intermolecular process, namely, that of unequal concentration of the two substrates in the later stages of the reaction, is therefore eliminated. On the other hand, abstraction by the free benzyl radicals, produced by disproportionation, could

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[1] Kooyman, van Helden, and Bickel, *Proc. k. ned. Akad. Wetenschap.*, 1953, **56***B*, 75.

[2] van Helden and Kooyman, *Rec. Trav. chim.*, 1954, **73**, 269; Walling and Miller, *J. Amer. Chem. Soc.*, 1957, **79**, 4181.

[3] (*a*) Russell, *J. Amer. Chem. Soc.*, 1956, **78**, 1047; (*b*) Walling and McElhill, *ibid.*, 1951, **73**, 2927.

[4] (*a*) Johnston and Williams, *J.*, 1960, 1446; (*b*) Walling and Jacknow, *J. Amer. Chem. Soc.*, 1960, **82**, 6113.

[5] Huyser, *J. Amer. Chem. Soc.*, 1960, **82**, 394.

[6] Huang and Yeo, *J.*, 1959, 3190.

[7] Huang and Si-Hoe, (*a*) *Proc. Chem. Soc.*, 1957, 354; (*b*) " Vistas in Free Radical Chemistry," ed. W. A. Waters, Pergamon Press, London, 1959, p. 242.

also occur. However, as these are resonance-stabilised radicals, the extent to which they abstract hydrogen is probably slight.[8]

Dehydrogenation by Benzoyloxy-radicals.—Although many atoms and radicals have been investigated with respect to their abstraction of benzylic hydrogen atoms, study of the benzoyloxy-radical has not been feasible because of the ease with which it is decarboxylated, and the tendency of benzoyl peroxide to suffer induced decomposition by free benzoyloxy-radicals and by attack of the secondary radical derived from the substrate.[9] Thus, decomposition of benzoyl peroxide in alkylbenzenes gives largely products which result from attack by free phenyl and not benzoyloxy-radicals,[10] whilst the reaction of the peroxide with diethyl ether involves [11] the induced decomposition:

$$\mathrm{Et{\cdot}O{\cdot}Et + Ph{\cdot}CO_2{\bullet} \longrightarrow Et{\cdot}O{\cdot}\overset{\bullet}{C}H{\cdot}Me + Ph{\cdot}CO_2H}$$

$$\mathrm{Et{\cdot}O{\cdot}\overset{\bullet}{C}H{\cdot}Me + (Ph{\cdot}CO)_2O_2 \longrightarrow Et{\cdot}O{\cdot}CH(O{\cdot}COPh){\cdot}Me + Ph{\cdot}COO{\bullet}},\ \text{etc.}$$

Since it is known that decarboxylation can be reduced by the use of a more reactive substrate (*e.g.*, a decrease from 96% to 30% when cyclohexane is replaced by cyclohexene),[12] and eliminated in the presence of a " scavenger " (*e.g.*, Hammond's reagent),[13] it should be possible to obviate decarboxylation by the use of a substrate from which hydrogen can be abstracted with great ease. The second difficulty can be circumvented if the substrate is one which on dehydrogenation gives rise to a radical that does not appreciably attack the peroxide. Benzyl ether appears to fulfil both of these requirements because of its high reactivity towards hydrogen-abstracting radicals (being about 150 times that of toluene towards the peroxy-radical,[3a] an entity similar in nature to free benzoyloxy-radicals), and the fact that the derived radical is resonance-stabilised, and itself disproportionates readily [14] into benzaldehyde and free benzyl radicals. These expectations were justified, as it has now been found that decomposition of benzoyl peroxide in an excess of dibenzyl ether, under conditions which ensure a low concentration of the peroxide at all times, gives benzoic acid in no less than 83—90% yield (*i.e.*, 1·7—1·8 moles from 1 mole of the peroxide), and benzaldehyde in 82—94% yield calculated on the benzoic acid formed. It must be taken into account that at least a few per cent of peroxide have been lost through intramolecular decomposition, or the " cage " reaction (to give phenyl benzoate),[13, 15] and that the yield of benzoic acid can be considered as being close to quantitative. These results contrast with those observed when benzoyl peroxide decomposed in diethyl ether,[11] from which the products consisted of (from 1 mole of the peroxide) 0·8 mole of benzoic acid and 0·9 mole of 1-ethoxyethyl benzoate, and indicate the absence of appreciable decarboxylation and induced decomposition. The high yield of benzaldehyde further shows that, under the reaction conditions, attack by the radical on the aldehyde was negligible.

In this work benzoyl peroxide was decomposed at 80—90° in dibenzyl ethers substituted with the *m*- and *p*-chloro-, *p*-t-butyl-, *p*-phenyl-, and *p*-methoxy-groups. In every case the benzaldehyde and substituted benzaldehyde produced were isolated by chromatography of the 2,4-dinitrophenylhydrazones.

Dehydrogenation by Free t-Butoxy-radicals.—A qualitative study of the dehydrogenation of dibenzyl ethers by this radical (generated from di-t-butyl peroxide at 110°) has been reported,[6] in which the main direction of abstraction for each ether was determined by the isolation, as the bisulphite compound, of one of the aldehydes in over 50% yield.

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[8] Cf. refs. 4*a* and 6.

[9] See Walling, " Free Radicals in Solution," Wiley and Sons, New York, 1957, p. 474.

[10] Dannley and Zaremsky, *J. Amer. Chem. Soc.*, 1955, **77**, 1588; see also Hey in ref. 7*b*, p. 209.

[11] Cass, *J. Amer. Chem. Soc.*, 1947, **69**, 500; 1950, **72**, 4915; see also Danney and Feig, *ibid.*, 1959, **81**, 5322.

[12] See ref. 9, pp. 481, 482.

[13] de Tar and Lamb, *J. Amer. Chem. Soc.*, 1959, **81**, 122.

[14] Cf. Huang and Singh, *J.*, 1959, 3183.

[15] Lynch and Pausacker, *Austral. J. Chem.*, 1957, **10**, 40.

The substituents *p*-chloro-, *p*-t-butyl, and *p*-methoxy- were thus found to be more effective than hydrogen in facilitating abstraction of the benzylic hydrogen atom. Results for the *m*-chloro-substituent were inconclusive. In this work the effects of the *p*-t-butyl and *p*-chloro-groups have been confirmed, and that of the *m*-chloro-group determined.

Besides dehydrogenation by free benzyl radicals, as mentioned above, another source of slight uncertainty could arise, *i.e.*, abstraction by free methyl radicals produced by disproportionation of the t-butoxy-radical. In the presence of a reactive substrate such as dibenzyl ether, however, breakdown of the t-butoxy-radical is probably negligible, from consideration of the following points. In the abstraction of hydrogen atoms from various hydrocarbons by this radical, the proportion of abstraction to disproportionation, as measured by the ratio t-butyl alcohol : acetone, has been successfully used to evaluate the relative reactivities of the substrates towards dehydrogenation.[16] This ratio, in the case of *p*-chlorotoluene, is [4a] about 7 : 1 at 110°. Since dibenzyl ether is approximately 175 times more reactive than *p*-chlorotoluene towards the peroxy-radical,[3a] and since it would be reasonable to expect the same order of reactivity with free t-butoxy-radicals, the t-butyl alcohol : acetone ratio with dibenzyl ether would be in the region of $(175 \times 7) : 1$. Interference by free methyl radicals must therefore be negligible.

EXPERIMENTAL

The substituted dibenzyl ethers were prepared as previously described.[17] Benzoyl peroxide (Eastman) was dissolved in AnalaR chloroform and precipitated with AnalaR methanol. This process was repeated, and the material so obtained was dried (P_2O_5). Iodometric titration showed it to be more than 99% pure. t-Butyl peroxide was distilled before use.

Chromatography of 2,4-Dinitrophenylhydrazones.—Reagent [18] *and materials.* 2,4-Dinitrophenylhydrazine (5 g.) was dissolved in warm 89% phosphoric acid (57 ml.), and the solution was made up with 95% ethanol to 100 ml. (For precipitation of the 2,4-dinitrophenylhydrazones from mixtures of aldehydes, a slight excess of the reagent was always used.) Kieselguhr and bentonite (British Drug Houses) were both sieved (80 mesh), and dried at 150° for 2 days. Chloroform was washed successively with concentrated sulphuric acid (10% v/v) and water (3—4 times) until completely free from cloudiness, and dried ($CaCl_2$) and distilled before use.

General procedure.[19] A mixture of the two aldehyde dinitrophenylhydrazones was dissolved in the minimum quantity of chloroform and adsorbed on a column of kieselguhr–bentonite (1 : 4 by weight) in the same solvent, then eluted first with chloroform, then with chloroform containing increasing amounts of analytical grade methanol (up to 4%). On chromatography, all the binary mixtures of dinitrophenylhydrazones obtained from cleavage experiments (except for a mixture of those from tolualdehyde and benzaldehyde) gave two distinct bands, and on elution the pure derivatives were obtained (m. p. and mixed m. p.). In a trial run, with material prepared from a synthetical mixture of freshly distilled benzaldehyde and anisaldehyde, recovery of the aldehydes as their 2,4-dinitrophenylhydrazones amounted to more than 95% of each component.

Decomposition of Benzoyl Peroxide in Dibenzyl Ether.—Benzoyl peroxide (1·36 g., 0·0056 mole) was added in 8 portions at intervals of 0·5 hr. to freshly distilled dibenzyl ether (27 g., 0·14 mole) at 80—90° (oil bath) under nitrogen. The odour of benzaldehyde was soon perceptible. When the addition was complete, the temperature was maintained at 80—90° for a further ½ hr., then raised to 110° for 1 hr., and the mixture was allowed to cool. Ether (150 c.c.) was added, and the solution was extracted, under nitrogen, with an air-free saturated solution of sodium hydrogen carbonate (3×60 c.c.), and then dried ($MgSO_4$). Acidification of the bicarbonate extract followed by isolation with chloroform yielded benzoic acid (1·21 g., 90%), m. p. and mixed m. p. 118—120°. The ethereal solution was concentrated under nitrogen through a 12-in. Vigreux column, and the residue was distilled under reduced pressure, with the receiver and trap at −80° (solid CO_2). The following fractions were collected: (*a*) a liquid (4·8 g.), b. p. 40—121°/0·1 mm., containing mainly benzaldehyde and unchanged dibenzyl ether

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[16] Brook, *Trans. Faraday Soc.*, 1957, **53**, 327.

[17] Huang and Si-Hoe, *J.*, 1957, 3988.

[18] Johnson, *J. Amer. Chem. Soc.*, 1951, **73**, 5888.

[19] Elvidge and Whalley, *Chem. and Ind.*, 1955, 589.

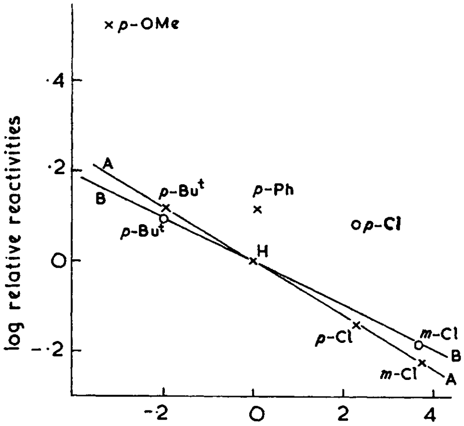
(fractionation was begun after the ether had begun to distil, in order to ensure removal of all benzaldehyde), and (*b*) the unchanged ether (19 g.), b. p. 121—124°/0·1 mm., n_D^{29} 1·5582. Fraction (*a*), diluted with ethanol (10 c.c.), was added to the 0·25M-solution of 2,4-dinitrophenylhydrazine (50 c.c.) described above, heated (steam bath) for 10 min., and set aside for 12 hr. After dilution with water (20 c.c.) the product was centrifuged, washed with water (2 × 30 c.c.), and dried. It was then dissolved in chloroform (800 c.c.) and chromatographed on bentonite–kieselguhr (60 g.) to give benzaldehyde 2,4-dinitrophenylhydrazone (2·66 g., 94%), m. p. and mixed m. p. 234—236°.

Decomposition of Benzoyl Peroxide in Substituted Dibenzyl Ethers.—Duplicate experiments were carried out on each ether as described above, using approx. 0·1 mole of the ether and 0·005 mole of the peroxide. At the end of the reaction the aldehydes were distilled from the reaction mixture and isolated as a mixture of 2,4-dinitrophenylhydrazones, which was chromatographed (samples of approx. 1 g. being used) to give the pure derivatives.

Decomposition of Di-t-butyl Peroxide in Substituted Dibenzyl Ethers.—(Cf. Huang and Yeo.[6]) A mixture of the ether (0·1 mole) and the peroxide (0·0125 mole) was heated for 46 hr. under argon at 110° (toluene bath), under an efficient reflux condenser. The aldehydes were distilled off and isolated as a mixture of 2,4-dinitrophenylhydrazones, duplicate samples (approx. 300—600 mg.) of which were chromatographed.

RESULTS AND DISCUSSION

In the Table are listed the results of dehydrogenation experiments in terms of the molar ratio, substituted benzaldehyde : benzaldehyde. This ratio for each ether expresses the relative rates of hydrogen-abstraction at the two benzylic carbon atoms.



Hammett plots for the benzoyloxy-radical (×) and the t-butoxy-radical (○).

Molar ratio $R{\cdot}C_6H_4{\cdot}CHO : Ph{\cdot}CHO$ from dehydrogenation of $R{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}Ph$.

	Abstraction by free benzoyloxy-group [a]			Abstraction by free t-butoxy-group [b]		
R	(*a*)	(*b*)	Mean	(*a*)	(*b*)	Mean
m-Cl	0·56	0·63	0·60	0·65	0·70	0·68
p-Cl	0·77	0·67	0·72	1·2	1·2	1·2
p-Bu^t	1·3	1·3	1·3	1·2	1·2	1·2
p-Ph	1·3	1·3	1·3			
p-OMe	3·3 [c]	—	3·3			

[a] Results of duplicate experiments. [b] Results of duplicate chromatographic analyses from single experiments. [c] Mean of duplicate chromatographic analyses.

A Hammett plot [20] for the benzoyloxy-radical is shown in the Figure. Although the present method is no more than semi-quantitative, the pattern of results is clear, and

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[20] σ values taken from Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 188.

indicates a polar effect in attack by the benzoyloxy-radical. The slope of the best straight line, obtained by the method of least squares (correlation coefficient r = —1·0), is found to be —0·6 which, not surprisingly, is the same as that obtained by Russell[3a] for the peroxy-radical at about the same temperature (90°). The point for the substituent *p*-phenyl is seen to be off the straight line (A), indicating the preponderance of other effects controlling the course of the reaction. This has been encountered before, *e.g.*, in the attack of chlorine atoms on substituted toluenes,[2b] and has been attributed to the fact that resonance stabilisation is here the over-riding factor. The abnormally high value for the *p*-methoxy-group has also been noted elsewhere,[1] and is probably due to side reactions.[21]

The results for the t-butoxy-radical afford a more quantitative appraisal of the effects of the *p*-t-butyl- and *p*-chloro-substituents than the earlier work,[6] and give an evaluation for the *m*-chloro-atom. In the Hammett plot for the t-butoxy-radical (r = —0·97), however, the point for the *p*-chloro-atom lies off the best straight line (B), and no explanation of this can at present be given. An attempt to substantiate the findings by dehydrogenating *p*-methyldibenzyl ether was not successful, as the aldehydes produced could not be separated by our method. The slope ρ (—0·5) is the same as that obtained by Johnston and Williams[4a] at the same temperature (110°), and is to be expected. It is worthy of note that, by using t-butyl hypochlorite, Walling and Jacknow[4b] have been able to study the reaction at 40°, and have found ρ = —0·8.

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[21] Harrison, Kebarle, and Lossing, *J. Amer. Chem. Soc.*, 1961, **83**, 777.