

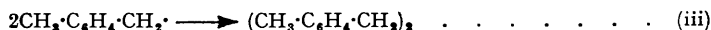
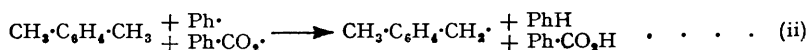
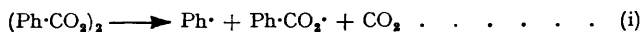
The Reactivity of p-Methylbenzyl Radicals. A Novel Application of the Kinetic Isotope Effect.

By J. I. G. CADOGAN, V. GOLD, and D. P. N. SATCHELL.

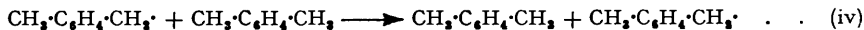
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The decomposition of dibenzoyl peroxide in [α - $^2\text{H}_1$]p-xylene produces 4:4'-dimethyldibenzyl containing the statistically expected proportion of deuterium atoms. The result indicates that, under the conditions of the experiment, the reaction of p-methylbenzyl radicals with p-xylene, $\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\dot{\text{C}}\text{H}_2 + \text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3 \longrightarrow \text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2 + \dot{\text{C}}\text{H}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$, occurs much more readily than their dimerisation.

It is well known that the decomposition of dibenzoyl peroxide in an aromatic solvent PhX (where X = NO₂, halogen, Ph, OMe, or H) gives, as the main products, benzoic acid and a mixture of monosubstituted diphenyls (Hey *et al.*, *J.*, 1954, 794, and earlier papers). The phenylation of alkylbenzenes is complicated by the possibility of attack in the side chain (Augood, Hey, Nechvatal, Robinson, and Williams, *Research*, 1951, 4, 386). Thus, when dibenzoyl peroxide in low concentration decomposes in p-xylene solution, 4:4'-dimethyldibenzyl is formed to an appreciable extent, which is consistent with the following mechanism:



The question arises as to whether the p-methylbenzyl radicals concerned in equation (iii) are only those resulting from reaction (ii), or whether fresh radicals arise owing to the presence of the following chain reaction:



Which of these two alternatives is correct will depend on the relative importance of hydrogen abstraction and dimerisation as the mode of reaction of the p-methylbenzyl radicals under the prevailing experimental conditions. This type of problem cannot be attacked by conventional methods of investigation but, as is now shown, can be solved by application on a hydrogen-isotope technique involving determination of the isotopic composition of the dimer resulting from p-xylene of known isotopic distribution.

EXPERIMENTAL

The method of hydrogen-isotope analysis employed has been described by Bryce-Smith, Gold, and Satchell (*J.*, 1954, 2743).

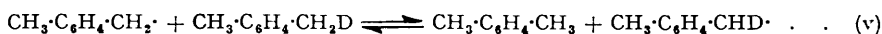
Preparation of [α - $^2\text{H}_1$]p-Xylene.—p-Methylbenzyl alcohol (m. p. 60°), prepared from p-toluic acid by reduction with lithium aluminium hydride, was converted into p-methylbenzyl bromide (m. p. 35°; 60%) by Kamm and Marvel's method (*Org. Synth.*, Coll. Vol. I, p. 25). The halide (0.23 mole), in ether, was converted into the Grignard reagent from which the deuterated hydrocarbon was prepared by the slow (20 min.; dropwise) addition of deuterium oxide (0.4 mole; 99.7% purity) to the vigorously agitated solution of the Grignard reagent, kept at its b. p. The mixture was stirred for a further 30 min., and solid carbon dioxide was then added in order to remove unchanged Grignard reagent. The mixture was acidified (N-hydrochloric acid) and the layers were separated. The ether solution was successively washed with water, 2N-sodium hydroxide (twice), and water, and dried (CaCl₂). Evaporation of the solvent from the filtered solution left a pale yellow oil, which was distilled (helix-packed column). The fraction of b. p. 138°/760 mm. was refractionated from sodium metal to give [α - $^2\text{H}_1$]p-xylene (yield 60%) of the same b. p., and m. p. 13° (unchanged by

fractional freezing) (Found: D, 6.95. Calc. for C_8H_9D : D, 10.00 atoms %).^{*} A portion of the product was oxidised by alkaline potassium permanganate. The resulting terephthalic acid was found to contain D, 0.47 atom %, indicating the presence of a small amount of deuterium in the nucleus (cf. Bryce-Smith, Gold, and Satchell, *loc. cit.*). On the assumption that no multiply deuterated compounds are formed in the reaction, the composition of the product was therefore: $CH_2D \cdot C_6H_4 \cdot CH_3$, 66.7; $CH_3 \cdot C_6H_3D \cdot CH_3$, 2.8; $CH_3 \cdot C_6H_4 \cdot CH_3$, 30.5 mole %.

Decomposition of Dibenzoyl Peroxide in [α - 2H_1]p-Xylene.—Dibenzoyl peroxide (1.9 g.) was added (10 min.) to the solvent (20 g.) kept at 80° in a thermostat. After 72 hr. the decomposition was considered to be complete and the excess of *p*-xylene was removed by distillation through a helix-packed column. The residual oil was boiled under reflux with 2*N*-sodium hydroxide (30 ml.) for 8 hr. in order to hydrolyse the esters present. The mixture was extracted with benzene (4 × 20 ml.), and the combined extracts were washed with water and dried (CaCl₂). The benzene was removed by distillation (10" column), and the pale yellow oil distilled *in vacuo*, giving a pale yellow semi-solid product (b. p. 60–90°/0.15 mm.; 1.10 g.). The liquid was removed by filtration through sintered glass, and the solid residue (0.75 g.) was recrystallised to constant m. p. (82°) from aqueous methanol, giving 4:4'-dimethyldibenzyl (0.23 g.) in colourless plates. The product contained D, 6.4 ± 0.1 atoms %.

DISCUSSION

When *p*-methylbenzyl radicals are formed by reaction of [α - 2H_1]-*p*-xylene with the free radicals resulting from the decomposition of benzoyl peroxide, there is competition between the rupture of C–H and C–D bonds. The theoretical considerations which predict that C–H bonds will break more rapidly than C–D bonds are well known, and have been abundantly verified experimentally—for the particular case of homolytic fission in solution by Kharasch, Rowe, and Urry *J. Org. Chem.*, 1951, 16, 905). Consequently, the *p*-methylbenzyl radicals formed in the reaction considered would be expected to contain more than the statistically calculated proportion of deuterium. If the dimer is formed by the combination of a pair of this "first generation" of radicals, then it will have the same deuterium content as these radicals. If, on the other hand, dimerisation is very unlikely compared with hydrogen abstraction [equation (iv)] then isotopic equilibrium between the *p*-methylbenzyl radicals and the *p*-xylene may be established, by reactions such as (v), before dimerisation occurs:



If, as would be expected, the equilibrium constants for such reactions are close to unity, isotopic equilibration will result in a statistical distribution of deuterium among the α -hydrogen atoms of the *p*-xylene. It can be shown that, for such a distribution,[†] the deuterium content of any reaction product, resulting from the replacement of an α -hydrogen atom, is that expected statistically and is independent of the relative rates of protium and deuterium abstraction. This circumstance illustrates a statement previously made (Bryce-Smith, Gold, and Satchell, *loc. cit.*) emphasising the dependence of the isotopic composition of the reaction product, not only on the relative ease of abstraction and abundance of the isotopic atoms, but also on their distribution.

The proportion of deuterium found in the 4:4'-dimethyldibenzyl was 6.4 ± 0.1 atoms %. The atom percentages calculated on the assumptions that protium abstraction is (a) as probable as deuterium abstraction, (b) twice as probable, and (c) infinitely more probable are 6.49, 6.88, and 7.30, respectively. (This calculation is based on the isotopic composition of the xylene sample employed, and takes into account the small amount of nuclear deuteration.) The experimental value agrees only with the first of these assumptions. This result can, in the light of previous discussion, be interpreted in two ways. It means either that the rates of protium and deuterium abstraction are identical

^{*} The atom percentage of deuterium represents the ratio, multiplied by 100, of the number of deuterium atoms in the compound to the total number of hydrogen (protium and deuterium) atoms in it.

[†] The fractional abundance of the species $X^2H_n^1H_{m-n}$, where m is the number of equivalent replaceable hydrogen atoms in the molecule, is given by $m!p^n(1-p)^{m-n}/n!(m-n)!$ where p is the fraction of deuterium atoms in the replaceable hydrogen atoms of the whole system.

or that the radicals thus formed attain, or at any rate approach, isotopic equilibrium with the solvent xylene before appreciable dimerisation occurs. In view of the experimental evidence to the contrary, the first of these alternatives seems untenable and we conclude that, under the specific conditions of our experiments, hydrogen abstraction occurs much more readily than dimerisation.

In a suitable case the validity of the assumption implicit in this view concerning the relative velocities of protium and deuterium abstraction by the initiating radical X· (phenyl or benzoyloxy-radicals in the present case) could be tested by carrying out an isotopic assay on the substance XH. The method could then be elaborated into a technique for measuring the chain length of the self-propagation reaction (iv). In the present work it was not experimentally possible to carry out an assay on the benzene or benzoic acid formed.

With the aid of a mass spectrometer, or by infra-red spectrometry, it might also be possible to observe the isotopic randomisation of deuterium among the *p*-xylene molecules produced by the chain reaction.

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