[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Reactions of Free Radicals with Aromatics. II. Involvement of Ring Hydrogens in the Reaction of Methyl Radicals with Alkylbenzenes[1]

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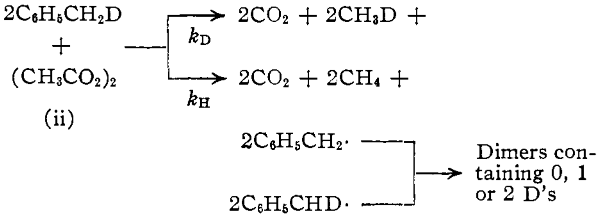
RECEIVED JANUARY 6, 1958

An attempt has been made to determine the isotope effect in the conversion of toluene-α-*d* to bibenzyl (using acetyl peroxide, benzoyl peroxide and di-*t*-butyl peroxide) both from the deuterium content of the bibenzyl and from the deuterium content of the methane, benzene or *t*-butyl alcohol formed concurrently. The two apparent isotope effects do not agree. Part of the discrepancy is due to abstraction of *ring*-hydrogen instead of side-chain hydrogen by the initiating radical, as shown by the reaction of acetyl peroxide with ring-deuterated toluene, ethylbenzene, cumene and *p*-xylene which gives rise to some methane-*d*. Abstraction of ring-hydrogen by methyl radicals is assumed to be preceded by addition of another methyl radical to the aromatic. This process competes quite favorably with α-hydrogen abstraction in toluene, less so in ethylbenzene and least in cumene. Partly because of this process, a previous determination of the isotope effect in the reaction of toluene-α-*d* with acetyl peroxide is in error. The upper limit of this isotope effect at 120° is now found to be 7, both from the deuterium content of the dimer (bibenzyl) and from the deuterium content of the methane produced in the decomposition of acetyl peroxide in toluene-α-*d* in very dilute solution where hydrogen abstraction from sources other than the side-chain becomes unimportant.

The reaction of alkylbenzenes possessing at least one α-hydrogen with free radicals of various origins is known to give rise to dimeric materials,[2] according to equation i

$$2C_6H_5CHRR' + 2M\cdot \longrightarrow 2MH + 2C_6H_5\dot{C}RR' \quad \text{(ia)}$$
$$2C_6H_5\dot{C}RR' \longrightarrow C_6H_5CRR'{-}CRR'C_6H_5 \quad \text{(ib)}$$
$$M = CH_3\cdot,\ C_6H_5\cdot,\ (CH_3)_3CO\cdot,\ \text{etc.}$$

Isotope effects in the hydrogen abstraction step (ia) involving alkylbenzenes with deuterium in the α-position of the side chain have been measured,[3] and a surprisingly high[4] value of 9.9 was found for the isotope effect in the dimerization of toluene-α-*d* by means of acetyl peroxide (eq. i, $R = H$, $R' = D$, $M = CH_3$). This value was calculated from the methane/methane-*d* ratio in the gas evolved (eq. ii) rather than from the deuterium content of the dimer.



(ii)

In connection with another investigation[5] we had occasion to re-examine the decomposition of acetyl peroxide in toluene-α-*d* as well as to study the decomposition of benzoyl peroxide and di-*t*-butyl peroxide in toluene-α-*d* and the decomposition of acetyl peroxide and benzoyl peroxide in *p*-xylene-α-*d*. In all instances the isotope effect was calculated from the deuterium content of the dimer, and in those cases (acetyl peroxide, di-*t*-butyl peroxide) where methane was produced, the isotope effect was also calculated from the methane/methane-*d* ratio in the gas. In one instance involving benzoyl peroxide, the isotope effect was also calculated from the benzene/benzene-*d* ratio. Moreover, in the case of the di-*t*-butyl peroxide induced reaction—which produces *t*-butyl alcohol as well as methane plus acetone—the deuterium content of the alcohol was determined by treating it with methyl Grignard reagent and finding the methane/methane-*d* ratio in the gas so produced, and from the resulting data an isotope effect was again calculated. As shown in Table I, whereas the isotope effect calculated from the dimer composition in the case of acetyl peroxide composition in toluene-α-*d* varied from 2.4 to 7.1, that calculated from the methane composition ranged from 8.8 to 9.6 (entries 1–5). A similar discrepancy was found in the benzoyl peroxide decomposition (entry 6) where the isotope effect calculated from dimer composition was 3.1 and that from benzene composition was 5.5 and in the di-*t*-butyl peroxide decomposition (entry 7) where the isotope effect calculated from dimer composition was 3.8, that from methane composition was 7.3 and that from *t*-butyl alcohol composition was 5.3. Only in the case of *p*-xylene-α-*d* (entry 9) did the isotope effects calculated in the two different ways agree within the limits of experimental error.

Although there is considerable scatter in the data derived from dimer composition,[6] there is no doubt

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(1) Presented in part before the Division of Petroleum Chemistry of the American Chemical Society at Atlantic City, N. J., September 20, 1956.

(2) (a) M. S. Kharasch, H. C. McBay and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945); (b) D. R. Augood, D. H. Dey, A. Nechvatal, T. S. Robinson and G. H. Williams, *Research (London)*, **4**, 386 (1951); (c) E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 131 (1951); (d) J. I. G. Cadogan, V. Gold and D. P. N. Satchell, *ibid.*, 561 (1955); (e) R. L. Dannley and B. Zaremsky, THIS JOURNAL, **77**, 1588 (1955); (f) C. S. Rondestvedt and H. S. Blanchard, *ibid.*, **77**, 1769 (1955); (g) D. H. Hey, B. W. Pengilly and G. H. Williams, *J. Chem. Soc.*, 1463 (1956); (h) G. W. K. Cavill and D. H. Solomon, *ibid.*, 3943 (1954); (i) H. C. McBay, O. Tucker and A. Milligan, *J. Org. Chem.*, **19**, 1003 (1954). We were not able to duplicate the high yields of bibenzyl referred to in this publication (footnote 3).

(3) W. H. Urry, Abstracts, Twelfth National Organic Chemistry Symposium, Am. Chem. Soc., Denver, Colo., 1951, p. 30. The result with toluene-α-*d* frequently has been quoted; *e.g.*, F. D. Greene, W. A. Remers and J. W. Wilson, THIS JOURNAL, **79**, 1416 (1957), and ref. 4.

(4) *Cf.* K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

(5) E. L. Eliel, Ph. H. Wilken, F. T. Fang and S. H. Wilen, THIS JOURNAL, **80**, 3303 (1958).

(6) The scatter does not appear to be a function of analytical peroxide concentration—*ca.* 1 *M* in runs 1–4, *ca.* 5 *M* in run 5—and in at least one case—entries 3 and 4, Table I—manifested itself as a serious lack of reproducibility between two apparently identical runs. We are led to believe that these difficulties are inherent in the technique of adding a relatively concentrated peroxide solution to a hot substrate, as the peroxide concentration at the moment of decomposition may differ widely from the analytical concentration and the temperature may fluctuate widely also. The ideal way to overcome these difficulties would be to decompose acetyl peroxide in a very dilute, homogeneous solution of toluene-α-*d*. Unfortunately, because of the low yield of bibenzyl, this would involve either the use of an impractically large amount of toluene-*d* or the recovery of an amount of bibenzyl insufficient for analysis.

TABLE I

ISOTOPE EFFECTS IN THE DECOMPOSITION OF PEROXIDES IN ALKYLBENZENES DEUTERATED IN THE α-POSITION OF THE SIDE CHAIN

Entry no.	Substrate	Isotopic purity, %[a]	Peroxide	Mole ratio[b]	Temp., °C.	Product, atom% D[c]	Isotope effect		Ref.
							Dimer	Methane	
1	$PhCH_2D$	98.7	Ac_2O_2[d]	4	125	13.1[e]	$7.1^{+1.3}_{-1.0}$	..	[f]
2	$PhCH_2D$	97.5	Ac_2O_2[d]	4	112–122	12.85[e]	$6.8^{+1.3}_{-0.9}$	9.0	[f]
3	$PhCH_2D$	97.7	Ac_2O_2	10.3	109–115	11.54	$2.5^{+0.1}_{-0.2}$	9.6	[f]
4	$PhCH_2D$	97.7	Ac_2O_2	10	109–115	12.43	$4.4^{+0.5}_{-0.4}$	8.8	[f]
5	$PhCH_2D$	97.5	Ac_2O_2	1.4[g]	Reflux	12.40	$4.4^{+0.5}_{-0.4}$	9.0	[f]
6	$PhCH_2D$	97.7	Bz_2O_2	10.6	110–116	11.92[e]	$3.1^{+0.2}_{-0.3}$	5.5[h]	[f]
7	$PhCH_2D$	97.7	DTBP[i]	10.1	107–116	12.25[e]	$3.8^{+0.4}_{-0.3}$	7.3(5.3[j])	[f]
8	$PhCH_2D$	[k]	Ac_2O_2	[k]	120	...	.....	9.9	3
9	p-$CH_3C_6H_4CH_2D$	95.05	Ac_2O_2	6	122–124	10.24[e]	$8.9^{+12.3}_{-3.3}$	6.6	[f]
10	p-$CH_3C_6H_4CH_2D$	95.05	Bz_2O_2	23.7	80	9.79[e]	$2.8^{+0.6}_{-0.5}$	..	[f]
11	p-$CH_3C_6H_4CH_2D$	66.7	Bz_2O_2	23.7	80	6.4	1.0	..	2d
12	$PhCHDCH_3$	[k]	Ac_2O_2	[k]	80	[k]	8.6	8.6	3
13	$PhCHDCH_3$	[k]	Ac_2O_2	[k]	120	...	.....	6.6	3
14	$PhCHDCH_3$	[k]	Ac_2O_2	[k]	135	...	.....	6.2	3
15	$PhCHDCH_3$	[k]	DTBP[i]	[k]	120	...	.....	5.5(4.1[j])	3

[a] ±0.2%. [b] Moles substrate/mole peroxide. [c] ±0.1%. [d] The commercial 25% solution in dimethyl phthalate was used. [e] Average of two combustion analyses. [f] This work. [g] See ref. 5. [h] From benzene-*d*/total benzene ratio. [i] Di-*t*-butyl peroxide. [j] Value in parentheses derived from *t*-BuOD/total *t*-butyl alcohol ratio. [k] Not available from published data.

that these data differ significantly from those derived from methane composition. In particular, although the methane data are in experimental agreement with the data of Urry,[3] the dimer data point to a considerably lower and more reasonable isotope effect for the hydrogen abstraction reaction than do the methane data.

It is unlikely that the dimer data are faulty. Two possible sources of error must be considered, namely, analytical difficulties and distortion of the isotope effect by some further reaction of the dimer which affects the various isotopic species unevenly. The former source of error is unlikely, as deuterium analyses are accurate to ±0.1% absolute and, as shown in Table II, the difference in deuterium content for dimer produced with an isotope effect of 4.5 and dimer produced with an isotope effect of 9.0 is 0.7%. Contamination of the dimer with deuterium-free impurities is also unlikely, as a low isotope effect was observed in no less than seven instances, and in each case the bibenzyl was purified carefully.[7]

TABLE II

DEUTERIUM CONTENT AS A FUNCTION OF ISOTOPE EFFECT IN BIBENZYL[a]

Isotope effect	1	2	3	4.5	6	9	∞
% D	9.6	11.5	12.3	12.9	13.2	13.6	14.3

[a] Assuming 98% isotopic purity of starting toluene.

Distortion of the isotope effect as calculated from either the dimer or the methane composition by further attack of radicals on dimer[8] cannot account for the discrepancy between the two sets of figures either. This is easily shown by the argument of *reductio ad absurdum*. Let us assume, in entry 2, Table I that the "real" isotope effect were 8, *i.e.*, between the "dimer isotope effect" of 6.8 and the "methane isotope effect" of 9.0. Now the dimer is a mixture of $PhCH_2CH_2Ph$, $PhCH_2CHDPh$ and (mainly) PhCHDCHDPh. Further attack of methyl (or other) radicals on these species would involve an intermolecular isotope effect leading to preferential destruction of the *least* deuterated isomer. The remaining bibenzyl would be *enriched* in deuterium and consequently the isotope effect calculated from its composition would be *higher* than 8 (*cf.* Table II) and could not possibly be 6.8. Moreover, the methane obtained in the reaction would come from attack of methyl radicals not only on $PhCH_2D$ but also on PhCHDCHDPh, and since the latter species has a higher proportion of abstractable deuterium than the former, the methane would be *enriched* in methane-*d*, and the isotope effect calculated from its composition would be *lower* than 8 rather than 9.0.

The conclusion is inevitable that some extraneous factor affecting the *methane* composition must account for the discrepancy between "dimer isotope effect" and "methane isotope effect," *i.e.*, that too

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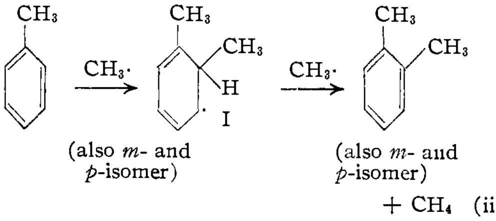
(7) To make an isotope effect (as calculated from dimer composition) of 9.0 appear like one of 4.5 due to impurity in the dimer requires 5.1% impurity (assumed isomeric with bibenzyl).

(8) Undoubtedly some such destruction occurs, as 1,2,3-triphenylpropane, the coupling product of a benzyl radical and the radical $Ph\underset{\cdot}{C}HCH_2Ph$, has been found among the products of pyrolysis of di-*t*-butyl peroxide in toluene.[2c]

much light methane is formed because methyl radicals abstract hydrogen from a source other than the side-chain of the toluene. The most likely source appeared to be the benzene ring and this point was checked by decomposing acetyl peroxide in ring-deuterated toluene.

Ring-deuterated toluene (mixture of d_5-, d_4-, d_3-, d_2-, d_1-, as well as d_0 species) was prepared by shaking toluene with deuteriosulfuric acid.[9] It was shown in two ways that the product contained no deuterium on the side chain. Mass spectrometric analysis at reduced ionizing voltage[10] showed the absence of toluene-d_6, -d_7 and -d_8 which species would have been expected to appear at least in small amount if side-chain deuteration had taken place. Moreover, it was shown that toluene-α-d lost none of its deuterium when shaken with light sulfuric acid of a higher concentration than the deuteriosulfuric acid used in the preparation of the ring-deuterated toluene.[11] Decomposition of acetyl peroxide in ring-deuterated toluene (average deuterium constant 3.3 atoms D) gave methane containing almost 8 atom % methane-d as shown by mass spectrometry, thus proving unequivocally that some of the methane obtained in the reaction of methyl radicals with toluene comes from the ring, and that therefore the methane/methane-d ratio in the reaction of methyl radicals with toluene-α-d is *not* a valid measure of the isotope effect.

In view of the strength of an aromatic C–H bond as compared to a benzylic C–H bond,[12] it is unlikely that formation of methane with ring hydrogens involves direct abstraction of these hydrogens by methyl radicals. Rather we believe that a methyl radical first adds to the benzene ring and that the resulting methylcyclohexadienyl radical (I) then undergoes hydrogen abstraction by another methyl radical to give methane and a methylated aromatic, as shown in equation iii for the case of toluene. Equation iii is analogous to the well-known free-radical *arylation* reaction[13] and implies that alkylation of aromatics with free radicals may also occur. This has been verified.[14]



(iii)

Evidence for the addition of methyl radicals to aromatics already has been adduced by Szwarc and co-workers.[15] Szwarc has postulated that the intermediate cyclohexadienyl radical (I) subsequently suffers disproportionation or dimerization. This process would not lead to the formation of methane-d from ring-deuterated toluene and our evidence suggests that at high (*ca.* 1 *M*) acetyl peroxide concentration the intermediate radical I (eq iii) loses hydrogen—either through abstraction by a methyl radical or, perhaps more likely in view of the concentration dependence, through an induced decomposition process involving acetyl peroxide—to give xylene and methane. At low acetyl peroxide concentrations, however, hydrogen abstraction becomes suppressed. Thus, in the decomposition of acetyl peroxide in 0.11 *M* solution in ring-deuterated toluene at 65°, the amount of methane-d in the gas drops to 0.4% of total methane. Since it is known[15] that even at these low concentrations methyl radicals add to the ring to give dimethylcyclohexadienyl radicals (I), it must be assumed that the latter now disappear largely by dimerization or disproportionation, to give olefins among other products.

Urry[3] has found that the methane/methane-d ratio in the decomposition of acetyl peroxide in ethylbenzene-α-d, $C_6H_5CHDCH_3$, is lower than for toluene-α-d and has concluded that the isotope effect for the abstraction of the α-hydrogen in ethylbenzene (6.6) is lower than in toluene (9.9). An alternative interpretation of the data is to assume that in the reaction of methyl radicals with ethylbenzene, more methane comes from the side-chain (which now has a more reactive secondary α-hydrogen) and correspondingly less from the ring than in toluene. To check this possibility, we have investigated the decomposition of acetyl peroxide in ring-deuterated ethylbenzene, cumene and p-xylene with the results summarized in Table III. Although the results are not susceptible of quantitative interpretation—in view of the fact that the substrates were not completely deuterated and that there may have been discrimination, both in the deuteration and the hydrogen abstraction by the radical, among the o-, m- and p-positions—it is evident that the extent of hydrogen abstraction from the ring *vs.* hydrogen abstraction from the

TABLE III

DECOMPOSITION OF ACETYL PEROXIDE IN RING-DEUTERATED SUBSTRATES: MOLE PER CENT. METHANE-d IN METHANE EVOLVED

Substrate	No. of D's[a]	Mole ratio[b]	Temp., °C.	Mole % CH_3D[c]
Toluene-d	3.31	6.9	131–147	7.8
p-Xylene-d	3.53	7.4	128–131	6.1
Ethylbenzene-d	2.82	7.1	129–131	2.1
Cumene-d	2.2	7.0	130–133	0.9

[a] Average number of deuterium atoms in ring. [b] Moles substrate/moles peroxide. The solutions were about 1-molar. [c] After reaching stationary state, *cf.* Fig. 1.

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[9] Following the general method of C. K. Ingold, C. C. Raisin and C. L. Wilson, *J. Chem. Soc.*, 915, 1637 (1936).

[10] D. P. Stevenson and C. D. Wagner, THIS JOURNAL, **72**, 5612 (1950); F. L. Mohler, V. H. Dibeler, L. Williamson and H. Dean, *J. Research Natl. Bur. Standards*, **48**, 188 (1952); F. H. Field and S. H. Hastings, *Anal. Chem.*, **28**, 1248 (1956). See also R. E. Honig, *ibid.*, **22**, 1474 (1950).

[11] S. Olsson and L. Melander, *Acta Chem. Scand.*, **8**, 523 (1954), already have demonstrated the same point for toluene-α-t.

[12] The bond dissociation energies of the phenyl–H and benzyl–H bonds are 102.5 and 77.5 kcal. per mole at 25°, respectively. See C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 50, and T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 1954. See, however, S. W. Benson and J. H. Buss, *J. Phys. Chem.*, **61**, 104 (1957).

[13] D. R. Augood and G. H. Williams, *Chem. Revs.*, **57**, 123 (1957); see also O. C. Dermer and M. T. Edmison, *ibid.*, **57**, 77 (1957).

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

[15] *E.g.*, M. Levy and M. Szwarc, THIS JOURNAL, **76**, 5981 (1954); **77**, 1949 (1955), and several later publications by M. Szwarc, *et al.*

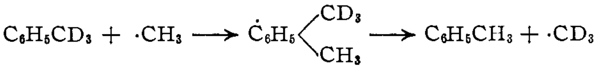
side chain is greatest for toluene, less for ethylbenzene and least for cumene.[16] This fact rather than a major difference in isotope effect, may account for some of the difference between toluene-α-*d* and ethylbenzene-α-*d* observed by Urry.[3]

Unfortunately, the amount of methane which originates from the ring in $C_6H_5CH_2D$ is not sufficient to account for the entire discrepancy between the isotope effect as calculated from dimer composition ($\lessdot$ 7.1) and that calculated from methane composition (9–10).[17] It is evident that there must be yet another source of unlabeled methane, other than the toluene molecule itself.

That this is so was emphasized in a decomposition of acetyl peroxide in toluene-α-d_3 containing but 6% of toluene-α-d_2 as an impurity. Taking into account ring attack and isotope effects, the methane/methane-*d* ratio should have been no higher than 1:1 whereas in fact it was 3:1.[18]

Regardless of the origin of the extraneous methane—whether from the ring or from sources other than the toluene[19]—it appeared that its formation could be suppressed at high toluene/peroxide ratios. Accordingly, acetyl peroxide was decomposed in toluene-α-*d* at concentrations of 0.15, 0.04 and 0.02 *M*. Calculation of the isotope effects from the methane/methane-*d* ratio gave values of 7.3, 6.8 and 7.2 which must be considered the upper limit to the true isotope effect in this reaction. Control experiments on the decomposition of acetyl peroxide in ring-deuterated toluene (about 3 D atoms per molecule) at concentrations similar to the above gave methane containing 0.9 and 0.7% methane-*d*, respectively, indicating little hydrogen abstraction from the ring under these conditions.

In the decomposition of acetyl peroxide in toluene-α-d_3, no methane-d_3 or methane-d_4 was evolved and the recovered substrate was free of toluene-d_0. These results indicate that a reversible addition of methyl radical to the C_1-carbon in toluene:



$$C_6H_5CD_3 + \cdot CH_3 \longrightarrow \dot{C}_6H_5\begin{matrix} CD_3 \\ CH_3 \end{matrix} \longrightarrow C_6H_5CH_3 + \cdot CD_3$$

does not occur to any appreciable extent.

As shown in Fig. 1, the methane-*d*/methane ratio in the decomposition of acetyl peroxide in ring-deuterated substrates increases with time at first and then becomes nearly constant. We take this to mean that the radicals formed by addition of methyl substrate (*e.g.*, I in eq. iii) will reach stationary state concentration only after some time. The alternative explanation[15] that two methyls add to substrate to give an alkyldimethylcyclohexadiene which is then aromatized by further methyl radicals (which abstract hydrogen from the diene to give methane and aromatic) is unlikely, as under these circumstances toluene should give rise to trimethylbenzene, whereas in fact it yields largely xylenes.[14]

Experimental[20]

The synthesis of and peroxide decomposition reactions in toluene-α-*d* and *p*-xylene-α-*d* are described in the preceding paper.[5]

Materials.—Ring-deuterated toluene was prepared by shaking toluene with twice to four times its volume of 51 mole per cent. aqueous deuteriosulfuric acid for 66 hours.[21] The acid was prepared by addition of stabilized liquid sulfur trioxide (Sulfan B, General Chemical Division, Allied Chemical and Dye Corporation) to deuterium oxide.[22] The deuteriosulfuric acid was assayed by titration and diluted to the desired concentration by addition of deuterium oxide.

Ring-deuterated *p*-xylene, ethylbenzene and cumene were prepared by exchange with 45 mole per cent. deuteriosulfuric acid. Preliminary experiments with light sulfuric acid showed that use of acid more concentrated than 45% led to extensive sulfonation. Aliquots, 7.5 ml. of each of the three aromatic hydrocarbons, were shaken in sealed ampoules with 25 ml. of the sulfuric acid solution for 45 hours. The volumes of the hydrocarbon layers served as an indication of the extent of sulfonation. The data obtained are shown in Table IV. The results with 55 mole per cent. sulfuric acid indicate the relative reactivities of the hydrocarbons to sulfonation.

TABLE IV

VOLUME OF RECOVERED AROMATIC HYDROCARBON[a]

H_2SO_4, mole %	44	55	60[b]
p-Xylene, ml.	7.0	0	0
Ethylbenzene, ml.	*ca.* 7.2	1.2	0
Cumene, ml.	7.3	2.7	0

[a] The volume measurement was subject to an error of 0.2–0.3 ml. due to mechanical losses. [b] Shaken for 20 hours only.

In the preparation of the deuterated alkylaromatics, 35.0

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(16) (a) Assuming no isotope effect, statistical distribution of the label and statistical attack of methyl radicals on the ring, one calculates the following figures for rate of abstraction of one side-chain hydrogen/rate of abstraction of one ring-hydrogen: toluene, 12.4; *p*-xylene, 9.0; ethylbenzene, 61.5; cumene, 217.1. The assumption of no isotope effect is unproved for this particular case and the statistical distribution assumptions are certainly unsound, since deuteration, being an electrophilic reaction, should be greatest in *ortho* and *para*, and methylation, being a free-radical substitution, should occur preferentially in the *o*-position.[18,14] However, setting aside the case of *p*-xylene and neglecting small hyperconjugative and inductive differences among the alkyl substituents and a possible small steric effect in cumene, what deviation from the statistical there is should be about the same for the three monoalkylbenzenes studied and the errors should thus approximately cancel out; (b) this order is in agreement with that reported in ref. 2g for the reaction of these alkylbenzenes with benzoyl peroxide, but not with that reported in ref. 2e (toluene < ethylbenzene > cumene) for the same reaction. It agrees, also, with the order of reactivity found by K. M. Johnston and G. H. Williams, *Chemistry & Industry*, 328 (1958), in reaction of these compounds with di-*t*-butyl peroxide.

(17) Again, because of the limitations pointed out in footnote 16, an exact calculation is not possible. Making the same assumptions as before[16]—which, for the reasons stated, are likely to lead to an *over*estimation of ring attack—one calculates that an apparent isotope effect of 10 as calculated from methane composition should correspond to a real isotope effect of 8.4 and an apparent isotope effect of 9 to a real one of 7.55. This correction is probably overgenerous, unless there is an isotope effect in the abstraction of hydrogen from the ring.

(18) Attack of methyl radicals on the unlabeled methyl group of xylene-α-d_3 formed according to equation iii is an unlikely source of so much light methane, as the xylene concentration in the substrate should not rise above 1 or 2%.[14] To get an equal amount of methane and methane-*d* from the side-chains of toluene-α-d_3 and xylene-α-d_3 assuming an isotope effect of 6 requires 17% of xylene in the substrate. Not enough acetyl peroxide was decomposed to produce that amount.

(19) The following sources of light methane must be considered: (a) the methyl groups of acetyl peroxide; (b) acetic acid and acetic anhydride which tend to be present as contaminants in solutions of acetyl peroxide in toluene prepared *in situ;* (c) dimethyl phthalate in cases where it was used as a solvent for acetyl peroxide. The proportion of all of these possible contaminants diminishes greatly as the concentration of acetyl peroxide in toluene decreases.

(20) All melting and boiling points uncorrected. Mass spectra by Mr. George Young, recorded on a Consolidated model 21-103A analytical mass spectrometer.

(21) The authors are indebted to Dr. M. P. Reddy for the preparation of the first sample of ring-deuterated toluene.

(22) E. F. Jenny and J. D. Roberts, THIS JOURNAL, **78**, 2008 (1956).

ml. of deuteriosulfuric acid was shaken for 65 hours with 10.0 ml. of the hydrocarbon in a sealed ampoule. Following this, the hydrocarbons were purified by distillation; 6–7 g. of each substance (purified) was obtained and analyzed by mass spectrometry at reduced ionizing voltage.[10] In the case of ring-deuterated toluene and ethylbenzene no species above d_5 and in the case of *p*-xylene no species above d_4 was found, suggesting that deuterium was confined to the ring. However, the ring-deuterated cumene contained an apparently significant amount of higher deuterated species (up to d_{10}), suggesting some deuteration in the β-positions of the side-chain.[23,24]

Toluene-α-d_3 was obtained from Merck and Co., Ltd., (Canada) and was used as received. Mass spectrometric analysis at reduced ionizing voltage indicated a composition of 94.5% $C_6H_5CD_3$, 5.4% $C_6H_5CHD_2$ and 0.1% $C_6H_5CH_2D$ corresponding to an average deuterium content of 2.94 atoms D/molecule and an isotopic purity of 98.1%.

Procedure.—Solutions of acetyl peroxide in ring-deuterated solvents were prepared by the method of Price and Morita,[25] ring-deuterated hydrocarbons being substituted for ethyl ether. The solutions were analyzed iodometrically by the method of Kokatnur and Jelling.[26] The apparatus utilized was similar to that described earlier.[5] The closed system consisted of a three-neck pear-shaped flask equipped with a gas inlet tube, a pressure equalized addition funnel and a condenser. A tube led from the top of the condenser to an inverted water-filled flask which served as a reservoir for the gas produced. Gas samples were withdrawn (using evacuated bulbs) through a stopcock-equipped side arm in the above-mentioned tube. Prior to each reaction, the entire system was flushed with dry carbon dioxide or argon.

In the apparatus described, a 15.9% solution of acetyl peroxide in ring-deuterated toluene (5.77 ml., containing 0.92 g., 0.0078 mole of acetyl peroxide, *i. e.* 1.2 *M*) was added dropwise to 0.6 g. of boiling ring-deuterated toluene (total amount of ring deuterated toluene taken, 5.1 g., 0.054 mole, average deuterium content[10,23] 3.31 atoms D per mole). Heating was continued throughout the addition, which took 30 minutes, and for 30 minutes more. Several samples of the gas collected were analyzed mass spectrometrically. The deuteriomethane content of the methane [100 $CH_3D/(CH_3D + CH_4)$] had a range of 6.06–7.85% (see Fig. 1).

Similar decompositions were carried out in ring-deuterated *p*-xylene, ethylbenzene and cumene. The average deuterium content of these solvents,[10,23] the molarity of the peroxide solutions and the methane-*d* content of the methane obtained [100 $CH_3D/(CH_3D + CH_4)$] in these decompositions were, respectively: 3.53 atoms D/molecule, 1.0 *M*, 5.13–6.14%; 2.82 atoms D/molecule, 0.98 *M*, 1.86–2.20%; and 2.2 atoms D/molecule, 0.93 *M*, 0.90–0.99% (see also Table III).

In the decomposition of acetyl peroxide in toluene-α-d_3 (same apparatus utilized as above), a 12.1% solution of acetyl peroxide in this solvent (5.3 ml., 4.94 g., containing 0.64 g., 0.0054 mole, of acetyl peroxide) was added dropwise to 0.37 g., of refluxing toluene-α-d_3 (total amount of solvent 4.67 g., 0.0492 mole; molar ratio solvent/peroxide = 9.1/1) in the course of 17 minutes (bath temperature 132–134°). The three gas samples taken had the following deuteriomethane contents [100 $CH_3D/(CH_3D + CH_4)$]: 24.23, 23.46, 23.54% (determined mass spectrometrically). No polydeuterated methane or polydeuterated ethane was present in the gas.

Decompositions at High Dilution.—These decompositions were carried out in glass cells constructed from 12 × 95 mm. Pyrex test-tubes which were equipped with a break-off tip in a side-arm. The appropriate solution of peroxide in deuterated solvent,[27] *ca.* 1 ml. (*ca.* 2 ml. was taken in the case of the more dilute solutions in order to afford sufficient gas for analysis), was placed in the cell, the cell was chilled in Dry Ice–acetone mixture, evacuated (to a pressure of 0.1 mm. or less) and sealed (the more dilute solutions were degassed several times prior to sealing while being cooled in liquid nitrogen). The cell was placed in an oil-bath or in an oven maintained at an appropriate temperature and kept there until decomposition was judged to be complete. The gas produced in the decomposition was removed from the cell in a vacuum line by means of a Toepler pump and analyzed mass spectrometrically (the side-arm of each cell was attached to the vacuum line, evacuation was begun and the break-off tip was broken thus allowing the gas to expand in the line). The data obtained are summarized in Table V.

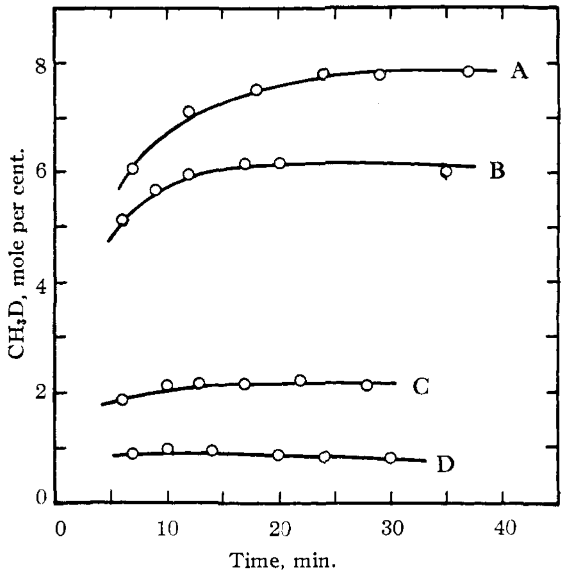

Fig. 1.—Extent of labeling of methane evolved as a function of time: A, toluene; B, *p*-xylene; C, ethylbenzene; D, cumene.

TABLE V

DECOMPOSITION OF DILUTE SOLUTIONS OF ACETYL PEROXIDE IN DEUTERATED TOLUENES

Solvent	Deuterium content (atoms D/molecule)	Mole[a] ratio	Concn., *M*	Bath or oven temp., °C.	Duration of decompn.	CH_3D content of gas produced[c]
Ring D	2.39	85/1	0.11	65	100 hr.	0.4%
Ring D	3.11	563/1	.02[b]	130 ± 6	3	0.9
Ring D	3.11	217/1	.04[b]	130 ± 6	3	0.7
	Mole % C_6H_5-CH_2D[d]					Isotope effect Calcd.
$C_6H_5CH_2D$	97.0	61/1	0.15	130 ± 5	70 min.	7.3
$C_6H_5CH_2D$	87.4	537/1	.02[b]	130 ± 6	3 hr.	7.2
$C_6H_5CH_2D$	87.4	218/1	.04[b]	130 ± 6	3 hr.	6.8

[a] Moles deuterated toluene/mole peroxide. [b] Calculated from the mole ratio using density of 0.87 for the solution. [c] $CH_3D/(CH_3D + CH_4)$. [d] Remainder is $C_6H_5CH_3$.

Isotope Effect Calculations.—Isotope effects from dimer composition were calculated as previously reported.[5] The limits of error indicated in Table I were calculated by combining, on one hand, the upper limit of the substrate analysis with the lower limit of the dimer analysis and, on the other, the lower limit of the substrate analysis with the

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[23] Typical analyses (mole %): Toluene: d_0, 0.6; d_1, 4.6; d_2 16.8; d_3, 32.3; d_4, 32.3; d_5, 13.3. Ethylbenzene: d_0, 0.8; d_1, 4.6; d_2, 22.7; d_3, 57.4; d_4, 13.5; d_5, 1.1. *p* Xylene: d_0, 0.1; d_1, 0.6; d_2, 6.4; d_3, 32.4; d_4, 60.5. Cumene: d_0, 8.9; d_1, 15.8; d_2, 28.1; d_3, 40.3; d_4, 6.1; d_4, 0.5; d_7, trace; d_8, 0.1; d_9, 0.2; d_{10}, trace.

[24] Analogous to the exchange of the methyl hydrogens in isobutane: J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck, THIS JOURNAL, **73**, 5741 (1951).

[25] C. C. Price and H. Morita, *ibid.*, **75**, 3686 (1953).

[26] V. R. Kokatnur and M. Jelling, *ibid.*, **63**, 1432 (1941).

[27] Acetyl peroxide solutions were made up as described above. In some cases the peroxide was added to the deuterated solvent in the form of a solution in dimethyl phthalate (*ca.* 25%, Becco Chemical Division, Food Machinery and Chemical Corp., Buffalo 7, N. Y.). Sufficiently small amounts were used so that abstraction by methyl radicals of hydrogen from the dimethyl phthalate would not interfere in the reaction or cause an appreciable error in the measurements.

upper limit of the dimer analysis. Isotope effects from methane composition were calculated using the formula

$$i = \frac{P(100 - y)}{y(300x - P)}$$

where

i = isotope effect
P = isotopic purity of substrate (%)
y = % methane-d in total methane $[100CH_3D/(CH_3D + CH_4)]$
x = 1 for toluene, x = 2 for p-xylene

Acknowledgment.—This paper is a contribution from the Radiation Project of the University of Notre Dame, supported in part under Atomic Energy Commission contract AT (11-1)-38 and Navy equipment loan contract Nonr-06900.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

Aromatic Substitution by a Highly Selective Radical—Triphenylmethyl. A Case of a Free Radical Reaction in Which Nitrobenzene Is Essentially Unreactive

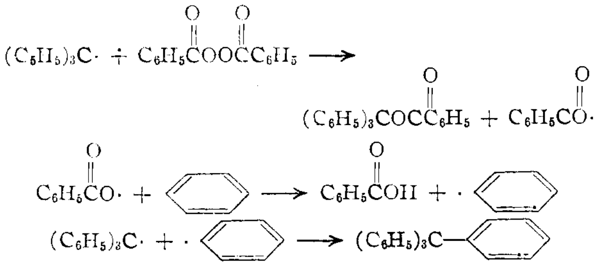
BY ROBERT A. BENKESER AND WILLIAM SCHROEDER

RECEIVED JANUARY 17, 1958

The Wieland reaction, which involves the attack of a triphenylmethyl radical on aromatic substrates in the presence of benzoyl peroxide, has been studied in detail. Isomer distributions and relative reactivities have been determined for substrates of anisole, chlorobenzene, methyl benzoate and benzotrifluoride. Nitrobenzene failed to react in this system. The order of reactivity observed ($C_6H_5OCH_3 > C_6H_5Cl > C_6H_5H > C_6H_5CO_2CH_3 > C_6H_5CF_3 > C_6H_5NO_2$) indicates the electrophilic nature of the triphenylmethyl radical. This order is explained in terms of the difficulty of formation of a complex between electron-deficient aromatic rings and and the highly selective, electrophilic triphenylmethyl radical. The arithmetical average of the isomer distributions obtained (43% *ortho*, 36% *meta*, 21% *para*) is amazingly close to the statistical values of 40–40–20, although this may be fortuitous. Possible interpretations of this distribution are discussed. An earlier report by Hammond and Ravve that nitrobenzene is reduced by triphenylmethyl radicals to form azobenzene and triphenylcarbinol is shown to be in error. The traces of phenol which are formed are shown to be independent of the presence of nitrobenzene.

The reaction between triphenylmethyl and benzoyl peroxide in benzene solution has been studied by Medwedew and Alexejewa[1] and Wieland and Meyer.[2]

These latter workers found the major product to be triphenylmethyl benzoate, accompanied by smaller amounts of tetraphenylmethane and benzoic acid. A later paper by Wieland and Meyer[3] disclosed that the solvent was playing a role in the formation of tetraphenylmethane. When di-p-phenylbenzoyl peroxide and triphenylmethyl were allowed to react in benzene, only tetraphenylmethane was found. Similarly the reaction of triphenylmethyl and benzoyl peroxide in chlorobenzene resulted in triphenylmethyl benzoate, benzoic acid and *chloro*tetraphenylmethane. These and several other similar experiments showed that the fourth ring of the tetraphenylmethane was originating exclusively from the solvent, and not from an induced decomposition of the peroxide. In every case the substituted tetraphenylmethanes which were formed were reported to have the substituent group in the p-position. Wieland and Meyer interpreted these results as an indication that triphenylmethyl was reacting with the peroxide to form triphenylmethyl benzoate accompanied by the liberation of a benzoyloxy radical. This radical in turn abstracted hydrogen from the solvent to given benzoic acid and a solvent generated free radical. The solvent free radical was then assumed to combine with more triphenylmethyl to give a substituted tetraphenylmethane



The only inconsistency with this postulate appeared to be that little or no carbon dioxide was liberated during the course of the reaction. On the other hand, the thermal decomposition of benzoyl peroxide, which is presumed to proceed *via* the homolytic fission of the O–O bond, affords large quantities of carbon dioxide, presumably by the subsequent decomposition of the benzoyloxy radical first formed.

Hammond, *et al.*,[4] reinvestigated the Wieland reaction on a more quantitative basis and came to the same general conclusions as to the mechanism, except that the possibility of the reaction occurring by a termolecular collision in a solvent cage[5] was suggested to explain the absence of carbon dioxide in the products.

During the course of a program designed to study the electrical effects of the triphenylmethyl group,[6] we had occasion to utilize the Wieland procedure as an alternate synthesis for some of the compounds

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(1) S. S. Medwedew and E. N. Alexejewa, *Ber.*, **65**, 137 (1932).

(2) H. Wieland and A. Meyer, *Ann.*, **532**, 179 (1937).

(3) H. Wieland and A. Meyer, *ibid.*, **551**, 249 (1942).

(4) G. S. Hammond, J. T. Rudesill and F. J. Modic, THIS JOURNAL, **73**, 3929 (1951).

(5) M. S. Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

(6) R. A. Benkeser and R. B. Gosnell, THIS JOURNAL, **78**, 4914 (1956); see also R. A. Benkeser and R. B. Gosnell, *J. Org. Chem.*, **22** 327 (1957).