served. The minor products, 1–2%, were believed to be 2,3-dimethyl-2-butane and 2,3-dimethyl-1-butene, resulting from dehydrohalogenation of the tertiary halide during analysis. The 2,3-dimethyl-2-butene structure was assigned to its corresponding peak by comparison of its retention time with that of an authentic sample. The two major products, >98% of the products obtained, were assigned the structures 2-chloro-2,3-dimethylbutane and 1-chloro-2,3-dimethylbutane. The tertiary chloride was prepared by the method described by Shiner,[14] and its retention time by glpc was found to be the same as that for the major isomer assigned that structure. The order of elution from the column was 2-chloro-2,3-dimethylbutane followed by 1-chloro-2,3-dimethylbutane.

Chlorinations at Incomplete Reaction. After initial reaction, dark or photoinitiated (see Table VII), the reactions were quenched in liquid nitrogen and the ampoules broken under acidified potassium iodide and titrated for active chlorine.[12] After titration the carbon tetrachloride layer was extracted, and the organic material was analyzed by glpc as previously described. Repeated extractions of the organic phase and reanalysis of the product mixture assured us that the product distribution determination was not affected by the contact of the reaction mixture with water during the titration.

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The Kinetic Hydrogen Isotope Effects in the Bromination of Some Polyalkylbenzene Systems[1]

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Abstract: The preparative, product analysis, and kinetic aspects for the determination of the kinetic hydrogen isotope effects, k_H/k_D, for the bromination of a number of polyalkylbenzene systems are described. The reaction is either bromination by molecular bromine in acetic acid and in nitromethane or silver ion catalyzed bromination in acetic acid–dioxane mixture (1,3,5-tri-*t*-butylbenzene). The isotope effect was found to be appreciably larger in nitromethane than in acetic acid solution (5-*t*-butylhemimellitene). Further evidence is presented in support of the view that steric hindrance at the reaction site is an important contributing factor for the occurrence of isotope effects in electrophilic aromatic substitution.

Since the first reports on the influence of steric hindrance on hydrogen isotope effects in electrophilic aromatic substitution[2–4] there has been cumulative evidence on the generality of this phenomenon.[5–9] More generally, the growing information on isotope effects for this reaction has been authoritatively discussed in recent reviews.[10]

In continuation of our studies in this field, we wish to report the results of a systematic investigation on the hydrogen isotope effects in the bromination of a number of polyalkylbenzenes characterized by a reaction center flanked by alkyl groups on both sides.

We also take this opportunity to include additional experimental information on the results reported in our previous reports.

Results

Except for 1,3,5-tri-*t*-butylbenzene (I), the hydrogen isotope effects were investigated for the dark bromination with molecular bromine under conditions for which the kinetics and mechanism of the reaction are fairly well known.[11] Anhydrous acetic acid and nitromethane were used as solvents depending on the reactivity of the substrate. Unlike mesitylene, the methylated analog, bromination in any of the latter conditions is exceedingly slow in the case of 1,3,5-tri-*t*-butylbenzene, which indicates a large steric hindrance effect upon the entrance of the halogenating species; therefore, the silver ion catalyzed bromination was used in this case.[4]

The hydrogen isotope effects, k_H/k_D, were evaluated from rate measurements in all cases except compound I. The course of the reaction was known from previous studies and had to be ascertained only with 5-*t*-butylhemimellitene that brominates smoothly with Br_2 to yield the 4-bromo derivative under conditions analogous to those adopted for the kinetics work.

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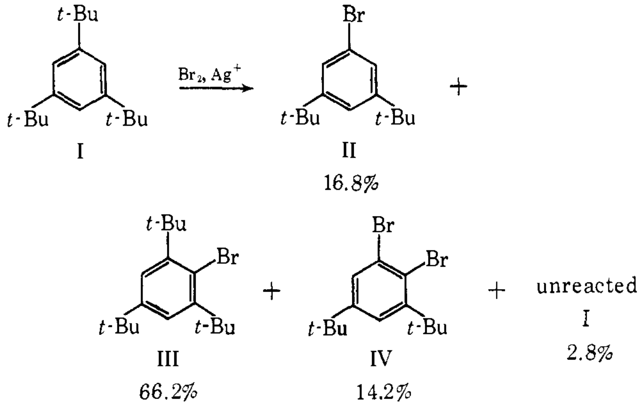
The isotope effect for the silver ion catalyzed reaction of compound I was estimated on the basis of the deuterium content of the reaction product (see Experimental Section). For our present purposes, a more careful examination of the reaction products than that previously reported[4] for this reaction was carried out. It was found that under conditions stated in the experimental part, the reaction can be described as follows.



I

II 16.8%

III 66.2%

IV 14.2%

I 2.8%

Under conditions identical with those used for the overall reaction, compound IV is formed either from III or II. The isotope effect under examination is affected neither by the latter reactions nor by the formation of II from I.

The results on the isotope effects are summarized in Table I.

Table I. Kinetic Hydrogen Isotope Effects for the Bromination of Some Polyalkylbenzenes and Their Derivatives at 30°

Substrate	Reagent	Solvent	k_H/k_D[a]	n[b]
Mesitylene	Br_2	AcOH	1.10 ± 0.02	13
Pentamethylbenzene[c]	Br_2	AcOH	1.20 ± 0.05	6
3-Methoxydurene	Br_2	AcOH	1.5 ± 0.1	4
5-*t*-Butylhemimellitene	Br_2	AcOH	1.6 ± 0.1	6
5-*t*-Butylhemimellitene	Br_2	$MeNO_2$	2.7 ± 0.2	11
3-Bromodurene	Br_2	$MeNO_2$	1.4 ± 0.1	6
1,3,5-tri-*t*-Butylbenzene[d]	Br_2, Ag^+	AcOH–dioxane	*Ca.* 3.6	

[a] Not corrected for the light hydrogen content in the deuterated compound. [b] Total number of determinations for the light and the deuterated compound. [c] At 18°. [d] Room temperature.

3-Bromodurene, 3-bromodurene-6-*d*, and 1,3,5-tri-*t*-butylbenzene-2-*d* were obtained upon hydrolysis of the appropriate organolithium intermediates with H_2O or D_2O. Comparative experiments showed that the organolithium intermediate was decidedly superior to the organomagnesium intermediate in the selective monohalogen–metal interconversion of dibromodurene. All the other deuterated compounds used in this work were obtained by exchange reactions (see Experimental Section).

Discussion

The relevant increase in the isotope effect, k_H/k_D, shown for 5-*t*-butylhemimellitene when the solvent is changed from acetic acid to nitromethane, can be properly related to our present knowledge of aromatic bromination with molecular bromine. A generally accepted mechanism for this reaction in diverse solvents consists of a two-step process, involving the complex (ArH, Br_2), as follows.[11c]

$$ArH + Br_2 \rightleftharpoons (ArH, Br_2) \qquad (1)$$

$$(ArH, Br_2) + Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (ArBrH)^+ + Br_3^- \qquad (2)$$

$$(ArBrH)^+ + B \xrightarrow{k_2} ArBr + HB^+ \qquad (3)$$

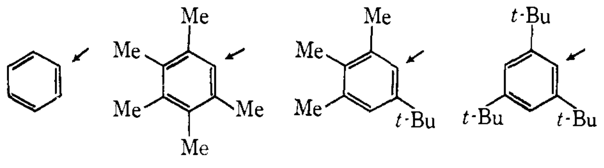
A hydroxylic solvent is known to assist specifically Br–Br bond breaking and, consequently, Br–C bond making, by H bonding.[11b] Hydrogen-bond interaction, however, also involves the tribromide ions, Br_3^-, and may thus influence the rate of the reversal of equilibrium 2. A hydroxylic solvent should make this rate relatively low and alter the k_{-1}/k_2 ratio in the direction of a decreased isotope effect, as can be shown if a steady-state treatment is applied. A synchronous mechanism would also accommodate the present results in terms of H-bond interaction.

Alternative explanations are also possible. For example, solvent may have a role in determining the symmetry[12] of the transition state relative to the step in which the proton is removed.

In the light of the solvent effect noted above, and because of the structural analogy among the compounds under examination, the isotope effect for the reactions of mesitylene, pentamethylbenzene, and methoxydurene in nitromethane is also expected to be greater than that found in acetic acid. If this is the case, the earlier observation concerning bromodurene[3] is now neatly confirmed by the results on mesitylene and pentamethylbenzene, and it is possible to conclude that in nitromethane solution the isotope effect for the bromination at a reaction center flanked by two methyl groups is no less than 1.4.

The k_H/k_D ratio for 1,3,5-tri-*t*-butylbenzene is not strictly comparable with the data in nitromethane owing to a solvent and a reagent effect as well. However, both such effects tend to lower the k_H/k_D ratio, because the solvent is largely hydroxylic, and the reagent involves a more powerful electrophile than molecular bromine.[13]

Thus, it appears that the isotope effect for a series of



V VI VII VIII

polyalkylbenzenes increases in the same order as the steric requirement at the reaction center does, along the sequence V to VIII.

Since in this sequence substituents of essentially the same polar character are involved, it is implied that steric hindrance is a major factor for the observed change in the isotope effects: the importance of this factor in this connection is then definitely established by the present results. In particular, even the small k_H/k_D value observed in the less hindered polymethyl-

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benzenes would appear to be a small primary, rather than a secondary, isotope effect.

The generality of this phenomenon, *i.e.*, its possible extension to other substitution reactions, is well illustrated by the very recent report[9] of the appearance of an isotope effect in nitration, a reaction heretofore reluctant to such effects. For this reaction it was possible to find a substrate so highly overcrowded (2,4,6-tri-*t*-butylnitrobenzene) as to yield a small, however clean-cut, isotope effect (1.8).

In contrast, the importance of polar contributions to the isotope effect is less firmly established. Recent reports on the isotope effects in the halogenation of dimethylaminobenzene derivatives indicate that the reaction site totally responsible for such effects is the one *ortho* to the electron-releasing group and not the one *para* to it.[5,7] Anisole[14] and 1,3,5-trimethoxybenzene[15] show slight or no isotope effects in bromination; again, the large k_H/k_D ratios associated with the reaction of 2-bromo- and 2,4-dibromo-1,3,5-trimethoxybenzene[8] are to be attributed to molecular overcrowding rather than to a special stability of any intermediate involved in the reaction. Use of a dipolar aprotic solvent, dimethylformamide, should also be noted in the latter examples.

The isotope effect found with methoxydurene, 1.5 in acetic acid, is significantly higher than that of pentamethylbenzene, a molecule of analogous steric characteristics at the reaction center (4-substituted durene series). It is doubtful whether a combination of steric and polar effects operates in this case. However, although methoxydurene is subject to steric inhibition of resonance, in bromination resonance interaction is still quite strong.[16] If a contribution came from the latter interaction, it would be one example of an isotope effect specifically related to a strongly electron-releasing group at a position *para* to the bromination site.

The appearance of an isotope effect in electrophilic aromatic substitution is due to a complex phenomenon[10c] that would be unsafe to interpret in an absolute way in separate cases. Accordingly, it is recommended that the assignment of structural contributing factors be made *via* a correlation of changes in k_H/k_D values with systematic changes in structure.

Experimental Section

Melting points are uncorrected, unless otherwise indicated.

Materials. Samples of mesitylene, pentamethylbenzene, and 3-bromodurene were available from earlier investigations.[17,18] However, the sample of 3-bromodurene used for the rate measurements was obtained by the method herein described for the preparation of 3-bromodurene-6-*d* (see further on). 3,6-Dibromodurene was obtained by adding bromine to bromodurene in acetic acid and keeping the reaction mixture in the dark for 1 week. The temperature was allowed to rise from room temperature to 50–55° in the last 4 days, yield 74%; recrystallization from absolute ethanol, mp 201.7–203.2° (lit.[19] mp 202°). The other aromatic compounds were prepared according to previously described procedures (original references and melting points are given): 5-*t*-butylhemimellitene,[20] 32–32.5°; 1,3,5-tri-*t*-butylbenzene,[21] 72.5–73°; 3,5-di-*t*-butylbromobenzene,[22] 65–66°; 3-methoxydurene,[16] 59–59.5°.

Bromination of 5-*t*-Butylhemimellitene by Molecular Bromine. To 2.64 g (0.015 mole) of 5-*t*-butylhemimellitene in 16 ml of acetic acid, 2.4 g (0.015 mole) of bromine in 12 ml of the same solvent was added. After standing in the dark for 2 weeks, the reaction mixture was diluted with water, and 3.3 g of crude 4-bromo-5-*t*-butylhemimellitene was collected. On recrystallization from ethanol, a product, mp 52–52.5°, was obtained (lit.[23] mp 49.5–51°).

Ag^+-Catalyzed Bromination of 1,3,5-Tri-*t*-butylbenzene. Product Analysis. This reaction was carried out in essential accordance with the procedure described by Myhre.[4] At the end of the reaction, any solid material was filtered off and extracted with *n*-pentane. The filtrate was poured into water, and the organic product was extracted with *n*-pentane. The *n*-pentane extracts were combined, washed with water, and dried over Na_2SO_4. On removal of the solvent, a waxy solid was obtained as the crude product of the reaction. This was analyzed by vpc with a 1-m silicone 710 column, at 195°, hydrogen being the carrier gas. The chromatogram revealed the presence of four well-resolved peaks. The areas of these peaks allowed the composition of the reaction product to be estimated as follows (% areas given in parentheses): I (2.8), II (16.8), III (66.2), and IV (14.2), the retention time increasing from compound I to compound IV. Compounds I and II were readily identified as the unreacted hydrocarbon and 3,5-di-*t*-butylbromobenzene, respectively, by vpc comparison with authentic specimens (see Materials). Compounds III and IV were isolated and identified by the following procedure. In a typical experiment, a saturated solution of 10.1 g of crude reaction product in petroleum ether, bp 30–50°, was applied on a chromatographic column of 400 g of alumina and eluted with the same solvent. Evaporation of a first group of combined fractions yielded 7.6 g of compound III, which was identified as 2,4,6-tri-*t*-butylbromobenzene, mp 173.5–174.5° after several recrystallizations from ethanol (lit.[4] mp 173–174°). From the subsequent group of fractions, on evaporation, a residue was obtained, which proved to be a mixture of compounds II and IV (vpc).

Mixtures of compounds II and IV as obtained from the chromatographic experiments of several batches were combined together (20 g) and distilled in a semimicro Todd column (packing: Monel spiral) at 20 mm to remove most of compound II (13.5 g). The distillation residue was again chromatographated on a column of alumina in petroleum ether (bp 30–60°) and recovered in eight fractions, the last of which appeared to consist of pure compound IV (the chromatogram showed a single peak on several different stationary phases). On removal of the solvent from this fraction, compound IV was obtained as a liquid, n^{20}D 1.5581. The nmr spectrum, obtained in CCl_4 with a Varian A-60 spectrometer, tetramethylsilane as an internal standard, showed peaks at τ 2.54 (2 H, AB quartet, J = 2.5 cps), 8.47 (9 H, singlet), and 8.70 (9 H, singlet). Such a spectrum and the elemental analysis are consistent with the structure of 1,2-dibromo-3,5-di-*t*-butylenzene. *Anal.* Calcd for $C_{14}H_{20}Br_2$: C, 48.30; H, 5.79; Br, 45.91. Found: C, 48.31; H, 5.82; Br, 45.72.

Either compound II or III, when brominated in the same conditions used for 1,3,5-tri-*t*-butylbenzene, form compound IV, as shown by vpc analysis of the reaction product.

Deuterium Analysis. The deuterated material was burned in a current of dry oxygen in accordance to the procedure described by Trenner, *et al.*[24] The water collected was then analyzed for heavy water by the falling-drop method at 27.7°, *o*-fluorotoluene being the inert liquid.[25] Since this method gives the best results when the heavy water content is near 2.5%, it was often necessary to burn mixtures of deuterated and light compound of convenient composition.

In the case of 3-methoxydurene-6-*d* and 5-*t*-butylhemimellitene-4,6-d_2, the deuterium content was estimated by nmr spectroscopy.

Deuterated Compounds *via* Halogen–Metal Interconversions. The following precautions have been used throughout the prepara-

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tions reported in this section to keep the contamination by moisture and light hydrogen to a minimum: use of all-glass apparatus and of especially smooth ground-glass joints; exhaustive drying of all parts by prolonged standing in a large oven and subsequent cooling in a desiccator; use of a dry nitrogen current or atmosphere depending on the operations. Outlets were protected with P_2O_5 pipes externally protected by $CaSO_4$; when parts were removed from the main apparatus, they were replaced by small anhydrone-containing bulbs. All reagents were carefully dried before use; anhydrous diethyl ether was obtained as described by Weldon and Wilson[26] and distilled directly into the desired container of the reaction apparatus.

A. **Bromoduryllithium and Bromodurylmagnesium Bromide.** A clear, freshly titrated[27] solution of *n*-butyllithium[28] (0.0056 mole) was added during 6 min into a solution of 1.46 g (0.0050 mole) of 3,6-dibromodurene under vigorous stirring. After an additional 4 min, the reaction mixture was poured onto Dry Ice and treated with 30 ml of 10% hydrochloric acid. The ether solution was then extracted with 180 ml of 3% sodium hydroxide, and the resulting alkaline extract was made acid with 50 ml of 10% hydrochloric acid. Subsequent extraction with diethyl ether yielded, on removal of the solvent, a crystalline residue. This material was washed repeatedly with petroleum ether to remove any valeric acid and recrystallized once from 95% ethanol to give 0.5 g, mp (cor) 233–234.5° subl. *Anal.* Calcd for $C_6(CH_3)_4BrCO_2H$: neut equiv, 256.1. Found: neut equiv, 249.2. In another experiment the aryllithium solution, as obtained in the 10-min reaction just described, was treated with 2.7 g of distilled water (0.15 mole); from the ether solution 3.18 g of bromodurene (99%) as a crystalline solid, mp 55–57.5°, was obtained. Recrystallization from methanol yielded the pure compound, mp 58.5–59°; a mixture melting point with an authentic specimen[18] was not depressed.

The following experiment shows that the Grignard reagent is a less suitable intermediate to the preparation of bromodurene from 3,6-dibromodurene. The latter compound (1.46 g, 0.0050 mole) was allowed to react for 1 hr under reflux with an equivalent amount of magnesium in diethyl ether in the presence of a small amount of ethyl magnesium bromide. The resulting arylmagnesium bromide solution was examined for carbonation and for hydrolysis in separate batches. Carbonation yielded a mixture of carboxylic acids, mp (corrected) 207–211.5° subl. *Anal.* Calcd for $C_6(CH_3)_4BrCO_2H$: neut equiv, 256.1. Calcd for $C_6(CH_3)_4(CO_2H)_2$: neut equiv, 111.1. Found: neut equiv, 224.6. Hydrolysis yielded a product, mp 41–47°, which, after chromatography on a column of alumina and recrystallization from methanol, was found to be a mixture containing unreacted 3,6-dibromodurene and 3-bromodurene, which were identified by mixture melting points with the corresponding authentic specimen.

B. **3-Bromodurene-6-*d*.** A 2-ml aliquot of 95.6% deuterium oxide (Abbott) was rapidly added under stirring into the bromoduryllithium reagent, as obtained from 4.38 g of 3,6-dibromodurene (see above). Stirring was continued for an extra 5 min. The ether solution was transferred into a separatory funnel, washed with water, and dried over sodium sulfate. From this solution 3.22 g of white scales, mp 51.5–54.8°, was obtained (100% yield). Several recrystallizations from absolute methanol gave a constant mp 58.5–59.1°. The extent of deuteration of this material was found to be 93.7% at the single, available nuclear position.

C. **1,3,5-Tri-*t*-butylbenzene-2-*d*.** A diethyl ether solution of 2,4,6-tri-*t*-butylphenyllithium was obtained by halogen–metal interconversion[29] of 10.4 g of 2,4,6-tri-*t*-butylbromobenzene (0.032 mole) with 0.0408 mole of *n*-butyllithium. A 15-ml aliquot of 97% deuterium oxide (Fluka, reagent grade) was then added, and the ether solution was worked up as usual to give 7.4 g of an oily solid. The latter was recrystallized from 2-propanol to constant mp 72–73°. The extent of deuteration of this material was found to be 94% at one of the three available nuclear positions.

Deuterated Compounds *via* Exchange Reactions. Deuterated trifluoroacetic acid was obtained by refluxing for 1 hr a mixture of equimolecular amounts of redistilled trifluoroacetic anhydride (Fluka, purum) and 99.6% heavy water (Fluka, reagent grade).

A. **Mesitylene-2,4,6-d_3.** A solution of 10.0 g of mesitylene (0.0833 mole), 2.6 mole of deuterated trifluoroacetic acid, and 0.9 mole of 99.6% deuterium oxide was allowed to stand at room temperature for 35 days. The deeply red solution was poured into an aqueous solution of potassium hydroxide containing some ice. The colorless mixture was extracted twice with CCl_4. The organic layer was washed and dried over Na_2SO_4. The solvent was distilled off, and the residue was fractionated in a Rose column (reflux ratio 1:10). A fraction with constant boiling point was collected (7.5 g, 76% yield). The exchange was repeated under similar conditions (mesitylene from the first exchange, 0.060 mole; CF_3CO_2D, 2.30 mole; D_2O, 0.62 mole). The extent of deuteration in the product *per* available nuclear position was found to be 87.8% after the first exchange, and 89.0% after the second.

B. **Pentamethylbenzene-6-*d*.** Pentamethylbenzene (0.95 g, 0.00641 mole), mp 49–50°, was allowed to react with 0.274 mole of deuterated trifluoroacetic acid for 6 days at room temperature. The deeply colored solution was then poured into an aqueous solution of potassium hydroxide containing some ice, and the organic material was thereafter extracted with petroleum ether, bp 30–60°. On removal of this solvent a white solid (0.85 g, mp 49.5–50.2°) was obtained (89% yield). The extent of nuclear deuteration was found to be 85.5%.

C. **5-*t*-Butylhemimellitene-4,6-d_2.** 5-*t*-Butylhemimellitene (2.5 g, 0.0142 mole) was treated with 0.54 mole of deuterated trifluoroacetic acid, and the solution was worked up as in the case of pentamethylbenzene. After removal of the solvent and recrystallization from methanol, 0.470 g of a product, mp 30.8–31.2°, was obtained. The extent of the nuclear deuteration was more than 90%.

D. **3-Methoxydurene-6-*d*.** 3-Methoxydurene (0.43 g, 0.0026 mole) was allowed to react with 0.290 mole of deuterated trifluoroacetic acid for 8 days, at room temperature. The solution was worked up as described above. The final product (0.290 g) was recrystallized from methanol, mp 59–59.5°. The extent of the nuclear deuteration was more than 95%.

Rate Measurements. Nitromethane and acetic acid were purified according to a procedure previously described.[30] The kinetics of bromination of 5-*t*-butylhemimellitene and 5-*t*-butylhemimellitene-4,6-d_2 in acetic acid and of 3-bromodurene (prepared from 3-bromoduryllithium) and 3-bromodurene-6-*d* in nitromethane were carried out as described in a preceding paper.[30] A simplified procedure, substantially identical with that described for the chlorination of halogenomesitylenes,[31] was instead used for the bromination in acetic acid of light and deuterated mesitylene and pentamethylbenzene and for the bromination in nitromethane of light and deuterated 5-*t*-butylhemimellitene. The only difference was that the halogen solution was added to that of the aromatic compound and that the kinetic flask had a volume of 25 ml. With this procedure, mesitylene gave 5.4 min as time at 10% reaction, a value in good agreement with that (5.6 min) obtained with the early procedure.[30] The kinetic experiments of bromination of light and deuterated 3-methoxydurene were brought about by the batchwise procedure, which has been previously described.[16,32] All the kinetic experiments were performed in a dark room (red lamp).

Isotope Effect in the Ag^+-Catalyzed Bromination of 1,3,5-Tri-*t*-butylbenzene-2-*d*. This reaction was carried out under conditions identical with those used for the corresponding "light" hydrocarbon; similarly, the main product of the reaction, 2,4,6-tri-*t*-butylbromobenzene, was isolated and purified by the method reported above. The extent of deuteration of this compound was 81.5% at one of the two available nuclear positions. 2,4,6-Tri-*t*-butylbromobenzene (P_H) and 2,4,6-tri-*t*-butylbromobenzene-3-*d* (P_D) are formed in a ratio, P_H/P_D, which can be related to the isotope effect, k_H/k_D, by means of the kinetic expressions for the rate of formation of these compounds from 1,3,5-tri-*t*-butylbenzene (R_H) and 1,3,5-tri-*t*-butylbenzene-2-*d* (R_D), which are both present in the starting material. From these expressions eq 4 is obtained.

$$d[P_H]/d[P_D] = (3k_H[R_H] + k_D[R_D])/2k_H[R_D] \quad (4)$$

If we assume that the R_H/R_D ratio remains unchanged during the run with respect to the initial value $(R_H/R_D)_0$, eq 4 may be integrated to give eq 5, from which the isotope effect is calculated. The above assumption is based on the fact that only one deuterium

$$P_H/P_D = [3k_H(R_H/R_D)_0 + k_D]/2k_H \quad (5)$$

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atom is present in the labeled 1,3,5-tri-*t*-butylbenzene and that the starting material contains just a minor amount (6%) of the light 1,3,5-tri-*t*-butylbenzene.

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The Decomposition of Acetyl Peroxide in Olefinic Solvents. The Acetyl Peroxide–Cyclohexene Reaction[1]

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Abstract: The reaction between cyclohexene and acetyl peroxide, I, yielding cyclohexyl acetate, II, proceeds, contrary to a prior report, with complete scrambling of the oxygen-18 label, initially in the carbonyl group of the peroxide. Four new minor products, the *cis* and *trans* isomers of 2-methylcyclohexyl acetate, III (0.4%), and 1,2-diacetoxycyclohexane, IV (0.9%), are shown also to be formed with complete scrambling of carbonyl label. Failure of added galvinoxyl scavenger to affect the yields of III and IV shows these to be radical-cage products. Cyclohexyl acetate yield is depressed on adding scavenger, suggesting its formation *via* an intermediate radical with a lifetime long enough to allow its escape from the solvent cage. Relative rates of ester formation in competitive reactions for a series of olefins show a qualitative parallel to the π basicities of the olefins, as measured by basicity toward dry HCl, and are consistent with a product-determining reaction of cage acetoxy radicals with olefin to yield a π complex which: (i) in a fast reaction within the solvent cage reacts with the other acetoxy radical to gives IV; (ii) reacts with methyl radical to give III; or (iii), in a subsequent reaction outside the cage, reacts with hydrogen donor to give II.

The thermal decomposition of acetyl peroxide is thought[5] to proceed by simple oxygen–oxygen bond cleavage to yield two acetoxy radicals which decarboxylate with a rate comparable to the rate at which they diffuse apart. Estimates of the lifetime of the acetoxy radical, made from a consideration[6] of the failure to detect typical radical reactions such as hydrogen abstraction by acetoxy radicals, fall in the range 10^{-9} to 10^{-10} sec. From the dependence of the yields of cage products, ethane and methyl acetate, on saturated hydrocarbon solvent viscosity, the rate constant for decarboxylation of acetoxy radical at 60° is calculated[7] to be 1.6×10^9 sec^{-1} (half-lifetime of the acetoxy radical 4.3×10^{-10} sec).

Such a short lifetime for these radicals makes them susceptible to capture only by the most rapid of radical scavenging reactions. For example, attempted[8] trapping of acetoxy radicals by reaction with "moist" iodine solution was not successful, although the intermediacy of the benzoyloxy radical in the thermal decomposition of benzoyl peroxide had been demonstrated by use of this reagent.[9] Rapid hydrolysis of acetyl peroxide makes the method inapplicable in the former case.[8] Addition of the stable free radical galvinoxyl,[8] or diphenylpicrylhydrazyl (DPPH),[8] leads to a reduction in the amount of carbon dioxide evolved from a solution of decomposing acetyl peroxide. Further investigation[10] has shown, however, that although this may reflect scavenging of acetoxy radical it also may result from a direct reaction between acetyl peroxide and the scavenger, at least for DPPH, the scavenger giving the largest effect on carbon dioxide evolution. In general,[11] attempts to scavenge acetoxy radicals before they decarboxylate have been unsuccessful, or at best ambiguous. An outstanding exception to this generalization is the reaction, reported by Shine and Slagle,[12] yielding cyclohexyl acetate from the decomposition of acetyl peroxide in cyclohexene. More than 15% of the acetoxy groups are present as cyclohexyl acetate in the product mixture, an indication of unexpectedly efficient scavenging by cyclohexene, if indeed acetoxy radicals are intermediates in its formation. Cyclopentyl acetate is formed[8] to an even larger degree (*ca.* 30%) when the solvent is cyclopentene.

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