bromination of the corresponding hydrocarbons. It was also shown that side chain brominated products produced by use of N-bromosuccinimide in carbon tetrachloride in the presence of benzoyl peroxide, gave peaks with different retention times. (1-Bromoacenaphthene decomposed on the column to give acenaphthylene.)

The chromatograph was calibrated directly with mixtures of the hydrocarbons and their *para* bromo derivatives and with 3-bromoacenaphthene. It was shown that 3- and 5-bromoacenaphthenes gave equal responses and equivalent result for the other pairs of bromo isomers was shown by checking the results with a gas chromatograph with a gas density balance as a detector.

Registry No.—**1**, 83-32-9; **2**, 569-41-5; **3**, 479-58-3; **4**, 14622-16-3; 6-bromoperinaphthane, 15733-72-9; 7-bromopleiadane, 15733-73-0.

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The Kinetic Isotope Effect in the Formation of Anthraquinone[1,2]

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The rate of formation of anthraquinone from 2-(2′-deuteriobenzoyl)benzoic acid is less than the rate for the protium analog, k_H/k_D varying from 1.28 in 97% sulfuric acid to 1.20 in 104% sulfuric acid. The product anthraquinone retains from 56 to 62% of one deuterium. The mechanistic implications of these results are discussed.

Isotope effects in aromatic substitution processes have been examined for many reactions by two different approaches. On the one hand there are direct comparisons of the rate of reaction of a protium compound and of its deuterium analog. Many examples typically show little or no isotope effect.[4] For example, in the nitration of nitrobenzene-d_5[5] k_H/k_D is 1.0 to within about 5%; similar results have been reported by De la Mare, Dunn, and Harvey[6] for the bromination of benzene and benzene-d_6. In other situations, however, there is observed a substantial deuterium isotope effect ($k_H/k_D \gg 1$). These situations have been characterized as ones in which the removal of the aromatic hydrogen is achieved by a general base in the rate-limiting step.[7,8] In still other cases intermediate values for k_H/k_D have been obtained. These results have been interpreted as indicating that the rate of proton loss from the Wheland intermediate is of about the same magnitude as the reversal of the attack of the substituting species upon the aromatic compound.[9]

The secondary isotope effects which accompany the formation of the Wheland intermediate are generally small. Berliner and Schueller[10] have concluded that in the bromination of biphenyl the formation of the Wheland intermediates is rate limiting with a secondary effect of $k_H/k_D = 1.15$. More recently Helgstrand and Lamm[11] have observed that the secondary isotope effect in the azo coupling reaction of *p*-chlorobenzenediazonium ion with trimethoxybenzene is inverse, $k_T/k_H = 1.13$. Very recently Kresge and Chiang[12] also reported an inverse secondary isotope effect in the aromatic hydrogen exchange of trimethoxybenzene, $k_H/k_D = 0.90$. Streitwieser[13] has pointed out that only modest secondary effects are to be expected in the formation of the Wheland intermediate as a result of the counterbalancing influences of the change in hybridization and of hyperconjugation. The results of Kresge and Chiang[12] and of Helgstrand and Lamm[11] suggest that the resultant of these influences will generally be a very small inverse effect. This is consistent with the results of Batts and Gold.[14]

Particularly pertinent to the present discussion are the results of Schubert and his students on the mechanism of the decarbonylation of aromatic aldehydes[15] which showed that proton attack on the aromatic ring of mesitaldehyde or of 2,4,6-triisopropylbenzaldehyde was not solely the rate-limiting step, but that the decomposition of the Wheland intermediate was partly rate limiting. Evidence for this was adduced from the observed isotope effect with mesitaldehyde-α-d and the solvent isotope effect.

There are studies of deuterium isotope effects in aromatic acylation reactions of the Friedel–Crafts type, which have been of the second-type, competitive experiments. Denney and Klemchuk[16] have reported that the cyclization of 2-(2′-deuteriophenyl)benzoic acid to fluorenone under a variety of conditions shows an isotope effect as measured by the deuterium content of the product. Jensen has reported[17] that benzene-d_6 is benzoylated 1.6 times more slowly than benzene; that toluene-4-d_1 shows k_H/k_D of 2.4 on benzoylation in

(1) Previous paper: D. S. Noyce and P. A. Kittle, *J. Org. Chem.*, **32**, 2459 (1967).

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(3) National Science Foundation Cooperative Graduate Fellow, 1961–1962; National Institutes of Health Predoctoral Fellow, 1962–1963.

(4) It is not the purpose of this discussion to attempt to present a comprehensive review. For leading references and an excellent discussion the reader is referred to the reviews by Melander ("Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960), by Zollinger ("Advances in Physical Organic Chemistry," Vol. II, V. Gold, Ed., Academic Press Inc., New York, N. Y., 1964, pp 163–200), and by Halevi ("Progress in Physical Organic Chemistry," Vol. I, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience Publishers, Inc., New York, N. Y., pp 109–221).

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benzoyl chloride solution; and that there is a kinetic isotope effect in the benzoylation of naphthalene.

In order to gain more insight into the later stages of the conversion of *o*-benzoylbenzoic acid into anthraquinone we have determined both the kinetic isotope effect and the product composition for the cyclization of 2-(2′-deuteriobenzoyl)benzoic acid under a variety of conditions.

Experimental Section[18]

2-Deuteriochlorobenzene.—In a 1-l., three-necked, round-bottomed flask, equipped with a pressure-equalized addition funnel, a stirring bar, and a condenser, was placed 28 g of magnesium turnings. The entire system was flushed carefully with dried nitrogen while warming. Through the third neck, ether (50 ml) dried over lithium aluminum hydride, was distilled directly into the flask. To complete the drying process 10.9 g, of ethyl bromide was added slowly. The remainder of the ether (500 ml) was distilled in and 191 g of *o*-bromochlorobenzene[19] was added slowly. After an additional 1 hr of stirring at room temperature, deuterium oxide (50 g) was added dropwise and cautiously. Working up in the usual fashion afforded 57.3 g (50%) of pure 2-deuteriochlorobenzene: bp 129–130° (spinning-band column), n^{20}D 1.5237 (lit.[20] bp 129.7–130.4°, n^{25}D 1.5210.

2-(2′-Deuteriobenzoyl)benzoic Acid.—The Grignard reagent was prepared from 8.75 g of magnesium and 37.5 g of 2-deuteriochlorobenzene in 75 ml of tetrahydrofuran following the procedure of Ramsden, *et al.*[21]

Occasional heating was required to maintain the reaction. The clear brown solution of 2-deuteriophenylmagnesium chloride was diluted with 170 ml of dry tetrahydrofuran and added slowly to a solution of 44.5 g of phthalic anhydride in 300 ml of tetrahydrofuran. After addition was complete, the resulting suspension was stirred at room temperature 1.5 hr, then heated under reflux 1 hr.

After cooling, most of the tetrahydrofuran was removed with a rotary evaporator. To the sticky, yellow residue was added 300 ml of cold water followed by enough concentrated hydrochloric acid to make the solution acidic. A yellow oily layer separated and was taken up by extraction with three portions of ether. The combined clear yellow ether layer was washed well with saturated sodium chloride solution, then extracted with three 120-ml portions of 10% sodium carbonate. The clear yellow combined aqueous extracts were boiled twice with charcoal and filtered (very little of the color was removed), cooled, and acidified with cold, concentrated hydrochloric acid. A light beige solid separated and was extracted with three 100-ml portions of ether. (A very intractable emulsion was encountered in these extractions.) The combined ether layers were filtered, washed with sodium chloride solution, and dried over sodium sulfate. After filtering, the ether was removed and the solid residue taken up in 200 ml of cold chloroform. Filtration removed a small amount of insoluble phthalic anhydride and evaporation of the chloroform gave 51.5 g of an ivory-colored solid, mp 122–130°.

This crude material was divided into four batches. Each batch was separately dissolved in the minimum amount of methylene chloride and pipetted onto a fresh 200 g column of silica gel wet packed in 2% methanol in methylene chloride. Elution with the same solvent mixture gave a combined total of 41.6 g (61.5%) of off-white material, mp 126–128°. Recrystallization from 40% benzene in cyclohexane yielded 37.6 g (55.5%) of 2-(2′-deuteriobenzoyl)benzoic acid as white platelets, mp 127.5–128.5°.

An analytical sample, mp 128–129°, was prepared by four recrystallizations from benzene–cyclohexane and sublimation at 100° (0.05 mm).

Anal. Calcd for $C_{14}H_9DO_3$: 10.00 atom % excess D. Found:[22] 9.50 atom % excess D.

2-Chloro-6-deuteriotoluene.—Freshly distilled 3-chloro-2-methylaniline was converted into 2-bromo-6-chlorotoluene by the procedure of Carpenter and Easter:[23] bp 68–69° (4 mm) [lit.[23] bp 60° (3 mm)], n^{20}D 1.5790 (lit.[23] n^{20}D 1.5791). The conversion of 2-bromo-6-chlorotoluene into 2-chloro-6-deuteriotoluene was carried out as described for the preparation of 2-deuteriochlorobenzene. The yield of material, bp 67° (35 mm), n^{20}D 1.5257, was 77%.

3-Deuterio-2-methylbenzhydrol.—The Grignard reagent was prepared from 5.15 g of magnesium and 27.0 g of 2-chloro-6-deuteriotoluene in 50 ml of dry tetrahydrofuran, initiated with a few drops of ethyl bromide and maintained at reflux for 1.5 hr. To the Grignard solution was added slowly 22.5 g of freshly distilled benzaldehyde in 35 ml of tetrahydrofuran.

After cooling, the suspension was hydrolyzed with 200 ml saturated ammonium chloride solution. Organic material which separated as a yellow upper layer was extracted with three portions of ether. The combined ether extracts were washed several times with brine and dried over sodium sulfate. Filtration followed by removal of ether with a rotary evaporator produced an oily yellow semisolid. Recrystallization of this material from 300 ml of petroleum ether (30–60°) gave 29.8 g (71%) of ivory-colored prisms, mp 90.0–92°. Further recrystallization including two treatments with Norit gave pure 3-deuterio-2-methylbenzhydrol as brittle clumps of white prisms, mp 90.5–92° (lit.[24] mp 90.5–91.0°).

The C–D band at 4.45 μ is clearly visible in the infrared spectrum of this material. In contrast, the spectrum of 2-methylbenzhydrol is completely free of absorption in this region. The two spectra also show subtle differences in the fingerprint region and in the intensity of the two strong bands at 6.7 and 6.9 μ.

2-Benzoyl-6-deuteriobenzoic Acid.—Chromium trioxide (40 g, 0.4 mol) was stirred into a mixture of 350 ml of glacial acetic acid, 10 ml of concentrated sulfuric acid and 100 ml of water. To this solution was added 11.92 g (60 mmol) of 3-deuterio-2-methylbenzhydrol in several portions. After the initial exothermic reaction subsided, the reaction mixture was heated under reflux 8.5 hr, cooled, and poured over 500 g of ice. Sodium bisulfite was added to destroy excess chromium trioxide. The solution was further diluted with 2 l. of cold water and extracted with two 500-ml portions of ether. The combined ether extracts were washed carefully with water to remove residual chromium salts. The concentrated ether extracts were extracted with 125 ml of 10% sodium bicarbonate and the basic solution was cooled and acidified with concentrated hydrochloric acid to give a white solid. One recrystallization from 30% benzene in cyclohexane yielded 6.4 g (47%) of white crystals of 2-benzoyl-6-deuteriobenzoic acid, mp 124.5–126.5°. An additional recrystallization provided material melting at 127–128.5°. The infrared spectrum of this material differed substantially from that of 2-(2′-deuteriobenzoyl)benzoic acid as well as from that of ordinary *o*-benzoylbenzoic acid.

1-Deuterioanthraquinone.—In a 100-ml flask was placed 2.5 g of 2-benzoyl-6-deuteriobenzoic acid and 20 ml of concentrated sulfuric acid. The resulting clear solution was protected with a calcium chloride drying tube and magnetically stirred while heated to 100° for 4 hr. The reaction mixture was then cooled and poured over 100 g of ice to give a woolly, voluminous tan solid. To coagulate the solid, this aqueous suspension was heated to boiling for a few minutes. After cooling, the solid was collected by suction filtration and washed well with several portions of hot water, then with dilute ammonium hydroxide, and again with hot water. The crude product was dried in the oven and recrystallized from toluene. A second recrystallization gave 2.05 g (90%) of 1-deuterioanthraquinone as long, silky needles, mp 284–286° (Kofler hot stage, corrected).

Three recrystallizations from toluene followed by drying (78° at 0.1 mm) and sublimation (135° at 0.05 mm) provided an analytical sample, mp 285–286° (hot stage).

(18) Melting points were determined in a Hershberg apparatus except as noted. Infrared spectra were taken using a Perkin-Elmer Model 137 Infracord.

(19) *o*-Bromochlorobenzene was purified by careful distillation through a 90-cm spinning-band column. A center cut boiling at 72° (9 mm) was collected. Vapor phase chromatography (silicon oil column at 142°) showed this material to be homogeneous except for a trace impurity which had the same retention time as *p*- or *m*-bromochlorobenzene. Authentic 1% solutions of these isomers in the distilled *o*-bromochlorobenzene were prepared and analyzed by vpc. Comparison of the relative peak heights with these chromatograms showed that the trace impurity present in *o*-bromochlorobenzene amounted to no more than 0.1%.

(20) J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *J. Amer. Chem. Soc.*, **78**, 601 (1958).

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(22) Deuterium analyses were by J. Nemeth, Urbana, Ill., unless otherwise indicated.

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(24) S. W. Kantor and C. R. Hauser, *J. Amer. Chem. Soc.*, **73**, 4122 (1951).

Anal. Calcd for $C_{14}H_7DO_2$: 12.50 atom % excess D. Found: 12.30 atom % excess D (98.5%) (an independent mass spectral analysis gave a value of 98.4%).[25]

This experiment also serves to establish that deuterioanthraquinone is stable under the experimental conditions for its formation and does not suffer loss of deuterium.

Kinetic Procedures. General Method.—All kinetic runs were conducted in "twinned pairs" using 1-cm quartz cells mounted within the cell compartment of a Beckman DU spectrophotometer equipped with dual thermospacers. For any given run, solutions of 2-(2′-deuteriobenzoyl)benzoic acid and *o*-benzoylbenzoic acid in the appropriate sulfuric acid were prepared just before use (as described below). The acid used to make these solutions was always withdrawn by pipet from the same batch of sulfuric acid which had been previously standardized. Acid used for the reference cell was likewise removed from the same batch of sulfuric acid for any given run. All three cells were then placed in the Beckman compartment and allowed to equilibrate for 20–25 min. Changes in optical density due to absorption of the product anthraquinone were recorded in the usual fashion by taking readings at appropriate intervals, first of the 2-(2′-deuteriobenzoyl)benzoic acid solution and then of the *o*-benzoylbenzoic acid solution. The wavelength used varied in the range 269–281 mμ depending on the strength of the sulfuric acid solvent. Infinity points were taken after (at least) 10 half-lives.

Calculation of the Data.—Raw optical density data were converted into per cent unreacted and were plotted *vs.* time. The first-order plots remained linear to at least 90% reaction. Rate constants were obtained from slopes of lines in the usual fashion.

Preparation of Solutions.—Stock amounts of the kinetic acids were prepared by diluting 30% fuming sulfuric acid to the desired concentration with sulfuric acid. Ordinary reagent grade sulfuric acid was used without further purification. All kinetic acids were titrated in triplicate using approximately 1 *N* sodium hydroxide which had been freshly standardized against potassium acid phthalate.

Stock solutions of 2-(2′-deuteriobenzoyl)benzoic acid and *o*-benzoylbenzoic acid were prepared by weighing out approximately 1.7 mg of each material in 100-ml volumetric flasks. Filling to the mark with chloroform provided solutions close to 7.5×10^{-5} *M*. Just before a kinetic run, a 1-ml aliquot of each solution was withdrawn and pipetted into a separate 10-ml volumetric flask. The chloroform was then evaporated in a gentle stream of dry nitrogen, and both flasks were dried for a short time in the oven before being filled to the mark with stock sulfuric acid of the desired concentration. After being thoroughly shaken these sulfuric acid solutions were transferred to 1-cm cells by means of a pipet. The concentration of the solutions used for kinetic runs was thus approximately 7.5×10^{-6} *M*.

Analysis of Standard Mixtures.—Approximately 20 mg of pure anthraquinone and 40 mg of pure 1-deuterioanthraquinone were accurately weighed into a small flask. The mixture was dissolved in benzene to assure homogeneity. After evaporation of the benzene in a stream of dry nitrogen, the anthraquinone was sublimed to give a sample for mass spectral analysis. Mass spectra were obtained at low ionizing voltages (10–15 V)[25] and the parent peaks were used to calculate the percentage of 1-deuterioanthraquinone present. Table I presents results of five determinations.

TABLE I

ANALYSIS OF STANDARD MIXTURES OF ANTHRAQUINONES

% 1-deuterioanthraquinone by weight	62.9	60.6	63.6[a]
% 1-deuterioanthraquinone by mass spectra	63.0	61.2	64.2, 63.4, 64.1

[a] This sample was sublimed in three successive fractions and each analyzed.

Product Isolation.—Approximately 1 g of 2-(2′-deuteriobenzoyl)benzoic acid was weighed out into a 25-ml volumetric flask. The flask was filled with sulfuric acid of the appropriate concentration and placed in an oil bath at 70°. After a period of time corresponding to 10–12 half-lives, the flask was removed from the bath and cooled, and the contents were poured over ice. The precipitate was filtered and washed thoroughly with water, a small amount of ammonia, and then again with water. The dried anthraquinone was crystallized from toluene, and sublimed to give a sample for mass spectral analysis.

A further control experiment in which a sample of 1-deuterioanthraquinone was heated with fuming sulfuric acid showed no loss of deuterium.

(25) The mass spectra were determined with a CEC Model 21-103 C mass spectrometer equipped with an ion multiplier. We thank Miss S. Firth for obtaining the mass spectra.

Results and Discussion

Kinetic Measurements.—The results of a series of kinetic measurements are presented in Table II. Above 100% sulfuric acid, the kinetic isotope effect k_H/k_D remains nearly constant. Below 100% sulfuric acid the value for k_H/k_D gradually increases. However, concurrently the rate of formation of anthraquinone remains nearly constant from 97 to 100% sulfuric acid, and is somewhat higher in fuming sulfuric acid. In 97% sulfuric acid (at 70°) *o*-benzoylbenzoic acid is substantially, but not entirely, converted into the lactol carbonium ion. It, therefore, appears that the kinetic isotope effects below 100% sulfuric acid are mediated by a secondary isotope effect on the equilibrium formation of the lactol carbonium ion.

TABLE II

RATE OF CYCLIZATION OF *o*-BENZOYLBENZOIC ACID AND 2-(2-DEUTERIOBENZOYL)BENZOIC ACID AT 70.0°

Run	Wt % H_2SO_4	$10^4k_{obsd}^H$, sec^{-1}	$10^4k_{obsd}^D$, sec^{-1}	k_H/k_D	Average k_H/k_D
1	97.13	1.27	0.987	1.29	
2	97.13	1.28	0.998	1.28	1.28 ± 0.02
3	97.13	1.26	0.998	1.26	
4	98.18	1.46	1.20	1.22	1.22
5	98.18	1.45	1.20	1.21	
6	99.23	1.56	1.35	1.16	1.16
7	99.23	1.56	1.34	1.16	
8	100.3	1.53	1.39	1.10	
9	100.3	1.56	1.38	1.13	1.13 ± 0.03
10	100.3	1.61	1.39	1.16	
11	101.3	1.98	1.66	1.19	1.19 ± 0.01
12	101.3	1.97	1.67	1.18	
13	101.3	1.97	1.65	1.19	
14	102.1	2.39	2.03	1.18	1.18
15	102.9	2.98	2.45	1.22	
16	102.9	2.85	2.40	1.19	1.20 ± 0.02
17	102.9	2.90	2.41	1.20	

Product Isolation.—Cyclization of 2-(2′-deuteriobenzoyl)benzoic acid gives a mixture of anthraquinone and 1-deuterioanthraquinone. The percentage of 1-deuterioanthraquinone formed in eight different sulfuric acid media is given in Table III.

TABLE III

PERCENTAGE OF 1-DEUTERIOANTHRAQUINONE IN ANTHRAQUINONE PRODUCT MIXTURES

Wt % H_2SO_4	% 1-Deuterioanthraquinone
97.13	56.6
98.18	57.5
99.23	58.3
100.3	59.2
101.3	60.0
102.1	60.7
102.9	61.2
104.9	62.6

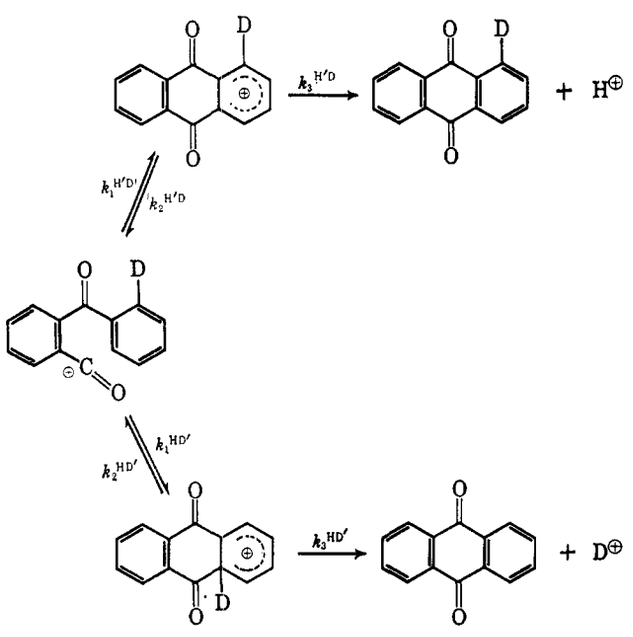
It is to be noted that the fraction of deuterium retained increases smoothly from 97% sulfuric acid to 105% sulfuric acid. This is in contrast to the behavior of the measured kinetic isotope effects discussed above.

In evaluating the significance of these results it is worthwhile to consider first the possibility that formation of the Wheland intermediate is rate limiting and followed by a fast collapse to products. This picture of the reaction sequence is inconsistent with the generally accepted conclusion that there is not a substantial isotope effect in the formation of the Wheland intermediate. Were this picture correct the ratio ($k_1^{H'D}/k_1^{HD'}$) (H'D superscript signifies attack at the hydrogen site; HD' superscript signifies attack at the deuterium site) would have to vary from 1.3 to 1.6, very much larger than any previously observed secondary isotope effects in the aromatic substitution process.

Thus, we conclude that these kinetic and product isotope effects demonstrate that decomposition of the Wheland intermediate is partially rate limiting. Denney and Klemchuk[16] have concluded that this same situation obtains in the formation of fluorenone from *o*-phenylbenzoic acid.

Consider the situation summarized in Chart I.

CHART I



The rate of formation of deuterated anthraquinone from 2-(2'-deuteriobenzoyl) acid may be directly obtained by making use of the knowledge of the fraction of deuterium retained in the product anthraquinone. Correcting the observed total rate of formation of anthraquinone in this fashion leads to the results tabulated in column 2 of Table IV. This rate is given by eq 1 in which it is to be noted that the rate constants

$$k_{obsd}^{H'D} = k_1^{H'D}k_3^{H'D}/(k_2^{H'D} + k_3^{H'D}) \quad (1)$$

involve only indirect and secondary isotope effects. This rate of reaction may further be compared with the rate of formation of ordinary anthraquinone from benzoylbenzoic acid (statistically corrected by factor of 2) with the results given in column 4 of Table IV. It

TABLE IV

DERIVED ISOTOPE EFFECTS

Wt % H_2SO_4	*a*, $10^4 \frac{k_1^{H'D}k_3^{H'D}}{k_2^{H'D} + k_3^{H'D}}$, sec^{-1}	*b*, $10^4 \frac{k_1^{HD'}k_3^{HD'}}{k_2^{HD'} + k_3^{HD'}}$, sec^{-1}	*c* $\frac{1/2k^{HH}}{k^{H'D}}$	*c* $\frac{1/2k^{HH}}{k^{HD'}}$
97.13	0.56	0.43	1.13	1.48
98.18	0.69	0.51	1.06	1.43
99.23	0.78	0.56	0.994	1.39
100.3	0.82	0.57	0.957	1.39
101.3	1.00	0.66	0.990	1.48
102.1	1.23	0.80	0.971	1.50
102.9	1.48	0.90	0.980	1.55

[a] Rate of formation of deuterioanthraquinone. [b] Rate of formation of ordinary anthraquinone. [c] Average in region 99–103% H_2SO_4, 0.978 ± 0.01.

is to be noted that the resulting isotope effect is very small and slightly inverse; in the region between 99 and 103% sulfuric acid, k_H/k_D is 0.978 ± 0.01.

Similarly, the fraction of ordinary anthraquinone obtained from 2-(2'-deuteriobenzoyl)benzoic acid allows calculation of the rate of reaction at the deuterium site (column 3, Table IV.) This rate (eq 2) now represents

$$k_{obsd}^{HD'} = k_1^{HD'}k_3^{HD'}/(k_2^{HD'} + k_3^{HD'}) \quad (2)$$

a combination of secondary isotope effects ($k_1^{HD'}$ and $k_2^{HD'}$) in the formation of the Wheland intermediate and its reversion to its precursor. In addition the important primary isotope effect involved in the decomposition of the Wheland intermediate to products ($k_3^{HD'}$) is encompassed in the rates given in column 3 of Table IV. The isotope effect involved is calculated in column 5 in Table V, and is 1.46 ± 0.05.

Thus, the secondary isotope effects are negligible; a primary isotope effect is operative, and hence, the decomposition of the Wheland intermediate is partially rate limiting.

Registry No.—Anthraquinone, 84-65-1; 2-(2'-deuteriobenzoyl)benzoic acid, 15733-67-2; 2-chloro-6-deuteriotoluene, 15733-68-3; 2-benzoyl-6-deuteriobenzoic acid, 15733-69-4; 1-deuterioanthraquinone, 7302-30-9; *o*-benzoylbenzoic acid, 85-52-9.