hours with absolute alcohol saturated with dry HCl gas, the alcohol was evaporated under nitrogen, and the residue worked up as in Fig. 3.

All the liquid–liquid extractions were carried out with equal volumes of ethyl acetate or alkali.

Preparation of 1,2,5,6-Dibenz-3,4-anthraquinone.—Crude dibenzanthracene-3,4-dihydrodiol, obtained from 9.4 g. of dibenzanthracene through its osmium tetroxide adduct by the method of Cook and Schoental,[32] was oxidized with sodium dichromate (9.2 g. in 27 ml. of water) and acetic acid (800 ml.) by modification of the method of Stephenson.[25] The reactants were mixed and slowly (1 hour) brought to reflux; the mixture turned red. It was refluxed for 30 min. and left at room temperature overnight. The red solid was filtered, washed with water and dried, yield 5.4 g. (53% based on DBA). The m.p. was 348–350° in contrast to the literature reports of 327–329°,[24,25] and 325°.[33] One recrystallization from ethyl acetate (not necessary for oxidation to the dicarboxylic acid) gave a m.p. of 349.5–350°. *Anal.*[34] Calcd. for $C_{22}H_{12}O_2$: C, 85.67; H, 3.92. Found: C, 85.22; H, 4.12. The mother liquor when poured into water gave a yellow crystalline solid, m.p. 208–210°, yield 0.46 g., which was not characterized further. It was not reported previously.[25]

Preparation of 2-Phenylphenanthrene-3,2′-dicarboxylic Acid (PDA).—This acid[25,33] was prepared from 1,2,5,6-dibenz-3,4-anthraquinone by a modification of the method used by Collins, *et al.*,[35] for the preparation of 2-phenylnaphthalene-1,2′-dicarboxylic acid. The quinone, 1.5 g., 900 ml. of *sym*-tetrachloroethane, 300 ml. of acetic acid and 420 ml. of 30% H_2O_2 were mixed in a 3-l. flask, heated for 18 hr. at 80–90° (when the organic layer turned yellow) and left overnight. The solvents were removed *in vacuo* when a yellow solid separated. The flask was cooled, the contents left for several hours, covered with an excess of 10% $NaHCO_3$ and then filtered. The crude dicarboxylic acid was precipitated from the filtrate by acidification with concd. HCl, and was cooled and filtered, yield 1.1 g. (67%), m.p. 300–309°. One recrystallization from acetone gave pure pale-yellow acid, m.p. 315–317°, yield 0.48 g., neutral equivalent 224 (calcd. 233).

In some of the carrier experiments, a sample of acid was used which, although its m.p. was 309–312° in accordance with the literature,[25] was shown later by neutral equivalent determinations to be only 80% pure.

Carrier Experiments.—(a) General techniques: The non-radioactive phenylphenanthrenedicarboxylic acid (PDA), mixed with the radioactive material was purified by repeated crystallizations from acetone and by sublimation. Less than 3 mg. of the acid was recrystallized from a 4:1 or 1:1 mixture of acetone with benzene or ligroin. Sublimations were carried out at less than 0.1 mm. and 280–320° (bath temperature). The acid was assayed for radioactivity by direct plating from acetone solution.

Dibenzanthracene carrier was purified by recrystallization from benzene and acetic acid and by chromatography on Florisil.[12] It was plated from benzene solution.

Carrier experiments which were repeated were reproducible.

(b) Carrier experiments on acidic materials obtained under hydrolysis condition (e): The radioactive material (2500–7000 c.p.m.) was mixed in the dry state with a known amount (15–70 mg.) of the *impure* PDA carrier. The mixture was dissolved in acetone, and sublimed 1–3 times. The non-acidic, more soluble impurity was removed and the dicarboxylic acid recrystallized to constant specific activity as illustrated in Fig. 4. Experiments 1–3 in Table V summarize the results obtained. In these three experiments, when neutralization equivalents of the samples of carrier acid obtained at various stages of purification after the initial sublimation(s) were plotted against their specific activities, a straight line was obtained.

The samples of PDA that had been purified to constant specific activity in experiments 1–3 (Table V), were combined and esterified with methanol as already described. The ester was isolated in the usual way. Two recrystallizations gave specific activities of 26 and 27 c.p.m./mg., respectively (calculated value 26); m.p. 142° (Cook and Schoental[33] give m.p. 144–145°).

(c) Carrier experiments on materials obtained by oxidative hydrolysis: The pepsin-soluble and pepsin-insoluble fractions derived from large-granular protein and the pepsin treated soluble protein (10,000–20,000 c.p.m.) were hydrolyzed according to method (h), using the pure carrier. The dicarboxylic acid was precipitated from the alkaline solution (after removal of MnO_2 and neutral substances) as already described. Three to six recrystallizations interspersed with two to three sublimations sufficed to achieve radiochemical purity.

(d) Carrier experiments on acidic and neutral materials obtained from pepsin-insoluble large-granular protein by hydrolysis method (j): The experiment using PDA as the carrier on the acidic material was done as in (a), except that the pure acid was used. The neutral fraction was mixed with carrier DBA, which was then purified to constant specific activity as already described.

MADISON, WISCONSIN

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(32) J. W. Cook and R. Schoental, *J. Chem. Soc.*, 170 (1948). After the decomposition of the adduct, only the diol (almost colorless) obtained on filtration and washed with water was used.

(33) J. W. Cook and R. Schoental, *J. Chem. Soc.*, 47 (1950).

(34) Microanalysis carried out by Clark Microanalytical Laboratory, Urbana, Ill.

(35) C. J. Collins, D. N. Hess, R. H. Mayor, G. M. Toffel and A. R. Jones, THIS JOURNAL, **75**, 397 (1953).

NOTES

The Infrared Intensity of the C–D Stretching Vibration in Deuterobenzene, *m*-Deuteronitrobenzene and *m*-Deuteroaniline

BY WILLIAM G. DAUBEN, GEORGE C. PIMENTEL AND C. WHEATON VAUGHAN, JR.[1]

RECEIVED DECEMBER 20, 1954

It has recently become of interest in this Laboratory to employ infrared spectroscopy to determine the percentage of deuterium in certain aromatic compounds. In this regard it has been reported by Alexander and Burge[2] that "with nitrobenzene and aniline hydrochloride, the absence of a characteristic infrared absorption in the C–D stretching frequency cannot be taken as evidence for the absence of small amounts of deuterium in the *meta* position." Such a conclusion was based upon a comparison of the infrared spectrum of deuterobenzene in benzene solution with the spectrum of a sample of *m*-deuteronitrobenzene containing 2.55 atom per cent. excess deuterium. These observations cast doubt upon the utility of

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(1) Du Pont Postgraduate Teaching Fellow in Chemistry, University of California (Berkeley), 1953–1954.

(2) B. R. Alexander and R. E. Burge, Jr., THIS JOURNAL, **72**, 3100 (1950).

infrared spectroscopy as a means of estimating deuterium content in deuterated aromatic compounds. To clarify the infrared spectral characteristics of *m*-deuteronitrobenzene, a sample of the compound was prepared with a higher deuterium content (11.51 atom per cent. excess) than that employed by Alexander and Burge[2] and the infrared spectrum carefully examined. In addition, the deuterated aniline derived from the nitrobenzene was studied.

It was found, in contrast to the earlier work,[2] that the spectra of the deuterated compounds did possess absorption bands in the characteristic C–D stretching vibration region which were not present in the spectra of the undeuterated compounds. The positions of the bands were 2285 ± 3 cm.$^{-1}$ for *m*-deuteronitrobenzene and 2270 ± 3 cm.$^{-1}$ for *m*-deuteroaniline as compared to 2272 ± 3 cm.$^{-1}$ for monodeuterobenzene.

To permit comparison of the intensities of the C–D stretching absorptions in the spectra of these three compounds, it is desirable to employ the integrated areas in view of the known sensitivity of band width to solvent environment.[3] Since the deuterium concentrations were not equal in the three compounds, each area was divided by the appropriate mole fraction of the deutero compound. The intensities so obtained are listed in Table I. The intensity of the *m*-deuteronitrobenzene band was found to be about half the intensity of the deuterobenzene band. The *m*-deuteroaniline band was found to be equal in intensity to the deuterobenzene band.[4] Thus, the above results are in contrast to the report[2] that no absorption associated with the C–D stretch was observed in a sample of *m*-deuteronitrobenzene containing 2.55 atom per cent. excess deuterium under conditions in which 0.2 atom per cent. excess of deuterium could be detected in deuterobenzene.

To investigate the possibility that this intensity behavior is caused by intermolecular interactions, "solvent perturbations," the intensity of the 2272 cm.$^{-1}$ band in deuterobenzene was studied in nitrobenzene solution and triethylamine solution. The solutions were prepared by dissolving one volume of deuterobenzene in four volumes of the solvent. The intensities observed are shown in Table I. As far as the experimental uncertainty permits a conclusion, the intensity of the C–D stretch in deuterobenzene is lowered by about 30% in nitrobenzene solution and by about 20% in triethylamine solution. The solvent effect of aniline was not studied.

The accuracy of these measurements is limited because of the inherently weak absorption of the C–D stretching motion and because pure *m*-deuteronitrobenzene was not prepared. However, the results do indicate that the intensity of the C–D stretch of *m*-deuteronitrobenzene is lower by a factor of two than that of deuterobenzene and that the intensity of the C–D stretch of deuterobenzene is significantly reduced when it is dissolved in nitrobenzene. It can be concluded that a large portion of the intensity difference of the C–D stretch in *m*-deuteronitrobenzene and deuterobenzene must be attributed to solvent environmental disturbances rather than to intramolecular perturbations.

TABLE I

INTENSITIES OF THE C–D STRETCHING FREQUENCIES OF SOME MONODEUTERATED AROMATIC COMPOUNDS

Compound	Solvent	Cell thickness, cm.	Intensity × 10^{-4}, liter cm.$^{-2}$ mole^{-1}
Deuterobenzene	Benzene	0.0094	36.6
		.008	34.9
		Av.	35.8
m-Deuteronitrobenzene	Nitrobenzene	.008	16.0
m-Deuteroaniline	Aniline	.0094	36.5
		.0094	41.6
		Av.	39.5
Deuterobenzene	Nitrobenzene	.0094	25.0
Deuterobenzene	Triethylamine	.0094	28.6

Experimental

m-Deuteronitrobenzene.—A solution of hydrochloric acid in deuterium oxide, prepared by dissolving 0.211 mole of hydrogen chloride in 26 ml. of 99.5% deuterium oxide, was added to 5.54 g. (0.04 mole) of *m*-nitroaniline and the mixture stirred at 60° for 15 minutes to ensure complete salt formation. After cooling to −10°, a solution of 3.10 g. (0.045 mole) of sodium nitrite in 8 ml. of 99.5% deuterium oxide was added, with stirring, over a period of 1 hour and the temperature was not allowed to rise above 0°.

To this diazonium solution, cooled to −15°, was added 24.0 g. (0.363 mole) of prechilled deuterohypophosphorus acid, prepared from anhydrous hypophosphorus acid obtained by dehydration of the commercially available 50% aqueous solution under reduced pressure at 35°. This anhydrous acid was allowed to exchange with an equal weight of 99.5% deuterium oxide, the acid again dehydrated and the resultant anhydrous acid was dissolved in an equal weight of 99.5% deuterium oxide. Upon the addition of the reducing agent, evolution of nitrogen was observed almost immediately but the reaction was allowed to stand for 12 hours at 0°.

The mixture was extracted twice with ether, the ethereal solution evaporated and the residual oil was steam distilled. The dried distillate then was distilled through a micro-column, yield 1.2 g. (23%). The product contained 11.55 atom per cent. excess deuterium which corresponds to a mole fraction of 0.578 of deuterated material.

m-Deuteroaniline.—*m*-Deuteronitrobenzene (0.460 g., 3.7 mmoles) was hydrogenated in alcoholic hydrochloric acid over palladium-on-charcoal and the hydrochloride isolated in near quantitative yield. Treatment of the salt with sodium hydroxide gave the free amine which was distilled in a micro-column, yield 0.21 g. (60%). The product contained 7.88 atom per cent. excess deuterium which corresponds to a mole fraction of 0.552 of the deuterated material.

Deuterobenzene.—Bromobenzene (78 g., 0.50 mole) was converted into the Grignard reagent in the usual manner and the latter material was decomposed with 12 g. of 99.5% deuterium oxide. After standing for 12 hours, hydrochloric acid was added and the mixture processed. The product was distilled through a column packed with Podbielniak Heli-pak, b.p. 80–81°, yield 30.3 g. (78%). The product contained 12.28 atom per cent. excess deuterium which corresponds to a mole fraction of 0.737 of the deuterated material.

Infrared Spectroscopy.—The infrared spectra were obtained using a Perkin–Elmer model 21 spectrophotometer equipped with CaF_2 and NaCl optics. All compounds were examined as pure liquids in cells near 0.1 mm. in thickness. The carbon dioxide absorption at 2349 cm.$^{-1}$ was used for frequency calibration shortly before and after each spectrum was completed. Intensities were estimated by integration of the bands over spectral regions 60 cm.$^{-1}$ in width. A small correction for absorption by nitrobenzene was necessary in the determination of the C–D stretch of *m*-deutero-

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(3) D. H. Whiffen, *Trans. Faraday Soc.*, **49**, 878 (1953).

(4) Alexander and Burge[2] examined only the spectrum of *m*-deuteroaniline hydrochloride.

nitrobenzene. Duplicate determinations differed by 5 to 13% but the intensities are assigned an uncertainty of ±20% because of difficulties inherent in the integrations. The spectral slit width at 2280 cm.$^{-1}$ was 8 cm.$^{-1}$.

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CHEMICAL LABORATORIES
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIFORNIA

Reactions of Anisic Acid and Ethyl Anisate in 100% Sulfuric Acid

BY ARTHUR BRADLEY

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Anisic acid (I) has been described as "the first aromatic acid without an *ortho*-substituent which exhibits acylization" in 100% sulfuric acid.[1] This statement was based on (a) the high "*i*" factor observed in this solvent (3.38), and (b) the fact that a solution of I in sulfuric acid gave 15% ethyl anisate on pouring into cold ethanol.

Since in theory an acid undergoing acylization would be expected to have an "*i*" factor of 4.0 and give nearly a quantitative yield of ester in (b) above,[2] Kuhn and Corwin[1] suggested that the acylcarbonium ion was partially removed as the anisyl sulfate, equation 1. This substance would be expected to react with an alcohol to give I, equation 2.

$$CH_3OC_6H_5CO^+ + HSO_4^- \rightleftharpoons CH_3OC_6H_5COOSO_3H \quad (1)$$

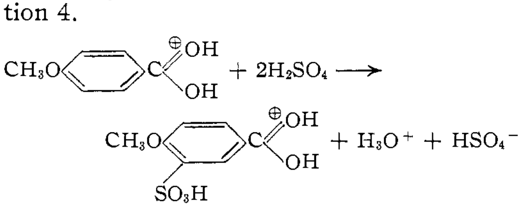
$$CH_3OC_6H_5COOSO_3H + ROH \longrightarrow CH_3OC_6H_5COOH + ROSO_3H \quad (2)$$

It also was implied that the benzoyl and acetyl cations, formed by acylization of certain of their esters, entered similarly into covalent bonds with bisulfate. The predicted "*i*" factor of a completely ionized ester of one of these acids (anisic, benzoic, acetic) would then be 4.0 or above, equation 3. This theory has been incorporated into a treatise on the behavior of organic compounds in sulfuric acid.[3]

$$RO{-}CO{-}R' + 2H_2SO_4 \rightleftharpoons ROSO_3H + H_3O^+ + RCO{-}OSO_3H + HSO_4^- \quad (3)$$

It has been shown recently[4] that in sulfuric acid, complete cleavage of acetic and non *ortho*-substituted benzoic esters consistently gave three particles ("*i*" = 3.0). Since this precludes acyl sulfate formation, it was felt that re-evaluation of the experimental observations that led to this theory might be possible. This has been accomplished, and the suggestion that anisate esters yield anisyl sulfate[1] may be considered unwarranted.

Newman and Deno[5] had reported that the "*i*" factor of I increased on standing to 3.8, whereupon it could no longer be recovered by quenching the acid and extracting with ether. They attributed the change of "*i*" factor to slow sulfonation, equation 4.

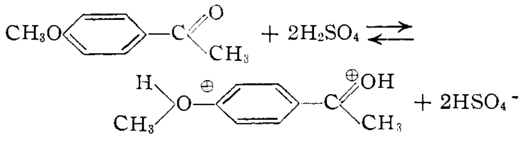


(4)

In repeating this work we found that the "*i*" factor of I as first measured was nearly 3.0, increasing to a fairly stable value of 3.9 after four hours at 50°. Percentage recoveries of I from sulfuric acid solutions at this temperature showed a large drop in the first hour, and then a slow decrease to zero (Table I). Esters of anisic acid have been shown to undergo cleavage to I at a rapid rate.[1,6] In this investigation trichloroethyl anisate gave 80% of I after two minutes. The yields of acid from II showed an early maximum followed by a gradual decline.

In order to obtain a better understanding of the behavior of I and II in 100% sulfuric acid, many "*i*" factor measurements at short intervals at approximately 10° were made (Fig. 1). At this temperature both sulfonation and cleavage are slow, and it is unlikely that either or both of these reactions could completely account for the observed rapid increase of "*i*" factors. A cryoscopic run on I at 10° was interrupted after 90 minutes ("*i*" = 3.1) and the contents thrown on ice, whereupon 63% of the acid was recovered. Since quantitative recoveries are never obtained,[1] less than 37%, and probably no more than 20% (*i.e.*, "*i*" = 2.4) of the acid had sulfonated. Similarly, the "*i*" factor of II observed after 60 minutes at 10° (3.0) is considerably higher than predicted by 9% cleavage (Table I), even if accompanied by some sulfonation. Evidently another effect contributes to the high "*i*" factor.

The possibility that multiple protonation accounted for the unexpectedly high "*i*" factors in the early stages of the reactions of I and II was considered. It was found that *p*-dimethoxybenzene and *p*-methoxyacetophenone (III) both gave initial values of about 3.0 (Fig. 2). The latter compound (III) was stable indefinitely in 100% sulfuric acid at 10°, and was recovered unchanged in good yield (66%) after one hour at 25°. Since III undoubtedly dissolved as the diprotonated ion (equation 5), it is surprising that both I and II were initially only monoprotonated.



(5)

It would be of great theoretical interest if a proton transfer analogous to 5 could be found to proceed at a measurable rate.[7] Unfortunately the addition of a second proton to anisic acid or ethyl anisate is difficult to establish, and if it occurs is too

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(1) L. P. Kuhn and A. H. Corwin, THIS JOURNAL, **70**, 3370 (1948).

(2) M. S. Newman, *ibid.*, **63**, 2431 (1941).

(3) L. F. Andrieth and J. Kleinberg, "Non-Aqueous Solvents," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 186.

(4) A. Bradley and M. E. Hill, THIS JOURNAL, **77**, 1575 (1955).

(5) M. S. Newman and N. Deno, *ibid.*, **73**, 3644 (1951).

(6) L. P. Kuhn, *ibid.*, **71**, 1575 (1949).

(7) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 11.