[Contribution from the Chemical Laboratories of Iowa State College]

Aromatic Nitration. I. The Ultraviolet Spectra of Aromatic Nitro Compounds in Sulfuric Acid

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The ultraviolet absorption spectra of mono and dinitro derivatives of 1,4-dihalobenzenes show three maxima in the near ultraviolet. Two are believed to be due to transitions in which the nitro group is intimately involved. These latter show very large bathochromic shifts as the ability of the solvent to form hydrogen bonds is increased. The transition occurring near 2500 Å. in nitrobenzene is affected in a similar manner. Using the shift as a criterion, it is found that the extent of hydrogen bonding to nitrobenzene is not increased materially by removal of the last 10% water from sulfuric acid solution. The implications of these results are discussed in relation to the nitration process.

While extensive and brilliant work[1] in several laboratories has rendered the process of aromatic nitration one of the best understood of all organic reactions, an unambiguous explanation has not been offered for the decrease in rate which is observed, in sulfuric acid solutions, as the last few per cent. of water is removed from the nitration medium. Bennett and co-workers[2] attempted to account for the phenomenon by invoking a termolecular mechanism but their interpretation has been shown to be untenable by Melander.[3] Westheimer and Kharasch[4] suggested that the decrease in rate might parallel the increase in the acidity function which accompanies the decrease in water content of the medium. It is not entirely clear whether or not these authors intended to suggest that the substrate is, in all cases, converted to a less reactive conjugate acid. Such an ionization has been shown by cryoscopic measurements[5] to occur with many compounds, such as benzoic acid, which show the fall off in nitration rate. However, Gillespie found that most nitroaromatics are only slightly ionized in solutions containing more than a per cent. or so of water.[5,6] Gillespie and Millen have suggested that these compounds are rendered less reactive by the formation of hydrogen bonded complexes with the solvent.[5] We have found that the study of the ultraviolet absorption spectra of aromatic nitro compounds in hydroxylic solvents indicates that considerable interaction does occur. We have, therefore, attempted to exploit this behavior as a test of Gillespie's hypothesis concerning the kinetic anomaly.

Experimental

Nitrobenzene, Eastman Kodak White Label, was distilled through a 44-plate column and a fraction boiling at 208.2° (745 mm.) was collected for use.

2,5-Dichloronitrobenzene, Eastman Kodak, was used without further purification, m.p. 54°.

2,5-Dibromonitrobenzene was obtained by the nitration of *p*-dibromobenzene with fuming nitric acid at room temperature. The product was recrystallized first from 95% ethanol and then from Skellysolve B, m.p. 82–82.5°.

2,3-Dinitro-1,4-dibromobenzene and 2,5-dinitro-1,4-dibromobenzene were isolated from the mixture produced when *p*-dibromobenzene was nitrated at 95° with concentrated nitric acid in 95% sulfuric acid. The fractionation procedure used by Jackson and Calhane[7] was used to obtain the crude fractions but it was found that the 2,5-isomer was best purified by recrystallization from dioxane as suggested by Sunde, *et al.*[8,9] Both isomers were recrystallized to constant melting points; 2,3-isomer, m.p. 157°; 2,5-isomer 128–129°.

Nitration of 2-Nitro-1,4-dichlorobenzene.—One hundred grams of *p*-dichlorobenzene, 220 cc. of concentrated nitric acid and 200 cc. of concentrated sulfuric acid were heated for two hours on the steam-bath. The reaction mixture was poured over a kilogram of cracked ice and the solid was removed by suction filtration. The damp filter cake weighed 132 g. and was dissolved in 400 cc. of hot benzene and the hot solution was filtered through about 30 g. of alumina to remove water and acid. Skellysolve B (700 ml.) was added to the benzene solution and on cooling overnight in the refrigerator the solution deposited 60 g. of solid which melted at 76–98°. Repeated recrystallization of this fraction from Skellysolve B and carbon tetrachloride gave **2,6-dinitro-1,4-dichlorobenzene**, m.p. 104.5–105°. The mother liquor was concentrated nearly to dryness and the residue was dissolved in 35 ml. of hot glacial acetic acid. On cooling the solution deposited 15 g. of crystals melting 84–98°. Repeated recrystallization of this material from glacial acetic acid gave **2,3-dinitro-1,4-dichlorobenzene**, m.p. 101–102°. Water was added to the acetic acid mother liquor and the solid deposited was filtered off and dissolved, while still damp, in 50 ml. of hot dioxane. On cooling the dioxane solution deposited 23 g. of solid, m.p. 105–110°. Repeated recrystallization of this fraction from dioxane and alcohol gave pure **2,5-dinitro-1,4-dichlorobenzene**, m.p. 117.5–118.5°. Ultimate yields are not included as they were very low, partly because the recrystallization was carried on exhaustively to ensure purity of final products. However, it is clear that obtaining a reasonable yield of any isomer by the above procedure would be exceedingly tedious.

2-Nitro-4-chlorobromobenzene was prepared from 2-nitro-4-chloroaniline by the Sandmeyer reaction. The amine was diazotized in 40% hydrobromic acid and the cold solution of the diazonium salt was added to a suspension of cuprous bromide in 48% hydrobromic acid. The product was removed by steam distillation of the acid solution and was washed with 5% sodium hydroxide to remove phenols. The crude product was recrystallized twice from ethanol, m.p. 68–68.5°.

4-Bromo-2-nitrochlorobenzene was prepared by the bromination of 2-nitrochlorobenzene by the procedure developed by Derbyshire and Waters.[11] To a mixture of 17 g. of silver sulfate and 6 ml. of bromine in 100 ml. of concd. sulfuric acid was added 16 g. of 2-nitrochlorobenzene. The mixture was heated on a steam-bath for 10 hours and then

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[1] For an account of the very extensive studies carried out in the laboratories of University College, London, see the series of papers by C. K. Ingold, *et al.*, *J. Chem. Soc.*, 2400 (1950).

[2] G. M. Bennett, *ibid.*, 474 (1947).

[3] L. Melander, *Nature*, **163**, 599 (1949); *Arkiv. Kemi*, **2**, 211 (1950).

[4] F. H. Westheimer and M. S. Kharasch, This Journal, **68**, 1871 1946).

[5] R. J. Gillespie and D. J. Millen, *Quart. Revs.*, **2**, 277 (1948).

[6] R. J. Gillespie, *J. Chem. Soc.*, 2537 (1950).

[7] C. L. Jackson and D. F. Calhane, *Am. Chem. J.*, **28**, 451 (1902).

[8] C. J. Sunde, C. Johnson and C. F. Kode, *J. Org. Chem.*, **4**, 548 (1939).

[9] Neither of the above procedures yielded the third isomer 2,6-dinitro-1,4-dibromobenzene, in pure form. See paper II[10] of this series for a synthesis of this compound which was not included in the present study.

[10] G. S. Hammond, F. J. Modic and R. M. Hedges, This Journal, **75**, 1388 (1953).

[11] D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 576 (1950).

poured over cracked ice. The excess bromine was removed by the addition of solid sodium bisulfite. The crude solid was filtered and extracted with ethanol and ether. After removal of the ether the product was recrystallized twice from ethanol giving 6 g. of fine yellow crystals, m.p. 69–70°.

Absorption spectra were determined with a Cary recording spectrophotometer (model 12). All measurements were made at room temperature.

Results and Discussion

Since we had available a number of nitro- and dinitro-1,4-dihalobenzenes they were utilized for the present study along with nitrobenzene itself. We have studied the spectra of these compounds in three solvents, 95% ethanol, water and concentrated sulfuric acid. The positions and intensities of the absorption maxima are presented in Table I and the spectra of 2,5-dinitro-1,4-dichlorobenzene in 95% ethanol and in sulfuric acid are shown in Fig. 1. This compound shows the typical spectral characteristics which we wish to discuss. In sulfuric acid, there are maxima at 2240, 2575 and 3345 Å. with respective molar extinction coefficients of 20,700, 5,080 and 1,990. These three maxima will be numbered consecutively from shorter wave lengths for purposes of discussion. It is of interest that the *p*-dihalobenzenes themselves have high intensity maxima in the vicinity of 2,200 Å. Therefore, it is quite probable that the first band is related to the 1950 Å. transition in benzene and has an electric moment oriented approximately along the axis connecting the halogen atoms. The second band is found in the spectra of nearly all aromatic nitro compounds and is found at 2670 Å. in the spectrum of nitrobenzene in water solution. This band is shifted to shorter wave lengths by the introduction of a second nitro group in the cross conjugated meta and para positions. The hypsochromic shift indicates, as would be anticipated, that electron migration to the nitro group is of more consequence in the excited state than in the ground state. Ortho substitution shifts the maximum to even shorter wave lengths. This is attributed to the decreased accessibility of the low energy orbitals of the nitro group to the π-electrons of the nucleus because of the steric distortion from coplanarity. The effect is illustrated by 2,3-dinitro-1,4-dichlorobenzene which shows the second maximum only as an inflection at 2450 Å. and by the corresponding dibromo compound which does not show the maximum at all. A minor anomaly is found in 2,5-dinitro-1,4-dichlorobenzene which has a shoulder at 2360 Å. in water. The position at short wave length may be due, in part, to the fact that the first maximum of this compound, as judged by the spectrum in sulfuric acid, occurs at shorter wave lengths than with any of the other dihalo compounds. Since the position of the point of inflection is sensitive to the location of both of the unresolved bands, some of the apparent shift may be illusory. In addition, the buttressing effect[12] arising from the juxtaposition of the three groups may force the nitro groups out of the plane of the nucleus.

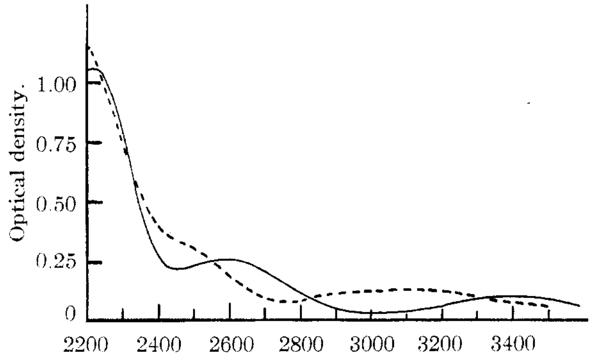

Fig. 1.—Absorption spectrum of 2,5-dinitro-1,4-dichlorobenzene, —, concentrated sulfuric acid (2.56 × 10^{-5} molar); ---, 95% ethanol (2.22 × 10^{-5} molar).

Table I

Absorption Spectra of Nitrodihalobenzenes

Compound	95% ethanol λ_{max}	95% ethanol ϵ_{max}	Water λ_{max}	Water ϵ_{max}	Concd. sulfuric acid λ_{max}	Concd. sulfuric acid ϵ_{max}
2-Nitro-	3090	1520	3150	1520	3400	1500
1,4-dibromo-			2580^a	2870	2725	3140
benzene	2235	17,400	2256	14,900	2265	15,500
2-Nitro-4-	3100	1620	3130	1530	3375	1535
bromochloro-	2500^1	4000	2580^a	2900	2745	3080
benzene	2235	19,300	2250	17,550	2245	15,500
2-Nitro-4-	3050	1680	3150	1530	3300	1680
chlorobromo-			2550	2780	2780	2300
benzene	2225	18,200	2225	15,750	2238	14,250
2,3-Dinitro-	3100	1570	3165	1900	3290	1900
1,4-dichloro-	2400^a	5970	2450^a	4890	2475^a	3260
benzene	2200^b	18,500	2190^b	19,100	2225	17,100
2,5-Dinitro-	3125	2660	3225	2720	3345	1990
1,4-dichloro-	2415^a	7420	2525	6250	2575	5080
benzene	2200^b	25,800	2210	23,900	2240	20,700
2,6-Dinitro-	3050	1520	3125	1750	3375	1460
1,4-dichloro-	2360^a	9100	2365^a	8600	2440^a	7550
benzene	2200^b	19,300	2150^b	19,800	2210	17,650
2,3-Dinitro-1,4-	3125	1430	3210	2280	3450	1300
dibromobenzene	2250	18,100	2225	18,550	2260	15,650
2,5-Dinitro-	3175	2510	3265	2780	3525	1960
1,4-dibromo-	2465^a	9070	2615^a	4970	2625^a	3720
benzene	2272	23,100	2290	22,800	2330	19,060

^{a} Point of inflection. ^{b} Short wave length limit, maximum not actually recorded.

The third transition is represented by a very broad, low intensity band with a maximum above 3000 Å. The intensity of the band is uniformly low and does not show pronounced steric effects. It is unresolved in the nitrobenzene spectrum but is represented by a persistent "tail" in the 3000–4000 Å. region.

The influence of environment on the position of the bands is striking, both because of the magnitude of the effects and because the sensitivity of the bands varies considerably. The position of the first maximum is influenced the least although it does shift in a small regular manner as the solvent is changed. The exact amount of the variation cannot be specified in every case as the maximum was not actually observed in all cases in water and ethanol. However, comparison of the extinction coefficients at the short wave length limit of the instrument with the values observed at the maximum with the other compounds shows that the unobserved maxima must lie very close to the last recorded measurements. A typical example is shown in Fig. 1. In those instances in which the maxima are observed in all three solvents there is,

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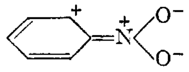
(12) M. Rieger and F. H. Westheimer, This Journal, **72**, 28 (1950).

with a single exception, a regular bathochromic shift as the solvent is changed from ethanol to water to concentrated sulfuric acid. However, the changes are rather small with the maximum difference between ethanol and sulfuric acid being 58 Å.

The second and third bands shift in the same direction but the changes are much more spectacular. The maximum shifts are 230 Å. for the second band and 350 Å. for the third band. The over-all effect of these changes is a marked sharpening up of the spectra in sulfuric acid as contrasted with other solvents. This effect should be of some use in characterizing aromatic nitro compounds which are not converted to new species by the highly acidic medium.

The fact that the first band is much less sensitive to solvent than the other two leads us to believe that the influence is not due entirely to the change in dielectric constant of the medium but is also due to hydrogen bonding of solvent molecules to the oxygens of the nitro functions. The presence of one or more hydrogen bonds would stabilize those excited states to which structures such as the following make prominent contributions.



This is qualitatively similar to the generalized solvent effects which are to be expected but attributes a much more potent influence to intimately bound solvent molecules than to those which are oriented by long range forces. The influence of solvents on the first band is, perhaps, more typical of generalized solvent influences. The order of influence of the various solvents is certainly that which would be expected. Comparison of water with hydrocarbon solvents is available from the data in Table II. It is clear that a considerable bathochromic shift accompanies the replacement of a hydrocarbon by water. A direct comparison is not available but there can be little doubt that 95% ethanol is intermediate between hydrocarbons and water since there is only a small difference between the spectra in alcohol and in water. It is to be expected that water should form the stronger hydrogen bonds of the two solvents. Concentrated sulfuric acid should be still more completely and firmly bound than water, especially in those solutions which contain very little water.

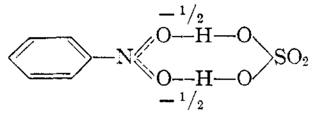
TABLE II

ULTRAVIOLET ABSORPTION MAXIMA IN NITROBENZENE SPECTRA

Solvent	$\lambda_{\max}$
n-Hexane[a]	2520
Water	2670
69.6% H_2SO_4	2760
84.4% H_2SO_4	2840
87.9% H_2SO_4	2865
93.6% H_2SO_4	2890
96.8% H_2SO_4	2885
98.4% H_2SO_4	2885

[a] E. A. Braude, *Ann. Reports*, **42**, 126 (1945).

Since the formation of hydrogen bonded complexes has been suggested as being responsible for the decrease in the rate of dinitration of mononitro compounds in concentrated sulfuric acid, we carried out a study of the position of the second maximum in the nitrobenzene spectrum as function of the composition of water–sulfuric acid solvent mixtures. The results are summarized in Table II. The bathochromic shift is observed as the sulfuric acid content is increased from zero to about 90% but then becomes constant between 90 and 98% acid. This result is only consistent with the rest of our spectral analysis if it assumed that hydrogen bonding is essentially complete in 90% acid. This would mean that in such a solution both oxygens must be covered by hydrogen bonds. This could be accomplished either by binding two solvent molecules per nitro function or by the formation of the symmetrical complex



This conclusion is of considerable consequence to the interpretation of the decrease in nitration rate in solutions of above the optimum concentration of sulfuric acid. It is clear that, at least in some solutions, nitration must occur by way of two reactions.

$$\mathrm{ArNO_2} + \mathrm{NO_2^+} \xrightarrow{k_1} \mathrm{Ar(NO_2)_2} + \mathrm{H^+} \quad (1)$$

$$\mathrm{ArNO_2{\cdot}H_2SO_4} + \mathrm{NO_2^+} \xrightarrow{k_2} \mathrm{Ar(NO_2)_2{\cdot}H_2SO_4} + \mathrm{H^+} \quad (2)$$

It is to be expected, as postulated by Gillespie and Millen,[5] that k_2 should be smaller than k_1. Determination of the relative importance of the two reactions in any given medium cannot be accomplished without the aid of quantitative measurements of the relative concentrations of the free nitro body and the hydrogen-bonded complex. We believe that the concentration of the complex is not changed materially by reducing the water content of the medium from 10 to 2%. However, the concentration of the free nitro compound may vary enormously. If this is the case, it is not feasible to attribute the small decrease in reaction rate to a *gradual* change from reaction (1) to reaction (2). We feel that a more likely explanation is to be found in the view that no appreciable fraction of the reaction proceeds by reaction (1) in the critical region. If this is the case the decrease in rate should be attributed to a decrease in the value of k_2 as a function of the change in medium.

A consideration of the modified Brönsted rate law[13-15] shows that such a change might be anticipated.

$$k_r = \frac{kT}{h}\,\frac{\gamma_{\mathrm{ArNO_2}}\gamma_{\mathrm{NO_2^+}}}{\gamma\ddagger}\,e^{-\Delta F/\ddagger RT} \quad (3)$$

Gillespie and Millen have, in essence, attributed the decrease in the rate constant, k_r, to a decrease in the activity coefficient of the nitro compound as it is converted to its complex. We suggest that even if the actual process is insensitive to such a

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[13] For a concise review of the concepts see L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapt. IV.

[14] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

[15] V. K. LaMer, *Chem. Revs.*, **10**, 179 (1932).

change (because too little uncomplexed material is present) the decrease in rate may be attributed to a decrease in the ratio $\gamma_{\mathrm{NO}_2^+}/\gamma^{\ddagger}$. The nitronium ion is much smaller than the positively charged transition state and therefore $\gamma_{\mathrm{NO}_2^+}$ should decrease more rapidly than $\gamma^{\ddagger}$ as the solvating power of the medium is increased. The assumption that the solvating power of sulfuric acid solutions increases with increasing water content cannot be defended rigorously but seems reasonable and has been previously rationalized by Hughes, Ingold and Reed.[16]

Further clarification of the situation would be aided by specific measurement of the activity of nitro compounds in these solutions. It is our plan to undertake such measurements in these laboratories.

(16) E. D. Hughes, C. K. Ingold and R. I. Reed, *J. Chem. Soc.*, 2400 (1950).

AMES, IOWA

[CONTRIBUTION NO. 214 FROM THE DEPARTMENT OF CHEMISTRY AND THE INSTITUTE FOR ATOMIC RESEARCH, IOWA STATE COLLEGE]

Aromatic Nitration. II. The Influence of Solvent on Anomalous Orientation by the Nitro Group[1]

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The mixtures of dinitration products formed in the nitration of 2,5-dibromonitrobenzene and 2,5-dichloronitrobenzene have been analyzed by an infrared method. The results are interpreted in terms of the interaction between the entering nitronium ion and the nitro group of the substrate molecule. In those media in which the attacking ion is believed to be least strongly solvated a considerable preference for the ortho position is evidenced. A framework for the discussion of "anomalous" ortho direction by non-linear, unsaturated substituents is established.

The qualitative theory of substituent influences[2] in reactions leading to aromatic substitution by electrophilic reagents has failed to give a really adequate explanation of the gross variations in the ortho/para ratio. Those cases in which the ratio falls below that to be expected on statistical grounds have been explained either on the basis of steric hindrance to attack at the ortho position[3] or by charge–dipole repulsion in the transition state for ortho substition.[4] The fact that the ratio may also become very much larger than the statistical value is frequently overlooked. An extensive survey of the literature reveals that a number of functional groups to which a strong meta directive influence is usually ascribed should actually be considered to direct meta and ortho.

These groups are all non-linear unsaturated functions such as $-\mathrm{NO_2}$, $-\mathrm{CO_2H}$, $-\mathrm{CO_2R}$, $-\mathrm{COR}$ and $-\mathrm{SO_3H}$. It would be inappropriate to review the pertinent literature[5] completely but a few examples, which are striking rather than typical in the order of magnitude of the effect, are worthy of mention.

Holleman[5,6] found that the nitration of nitrobenzene in 94.5% nitric acid at 30° gave the ortho, meta and para dinitro compounds, respectively, in 8.1, 91.2 and 0.7% yields. Similarly, the nitration of methyl benzoate with concentrated nitric acid at −30° gave the products in the ratio, $o:m:p = 23:74:2$. More recently Kleene[7] found that *p*-bromotoluene gives largely the 2,3-dinitro derivative when nitrated with mixed acid.

Kobe and Levin[8] have reported that in the dinitration of *p*-xylene with mixed acid the 2,3-dinitro derivative is formed in 60–80% yield and the 2,6-isomer in 40–20% yield. Apparently the third isomer is produced in vanishingly small amounts.

Obermiller[9] called attention to several instances of meta–ortho direction in nitrations. He also pointed out that similar ortho orientation was not observed in the sulfonation of the same or analogous compounds. The significance of the latter observation is not clear in the light of the well known reversibility of sulfonation reactions.

This interesting behavior has not been entirely neglected but no particularly satisfactory explanation has been offered. Some years ago, Lapworth and Robinson[10] suggested a cyclic mechanism for ortho nitration. The explanation seems reasonable but needs modification in light of recent studies[11] which make it seem improbable that molecular nitric acid is ever the attacking species in nitrations. Dewar[12a] has applied Wheland's method[12b] to the calculation of relative activation energies for attack at the various open positions of a monosubstituted benzene. Since the results, but not the details of the calculations, are presented one is impressed but at the same time unsatisfied because the "anomalous" ortho effect appears to develop as a natural conclusion. These results appear to be

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(1) Work was performed in part in the Ames Laboratory of the Atomic Energy Commission.

(2) A. E. Remick, "Electronic Interpretations of Organic Chemistry," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 85.

(3) R. J. LeFevre, *J. Chem. Soc.*, 977 (1933); 1501 (1934).

(4) In our opinion this description is equivalent to the "direct field effect" cited by C. K. Ingold and C. C. N. Vass, *ibid.*, 497 (1928).

(5) A large number of examples may be found in the classic studies by A. F. Holleman, "Die Direkte Einfuhrung von Substituenten in den Benzolkern," Leipzig, 1910.

(6) A. F. Holleman, *Chem. Revs.*, **1**, 187 (1924).

(7) R. D. Kleene, THIS JOURNAL, **71**, 2259 (1949).

(8) K. A. Kobe and H. Levin, *Ind. Eng. Chem.*, **42**, 352, 356 (1950).

(9) J. Obermiller, *J. prakt. Chem.*, **89**, 70 (1914); **126**, 257 (1930).

(10) A. Lapworth and R. Robinson, *Mem. Proc. Manchester Lit. Phil. Soc.*, **72**, 43 (1928).

(11) V. Gold, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2467 (1950).

(12) (a) M. J. S. Dewar, *ibid.*, 463 (1949); (b) G. Wheland, THIS JOURNAL, **64**, 1900 (1942).