[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, NEW MEXICO HIGHLANDS UNIVERSITY]

Near Ultraviolet Absorption Spectra of Halogenated Nitrobenzenes

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Ultraviolet absorption spectra are reported for the twelve monohalonitrobenzenes in ethanol. The absorption bands have been related to the corresponding transitions in benzene. Ortho effects in these compounds are observed by comparison of the absorption intensities of the 260 $m\mu$ bands.

Although ultraviolet absorption spectra have been determined for the three chloronitrobenzenes[2,3] and for *p*-fluoronitrobenzene,[4] no systematic study has been made to evaluate the effect of halogen substitution on the spectrum of nitrobenzene. In the present work absorption spectra have been obtained for each of the substances between 208 and 400 $m\mu$. The observed bands are classified and compared with the absorption spectra of nitrobenzene and the halogen benzenes.

Experimental

Point by point absorbence measurements were made in 2 $m\mu$ intervals or less with a model DU Beckman spectrophotometer.[5] The fluoro and iodo compounds were rechecked with a Cary recording spectrophotometer.[6] While the molar absorptivities obtained with the two instruments were in good agreement, the values given are those from the Beckman instrument. Reagent quality nitro compounds were used. The iodo compounds were resublimed immediately before use and the fluoro compounds[7] were redistilled. Absorbence measurements were carried out at 25° with freshly prepared 95% ethanol solutions in concentrations of 1×10^{-3} to 1×10^{-5} mole per liter. The experimental results are given in Figs. 1–3.

Discussion

The halogen benzenes have two prominent absorption bands above 200 $m\mu$ which correspond to primary and secondary bands of Doub and Vandenbelt,[3] both on the basis of relative intensities and wave lengths.[8,10] The intensities of the primary bands and their wave lengths increase from fluorine to iodine.[11] The secondary bands decrease in intensity in the same sequence if the absorption for iodide (ϵ 400–500) is subtracted from the molar absorptivity of iodobenzene.[12] The behavior of the secondary bands is therefore parallel to the resonance interaction of the halogens with benzene. Since these bands are also blue-shift bands,[13] they may be attributed to $n \rightarrow \pi$ transitions.[14]

Nitrobenzene has an intense primary band at 260 $m\mu$.[15] This band has a weak shoulder or tail of low intensity indicative of a hidden transition which may be related to the secondary band or to an absorption band due to the nitro group.[16]

In the halogenated nitrobenzenes only three bands are observed above 205 $m\mu$.[17] According to their intensities the bands around 210 and 260 $m\mu$ are primary bands. The weak bands near 310 $m\mu$ are probably related to the hidden transition in the nitrobenzene spectrum. The 260 $m\mu$ band is characteristic of the nitrobenzene chromophore and is found in nearly all aromatic nitro compounds.

In *o*-substituted nitrobenzenes, alkyl substituents decrease the molar absorptivity of the 260 $m\mu$ band and the decrease is proportional to the size of the alkyl group.[19] Similar steric effects have been observed with *o*-C_6H_5,[20] OMe,[21] OC_6H_5,[22] SMe,[23] SC_6H_5,[24] COMe[25] and COOH.[26]

Francel has presented evidence[27] which shows that the nitro group in *o*-chloro- and *o*-bromonitrobenzene is twisted out of the plane of the ring. To account for the ortho effects Burawoy proposes repulsive interaction of electrons and nuclei in the adjacent groups[28] of such compounds as *o*-chloro-, methyl- and methoxynitrobenzene.

The spectra of the *o*-halonitrobenzenes show the expected decrease in the 260 $m\mu$ band in the order $F < Cl < Br$. *o*-Iodonitrobenzene has only a shoulder in this region and its molar absorptivity at 260 $m\mu$ is smallest among these compounds if the iodide absorption is allowed for. Slight decreases in intensity of the 260 $m\mu$ band also occur in the meta isomers but in each case these compounds absorb far more strongly in this region than the ortho isomers. The *m*-iodo compound again is

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(1) Chemistry Department, Purdue University, Lafayette, Indiana.

(2) R. A. Morton and A. McGookin, *J. Chem. Soc.*, 901 (1934).

(3) L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947); **71**, 2414 (1949).

(4) F. Smith and L. M. Turton, *J. Chem. Soc.*, 1702 (1951).

(5) The author is indebted to Frida Lutz and Robert Smith for a number of the determinations.

(6) Measurements by Robert P. Curry, Purdue University.

(7) The author wishes to express his appreciation to Dr. Glen C. Finger, State Geological Survey of Illinois, for a generous sample of *m*-fluoronitrobenzene.

(8) The bands in iodobenzene actually represent a combination of two chromophores absorbing in the same region.[9] This may explain the low value (1.13) for $\lambda_{sec.}/\lambda_{prim.}$ For the other halogen benzenes $\lambda_{sec.}/\lambda_{prim.} = 1.25$.

(9) L. Doub and J. M. Vandenbelt, *Anal. Chem.*, **24**, 601 (1952).

(10) Since our values for λ_{max} and ϵ for the halogen benzenes agreed closely with those of Bowden and Braude,[11] they are not given here.

(11) K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

(12) T. M. Dunn and T. Iredale, *ibid.*, 1592 (1952).

(13) H. E. Ungnade, THIS JOURNAL, **75**, 432 (1953).

(14) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

(15) All bands and intensities are for ethanol solutions.

(16) Nitroparaffins absorb near 200 and 280 $m\mu$.

(17) The same three bands were also observed in the nitro- and dinitrodihalobenzenes.[18]

(18) G. S. Hammond and F. J. Modic, THIS JOURNAL, **75**, 1386 (1953).

(19) D. W. Sherwood and M. Calvin, *ibid.*, **64**, 1350 (1942); W. G. Brown and H. Reagan, *ibid.*, **69**, 1032 (1947); W. R. Remington, *ibid.*, **67**, 1838 (1945); P. Fielding and R. J. W. LeFevre, *J. Chem. Soc.*, 2812 (1950).

(20) M. Pestemer and E. Mayer-Pitsch, *Monatsh.*, **70**, 104 (1937).

(21) H. E. Ungnade and I. Ortega, *J. Org. Chem.*, **17**, 1475 (1952).

(22) H. E. Ungnade and E. Hansbury, *ibid.*, **17**, 742 (1952).

(23) E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 2892 (1949).

(24) A. Mangini and R. Passerini, *J. Chem. Soc.*, 1168 (1952).

(25) M. Pestemer, T. Langer and F. Manchen, *Monatsh.*, **68**, 326 (1936).

(26) L. Marchlewski and J. Mayer, *Bull. intern. acad. polon. sci.*, [A] 178 (1929).

(27) R. J. Francel, THIS JOURNAL, **74**, 1265 (1952).

(28) A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, 2315 (1952).

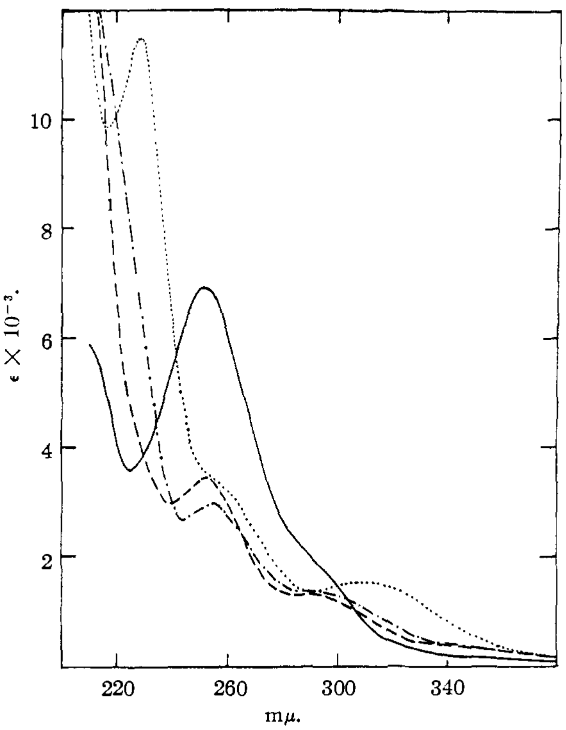

Fig. 1.—Ultraviolet absorption spectra of *o*-halonitrobenzenes: —, fluoro; — — —, chloro; —·—·, bromo; ...., iodo.

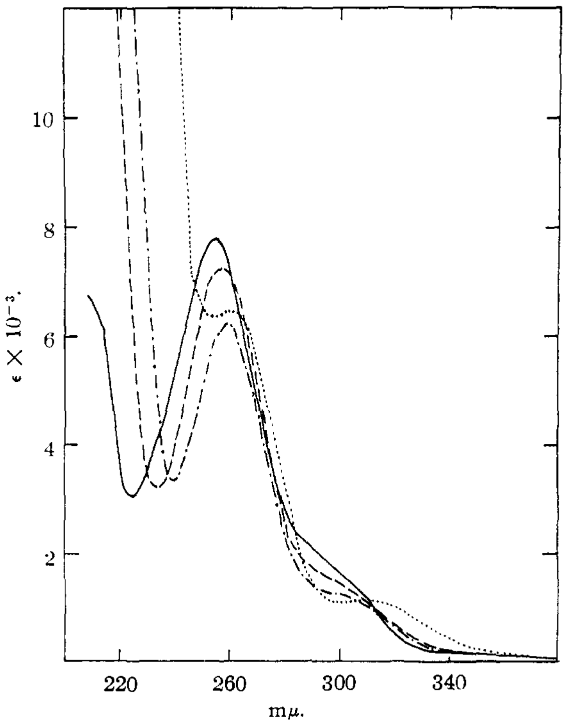

Fig. 2.—Ultraviolet absorption spectra of *m*-halonitrobenzenes: —, fluoro; — — —, chloro; —.—., bromo; ...., iodo.

comparable with the other *m*-halonitrobenzenes if the iodide absorption is subtracted.

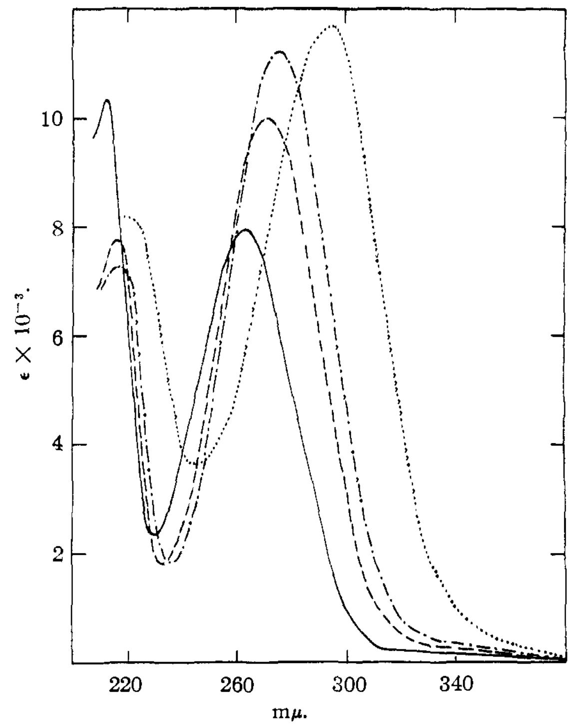

Fig. 3.—Ultraviolet absorption spectra of *p*-halonitrobenzenes: —, fluoro; — — —, chloro; —·—·, bromo; ...., iodo.

The *p*-halonitrobenzenes each contain a broad band of high intensity. In fluoronitrobenzene this primary band is almost identical with the 260 mμ band in nitrobenzene. With increasing atomic weight of the halogen the bands shift to the red and the molar absorptivity increases. The iodide absorption need not be considered at the maximum for *p*-iodonitrobenzene because it is negligible at 294 mμ. It may be responsible for the unsymmetrical broadening of the band between 260 and 280 mμ.

The weak secondary bands (near 310 mμ) are almost completely fused with the 260 mμ band in the *p*-halonitrobenzenes. They show clearly in the ortho and meta isomers and have separate and distinct maxima in the *o*- and *m*-iodo compounds. In each case the secondary band of the ortho compound is more intense than the band of the corresponding meta isomer and the molar absorptivities of the bands increase from fluorine to iodine. Steric effects are therefore unimportant in these bands.

The second primary bands at around 220 mμ cannot always be observed since they occur close to 200 mμ. They shift to the red with increasing atomic weight of the halogen, are most intense in the meta compounds and least in the para isomers. In *o*-iodonitrobenzene this band is virtually identical with the primary band in iodobenzene. According to Bowden and Braude such bands would be regarded as partial chromophore bands due to para dipolar structures not involving the substituents.[11] In view of the considerable resonance interaction between the substituents and the nucleus in these compounds it is felt that the transition represented by the first primary band has lost the vibrational fine structure bands which occur in benzene at 193, 195, 201 and 204 mμ[29] (as is the case in dimethylaniline[30]).

Consequently the second primary band would correspond to the 183 mμ transition in benzene.[31]

The behavior of the absorption bands permits the conclusion that the first primary bands in the halonitrobenzenes (around 260 mμ) are characteristic for transitions in which ionic resonance forms with coplanar arrangement of nitro group and nucleus contribute largely to the excited states. This is evidently not the case for the secondary and first primary bands which appear independent of steric effects.[32]

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[29] J. R. Platt and H. B. Klevens, *Chem. Revs.*, **41**, 301 (1947).

[30] H. B. Klevens and J. R. Platt, THIS JOURNAL, **71**, 1714 (1949).

[31] The assignment can be made with certainty only when measurements in the vacuum ultraviolet are available.

[32] NOTE ADDED IN PROOF.—Since the acceptance of this paper the absorption spectra of the iodonitrobenzenes have been described by J. Ferguson and T. Iredale [*J. Chem. Soc.*, 2959 (1953)] and those of the fluoronitrobenzenes by W. Gruber [*Can. J. Chem.*, **31**, 1020 (1953)]. Their results are qualitatively in agreement with those reported here.

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The Effects of Deuterium Substitution on the Rates of Organic Reactions. III.[1,2] Solvolysis Rates and Arrhenius Parameters for 2,3-Dimethyl-2-chlorobutane and its 3-Deutero Analog

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The observations of the effect of the β-deuterium substitution on the solvolysis rates of tertiary alkyl chlorides have been extended to include the case of a tertiary deuterium atom. The solvolysis rate constants in 80% aqueous alcohol at 25° for 2,3-dimethyl-2-chlorobutane and its 3-deutero analog are 8.68 and 6.76 × 10^{-6} sec.$^{-1}$, respectively. The deuterium compound has an activation energy 580 ± 70 calories higher and a log frequency factor 0.32 ± 0.03 unit higher than the hydrogen compound. The order of the isotope rate effect in the series $-CD_3$, $-CD_2-$, $-CD-$ and the hypothesis of elimination type driving forces suggests a reinterpretation of the effect of β-branching on solvolysis rates which does not involve two conflicting electronic influences. Similarly suggested is a possible reinterpretation of the polar effects of alkyl groups in ionic reactions, customarily explained by hyperconjugation.

In part II[2] which initiated the study of the effect of deuterium substitution on the rates of the S$_N$1-E1 solvolysis reactions of tertiary alkyl compounds, the effect of deuterium substitution for primary and secondary hydrogens adjacent to the reaction center was reported. In this paper the observations are extended to include the effects of deuterium substitution for an adjacent tertiary hydrogen atom. This example also has been used to analyze the effect of β-deuterium substitution in terms of the parameters in the Arrhenius equation. In the previous paper it was assumed that the most important effect was the change in the activation energy and for this case the validity of this assumption is tested.

$$\underset{\text{I}}{(CH_3)_2{-}CH{-}C(CH_3)_2{-}Cl} \qquad \underset{\text{II}}{(CH_3)_2{-}CD{-}C(CH_3)_2{-}Cl}$$

Compound I was prepared in the conventional manner by treatment of dimethylisopropylcarbinol with concentrated hydrochloric acid. The deuterium analog II was prepared by the addition of deuterium chloride to tetramethylethylene. This was accomplished by the slow addition of deuterium oxide[3] to a stirred solution of tetramethylethylene in excess acetyl chloride.[4]

The solvolysis reactions were followed by the titration of developed acid in aliquots taken at suitable time intervals to more than 75% completion. The solvolysis rate constants and their standard deviations, given in Table I, were obtained from the slope of the least squares plot of t *vs.* $\log b/(b - x)$.

In the olefin determinations a series of tubes was filled with a solution of each of the halides in the same 80% aqueous alcohol solution containing just enough sodium hydroxide to ensure that the solution remained basic throughout. These tubes were sealed off and a set of each was allowed to react for 10 to 20 half-lives at each of the four temperatures. The amount of olefin in each tube was determined by the reaction with standard bromine in cold chloroform[2] and the total reaction determined by titration of the remaining base. The olefin fractions were calculated from these values. Whereas the absolute accuracy would be somewhat poorer the parallel nature of the experiments made the reproducibility and the relative accuracy of the olefin fractions of the order of 0.005.

TABLE I

RATE DATA FOR THE SOLVOLYSIS OF 2,3-DIMETHYL-2-CHLOROBUTANE (I) AND ITS 2-DEUTERO ANALOG II IN 80% AQUEOUS ALCOHOL

Temperature, °C.	25.00	36.00	45.00	55.00
Number of points				
I	13	13	14	14
II	15	13	14	15
K (10^{-6} sec.$^{-1}$)				
I	8.680	35.01	98.74	294.2
II	6.765	28.54	82.56	250.4
Std. deviation of K				
I	0.053	0.18	0.28	1.4
II	0.055	0.17	0.17	1.0
Olefin fractions				
I	0.693	0.701	0.708	0.712
II	0.630	0.640	0.660	0.665

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[1] Part I, THIS JOURNAL, **74**, 5285 (1952).

[2] Part II, *ibid.*, **75**, 2925 (1953).

[3] Obtained from the Stuart Oxygen Company on allocation from the United States Atomic Energy Commission.

[4] Preparation suggested by Professor C. E. May.