change (because too little uncomplexed material is present) the decrease in rate may be attributed to a decrease in the ratio $\gamma_{NO_2^+}/\gamma^{\ddagger}$. The nitronium ion is much smaller than the positively charged transition state and therefore $\gamma_{NO_2^+}$ 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 $-NO_2$, $-CO_2H$, $-CO_2R$, $-COR$ and $-SO_3H$. 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).

closely akin to the reasonable argument, based upon charge distribution in the transition states, offered by Branch and Calvin.[13]

We have determined the relative amounts of the isomeric dinitro compounds formed when 2,5-dibromo- and 2,5-dichloronitrobenzene are nitrated under varying conditions. These compounds recommend themselves for study for two reasons. The second nitro group can enter at any of three open positions which are ortho, meta and para to the first. Each position is ortho to one halogen atom and meta to a second. The second important feature is that all three isomers are formed in substantial amounts which facilitates the determination of relative yields with reasonable precision. We were fortunate in finding a very simple infrared method for the analysis of the reaction mixtures.

Experimental

The preparation of the three **dinitro-1,4-dichlorobenzenes, 2,3-dinitro-1,4-dibromobenzene and 2,5-dinitro-1,4-dibromobenzene** has been described elsewhere.[14]

2,6-Dinitroaniline was prepared by the method of Welsh.[15]

2,6-Dinitro-4-bromoaniline was prepared by the bromination of 2.0 g. of 2,6-dinitroaniline with 3.0 g. of bromine and 1.6 g. of silver sulfate in 50 ml. of concentrated sulfuric acid. The mixture was heated to 120° for 12 hours and then poured over ice. The solid was filtered off and extracted with 300 ml. of hot ethanol. Concentration of the ethanol extract yielded 2.1 g. of orange solid m.p. 150–157°. Repeated recrystallization from ethanol gave material melting 157–158°.

2,6-Dinitro-1,4-dibromobenzene was prepared by the Sandmeyer reaction from the above amine. One and eight-tenths grams of 2,6-dinitro-4-bromoaniline was dissolved in 20 ml. of concentrated sulfuric acid and cooled to 0°. The cold solution of the amine was added slowly to a cold solution of 0.48 g. of sodium nitrate in 20 ml. of concentrated sulfuric acid. One-half hour after the addition was completed the solution of the diazonium salt was added slowly to a cold solution of cuprous bromide in 48% hydrobromic acid. The product was extracted with Skellysolve B and on evaporation 1.1 g. (50% yield), m.p. 112–115°, was obtained. This product was recrystallized from cyclohexane and Skellysolve B to a constant melting point of 119–119.5°. The infrared spectrum showed no evidence for the presence of either position isomers or 2,6-dinitrobromobenzenes.

2,6-Dinitrobromobenzene was prepared for comparison of its infrared spectrum with that of the dibromo compound. Two grams of 2,6-dinitroaniline was diazotized and treated with cuprous bromide by essentially the same procedure as was utilized in the preparation of the dibromo compound. The product was isolated in 50% yield and was recrystallized from Skellysolve B, m.p. 103–103.5°.

Transbromination Reaction.—When 2-nitro-1,4-dibromobenzene was nitrated in fuming sulfuric acid a white solid was observed to separate from the hot solution after a time. At 140° the product began to form within a half-hour and it was produced in all cases after long heating. When 2 g. of 2,5-dinitro-1,4-dibromobenzene was heated overnight at 140° with 200 cc. of concd. sulfuric acid and 50 g. of potassium nitrate, a white solid separated which was removed by filtration; yield 0.5 g., m.p. 206–211°. Recrystallization from benzene gave material melting at 313–315°. Two hundred milligrams was recrystallized from two liters of Skellysolve B giving stout white prisms, m.p. 315°. *Anal.* Calcd. for $C_6O_4N_2Br_4$: N, 5.78; Br, 66.1. Found: N, 5.83; Br, 67.1.

Concentrated sulfuric acid was diluted with water to give approximately the desired concentrations and the resulting solutions were assayed by titrating with standard base. Fuming sulfuric acid, Baker and Adamson C.P., was used as drawn from the reagent bottle.

Nitration Studies.—A typical run will be described in detail. To a 100-ml. round bottom flask were added 2 g. of 2,5-dichlorobenzene (0.0104 mole) and 4.4 g. of sodium nitrate (0.052 mole). Then 40 ml. of concentrated sulfuric acid was added and the flask was immediately immersed in a steam-bath. The solution was heated for five hours and then added to cracked ice. The crude solid was recovered by suction filtration and was dried under an infrared lamp. A weighed sample was then dissolved in 10 ml. of carbon disulfide and the infrared spectrum of the solution was measured.

Infrared spectra were studied with a Baird Associates infrared spectrophotometer using a sodium chloride prism. Qualitative characterization was carried out with Nujol mulls and carbon disulfide solutions were used in the quantitative analysis. The spectra of all compounds studied are presented in Figs. 1–11. Examples of both solution spectra (which are not significant in the region above 1500 cm.$^{-1}$ because of strong absorption by the solvent) and mull spectra are included. In the latter spectra the strong band at 2900 cm.$^{-1}$, the strong doublet between 1450 and 1600 cm.$^{-1}$ and the weak band at 723 cm.$^{-1}$ are due primarily to Nujol.

Quantitative Analysis.—The bands which were used for analysis are listed in Table I. The excellent separation of the bands is indicated in Fig. 10 which shows the spectrum of the crude mixture obtained in the partial nitration of 2-nitro-1,4-dibromobenzene. Control experiments showed that Beer's law holds closely for each of the individual components. An uncertainty of about 0.5% transmission can be assigned to the readings because of line thickness and the noise level of the instrument. In order to ascertain that the substances involved do not interact appreciably in solution and to give an independent check on the accuracy of the method, a number of artificial mixtures were analyzed by the method. The results are shown in Table II.

TABLE I

ANALYTICAL INFRARED FREQUENCIES

Compound	Frequency of characteristic band in cm.$^{-1}$
2,5-Dichloronitrobenzene	1050
2,3-Dinitro-1,4-dichlorobenzene	822
2,5-Dinitro-1,4-dichlorobenzene	842
2,6-Dinitro-1,4-dichlorobenzene	718
2,5-Dibromonitrobenzene	1032
2,3-Dinitro-1,4-dibromobenzene	818
2,5-Dinitro-1,4-dibromobenzene	840
2,6-Dinitro-1,4-dibromobenzene	718

TABLE II

ANALYSIS OF ARTIFICIAL MIXTURES OF DINITRO-1,4-DICHLOROBENZENES

Mixture no.	Position of nitro groups	Per cent. Actual	Per cent. Found
1	2,3	48.3	46.6
	2,5	16.7	16.9
	2,6	34.9	36.5
2	2,3	49.8	47.4
	2,5	21.8	21.2
	2,6	28.4	31.3
3	2,3	26.9	26.7
	2,5	21.7	21.8
	2,6	51.4	51.5

Results and Discussion

In order to determine the applicability of the infrared method to the determination of the relative yields in the nitration reactions it was necessary to obtain each of the dinitration products in pure form.

All six of the desired compounds have previously been isolated by fractional recrystallization of the mixtures obtained by the dinitration of *p*-dichloro- and *p*-dibromobenzene.

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[13] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 477.

[14] G. S. Hammond and F. J. Modic, THIS JOURNAL, **75**, 1385 (1953).

[15] L. H. Welsh, *ibid.*, **63**, 3276 (1941).

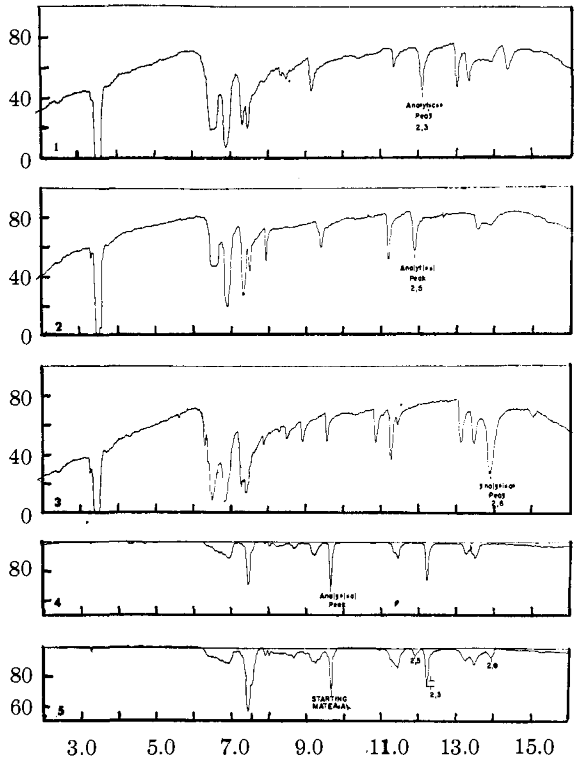

Fig. 1.

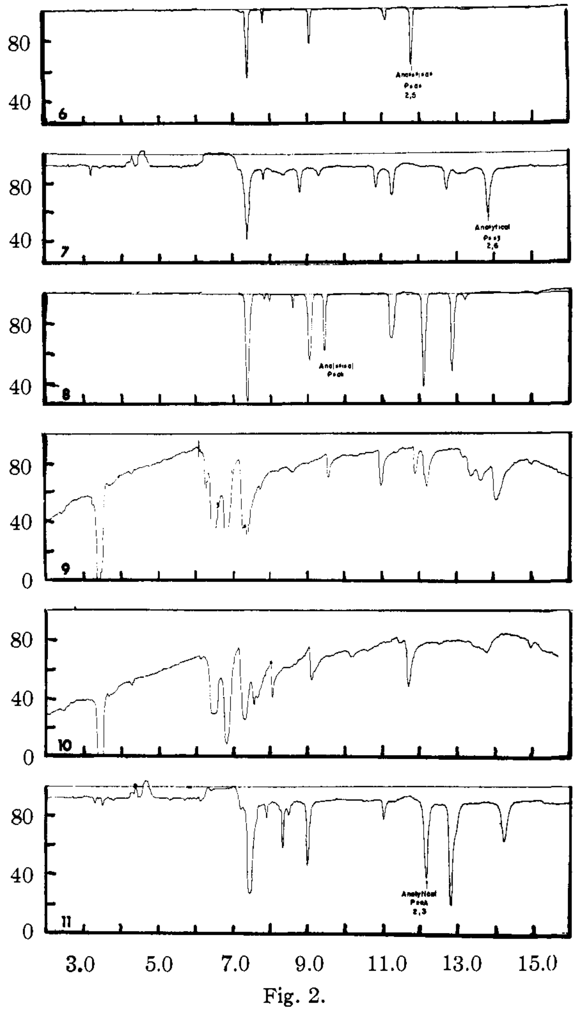

Fig. 2.

Figs. 1 and 2.—Infrared spectra. Designation in parentheses indicates whether the particular sample spectrum was run in a Nujol mull or in carbon disulfide solution: 1, 2,3-dinitro-1,4-dibromobenzene (Nujol); 2, 2,5-dinitro-1,4-dibromobenzene (Nujol); 3, 2,6-dinitro-1,4-dibromobenzene (Nujol); 4, 2-nitro-1,4-dibromobenzene (CS_2); 5, mixture from nitration of 2-nitro-1,4-dibromobenzene (run 16, CS_2); 6, 2,5-dinitro-1,4-dichlorobenzene (CS_2); 7, 2,6-dinitro-1,4-dichlorobenzene (CS_2); 8, 2-nitro-1,4-dichlorobenzene (CS_2); 9, 2,6-dinitrobromobenzene (Nujol); 10, transbromination product (Nujol); 11, 2,3-dinitro-1,4-dichlorobenzene (CS_2).

We were unable to obtain pure 2,6-dinitro-1,4-dibromobenzene by such a procedure so it was prepared by an alternative route. The bromination of 2,6-dinitroaniline gave 2,6-dinitro-4-bromoaniline and this substance was diazotized in concentrated sulfuric acid and converted to the dibromo compound by the Sandmeyer reaction. The purified product melted sharply at 119–119.5° which is in agreement with the melting point reported by Jackson and Calhane[16] but is lower than the value of 127° reported by Sunde, Johnson and Kode.[17] Since we have frequently encountered eutectic mixtures in our work with nitrohalobenzenes the purity of our product was checked carefully. The infrared spectrum showed no evidence of N–H or O–H bands indicating the absence of unreacted amine and phenolic by-products and another possible contaminant, 2,6-dinitrobromobenzene, was prepared and shown by spectroscopic examination not to be present in our product. It is also noteworthy that the spectrum of our compound is very similar to that of the corresponding dinitrodichlorobenzene.

The results of the analysis of nitration mixtures obtained under various conditions are summarized in Tables III and IV. The nitration of 2,5-dichloronitrobenzene was easily controlled so as to give a stoichiometric yield of dinitro compounds. This is indicated by the fact that the sum of the amounts of the three isomers in weighed samples of the crude mixtures was equal to the sample weight, within the limits of the expected experimental errors, in all cases.

The nitration of 2,5-dibromonitrobenzene was complicated by concurrent reactions which destroyed the dinitration products. The only product of these changes which has been isolated is a white crystalline solid which melts sharply at 315°. The bromine and nitrogen analyses are compatible with the formula $C_6O_4N_2Br_4$. The infrared spectrum, shown in Fig. 11, is quite compatible with the assignment of the structure as an aromatic nitro compound. The characteristic aromatic nitro frequency at 1360 cm.$^{-1}$ is very prominent. The fact that the compound is produced readily from 2,5-dibromo-1,4-dinitrobenzene suggests that it is 2,3,5,6-tetrabromo-1,4-dinitrobenzene. The compound is not the known[18] 2,4,5,6-tetrabromo-1,3-dinitrobenzene which melts at 235°. The very high melting point is in accord with the symmetrical structure. The formation of this compound must involve the acid-catalyzed transfer of bromine from one aromatic molecule to another. Such transbrominations have been previously observed under similar conditions. Thus, *sym*-tetrabromobenzene has been obtained from *p*-dibromobenzene[19] and hexabromobenzene has been produced from the *sym*-tetrabromo compound.[20]

It was not possible to produce a mixture which did not contain substantial amounts of either the starting material or the by-product. Since the rates of formation of the latter from each of the dinitro compounds should not be equal it is evident that significant results can be obtained only in runs in which very little is formed. The reactions were, therefore, run for only a short time and the amount of starting material was determined in the resulting quaternary mix-

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

(17) C. J. Sunde, C. Johnson and C. F. Kode, *J. Org. Chem.*, **4**, 548 (1949).

(18) C. L. Jackson and F. B. Gallivan, *Ber.*, **28**, 190 (1895).

(19) Riche and Berard, *Compt. rend.*, **59**, 142 (1864).

(20) C. L. Jackson and F. B. Gallivan, *Am. Chem. J.*, **18**, 250 (1896).

TABLE III

NITRATION OF 2,5-DICHLORONITROBENZENE

Run no.	Temperature, °C.	Sulfuric acid,[a] %	Percentage isomer in product			Isom reratios	
			Ortho	Para	Meta	*o/p*	*o/m*
1	100	Fuming	14.5	32.5	53.0	0.45	0.27
2	100	96.2	21.4	27.7	50.8	.77	.42
3	100	95	24.5	25.8	49.6	.95	.49
4	100	89	29	24.1	46.8	1.2	.62
5	140	96.2	25	27.5	47.5	0.91	.53
6	140	Fuming	11.4	34.8	53.8	.33	.21
7	100	96.2[b]	24.2	27.3	48.4	.89	.50
8	100	96.2[c]	25.8	26.4	47.8	.98	.54
9	100	96.2[d]	35.0	19.3	45.7	1.8	.76
10	100	HNO_3[e]	33.1	21.1	45.7	1.6	.72

[a] Unless otherwise noted the nitration mixture was prepared from 40 ml. of acid of the indicated composition and 4.4 g. of sodium nitrate. [b] Same as *a* except 9.0 g. of potassium bisulfate added. [c] Same as *a* except 9.0 g. of potassium perchlorate added. [d] Fifty ml. of acid and 11.0 g. of sodium nitrate. [e] Fuming nitric acid plus 20% by volume of 60% perchloric acid.

TABLE IV

NITRATION OF 2,5-DIBROMONITROBENZENE

Run no.	Temperature, °C.	Sulfuric acid,[a] %	Percentage isomer in product			Isomer ratio	
			Ortho	Para	Meta	*o/p*	*o/m*
11	100	Fuming	2.9	43.1	53.9	0.07	0.05
12	100	Fuming	2.6	41.8	55.3	.06	.05
13	100	96.8	13.7	36.3	50.0	.38	.27
14	100	90	29.2	20.8	50.0	1.4	.58
15	120	96.8	19.6	29.4	51.0	0.67	.38
16	100	96.8[b]	19.2	37.5	43.2	.51	.44
17	100	HNO_3[c]	29.9	21.3	48.8	1.4	.61

[a] Nitration mixtures prepared from 40 ml. of acid of indicated composition and 4.4 g. of sodium nitrate. [b] Forty ml. of acid and 6.6 g. of sodium nitrate. [c] Fuming nitric acid with 20% by volume of 60% perchloric acid.

ture. The presence of a very small amount of the transbromination product was easily detected because of its very low solubility in carbon disulfide, the solvent used in the determination.

The results are summarized in Tables III and IV and are normalized to give a total of exactly 100%.

The nitration of 2,5-dichloronitrobenzene is the less complicated of the two reactions and should be considered first. The three open positions will be described as ortho, meta or para with reference to the nitro group. Meta nitration predominates in all cases and the maximum yield of the meta isomer is produced at 140° in fuming sulfuric acid as a medium. That these conditions represent an extremum is also indicated by the fact that they also give the maximum yield of the para isomer and minimize the ortho/para ratio. This ratio is increased both by lowering the temperature and by increasing the water content of the medium. In this connection it should be noted that the percentages listed in the tables represent the acid strength prior to the addition of substantial amounts of potassium nitrate. The water content was somewhat higher in the final nitration mixtures since it is produced by the ionization of nitrate. The substantial effect of this change is illustrated by comparison of runs 2 and 12. In the former the solvent was prepared by the addition of 50 ml. of acid to 5.5 g. of nitrate and in the latter the same volume of acid was added to 11 g. of nitrate. The effect must be due, primarily, to the influence of water rather than to the increase in electrolyte concentration since the addition of gross amounts of potassium bisulfate or potassium perchlorate (runs 8 and 9) altered the results in a much less spectacular manner. Since ortho direction is believed to be minimized in sulfuric acid[21] we also carried out the reaction in fuming nitric acid. Unreacted starting material was recovered after three days heating at 100° when either fuming nitric acid or fuming nitric with 5% perchloric acid was used as the nitration medium. However, complete conversion was realized in 24 hours with 20% perchloric acid. The isomers ratios were very close to those obtained in run 12 in which the water content of the sulfuric acid was at a maximum.

$$NO_3^- + 3H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 3HSO_4^- \quad (1)$$

The nitration of 2,5-dibromonitrobenzene is considerably slower than that for the corresponding dichloro compound. Furthermore, the isomer ratios vary over much wider limits. Very little ortho isomer is produced in fuming sulfuric acid and the yield of the para isomer becomes almost as large as that of the meta compound. Again, an increase in the water content of the medium increases both the ortho/para and ortho/meta ratios and 20% perchloric (run 18) in nitric acid gives a result quite similar to that of run 17 in which the concentration of water in sulfuric acid was the highest used in the series. At 120° in fuming sulfuric and at 140° in 96.8% acid, the rate of transbromination was so close to that of dinitration that we were unable to study products formed under these conditions. The yield of ortho isomer in 96.8% acid is decreased considerably by raising the reaction temperature to 120°.

These results are not readily explained by the conventional arguments since none of these take any account of the influence of the solvent on the course of the reaction unless it is specifically combined with the compound undergoing nitration. We have previously presented evidence[11] that very little change occurs in the state of nitrobenzene in sulfuric acid solutions of from 90 to nearly 100% acid. In fuming sulfuric acid ionization may become extensive but one would expect that the conjugate acids would be considerably less reactive than un-ionized species. If such is the case, the bulk of the reaction would still occur with the same species as in, for example, 95% acid. It is possible that the sharp change in the isomer ratio when the dibromo compound is nitrated in fuming acid is actually due to the fact that this compound is almost entirely ionized with the consequence that nitration of the conjugate acid becomes important. The reaction medium actually becomes blood red immediately upon addition of the nitro compound whereas the dichloro compound gives only a pale yellow solution. If we disregard the reaction of the bromo compound in fuming acid, the isomer ratios vary in much the same way with both compounds.

Since the nitro function is generally considered to be a rather bulky group it would be anticipated that it would resist ortho nitration in much the same way as the *t*-butyl group.[22] There is ample evidence that the ortho disposition of two nitro groups results in considerable strain.[23] It is, therefore, apparent that in the transition state of the reaction which produces the ortho isomer there must be some stabilizing features which are either absent or less important in both the para transition state and in the final products of both reactions. There are two important differences between the transition states and the final products which are immediately apparent. Since Melander[24] has shown that hydrogen ion is not lost in the rate-controlling step of nitration reactions the transition state must bear a positive charge and the carbon atom at which substitution occurs must be approaching the tetrahedral configuration. The latter effect will remove the entering group from the plane of the nitro group which will result in steric strains being less than in the ortho dinitro product and perhaps less than in the transition state involved in substitution ortho to a bulky, non-planar group such as *t*-butyl. The distribution of the positive charge in the transition state has been discussed frequently. Roberts, Clement and Drysdale[25] have recently presented a very direct argument to show that, even in a very unfavorable case, a considerable charge is located on the carbon atoms ortho and para to the entering group. On the other hand, Ree and Eyring[26] obtained reasonable values for expected isomer ratios in aromatic substitutions by the use of model which treats the entering group as a

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

[22] D. Craig, THIS JOURNAL, **57**, 195 (1935).

[23] G. W. Wheland, "The Theory of Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1945, p. 189.

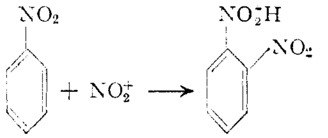
[24] L. Melander, *Arkiv Kemi*, **2**, 211 (1950).

[25] J. D. Roberts, R. A. Clement and J. S. Drysdale, THIS JOURNAL, **73**, 2182 (1951).

[26] T. Ri (Ree) and H. Eyring, *J. Chem. Phys.*, **8**, 433 (1940).

point charge. The actual charge distribution is doubtless intermediate between these extremes. We can consider that there is actually a fairly strong dipole with a component directed along the axis of the new bond. In the ortho transition state this dipole will interact in an attractive manner with the moment of one of the nitrogen–oxygen bonds of the adjacent nitro group.[27] The interaction cannot be other than repulsive for the meta and para transition states with the effect being the strongest with the latter. An interaction such as this would be sensitive to the extent to which the nitronium ion retains its shell of oriented solvent molecules in the transition state. Dispersal of the charge to the solvent would be expected to decrease the preferential stabilization of the ortho transition state. It is observed that the less polar solvents, *i.e.*, those containing the larger amounts of water or the nitric acid solutions, show the largest ortho/para ratios. We have shown earlier[12a] that the decrease in nitration rates with decreasing water content of sulfuric acid solutions can be most easily explained by assuming that the activity coefficient of the nitronium ion decreases appreciably. The assumption that the specific influence of solvent on the nitronium ion will persist in the transition state is reasonable.

An alternative to the above explanation of the ortho effect is one in which it is assumed that the ortho reaction proceeds by a new mechanism in which the proton is actually displaced in one concerted process and appears first on the oxygen of a neighboring group. The similarity in the rates



(2)

of nitration at all positions in our systems, suggests that if it is possible to carry out a concerted nitration at the ortho positions, there must be a very fine line of demarcation between the free energies of activation of the two step and concerted mechanisms. If this were the case, it might well be possible to induce the meta and para reactions to go by a concerted mechanism by the addition of gross amounts of bisulfate ion. This was done in the nitration of the chloro compound (run 8). A minor increase in the ortho/para ratio was observed indicating that no new mechanism for para nitration was brought into play. The addition of the same amount of potassium perchlorate gave a slightly larger increase in the ratio indicating that the influence of the anions does not depend upon their basicity. The exact significance of the generalized electrolyte effect is not obvious. It might have been anticipated that an increase in the ionic strength would decrease the ortho/para ratio. However, massive amounts of electrolytes may increase the activity of the nitronium ion, by decreasing its solvation energy.

The variation in the isomer ratios with temperature is interesting and indicates the intrusion of a second mechanism at high temperatures in the nitration of dichloronitrobenzene in fuming sulfuric acid. One would anticipate that meta substitution would involve the smallest activation energy since the classical explanation for meta orientation by the nitro function implies that the meta reaction derives its advantage from the relatively low potential energy of the transition state. The decrease, with increasing temperature, in the yields of meta isomers in 96% acid is consonant with this concept. However, in fuming acid the yield of meta product is virtually unchanged by an increase of the reaction temperature from 100 to 140° and the ortho–meta ratio is actually decreased. This can be accounted for if one assumes that at the higher temperature an appreciable amount of material is produced by the nitration of the conjugate acid of the mono nitro compound. The nitration of this species should involve a higher activation energy than the reaction of the neutral molecule and it would be expected that the presence of the positive charge on the first nitro group would increase the preference for the meta position and completely destroy the ortho direction through the interaction described above. The lower reactivity of the bromo compound as compared to the chloro analog may be attributed to the steric requirements of the bromine atoms.

As a general conclusion we can tentatively assume that all planar, non-linear substituents, in which the atom is at the negative end of a dipole, will exert an ortho orienting influence. The magnitude of this effect will be decreased by: (1) an increase in the dielectric constant of the medium, (2) a decrease in the ionic character of the new bond in the transition state or (3) an increase in the steric requirements of either the entering or the orienting group. The ortho influence should be virtually destroyed by addition of a proton to the orienting group. Since the dipolar attraction in attack at the ortho position cannot become positive for a linear group, the orientation influence of the cyano function is of great interest. As little reliable information can be gleaned from the literature we have undertaken a study of the dihalocyanobenzenes which are structurally analogous to the nitro compounds used in this investigation.

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[27] An equivalent statement is that the positively charged entering group is closer to one of the oxygens of the nitro group than it is to the positively charged nitrogen of the latter function.

[CONTRIBUTION FROM SHELL DEVELOPMENT COMPANY]

The High Temperature Chlorination of Various Mono- and Dichloropropenes

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The products from the high temperature substitutive chlorination of mono- and dichloropropenes have been characterized. The results are explained by a mechanism involving allylic radicals capable of reaction at two sites.

Introduction

The chlorination of propylene at elevated temperatures has been shown in an earlier publication[1] to lead predominantly to allyl chloride with a relatively small amount of dichloropropenes, dichloropropane and higher boiling chlorides. In recent years there has been an increasing interest in the polychlorides, known commercially as "D–D," because of their effectiveness as a nematocide. "The present work was undertaken to characterize some of the products which might be present in this mixture. The results were useful also in providing a better understanding of the nature of the high temperature substitutive chlorination of olefins.

Apparatus.—The reactor consisted of a quartz tube 2.0 cm. × 50 cm. surrounded by an electrically-heated steel block. The temperature throughout the reactor was measured by a thermocouple inserted in a quartz tube liner. The material to be chlorinated was fed from a 500-cc. graduate through a rotameter into a Pyrex evaporator heated with decalin. It was mixed with gaseous chlorine supplied from a weighed cylinder with the flow rate measured by an orifice meter. The reactants were mixed in a jet of quartz tubing 0.2 cm. in diameter attached directly to the reactor and arranged so that the chlorine entered as a side stream at right angles to the flow of the organic chloride. The re-

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[1] H. P. A. Groll and G. W. Hearne, *Ind. Eng. Chem.*, **31**, 1530 (1939).