

and 5 at the lower concentrations than those reported here. They employed benzene concentrations more nearly equivalent to the nitric acid concentrations and measured "initial" rates of nitrobenzene formation over time intervals of order 30–90 minutes. The present investigation indicates that the solvent reaction could slow the benzene nitration rate considerably (the half-life for nitric acid in equation 2 is about one hour) during such a time interval. The effect furthermore would be relatively greater at the lower nitric acid concentrations than at the higher because the rate of the solvent reaction varies as the first power of the nitric acid concentration whereas the benzene nitration rate varies as a higher power. They thus reported a higher-order dependence of rate on nitric acid concentration, close to third, than that reported here.

Cohen and Wibaut measured the rate of disappearance of nitric acid in acetic anhydride with time, obtaining results considerably lower than the present experiments indicate. Their analytical procedure, however, the determination of unreacted nitrate ion by Devarda's method, may well reduce some of the combined nitrogen in the lower products of nitration, as they have pointed out. An attempt was made in the present investigation to determine nitric acid in acetic anhydride or in acetic acid by non-aqueous titration with pyridine but the end-point, indicated by glass-electrode potentiometry, is insufficiently sharp for analytical precision.

The nitric acid-acetic anhydride reaction itself is clearly not a simple one and merits further study in view of the practical importance of the system.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

### *Ortho-Para* Directive Effects for Aromatic Nitration in Acetic Anhydride

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The nitration of chlorobenzene and of bromobenzene in nitric acid-acetic anhydride solutions containing a relatively low concentration of sulfuric acid as catalyst yields a higher proportion of the *para*-substituted product than is obtained by nitration with aqueous 90% nitric acid. This effect is opposite to that observed with anisole and other compounds previously studied, where nitration in acetic anhydride yields a higher proportion of the *ortho*-substituted isomer. The results are consistent with a nitronium ion mechanism for both media on the supposition that in the medium of lower dielectric constant, electrostatic interaction between ion and dipole plays a significant role.

Existing data for the nitration of aromatic compounds containing an *ortho-para* directing group suggest that if one uses acetic anhydride as solvent in place of water, there is an increase in the proportion of *ortho*-substituted to *para*-substituted product. The effect is well established for the nitration of anisole,<sup>2,3</sup> acetanilide<sup>4,5</sup> and propionanilide<sup>5</sup> but there is practically no effect in the case of toluene.<sup>6</sup> For anisole, an attempt has been made recently to account for the "ortho effect" on steric grounds.<sup>3</sup> If the nitrating agent in acetic anhydride is a molecular compound such as acetyl nitrate, one can envision a mechanism whereby the directing group assists the incoming molecule, thus favoring substitution at the *ortho* position. The absence of a hydrogen-isotope effect in this position,<sup>3</sup> however, shows that displacement of the proton is not involved in the rate-determining transition state. If on the other hand the actual mechanism is electrophilic addition of nitronium ion,<sup>7,8</sup> as in aqueous solutions, then a different explanation is suggested, based on the polar character of the directing group and the dielectric constant of the solvent.

Because of the inhomogeneous nature of the intervening medium,<sup>9</sup> it is difficult to estimate the electrostatic free energy between the attacking positively charged ion and the dipole moment associated with the *ortho-para* directing substituent. Qualitatively, however, one would expect that for a dipole with its positive end directed outward from the ring, as in the cases of the methoxy and the anilide groups, electrostatic interaction would favor the nearer *ortho* position relatively to the more distant *para* and that this effect might be enhanced to some extent in a solvent of lower dielectric constant. One does not have to suppose that the polar effect is predominant but only that it will be superimposed on other factors determining the actual rates of reaction at the respective sites. On the basis of this argument, the small effect of the solvent in the case of toluene nitration could be associated with the comparatively small dipole moment contributed by the methyl group itself.

It would follow that for substituents providing dipole moments with the negative end directed outward from the ring, such as the chloro and bromo groups, *ortho* substitution should be suppressed relatively to *para* in acetic anhydride as compared with water. The present investigation shows that this is the case. When chlorobenzene is nitrated at 0° in acetic anhydride containing 2 M HNO<sub>3</sub> with 0.04 M H<sub>2</sub>SO<sub>4</sub> present as acid catalyst,<sup>8</sup> the proportion of *o*- to *p*-chloronitrobenzene in the product is 10–90 as compared with 30–70 obtained by nitration with

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aqueous 90% HNO<sub>3</sub>.<sup>10</sup> When bromobenzene is similarly nitrated, the proportion of *o*- to *p*-bromonitrobenzene is 25-75 from the acetic anhydride mixture as compared with 38-62 from the aqueous.<sup>11</sup>

These findings do not ensure that the explanation here suggested for their origin is correct. They do cast doubt however on any theory postulating that the "ortho effect" of acetic anhydride is general.

### Experimental

Conditions for nitration in acetic anhydride are given: to 22.5 ml. of B. & A. A.C.S. reagent acetic anhydride cooled in an ice-bath, 2.5 ml. of B. & A. A.C.S. reagent fuming nitric acid containing approximately 90% HNO<sub>3</sub> was added slowly, with one drop (0.05 ml.) of 96% H<sub>2</sub>SO<sub>4</sub> as catalyst. Then 0.02 mole of E. K. Co. chlorobenzene or bromobenzene, respectively, was added dropwise. Reaction was quite rapid, as evidenced in the case of bromobenzene by partial separation of crystalline product before the last of the reactant had been added. The reaction mixture was allowed to stand at 0° for 20 minutes.

Recovery of the nitration product was effected by two procedures. In one the reaction mixture simply was poured into 175 ml. of water at 0°. In the other, to counter the slight but significant solubilities of the products in the resulting aqueous acetic acid solution, approximately 20 g. of NaOH was also present to neutralize the acid. After standing at 0° for at least 30 minutes after all the acetic anhydride had been decomposed, the crystalline product was filtered in a sintered glass crucible, washed with ice-water until free of acid or alkali and then dried for several days in a vacuum desiccator over Drierite.

The samples were analyzed at a standard concentration of 0.1000 g. per ml. of benzene solvent by means of a Perkin-Elmer Model 21 double-beam infrared spectrometer. Known mixtures of the *ortho* and *para* isomers were run for comparison. These were made up from recrystallized E. K. Co. products except for *o*-chloronitrobenzene, which was prepared by diazotization of E. K. Co. *o*-nitroaniline. Compositions determined from the spectra are estimated to be uncertain by plus or minus two percentage points. There was no indication of any other compounds in the reaction products except the mononitro *ortho* and *para* isomers.

To test the recovery procedures, known mixtures were prepared with compositions adjusted to match the reaction products. They were dissolved in acetic anhydride at comparable concentrations and recovered by the same procedures. By this means it was established that known samples containing 25% *o*-bromonitrobenzene and 75% *p*-

bromonitrobenzene gave the same spectrum as the nitration product from bromobenzene recovered by the same procedure. Recovery from the NaOH solutions was at least 98% and the composition was not altered significantly by the recovery procedure. Recovery from aqueous solutions not neutralized by NaOH was about 88% and the product contained actually about 19% *ortho* and 81% *para* isomer. The shift was due to differences in the relative solubilities in the dilute acetic acid solutions under the stated conditions, as was confirmed by recovery tests on separate samples of each isomer. With chloronitrobenzene, similar tests showed that known samples containing 10% *ortho* and 90% *para* when recovered by either procedure gave the same spectrum as the nitration product from chlorobenzene recovered by the same procedure. Actual recovery from the NaOH solutions was about 94% and the product contained 91% *para* while from aqueous solutions not neutralized with NaOH, recovery was 89% and the product contained 93% *para*. With allowance for solubility losses, the over-all nitration yields were between 95 and 100% of theoretical.

"Aqueous nitration" products were prepared by adding 0.02 mole of chlorobenzene or bromobenzene, respectively, to 10 ml. of 90% HNO<sub>3</sub> dropwise at 0°. The reaction mixture solidified after half the organic reactant had been added and its fluidity was restored by the addition of two further 2-ml. portions of the nitric acid during the latter part of the run.<sup>10,11</sup> After standing at 0° for 20 minutes, the products were recovered by diluting the reaction mixtures to 200 ml. with ice-water. In agreement with previous observations by Holleman and de Bruyn,<sup>10,11</sup> the infrared analyses showed that the bromonitrobenzene contained 62% *para* and 38% *ortho* while the chloronitrobenzene contained 70% *para* and 30% *ortho*.

When 0.02 mole of bromobenzene was added at 0° to 22.5 ml. of acetic anhydride containing 2.5 ml. of 90% HNO<sub>3</sub> in the absence of sulfuric acid, only a trace of nitration product was obtained, even when the mixture was kept at 25° for six hours before dilution. With 2.5 ml. of 100% HNO<sub>3</sub> (obtained by fractional distillation under reduced pressure from a mixture of 90% HNO<sub>3</sub> and concentrated sulfuric acid) in 22.5 ml. of acetic anhydride under similar conditions, the yield of bromonitrobenzene was about half that obtained at 0° in the presence of 0.04 *M* sulfuric acid and it was contaminated with some of the unreacted bromobenzene. So far as could be ascertained, the proportion of *p*- to *o*-bromonitrobenzene was not significantly influenced by the presence or absence of the catalyzing acid.

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