[Contribution from the Department of Industrial Chemistry, the Faculty of Engineering, Kyoto University]

THE ACCELERATIVE *ORTHO* EFFECT. II. THE ORIENTATION IN THE MERCURATION OF NITROBENZENE

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The mercuration of some substituted aromatic compounds has been known often to produce predominantly *ortho* compounds (1), (2), but an accurate analysis of the products has yet to be reported. Recently, Klapproth and Westheimer (3) have estimated the *meta* and (*ortho* + *para*) yields in the mercuration of nitrobenzene. However, they did not determine an *o*:*p* ratio. In addition, it is of importance to know how the mercuration occurs — whether it is homolytic or heterolytic. Although Westheimer and co-workers (4) showed in their other reports that the mercuration of benzene was an ordinary second-order electrophilic substitution, they concluded from their own data that the mercuration in non-polar solvents at high temperature might involve a statistical (non-oriented) attack of the reagents (2). Also Ingold (4) states from the orientation of the substitution that the mercuration is usually electrophilic, but that with mercuric acetate in non-polar solvents as reagent, it is often homolytic.

Our main object was to determine an accurate orientation in the mercuration of nitrobenzene and to discuss the results on the basis of the electrostatic interaction of atomic charges in the activated complex (5).

The mercuration of nitrobenzene was accomplished with mercuric nitrate (or perchlorate) in concentrated nitric (or perchloric) acid and with mercuric acetate in nitrobenzene as reagent. In both cases, the isomeric mixture of nitrophenylmercuric chlorides produced was converted into the mixture of bromonitrobenzenes by the ordinary method and then the mixture was analyzed by a newly established ultraviolet spectrophotometric method. The results are shown in Table I.

The table indicates that the *ortho* compound amounts to 30–40% and the yield of the *para* isomer is low. This fact appears abnormal in the ordinary electrophilic substitution on nitrobenzene, even though 60–70% of the normal *meta* compound is obtained. The table also shows that in the solvent nitric acid the *o*:*p* ratio is larger than it is in nitrobenzene.

The above facts can be accounted for by the assumption of an electrostatic interaction in the transition state of the reaction similar to that reported previously (6). The attraction between the oppositely charged mercury and oxygen will stabilize the transition state and will certainly accelerate the *ortho* substitution. The atomic charges and atomic distances were evaluated similarly as in Part I (6). The calculation for the electrostatic interaction energy between the positive charge on mercury and atomic charges on the nitro group, ΔE, and that between atomic charges on the nitro group and the positive charges located on the *o*- and *p*-position of mercury, $\Delta E'$, were both carried out in the same manner as Part I; thus for *o*-substitution:

$$\mathrm{E}_o = \frac{4.77 \times 6.062 \times 10^{23}}{4.185\ \epsilon}\left[2.025\left(\frac{1}{3.12}+\frac{1}{4.46}\right)-\frac{3.476}{3.44}\right]$$

$$= \frac{6.5}{\epsilon}\ \text{k cal./mole}$$

$$\mathrm{E}_o' = \frac{\left(1.59+\dfrac{0.574}{3}\right)6.062\times 10^{23}}{4.185\ \epsilon}\left[2\left\{2.025\left(\frac{1}{4.08}+\frac{1}{4.66}\right)-\frac{3.476}{3.67}\right\}+2\left(\frac{2.026}{2.20}\right)-\frac{3.746}{1.35}\right]$$

$$= -\frac{20.0}{\epsilon}\ \text{k cal./mole}$$

$$\mathrm{E}_o + \mathrm{E}_o' = \frac{-13.5}{\epsilon}\ \text{k cal./mole}$$

and those with *m*- and *p*-substitutions:

$$\Delta\mathrm{E}_m + \Delta\mathrm{E}_m' = \frac{2.7-6.0}{\epsilon} = -\frac{3.3}{\epsilon}\ \text{k cal./mole}$$

$$\Delta\mathrm{E}_p + \Delta\mathrm{E}_p' = \frac{1.8-20.0}{\epsilon} = -\frac{18.2}{\epsilon}\ \text{k cal./mole}$$

where the negative sign means a repulsion. Hence the rate of mercuration should be in the order, $m > o > p$, and this is in accord with our results.

EXPERIMENTAL

Materials. The nitrobenzene used was purified by duplicate vacuum-distillations. The mercuric oxide and acetate was of the best grade. The *o*- and *p*-bromonitrobenzene were prepared from the corresponding nitranilines and melted at 43.0° and 127.5°, respectively. The *m*-isomer was prepared by the bromination of nitrobenzene, m.p. 56.5°.

The mercuration procedures. (A) *The mercuration with mercuric nitrate in nitric acid.* A mixture of conc'd nitric acid (120 ml.), nitrobenzene (90 ml.), mercuric oxide (25 g.), and some urea was placed in a 500-ml. flask and heated under stirring at 97–98° for 7 hours. The reaction mixture then was cooled, 300 ml. of water was added, and the aqueous layer was sepa-

TABLE I

THE PERCENTAGE COMPOSITION OF ISOMERS IN THE REACTION PRODUCTS IN THE MERCURATION OF NITROBENZENE

Reaction conditions		Isomeric nitrobenzenes, %		
		o	*m*	p^a
Solvent, HNO_3. Reagent, HgO. Temp. 99°. Time, 7 hr.	1	37.1	56.5	6.4
	2	37.4	56.2	6.5
	3	37.5	57.0	5.5
Solvent, $C_6H_5NO_2$. Reagent, $Hg(OAc)_2$. Temp. 155°. Time, 2.5 hr.	1	26.1	68.8	5.1
	2	28.0	66.0	6.0
	3	26.3	68.5	5.2

[a] For the comparison of the orienting power, these yields of *p*-substitution should be duplicated.

rated from the oily layer. Sodium chloride (100 g.) was added to the aqueous layer, and the precipitated nitrophenylmercuric chloride was filtered, washed with water, and then was introduced into a 1 l. flask together with 200 g. of sodium chloride, 100 ml. of water, and the oily layer obtained before. The solvent nitrobenzene then was steam-distilled, and the residual isomeric nitrophenylmercuric chlorides were converted to the corresponding bromonitrobenzenes by Dimroth's method (1). The product was freed from dibromonitrobenzene derived from dimercurated product by cautious vacuum-distillation. It was ascertained that neither nitration, oxynitration, nor decomposition of mercurated compounds occurred during the steam-distillation.

(B) *The mercuration with mercuric acetate in nitrobenzene as reagent.* Nitrobenzene (60 ml.) and mercuric acetate (20 g.) were heated with stirring for 2.5 hours at 150–155°.

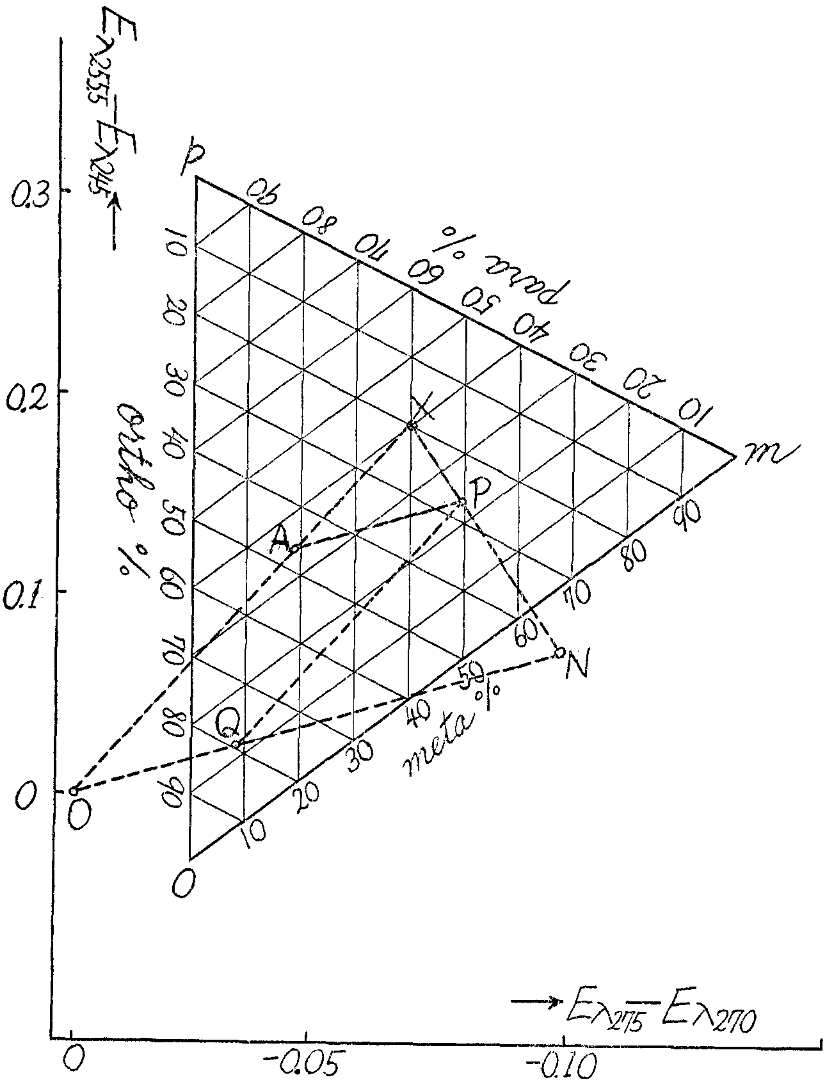

FIG. 1. VAUGHN'S CHART MODIFIED FOR FOUR-COMPONENT MIXTURES; WAVE LENGTHS AS SHOWN.

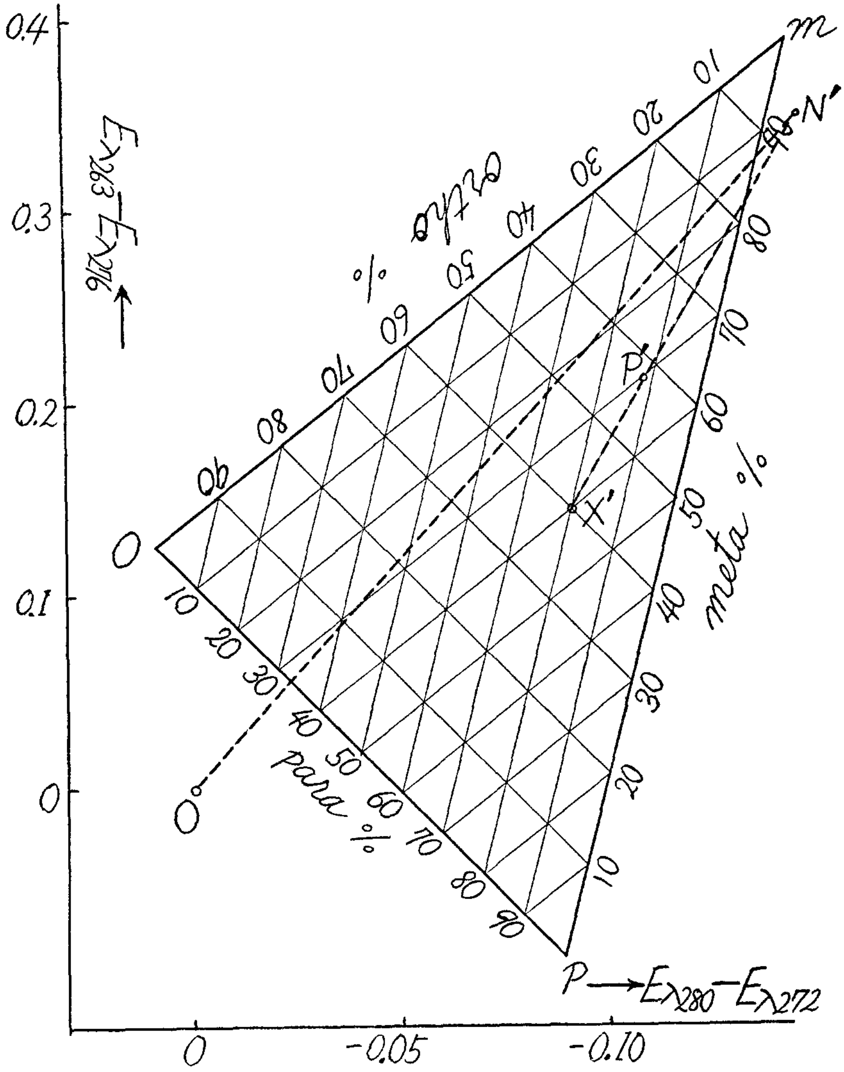

FIG. 2. VAUGHN'S CHART MODIFIED FOR FOUR-COMPONENT MIXTURES; WAVE LENGTHS AS SHOWN.

The resulting mixture was added with 300 ml. of a saturated aqueous solution of sodium chloride, steam-distilled, and then was treated with bromine as mentioned above.

The method of analysis. Many authors have postulated various methods for estimating the *o*:*m*:*p* ratio in an isomeric mixture, most of them by using inaccurate chemical processes (2), or some workers by measuring the freezing point of the isomeric mixture (7). Although the latter method has recently been well revised (8) and proven to be reliable with pure materials, the freezing point often varies largely with traces of impurities, and in this case the unreacted nitrobenzene was difficult to separate sharply from the bromocompounds even by a cautious fractional vacuum-distillation.

Therefore, we revised Vaughn's ultraviolet spectrophotometric method (9) for the estimation of a three-component system and applied the method to our four-component system, *i.e.*, nitrobenzene, and *o*-, *m*-, and *p*-bromonitrobenzene. For measurement of the optical densities, a Beckman quartz spectrophotometer, model DU, was used.

Pure *o*-bromonitrobenzene (40 mg.) was weighed accurately on a semi-micro balance and was dissolved in optically pure cyclohexane in a 25-ml. volumetric flask. One ml. of the solution was diluted to 50 ml. and the optical densities of this standard (concentration) solution were measured at eight points at various wave lengths. The same operations were repeated with the pure *m*- and *p*-isomers and with nitrobenzene.

By using four values of these optical densities, a Vaughn's working chart (Fig. 1) was prepared, and on it, a point N corresponding to pure nitrobenzene was plotted from the density data. Suppose that a mixture which contains *o*-, *m*-, and *p*-isomers in a ratio represented by X is mixed with nitrobenzene in a ratio of m.n and then by diluting to the standard solution, a mixture P of four components is produced. The same mixture of the same concentration will be obtainable by mixing a standard solution of mixture X diluted to m/(m + n) with a standard solution of nitrobenzene diluted to n/(m + n). The m/(m + n) dilution of mixture X is represented by a movement of a corresponding point along line XO to A where O is an origin and XA:AO = n:m. Similarly, the n/(m + n) dilution of nitrobenzene is expressed by a movement from N to Q where NQ:QO = m:n. When the diluted mixture A is mixed with nitrobenzene, the procedure is represented by a line passing A and parallel to ON, since optical densities are additive functions in regard to those of the components. In the same way, the admixture of nitrobenzene with mixture X will be represented by a line passing Q and parallel to XO. Therefore, mixture P must be expressed as a crossing point of the two lines and moreover P must lie on line XN, since AP:ON = n:(m + n). Conversely, if a mixture consisting of unknown quantities of the four components is measured at the standard concentration and its optical densities are represented by P, the true *o*:*m*:*p* ratio of the mixture should be represented by a point situated somewhere on line NP or its extension. Since the positions of P and N in Fig. 2 are known, then

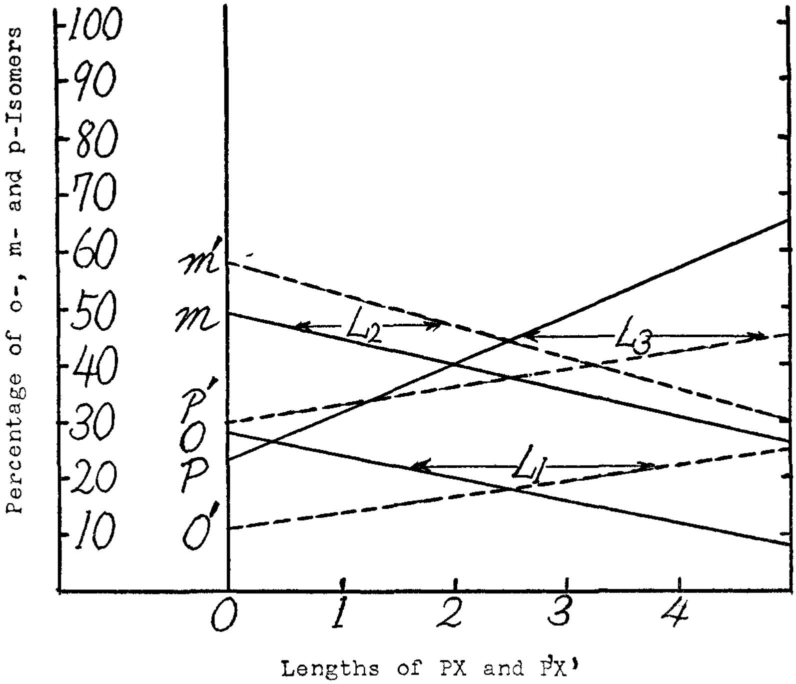

FIG. 3. CHANGE IN LENGTH OF PX AND PX′ *versus* PERCENT OF *o*-, *m*-, AND *p*-ISOMERS.

it will be sufficient to decide only the length of either NX or PX. For this purpose, it is necessary to make another chart (Fig. 2) by measuring the previous points in the other four wave lengths, where X′, P′ etc. correspond to mixture X, P etc., respectively.

Then in Fig. 3 are plotted six lines which show the change of percentages of *o*-, *m*-, and *p*-isomers with variation of the length of PX or P′X′. These lines are, of course, drawn from the variation of the *o*-, *m*-, and *p*-percentages with the unit length change of PX in Fig. 1 and P′X′ in Fig. 2. Since X and X′ represent a mixture of the same composition, the height of the *o*- line at abscissa PX must be equal to that of the *o*′-line at P′X′, and the same is true with the *m*- and *p*-lines. Accordingly, if the horizontal distance L between the *o*- and *o*′-line *versus* the length of PX is plotted, and if data similarly are worked up for *m* and *p*, the three lines obtained must meet at one point (Fig. 4). The abscissa of the point gives the length of PX and hence the position of X in Fig. 1, *i.e.*, the *o*:*m*:*p* composition of mixture X, may be determined.

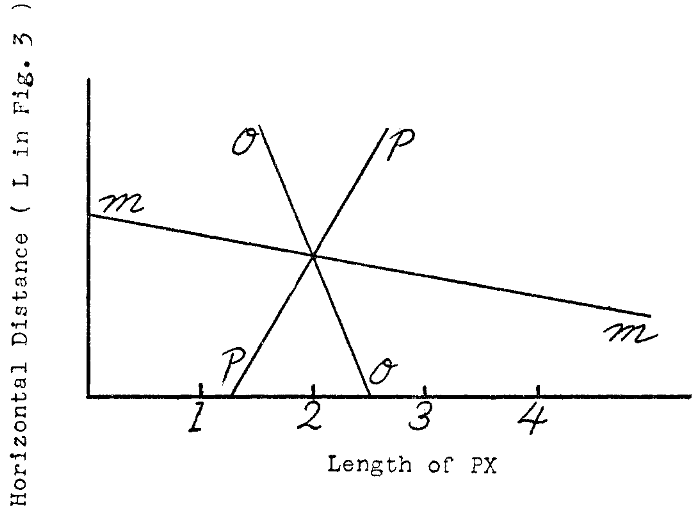

FIG. 4. PLOT OF DISTANCES L IN FIG. 3 *versus* LENGTH OF PX.

TABLE II

EXPERIMENTS WITH KNOWN MIXTURES IN ESTABLISHING THE SPECTROPHOTOMETRIC ANALYSIS OF MIXTURES CONTAINING *o*-, *m*-, AND *p*-BROMONITROBENZENES AND NITROBENZENE

		Bromonitrobenzenes (%)			Nitrobenzene (%)
		o	*m*	*p*	
1	Calc'd	50.0	14.3	35.8	13.4
	Obs'd	50.5	14.0	35.5	14.2
2	Calc'd	15.3	77.0	7.7	19.8
	Obs'd	14.4	77.3	8.3	19.7
3	Calc'd	29.5	11.7	58.8	50.0
	Obs'd	28.9	12.5	58.6	50.7
4	Calc'd	58.8	11.7	29.5	23.1
	Obs'd	58.7	12.4	28.9	22.9
5	Calc'd	6.3	62.5	31.2	18.1
	Obs'd	7.0	62.7	30.4	18.3

Furthermore, the weight percentage of nitrobenzene in the mixture P can be estimated from a quotient AP/ON or n/(m + n). Table II shows our result on tests with known amounts of the samples.

SUMMARY

The orientation in the mercuration of nitrobenzene with mercuric nitrate or acetate has been studied by converting the product with bromine into an isomeric mixture of bromonitrobenzenes and then by measuring their composition using an unique analytical method of ultraviolet spectrophotometry. The yields of the mercurated nitrobenzenes have been found to be in the order $m > o \gg p$. This fact suggests that the electrostatic attraction between oppositely charged atoms in these activated complexes is strongest in the *ortho* substitution.

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