[CONTRIBUTION FROM THE DEPARTMENT OF GENERAL CHEMISTRY OF THE UNIVERSITY OF ROME]

# The Determination of Reactivities *meta* and *para* to Halogens. The Bromination of Some Halopolymethylbenzenes by Bromine in Nitromethane[1,2]

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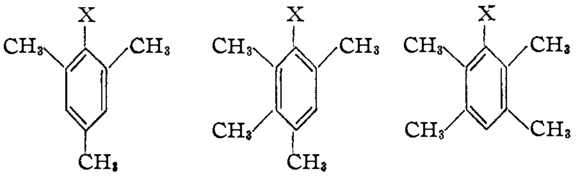
Bromination rates of halogen-substituted mesitylenes, isodurenes and durenes relative to the parent hydrocarbons have been measured in nitromethane, acetic acid and mixed solvents at 30°. Bromination by molecular bromine in nitromethane was found to be third order in the concentration range 0.01–0.02 *M*. The reactivities per position of attack $k/k_0$ are largely independent of the methyl substituents and indicate that the steric environment at the reaction center keeps approximately constant along each of the three series examined. This is particularly evident from the excellent agreement of the present data for fluoro and chlorodurene with those by de la Mare and Robertson for fluoro and chloronaphthalene. The present structural approach has permitted, for the first time, the determination of reliable data for bromination *meta* to halogens and the estimation of *para/meta* ratios for the same reaction in monohalobenzenes. A linear free energy relationship of the present data was found with a set of $\sigma^+$-values as developed very recently by Brown and Okamoto. Correspondingly, a value of $-8.64$ was estimated for the $\rho$-constant of the reaction.

The electronic effects of halogens on the rate of electrophilic aromatic substitution have been given considerable attention by several authors in modern studies.[3-9] It appears that the relative reactivity of halobenzenes is appreciably affected by the nature of the reagent and that reactivity values for halogenation, especially bromination, are more widely spaced than those for nitration. While the isomer distribution in the nitration of halobenzenes has been the object of several investigations, similar information relative to halogenation reactions is more scanty. The relative amount of *meta* product for the latter reactions is vanishingly small and in many cases over-all rates can be taken as essentially *para* substitution data.[4]

In continuation of our studies on polymethylbenzenes,[1] one of the objects of our work was to devise a structural approach to the problem of determining the reactivities for aromatic bromination *meta* and *para* to halogens by using bromine as the reagent and utilizing current methods available for the measurement of over-all rates in this reaction.[10-12] To this end, we have examined the following series of substituted tri- and tetramethylbenzenes in which the positions available for substitution are either *meta* (I and II) or *para* (III) to the substituent X. A study of molecular patterns of this kind involves electronic as well as steric effects, on account of the overcrowding of the substituents around the benzene ring. The use of the present approach in order to obtain information on the electronic effects of halogens was based on the reasonable expectation that the effects of the substituents in compounds I to III would contribute to the energy of activation in an additive manner.[13,14] The relative importance of possible steric effects, as revealed by our results, will be considered in the Discussion.



I II III

X = H, F, Cl, Br, I

Another object of this work was to obtain further information regarding the possible mechanism of aromatic bromination in nitromethane since our recent preliminary report.[15] Because of the similarity of nitromethane to acetic acid as to the general kinetic behavior of aromatic bromination in these media and the much higher speed at which the reaction proceeds in the former solvent, a wide range of reactivity was expected to be covered by using the two solvents and mixtures thereof without the aid of other accelerating devices such as changing concentration, adding water or catalysts. In order to justify such a procedure, both kinetic and reactivity orders in varying media have been determined.

## Results and Discussion

**Kinetic Order and Relative Rates of Bromination in Nitromethane, Acetic Acid and Mixed Solvents.**—Aromatic bromination by bromine in acetic acid is a complex reaction involving the participation of more than one molecule of bromine in the kinetically significant stages of the process[9,10,16] and the reaction order depends on the concentration range in which it is determined. On extending our observations on the similar kinetic behavior of nitromethane as a solvent for this reaction,[15] we

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[1] This paper is part IV in the series "Substitution in Polymethylbenzenes." Previous papers: G. Illuminati and G. Marino, THIS JOURNAL, **75**, 4593 (1953); G. Illuminati and M. P. Illuminati, *ibid.*, **75**, 2159 (1953); G. Illuminati, *ibid.*, **74**, 4951 (1952).

[2] Presented in part to the XIVth International Congress of Pure and Applied Chemistry, Zurich, July, 1955.

[3] M. L. Bird and C. K. Ingold, *J. Chem. Soc.*, 918 (1938); G. A. Benford and C. K. Ingold, *ibid.*, 929 (1938).

[4] P. B. D. de la Mare and P. W. Robertson, *ibid.*, 100 (1948).

[5] P. W. Robertson, P. B. D. de la Mare and B. E. Swedlung, *ibid.*, 782 (1953); P. B. D. de la Mare, *ibid.*, 4450 (1954).

[6] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

[7] J. D. Roberts, J. K. Sanford, F. L. J. Sixma, H. Cerfontain and R. Zagt, THIS JOURNAL, **76**, 4525 (1954).

[8] S. J. Branch and B. Jones, *J. Chem. Soc.*, 2921 (1955).

[9] P. W. Robertson, *Science Progress*, 418 (1955).

[10] P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, *J. Chem. Soc.*, 276 (1943).

[11] E. Berliner and F. Berliner, THIS JOURNAL, **71**, 1195 (1949).

[12] P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 1764 (1951).

[13] F. E. Condon, THIS JOURNAL, **70**, 1963 (1948).

[14] B. Jones and J. P. Sleight, *J. Chem. Soc.*, 1775 (1954), and refs. thereof.

[15] G. Illuminati and G. Marino, *Gazz. chim. ital.*, **84**, 1127 (1954).

[16] R. M. Keefer, A. Ottenberg and L. J. Andrews, THIS JOURNAL, **78**, 255 (1956).

TABLE I

KINETIC DATA ON THE BROMINATION OF HALOGEN-SUBSTITUTED MESITYLENES (I), ISODURENES (II) AND DURENES (III) AND OF THE PARENT HYDROCARBONS IN 0.01 *M* SOLUTION AT 30.0°

| | | Time at 10% reaction, min. | | | | | Reactivity relative to parent hydrocarbon | |
|---|---|---|---|---|---|---|---|---|
| Aromatic compound | X | In $MeNO_2$ | In $MeNO_2$–AcOH, 1:1 in volume | In AcOH | Relative rate (durene = 1000) | *s* | $k/k_0$ | $\log (k/k_0)$ |
| 2-Substituted | H | | | 5.40 | 62,800 | 3 | 1 | 0 |
| 1,3,5-trimethylbenzenes | F | 28.3 | 150 | | 35.9 | 2 | $8.56 \times 10^{-4}$ | −3.068 |
| (mesitylene series, I) | Cl | 48.8 | 263 | | 20.6 | 2 | $4.93 \times 10^{-4}$ | −3.307 |
| | Br | 54.9 | | | 18.2 | 2 | $4.35 \times 10^{-4}$ | −3.361 |
| | I | 21.2 | | | 47.2 | 2 | $11.3 \times 10^{-4}$ | −2.947 |
| 4-Substituted | H | | | 2.99 | 113,000 | 2 | 1 | 0 |
| 1,2,3,5-tetramethylbenzenes | F | 14.5 | | | 69.0 | 1 | $12.2 \times 10^{-4}$ | −2.914 |
| (isodurene series, II) | Cl | 27.6 | | | 36.3 | 1 | $6.42 \times 10^{-4}$ | −3.192 |
| | Br | 28.2 | | | 35.5 | 1 | $6.28 \times 10^{-4}$ | −3.202 |
| | I | 5.34 | | | 187 | 1 | $33.1 \times 10^{-4}$ | −2.480 |
| 3-Substituted | H | | 5.47 | 339 | 1,000 | 2 | 1 | 0 |
| 1,2,4,5-tetramethylbenzenes | F | | | 147 | 2,310 | 1 | 4.62 | +0.664 |
| (durene series, III) | Cl | 13.8 | 75.4 | | 72.6 | 1 | $14.5 \times 10^{-2}$ | −0.839 |
| | Br | 33.1 | 173 | | 30.9 | 1 | $6.18 \times 10^{-2}$ | −1.209 |
| | I | 25.0 | | | 40.0 | 1 | $8.02 \times 10^{-2}$ | −1.096 |

have now found that in the case of halopolymethylbenzenes the reaction in nitromethane is third order as in acetic acid in the same concentration range (0.01–0.02 *M*). Typical values for the total order are as follows (see Experimental for details): bromodurene in nitromethane, 2.95; chloromesitylene in nitromethane, 3.01; fluorodurene in acetic acid, 3.07.

We also have gathered well-supported evidence that the relative rates of the compounds under examination are the same in the two solvents. To test this, since there was found too strong a difference in reaction rates for the accurate measurement of any one substance in both pure solvents, we have compared the relative rates of some of the compounds in pure nitromethane and in mixed solvents. The constancy in relative rates can be verified by comparing the data reported in Table I for chlorodurene, fluoromesitylene, bromodurene and chloromesitylene, as obtained from measurements in both nitromethane and nitromethane–acetic acid.

These results show that aromatic bromination by bromine in nitromethane and in acetic acid proceed by a similar mechanism and lend further support to our previous assumption[15] that in nitromethane molecular bromine is the halogenating entity. Also, they justify the use of both solvents and a mixture thereof to assess quantitative data for compounds varying in a broad range of reactivity. For the most reactive compounds, that is, the three hydrocarbons and fluorodurene, the measurements were carried out in acetic acid; for all the others, nitromethane was used. The relative rates for the whole set of compounds were established with the aid of a number of determinations in nitromethane–acetic acid mixtures carried out with some of the compounds of intermediate reactivity. The times for 10% reaction ($t_{10}$) as measured in the three media and the relative rates calculated therefrom are reported in Table I.

The acceleration of bromination in nitromethane with respect to acetic acid, which was previously stated[15] to be roughly in the order of $10^3$ has now been established more accurately; a value of 331, averaged from several determinations, was obtained. As to the purification of nitromethane to use for bromination studies, it is interesting to note that phosphorus pentoxide proved to be a very effective reagent in destroying the bromine-consuming impurities which often accompany commercial samples of the solvent.

**Reactivities *meta* and *para* to Halogens.**—The reactivities per position of attack relative to the parent hydrocarbon ($k/k_0$) in each of the three series examined are reported in Table I. They were deduced from the relative bromination rates by taking into account the number of equivalent positions available for substitution, expressed by the statistical factor *s*. These results are diagrammatically illustrated in Fig. 1 by plotting log ($k/k_0$) *vs.* the nature of the substituents. For comparison, the figure reports the *para* values diagram for the 1-halonaphthalenes (IV) as determined by de la Mare and Robertson.[4] Since the distribution of the methyl groups in each of the series examined by us is kept constant and only the halogen is varied, in the following any data concerning bromination *meta* and *para* to halogen atoms will be simply referred to as *meta* and *para* bromination data.

The major differential features concerning *meta* and *para* reactivities of the halopolymethylbenzenes can be qualitatively interpreted in terms of the electronic effects of the halogens. In the *meta* bromination series (I and II) a strong deactivation is observed on the order of $10^3$. The effects of the halogens are very similar in both series. The haloisodurene diagram (II) shows a slight shift toward higher reactivities with respect to the halomesitylene diagram (I), corresponding to differences in the $k/k_0$ values by a factor less than 1.5 for F, Cl and Br. The difference is somewhat higher for the iodo compounds being by a factor of *ca.* 3.

In the *para* bromination series (III), fluorine acts as an activating substituent and the other halogens exert a moderate deactivation by a factor on the order of 10. The reactivity diagram is closely similar to the one corresponding to the *para* bromination of the 1-halonaphthalenes (IV). The agreement is excellent for F and Cl; the small but increasing deviation observed for Br and I will be discussed in the next section.

As expected from the high selectivity[17] of aromatic bromination by molecular bromine, there is a very broad separation between *meta* and *para* reactivity showing the large extent of conjugation of the halogen atom *in the transition state* of the *para* reactions and, essentially, the sole operation of the electron attracting effects of the inductive type in the *meta* reactions. If the steric environment at the reaction center undergoes no appreciable change along each series (see next section), from inspection of the $k/k_0$ values in the *meta* series I and II it follows that *differences in the inductive effects of halogens in the transition state of bromination are small as compared with the observed strong deactivation with respect to the parent hydrocarbon.* Diagrams I and II (Fig. 1) show a minimum in the bromo member with a reactivity order $F > Cl \sim Br < I$. Susceptibility to resonance interaction at a reaction site *meta* to the halogen, which can be regarded as a minor effect, is expected to vary in the same order as the resonance interaction observed in the *para* reaction and may be appreciable in the case of fluorine, which displays such a large effect of this kind in the *para* reaction (diagrams III and IV). Since differences arising from the inductive effects are relatively small according to the above statement, even weak resonance interactions at the *meta* position may play a role in determining the observed irregular order.

**Estimation of *para/meta* Bromination Ratios in Monohalobenzenes.**—The deviations in reactivity observed in the present work when comparing *meta* to *meta* and *para* to *para* diagrams (Fig. 1) may be significant for the bulkiest halogens; however, they are generally small. Although the *para* series III and IV belong to markedly different patterns, those of durene and naphthalene, the effects of fluorine and chlorine on *para* reactivity are practically the same in the two series. The observed deviation in the bromo and iodo members, *if* considered as a shift of the durene diagram toward lower reactivities, could be interpreted in terms of decelerating steric effects.[18] However, at least part of the deviation is probably due to a shift of the bromo and iodonaphthalene values toward (apparently) higher reactivities and may depend on the experimental approximation used by de la Mare and Robertson[4] in taking over-all bromination rates as *para* rate data. It is possible that such an approximation becomes somewhat unsatisfactory with the bromo and iodo members in view of the trend shown by halogens in nitration[7,19] to increase the *ortho* reactivity from chlorine to iodine.

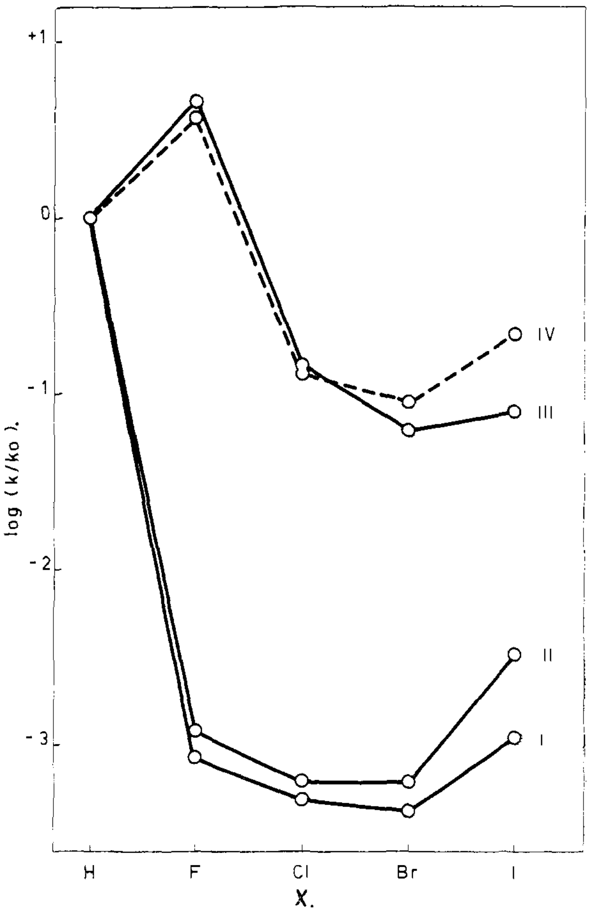

Fig. 1.—Effect of the halogen substituent on reactivity in *meta* (I, II) and *para* (III, IV) bromination: solid lines, this work.

The observed facts and the above considerations lead to the conclusion that activation energy and entropy contributions arising from steric effects[20] are approximately constant along each series, so that *the reactivities* $k/k_0$ (relative to the parent hydrocarbon) *essentially reflect the specific electronic effects of the halogen atom alone.* Accordingly, our $k/k_0$ values can be taken as a measure of *meta* and *para* partial rate factors in the monohalobenzenes ($f_m$ and $f_p$) and the following equation can be assumed to be approximately valid

$$\frac{f_p}{f_m} = \frac{(k/k_0)_p}{(k/k_0)_m}$$

where $(k/k_0)_p$ and $(k/k_0)_m$ are the reactivities corresponding to *para* and *meta* bromination as determined with the aid of the structural approach used in this work. Then, the ratio between percentages of *para* and *meta* isomerides obtained in the

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[17] H. C. Brown and K. L. Nelson, This Journal, **75**, 6292 (1953); K. L. Nelson, *J. Org. Chem.*, **21**, 145 (1956).

[18] Decelerating steric effects due to a bulky halogen atom at a position *para* to the reaction center of such an overcrowded molecule as that of a halodurene may consist of increased hindrance toward the incoming reagent and be electronic in nature as well. A bulky halogen atom may be forced out of the ring plane by stiffened adjacent methyl groups; sufficiently strong bond bending is theoretically expected to cause a decrease in the conjugation of the halogen with the aromatic system in the transition state of the reaction. It may be of interest to note that both halogen atoms and methyl groups have been found susceptible to out-of-plane bending in the crystal state (*cf.* O. Bastiansen and O. Hassel, *Acta Chem. Scand.*, **1**, 489 (1947); D. M. Donaldson and J. M. Robertson, *J. Chem. Soc.*, 17 (1953)). Crystal structure information on the halodurenes would also be desirable. We are grateful to Professor C. A. Coulson of the University of Oxford for clarifying discussion on the subject.

[19] A. F. Holleman, *Chem. Revs.*, **1**, 187 (1924).

[20] N. Ivanoff and M. Magat, *J. chim. phys.*, **47**, 914 (1950).

bromination of a halobenzene (*para/meta*) is related to the $k/k_0$ values by the simple equation

$$\frac{para}{meta} = \frac{(k/k_0)_p}{2(k/k_0)_m}$$

for, by definition of partial rate factors,[21] we may put $para/meta = f_p/2f_m$.

In estimating the *para/meta* ratios as $(k/k_0)_p$ values, we have directly used the data corresponding to the halodurenes, whereas the $(k/k_0)_m$ values were obtained by averaging the data reported for each halogen in the series I and II (Table I). The ratios thus calculated are as follows: Ph–F, 2230; Ph–Cl, 128; Ph–Br, 58; Ph–I, 18.

**Free Energy Relationships.**—The application of the Hammett equation to nuclear substitution has been discussed by several authors.[7,22,23,24] Side-chain σ-constants have been found unsuitable to yield linear free energy relationships with reactivities at *para* positions. A quantitative treatment of isomer distribution based on an extension of the Hammett equation has been given recently by Brown and his co-workers.[25] Lately Brown and Okamoto have developed a new set of substituent constants ($\sigma^+$) for use with electrophilic reactions.[26] It was of interest to examine the extent of agreement between the present data and these values. The result is shown in Fig. 2. We note at once that the general agreement is quite satisfactory and that the points showing significant deviations are the ones corresponding to iodonaphthalene and iodoisodurene (see preceding qualitative discussion). Also, the linearity of the plot can be considered as a mutual test for the new $\sigma_p^+$-constants and the validity of the present structural approach to the determination of reactivities *meta* and *para* to halogens in bromination by molecular bromine. From the slope of the line we have estimated a value of −8.64 for the ρ-constant of this reaction. Work is in progress in this Laboratory to extend the present study to other substituents.

## Experimental

**Purification of Nitromethane for Bromination Studies.**—The simple purification procedure reported previously[15] cannot be generally applied, as some commercial samples of nitromethane contain bromine-consuming impurities which could not be removed by fractionation alone. We have found that phosphorus pentoxide acts as a very effective reagent in removing this kind of impurities and have used a procedure similar to the one described by Evans, *et al.*[27] A commercial sample of nitromethane was first dried over calcium chloride and then treated with 60 g. of phosphorus pentoxide per kilogram of solvent. After one-day standing, the liquid was decanted, distilled twice at reduced pressure (20 mm.) and fractionated twice at atmospheric pressure in a 40-cm. long Fenske column. The fraction boiling at

TABLE II

PREPARATION AND PHYSICAL PROPERTIES OF THE TRIMETHYL AND TETRAMETHYLBENZENE COMPOUNDS EXAMINED IN THE PRESENT WORK

| Compound | B.p., °C.[a] | $n_D$[b] | M.p., °C.[c] |
|---|---|---|---|
| Mesitylene[d] | 164.5–164.8 (atm.) | 1.5005 (16) | |
| 2-Fluoromesitylene[e] | 164.8–165.1 (atm.) | 1.4861 (15) | |
| 2-Chloromesitylene[f] | 86.0–86.8 (∼14) | 1.5282 (15.5) | |
| 2-Bromomesitylene[g] | 47.0 (∼0.5) | 1.5520 (20) | |
| 2-Iodomesitylene[h] | | | 30.5–31 |
| Isodurene[i] | 81.0 (∼12) | 1.5131 (20) | |
| 4-Fluoroisodurene[j] | 87–88 (∼17) | 1.4951 (22.5) | |
| 4-Chloroisodurene[k] | 108.5–108.9 (∼12) | 1.5411 (20.5) | |
| 4-Bromoisodurene[l] | 125.7–126.1 (∼13) | 1.5639 (20) | |
| 4-Iodoisodurene[m] | 81.5–82.0 (∼0.5) | 1.6029 (21.2) | |
| Durene[n] | | | 79.5–80.3 |
| 3-Fluorodurene[o] | | | 54.5–55.0 |
| 3-Chlorodurene[p] | | | 45.5–46.1 |
| 3-Bromodurene[q] | | | 59.7–60.5 |
| 3-Iododurene[r] | | | 78.5–79.5 |

[a] The pressure (mm.) is given in parentheses. [b] The temperature (°C.) is given in parentheses. [c] All m.p.'s uncorrected. [d] Eastman Kodak reagent grade, redistilled. [e] See F. Brown, J. M. A. de Bruyne and P. Gross, THIS JOURNAL, **56**, 1291 (1934), and refs. therefrom. [f] Obtained by adding chlorine to mesitylene in acetic acid solution at 10° and keeping the reaction mixture at room temperature for six days in the dark. The crude yield was 83%; the oil was refractionated twice at reduced pressure. [g] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 95; refractionated twice at reduced pressure. [h] A. Klages and C. Liecke, *J. prakt. Chem.*, [2] **61**, 307 (1900); distilled once and recrystallized twice from 95% ethanol. [i] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 360; refractionated twice at reduced pressure. [j] G. Grassini, G. Illuminati and G. Marino, *Gazz. chim. ital.*, in press (1956). [k] Obtained by slowly adding chlorine to isodurene in acetic acid solution at 10° in the presence of a crystal of iodine and keeping the reaction mixture at room temperature for 45 minutes. The crude yield was 93%; the oil was fractionated at reduced pressure and the fraction with a refractive index of *ca.* 1.5440 (12.5°) was shaken with a small amount of finely powdered sodium thiosulfate and finally refractionated to give a colorless product. [l] L. I. Smith and C. L. Moyle, THIS JOURNAL, **55**, 1676 (1933). The crude product was fractionated at reduced pressure; the fraction with a refractive index in the range 1.5625–1.5641 (20°) was shaken with small amounts of finely powdered calcium carbonate and sodium thiosulfate and finally refractionated to give a colorless product. [m] Not recorded in the literature. Prepared in essential accordance with the method of Klages and Liecke (see note *h*). The crude product was fractionated at reduced pressure; the fraction with a refractive index of *ca.* 1.6020 (18°) was decolorized as described in note *l* but on refractionation it failed to give a colorless distillate. The latter was freed from the traces of iodine by extraction with a sodium thiosulfate solution. *Anal.* Calcd. for $C_{10}H_{13}I$: C, 46.17; H, 5.04. Found: C, 46.53; H, 5.29. Successive purifications by the same procedure gave the same kinetic results. [n] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 248. Recrystallized three times from 95% ethanol. [o] See note *j*. [p] A. Tohl, *Ber.*, **25**, 1521 (1892). The crude product was first steam distilled and then freed from durene by distilling off the unreacted hydrocarbon at atmospheric pressure. The residue from the distillation was treated with charcoal in methanol solution and recrystallized. [q] See ref. 15. [r] Prepared according to the iodination method of Klages and Liecke, note *h*. Recrystallized twice from 95% ethanol.

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(21) C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2918 (1927); C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *ibid.*, 1959 (1931).

(22) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 198.

(23) D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952).

(24) F. E. Condon, THIS JOURNAL, **74**, 2528 (1952).

(25) C. W. McGary, Y. Okamoto and H. C. Brown, *ibid.*, **77**, 3037 (1955).

(26) Private communication from Professor Herbert C. Brown of Purdue University. The $\sigma_p^+$-values for halogens are as follows: F, −0.0714; Cl, 0.112; Br, 0.148; I, 0.132. The $\sigma_m^+$-values were found nearly identical with Hammett's σ-values and it was suggested to use the latter. The $\sigma^+$-values are based on the solvolysis of substituted phenyldimethylcarbinyl chlorides and the experimental work related to such determinations will be published soon. We gratefully acknowledge Prof. Brown's kindness for giving permission to include the above unpublished values in the present paper.

(27) A. G. Evans, J. A. G. Jones and G. O. Osborne, *Trans. Faraday Soc.*, **50**, 16 (1954).

101.2–101.9° from the first fractionation was refractionated under a reflux ratio of *ca.* 10 to give a median fraction, b.p. 101.6–101.8° (763 mm.), $n^{20}\text{D}$ 1.3819, which was used for the kinetic measurements. Starting from samples of three different firms, the average yield was 400 g. per kilogram of the commercial solvent.

**Trimethyl and Tetramethylbenzene Compounds and Other Materials.**—The synthetic procedures and the relevant physical properties of the aromatic compounds examined in the present work are reported in Table II. Merck Co. (Darmstadt) bromine was used as such. C. Erba (Milan) glacial acetic acid for freezing point measurements was fractionated once and the median fraction used for the kinetic experiments. This fraction gave a negative test for bromine absorption.[28] The test was carried out by using a bromine solution in acetic acid prepared according to Orton and Bradfield.[29]

**Kinetic Measurements.**—The kinetic experiments were carried out at 30° with 22-ml. samples of solutions either 0.01 or 0.02 *M* with respect to both the aromatic compound and bromine. Kinetic solutions in nitromethane, acetic acid and mixed solvents were made up by mixing calculated volumes of approximately 0.1 *M* stock solutions of the reactants in either nitromethane or acetic acid with complementary amounts of either solvent or both. In the mixed solvent experiments no appreciable volume change was observed on mixing the two solvents. The exact concentration of the stock solution of bromine was determined by iodometric titration with a 0.02 *N* solution of sodium thiosulfate just before each experiment. The general procedure used was as follows. The solution of the aromatic compound and the solvents were placed in a straight-wall beaker of 105-mm. height and 30-mm. width and immersed in a thermostat regulated to within 0.05°. After ten minutes, the bromine solution was added under efficient mechanical stirring; the end of the addition was taken as the zero time of the reaction. The first 2-ml. sample for the analysis was withdrawn soon afterward. The remaining solution was then rapidly transferred into a thermostated 20-ml. storage flask and five successive 2-ml. withdrawals were evenly spaced in a suitable time interval corresponding to 15–20% of reaction. The storage flask was cylindrical-shaped, dark-colored and provided with a special glass stopper made in such a way as to occupy most of the free space in the relatively long neck.

TABLE III

TYPICAL KINETIC BROMINATION DATA AT 30.0°

| Compounds and conditions | Time, min. | $Na_2S_2O_3$, ml. | Reaction, % |
|---|---|---|---|
| 4-Fluoroisodurene | 0 | (4.01)[a] | 0 |
| (in nitromethane, 0.01 *M* | 1.13 | 3.98 | 0.75 |
| soln. in both reactants)[b] | 11.08 | 3.70 | 7.73 |
| | (14.3)[a] | (3.61)[a] | 10 |
| | 15.32 | 3.59 | 10.48 |
| | 20.38 | 3.46 | 13.72 |
| | 25.12 | 3.32 | 17.21 |
| | 30.10 | 3.21 | 19.95 |
| 3-Fluorodurene | 0 | (7.66)[a] | 0 |
| (in acetic acid, 0.02 *M* | 1.0 | 7.63 | 0.39 |
| soln. in both reactants)[c] | 11.1 | 7.40 | 3.39 |
| | 21.7 | 7.15 | 6.66 |
| | 32.5 | 6.925 | 9.59 |
| | (34.0)[a] | (6.89)[a] | 10 |
| | 45.2 | 6.65 | 13.19 |
| | 58.9 | 6.37 | 16.84 |
| 3-Chlorodurene | 0 | (4.31)[a] | 0 |
| (in mixed solvents, 1:1 in | 1.1 | 4.31 | 0 |
| vol.; 0.01 *M* soln. in both | 26.0 | 4.14 | 3.94 |
| reactants)[d] | 49.4 | 4.01 | 6.96 |
| | 73.9 | 3.89 | 9.74 |
| | (77.0)[a] | (3.88)[a] | 10 |
| | 100.2 | 3.78 | 12.30 |
| | 125.0 | 3.65 | 15.32 |

[a] The values in parentheses are based on graphic evaluation. [b] Kinetic soln. (22 ml.) made up as follows: fluoroisodurene, 0.06344 *M* stock soln., 3.47 ml.; solvent, 16.67 ml.; bromine, 0.1184 *M* stock soln., 1.86 ml. [c] Kinetic soln. (22 ml.) made up as follows: fluorodurene, 0.10847 *M* stock soln., 4.06 ml.; solvent, 13.92 ml.; bromine, 0.1095 *M* stock soln., 4.02 ml. [d] Kinetic soln. (22 ml.) made up as follows: chlorodurene, 0.09659 *M* stock soln. in nitromethane, 2.28 ml.; nitromethane, 8.72 ml.; acetic acid, 9.31 ml.; bromine, 0.1298 *M* stock soln. in acetic acid, 1.69 ml.

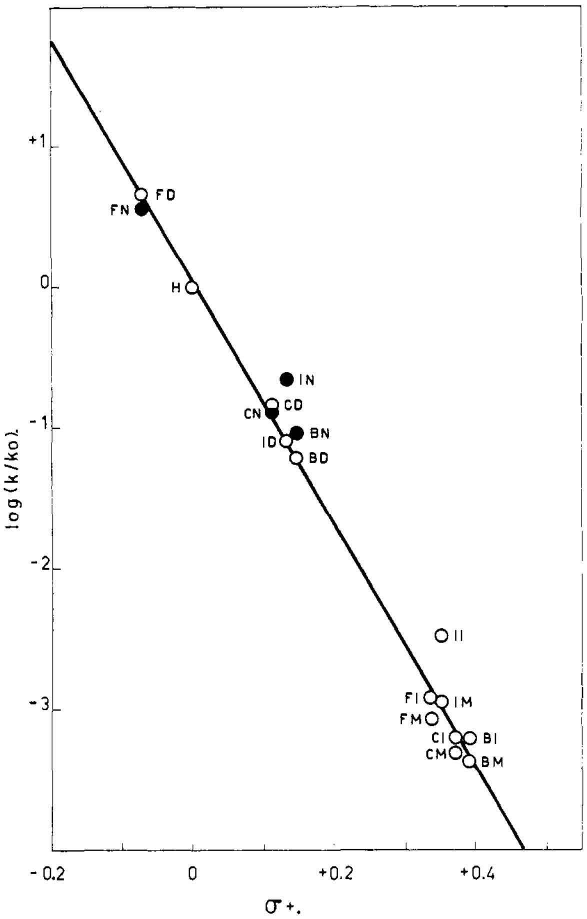

Fig. 2.—Relationship between log $(k/k_0)$ and nuclear substitution constants $(\sigma^+)$ for bromination by molecular bromine. FM, CM, BM, IM; FI, CI, BI, II; FD, CD, BD, ID; FN, CN, BN, IN: fluoro, chloro, bromo, iodo substituted mesitylenes, isodurenes, durenes and naphthalenes, respectively; white circles, this work.

The kinetic experiments were conducted in a dark room; red light was used in each experiment starting from the addition of bromine (zero time) up to the last sample withdrawal.

As to the analytical procedure, the reaction in the sample withdrawn from time to time was quenched by pouring the sample into 5 ml. of a solution of potassium iodide in 70% aqueous alcohol. The iodine thus set free was titrated with an approximately 0.01 *N* solution of sodium thiosulfate; the starch solution was added after dilution of the titration mixture with a sufficient excess of water. Typical runs are reported in Table III. The titer at 0% of reaction and the time of 10% of reaction $(t_{10})$ were evaluated graphically. Each experiment was repeated from four to six times and independently carried out by either investigator. A total of 120 runs was involved in the averaged values herein reported; the mean deviation of the $t_{10}$ values for each compound was in the average ±3.8%.

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(28) K. J. P. Orton, M. G. Edwards and H. King, *J. Chem. Soc.*, 1178 (1911).

(29) K. J. P. Orton and A. E. Bradfield, *ibid.*, 983 (1927).

The reaction orders were obtained from the $t_{10}$ values corresponding to reactions in solutions 0.01 $M$ (Table I) and 0.02 $M$ in both reactants. In the latter concentrations the $t_{10}$ values for bromodurene and chloromesitylene in nitromethane and for fluorodurene in acetic acid were found to be 8.6, 12.0 and 35.0 minutes, respectively.

The over-all acceleration of bromination in going from acetic acid to nitromethane solutions was obtained on multiplication of the acceleration observed with durene from acetic acid to mixed solvent solutions by the acceleration observed with a number of compounds from mixed solvent to nitromethane solutions. From the mean values of $t_{10}$ reported in Table I, the former acceleration is given by the ratio 339/5.47, whereas the latter acceleration is given by the ratio 150/28.3 as obtained from fluoromesitylene and by any similar ratio obtained from other compounds, such as chloromesitylene, chlorodurene and bromodurene. For the over-all acceleration a mean value of 331 ± 5 was obtained.

**Extent of Side-chain Bromination.**—Dark bromination in a polar solvent of alkylated aromatic compounds is expected to occur at the ring carbon atoms. In order to ascertain this point we have carried out side-chain bromination tests for a number of the compounds examined in this work under conditions essentially similar to the kinetic experiments. In all cases we found that the extent of side-chain substitution is so small that it affects over-all rates but negligibly. A side-chain bromination test for mesitylene in acetic acid solution has been recently reported by Keefer, *et al.*[16] By adopting such a test for isodurene, the extent of side-chain reaction was found to be 0.33%. In the case of the brominations carried out in nitromethane solution, we have worked out the following modified procedure. A solution (20 ml.) approximately 0.1 $M$ with respect to the aromatic compound and 0.05 $M$ with respect to bromine, was allowed to stand in the dark for ten days. After withdrawing a 1-ml. sample for the determination of the unreacted bromine, to the remaining solution aqueous potassium iodide and sodium thiosulfate were successively added under vigorous shaking. After addition of ether, the mixture was transferred into a separatory funnel and the organic layer thoroughly washed with distilled water to eliminate all halide ions. Then the ether was removed and the remaining liquid was treated with an excess of alcoholic silver nitrate solution and the bromide ion thus set free was determined gravimetrically. The extent of the total bromination was 72 to 87% depending on the aromatic compound used. In the case of bromomesitylene, fluoromesitylene, chloroisodurene and iododurene the extent of side-chain bromination was found to be 1.3, 0.3, 0.57 and 0.31%, respectively.

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ROME, ITALY

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[CONTRIBUTION FROM THE ROHM AND HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION]

# *aci*-Nitroalkanes. I. The Mechanism of the ter Meer Reaction[1]

BY M. FREDERICK HAWTHORNE

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The reaction of 1-chloronitroethane with nitrite ion to produce 1,1-dinitroethane (ter Meer reaction) has been found to proceed through the isomerization of the chloronitroethane to its *aci*-isomeride followed by a bond-making type of nucleophilic displacement of halogen by nitrite ion. This conclusion is based on the facts: (1) The reaction may be inhibited by the addition of excess strong base, (2) the reaction displays a first-order dependence on both nitrite ion and chloronitroethane at high nitrite ion concentrations and that under these conditions the rate-determining process is the nitrite ion (general base) catalyzed ionization of the chloronitroethane and (3) the substitution of deuterium for protium alpha to the chloro and nitro substituents produces a primary kinetic isotope effect of approximately 3.3 when the reactions are compared at high nitrite ion concentrations. It is suggested that the formation of *sym*-dialkyl dinitroethenes from 1-halonitroalkanes in basic solution and the solvolysis of 1-chloronitroethane proceed by similar mechanisms.

It is the purpose of this paper to prove that the *aci*-isomerides of 1-halo-1-nitroalkanes are reactive substrates in nucleophilic displacement reactions and that these displacement reactions furnish an explanation for certain syntheses and kinetic measurements which have been reported heretofore. As a model reaction, the synthesis of 1,1-dinitroethane from 1-chloronitroethane and nitrite ion in basic solution[2] has been chosen for kinetic study using the model compound 1-chloronitroethane in 50% (volume) aqueous ethanol at 29.8°.

## Results

In order to examine the kinetics of the ter Meer reaction using 1-chloronitroethane an analytical method for the determination of 1,1-dinitroethane was required as well as a method for the rapid quenching of the reaction mixtures. Spectrophotometric examination of solutions of 1,1-dinitroethane in approximately 0.10 $N$ sodium hydroxide (in 50% by volume aqueous ethanol) proved that the 1,1-dinitroethane anion was produced quantitatively, obeyed Beer's law at the 380 m$\mu$ maximum ($\epsilon$ 1.6 × $10^4$) and was stable under these conditions for reasonable periods of time.

Similarly, it was found that the anion of 1-chloronitroethane was produced quantitatively and at an immeasurably rapid rate when a few milligrams of the chloronitroalkane was added to a large excess of this basic solution. The ultraviolet absorption spectrum of this anion exhibited a well defined peak at 237 m$\mu$ ($\epsilon$ = 1.00 × $10^4$) which remained unchanged for at least one hour. Table I records the stability of 1-chloronitroethane dissolved in an excess of dilute ethanolic base at 30° in terms of the amount of chloride ion liberated by hydrolysis.

TABLE I

THE EXTENT OF DECOMPOSITION OF 1-CHLORONITROETHANE IN THE PRESENCE OF EXCESS HYDROXIDE ION IN 50% (VOLUME) AQUEOUS ETHANOL AT 30°

| Initial concentration, moles/l. | | | | |
|---|---|---|---|---|
| 1-Chloro-1-nitroethane | Hydroxide ion | Elapsed time, hours | Final chloride ion concn., mole/liter | Reaction, % |
| 0.0749 | 0.0949 | 17.0 | 0.0045 | 6.0 |
| .0402 | .0949 | 16.5 | .0021 | 5.2 |

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(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) E. ter Meer, *Ann.*, **181**, 4 (1876).