with solvent proceeded at approximately one-fifth the rate of the reaction with the aromatic. The data were corrected for this side-reaction. In all other cases the solvent reaction was negligible.

Isomer Distribution in the Bromination of Toluene.—A. To one liter of 85% acetic acid containing 82.9 g. (0.90 mole) of toluene was added 14.9 g. (0.093 mole) of bromine in one liter of the same solvent. The reaction was allowed to proceed in the dark for 13 hr. at 25.0 ± 0.5°. Analysis indicated that the reaction had proceeded to 39% completion, equivalent to 6.2 g. of bromotoluenes. The reaction mixture was quenched by adding aqueous sodium borohydride, and the organic materials were extracted with carbon disulfide. The extracts were subsequently combined and dried over calcium sulfate and calcium hydride. The carbon disulfide was removed by careful fractionation and triglyme (triethylene glycol dimethyl ether) was added as a chaser. The fraction (b.p. 130–205° (753 mm.)) was taken up in carbon disulfide, washed with water to remove triglyme, dried over calcium hydride, and the resulting solution used for infrared analysis.

B. A duplicate preparation was carried out to 42% completion and the distillation was carried out to include a small quantity of toluene (b.p. 112–212° (746 mm.)).

C. A synthetic mixture was prepared by dissolving 80.0 g. (0.88 mole) of toluene, 5.02 g. (29.3 mmoles) of *p*-, 2.21 g. (12.9 mmoles) of *o*-, and 0.080 g. (0.47 mmole) of *m*-bromotoluene in 2 l. of acetic acid. To this solution were added in rapid succession 14.0 g. (87.5 mmole) of bromine and 300 ml. of 1% aqueous sodium borohydride. The product was isolated as above.

The solutions were analyzed for the three isomeric bromotoluenes by utilizing the characteristic frequencies of 13.5 μ for *o*-, 13.1 μ for *m*-, and 12.5 μ for *p*-. Preliminary experiments with synthetic mixtures indicated that in order to determine the three components in the range of their expected concentrations, the analysis would have to be made in two parts, by different procedures. The analysis for *o*- and *p*- would utilize relatively dilute solutions (0.2 *M*) while the *m*-bromotoluene would be determined in a more concentrated solution (2 *M*).

Weighed samples of the carbon disulfide solutions (A, B and C above) were diluted with carbon disulfide to give solutions approximately 0.2 *M* in bromotoluenes. No absorption was noted at 13.1 μ for *m*- in solutions A and B, and only slight absorption in C (synthetic composition, 30.3% *o*-, 1.1% *m*-, 68.6% *p*-). The spectra were analyzed by the base line technique:

A. Found: 32.8% *o*-, 67.2% *p*-, 67.2% recovery.
B. Found: 33.2% *o*-, 66.8% *p*-, 75.5% recovery.
C. Found: 31.6% *o*-, 0.4% *m*-, 68.0% *p*-, 80.3% recov.

To determine the *meta* content of solutions A and B, the products were diluted with carbon disulfide to give solutions 2.0 *M* in bromotoluene. A series of standard solutions were prepared, 2 *M* in total bromotoluene with the *p*- to *o*-ratio maintained at 2.1. In these solutions, the *meta* isomer concentration was varied systematically from 0.005 to 0.017 *M*. These solutions gave a sharp absorption at 13.1 μ, in spite of the strong absorption of the high concentrations of the *o*- and *p*-isomers at 13.5 and 12.5 μ. Direct comparison of the spectra from solutions A and B with the spectra from these standard solutions indicated a *meta* content of 0.24% for A and 0.32% for B. These values were normalized with the *o*- and *p*-values and the results are listed in Table III. From the results with numerous test analyses, we believe that the *o*- and *p*-values are accurate to better than ±1.5% of the reported figures and the *m*-value to within ±0.1%.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

Kinetics of Aromatic Halogenation. IV. The Bromination of Naphthalene in 50% Aqueous Acetic Acid[1]

BY ERNST BERLINER AND MARJORIE C. BECKETT

RECEIVED SEPTEMBER 28, 1956

The bromination of naphthalene by bromine has been studied in 50% by volume aqueous acetic acid in an excess of bromide ion. Unlike in glacial acetic acid, the reaction under these conditions is second-order over-all, first-order in each reactant. The results of the kinetic study are in agreement with a mechanism involving a reaction between free molecular bromine and naphthalene. A very small amount of bromination by the tribromide ion is not excluded.

Aromatic bromination in glacial acetic acid is characterized by two features which complicate its kinetics. According to the extensive work of Robertson and his students,[2] bromination is usually of second and sometimes of third order with regard to bromine, so that the over-all reaction may be third or fourth order. In addition, since bromide ion is formed during the reaction, some of the bromine is continuously removed from the reaction as tribromide ion or HBr_3, which have either no, or only very weak, brominating properties. High-order bromination has also been observed in other solvents of low dielectric constant, such as 75% and 90% aqueous acetic acid,[3,4] carbon tetrachloride,[5] chlorobenzene,[4] methanol[2b] or benzene.[6] Following Robertson,[7] it is customary to regard bromination as a composite reaction of the type

$$-dx/dt = k_1(\mathrm{ArH})(\mathrm{Br_2}) + k_2(\mathrm{ArH})(\mathrm{Br_2})^2 + k_3(\mathrm{ArH})(\mathrm{Br_2})^3 \quad (1)$$

where the exact form of the rate equation and the relative importance of each term depend on various circumstances, such as the medium and the nature and concentration of the reactants.[2]

---

(1) Taken from a dissertation submitted by Miss M. C. Beckett to the Graduate School of Bryn Mawr College in partial fulfillment of the requirements for the Ph.D. degree, June, 1956. Presented in part before the Symposium on Aromatic Substitution at the 130th Meeting of the American Chemical Society in Atlantic City, N. J., September, 1956.

(2) (a) P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, *J. Chem. Soc.*, 276 (1943); (b) P. W. Robertson and P. B. D. de la Mare, *ibid.*, 100 (1948); P. W. Robertson, *Science Progress*, **171,** 418 (1955).

(3) A. E. Bradfield, G. I. Davies and E. Long, *J. Chem. Soc.*, 1389 (1949).

(4) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **78**, 3637 (1956).

(5) P. W. Robertson, J. E. Allan, K. N. Haldane and M. G. Simmers, *J. Chem. Soc.*, 933 (1949); J. H. Blake and R. M. Keefer, THIS JOURNAL, **77**, 3707 (1955); C. C. Price and C. E. Arntzen, *ibid.*, **60**, 2835 (1938). Also see R. A. Benkeser and A. Torkelson, *ibid.*, **76**, 1252 (1954); T. Tsurata, K. Sasaki and J. Turukawa, *ibid.*, **76**, 994 (1954).

(6) L. Bruner, *Z. physik. Chem.*, **41**, 514 (1902); C. C. Price, THIS JOURNAL, **58**, 2101 (1936).

(7) B. E. Swedlund and P. W. Robertson, *J. Chem. Soc.*, 630 (1947).

It is probably partly because of the kinetic complexities that bromination has been used less extensively in the study of aromatic substitution characteristics than nitration, and in those studies in which substituent effects were investigated, rate constants were not determined, but time intervals at which a definite percentage of reaction had occurred were compared.[8] However, a separate evaluation of the first- and second-order (in bromine) rate constants has since been reported for bromination in 75% acetic acid[3] and, more recently, also in 90%[4] and glacial acetic acid.[9]

Because of the potential usefulness of molecular bromination in studies of aromatic reactivity, it seemed desirable to find conditions which would simplify the kinetics and which would define the substituting agent uniquely under those conditions. The results of Robertson's work give valuable information about the factors that reduce the kinetics to simpler orders, namely, the addition of water to the acetic acid, low concentration of reactants and higher temperatures.[2] For the present study, 50% (by volume) aqueous acetic acid was chosen as the solvent and naphthalene as the aromatic compound. Naphthalene was selected, not only for reasons of solubility and conveniently measurable rates, but also for purposes of comparison, since in glacial acetic acid it had been found to react by fourth-order kinetics, third order in bromine.[2b] Other bromination studies on this hydrocarbon were also available.[10] To avoid the disturbing feature of the conversion of bromine to tribromide ion, a large excess of bromide ion was employed, so that the bromide ions formed during substitution could be neglected. This avoids the use of a rather cumbersome integrated rate equation.[11]

Although the substituting agent for various aromatic compounds has been shown to be molecular bromine in glacial acetic acid,[12] 75% acetic acid[3] and in water,[13] it had to be re-established under the present set of conditions. In addition to bromine, such species as HOBr, CH_3COOBr, H_2OBr^+ or $CH_3COOHBr^+$ seem possible substituting agents, which might be formed from bromine and the solvent and which had to be considered.

Experimental

Materials.—All inorganic compounds were best Reagent Grade chemicals and were used without further purification. Sodium bromide and anhydrous sodium perchlorate were dried at 110° before use. A middle portion of purified[14] glacial acetic acid of b.p. 118.0 and m.p. 16.4° was used. The 50% acetic acid was prepared by mixing equal volumes of thermostated acetic acid and boiled-out distilled water. Fresh batches of the 50% acid were made frequently and the kinetic data were found to be entirely reproducible in each solvent preparation. A Reagent Grade sample of naphthalene was recrystallized three times from 95% ethanol. Further crystallization produced no change in the m.p. of 80.1–80.8°. This sample was used in all kinetic runs. A sample of naphthalene of known sulfur content (0.002% by weight) and of m.p. 80.5–80.8° after one crystallization from alcohol was found to give the same kinetic results as the former compound.[15]

Kinetic Determinations.—A stock solution (200 ml.) was prepared of bromine (0.1 *M*) and bromide (2 *M*), which could be diluted with a 2 *M* bromide solution to bromine solutions of desired strength. Stock solutions of all other reagents were similarly prepared. Because only about 0.24 g. of naphthalene could be dissolved in 100 ml. of the solvent, it was often necessary to prepare the naphthalene solutions with the solutions of the other reagents. At the beginning of a run, 10 ml. of the bromine–bromide solution was added from a fast draining pipet to 90 ml. of the naphthalene solution, contained in a brown 125-ml. glass-stoppered bottle, all thermostated, while the bottle was continuously swirled. The bottle was briefly shaken, and a 10-ml. sample was withdrawn. Zero time was noted when this sample was added to a 5% solution of KI. This operation never exceeded 45 sec. With very fast runs, the initial titer was determined by a blank. The liberated iodine was titrated with sodium thiosulfate from a 5-ml. microburet graduated in hundredths. A thiosulfate solution of desired strength was daily prepared from a 0.1 *N* stock solution. Usually eight further samples were withdrawn at appropriate time intervals, and rate constants were obtained from the integrated second-order rate equation. The average deviation within one run was rarely greater than 1%. All runs were conducted at least in duplicate, and if the average rates of two independent runs differed by more than 2%, the experiment was repeated. Blank solutions of various concentrations were used to check for any error resulting from the volatility of bromine, but it was found that the loss due to volatility was negligible. The last two points in a reaction were sometimes affected, owing to the increased volume of the vapor phase, which caused the rate to apparently increase, although never more than 2%. Although reaction was conducted in darkened bottles in a semi-darkened room, it was found that the reproducibility of the data was unaffected when the bottles were exposed to sunlight.

Product Isolation.—The conditions of a typical kinetic run were reproduced on a one-l. scale (naphthalene 0.0168 *M*, Br_2 0.0085 *M*, NaBr 0.2 *M*). After all the bromine had been used up, the solution was diluted with one l. of water and extracted repeatedly with petroleum ether. The petroleum ether extracts were washed twice with a 5% sodium carbonate solution, twice with water and then dried over sodium sulfate. The ethereal extracts from 10 independent runs were combined, the solvent evaporated and most of the excess naphthalene was removed by sublimation by passing a current of dry air through the warm mixture. The remaining brown oil (12.4 g., 70%) was twice vacuum-distilled to yield 9.1 g. (52%) of a straw-colored liquid, b.p. 110–113° at 5 mm. A tarry residue (1.4 g.), possibly disubstitution products,[16] remained after the first distillation; small amounts of naphthalene were obtained in the forerun. The picrate, crystallized from alcohol, melted at 133.1–133.8° and gave no depression of the m.p. when mixed with the picrate of an authentic sample of 1-bromonaphthalene of m.p. 133.0–133.8° (lit.[17] 134–135°). The product had d^{25}_4 1.4768 and $n^{26}\mathrm{D}$ 1.6543; for an authentic commercial sample of 1-bromonaphthalene these constants were 1.4775 and 1.6545 (lit.[17] 1.4785 and 1.6558). The product is therefore 1-bromonaphthalene. No other product was isolated, although it is likely that traces of 2-bromonaphthalene were also formed.[18]

---

(8) P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943); P. W. Robertson, P. B. D. de la Mare and B. E. Swedlund, *ibid.*, 782 (1953); E. Berliner and F. Berliner, THIS JOURNAL, **71**, 1195 (1949); G. Illuminati and G. Marino, *ibid.*, **78**, 4975 (1956).

(9) R. M. Keefer, A. Ottenberg and L. J. Andrews, *ibid.*, **78**, 255 (1956).

(10) F. L. J. Sixma and J. P. Wibaut, *Rec. trav. chim.*, **69**, 577 (1950); and previous papers; F. R. Mayo and W. B. Hardy, THIS JOURNAL, **74**, 911 (1952).

(11) A. E. Bradfield, B. Jones and K. J. P. Orton, *J. Chem. Soc.*, 2810 (1929).

(12) P. W. Robertson, *ibid.*, 1267 (1954).

(13) W. J. Wilson and F. G. Soper, *ibid.*, 3376 (1949); D. H. Derbyshire and W. A. Waters, *ibid.*, 564 (1950). See also E. Grovenstein and U. V. Henderson, THIS JOURNAL, **78**, 569 (1956), for bromination in 80% acetic acid.

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

(15) We are indebted for this sample to Mr. M. Winicov of the Barrett Division, Allied Chemical and Dye Corporation, Philadelphia, Penna.

(16) H. T. Clarke and M. R. Brethen, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 121.

(17) "Elsevier's Encyclopaedia of Organic Chemistry," Series III, Vol. XIIB, Elsevier Publishing Co., New York, N. Y., 1948.

(18) J. F. Suyver and J. P. Wibaut, *Rec. trav. chim.*, **64**, 65 (1945).

Determination of the Tribromide Equilibrium Constant in 50% Acetic Acid.—The determination was based on the method of Jones.[19] The equilibrium constant, K_1, for the dissociation of tribromide, is given by the equation $K_1 = c(b - a + c)/(a - c)$ moles/l., where c, a and b are the concentrations of free bromine, total bromine (*i.e.* free bromine plus tribromide) and bromide ion, respectively. In order to measure c, a fine stream of nitrogen gas, saturated with solvent vapor, was passed through a known volume (V, l.) of a solution of bromine in 50% acetic acid at the thermostated temperature of 24.9° at a constant flow rate (n moles per sec.) for a known time (t sec.). The vapors were then absorbed in a 5% KI solution, and iodometric analysis of this and the bromine solution at the conclusion of flow gave respectively the amounts of bromine abstracted (x moles) and the total residual bromine concentration ($a - x/V$ moles/l.). From Henry's law relating the partial pressure of bromine to the concentration of free bromine in solution, the expression may be derived

$$k_H/f_{Br_2} = \frac{76(nt + x)}{2.303PV \log c/(c - x/V)}$$

where k_H is Henry's law constant, f_{Br_2} is the bromine activity coefficient and P is the total constant pressure in cm. above the bromine solution initially at a concentration of c moles/l.

The full details of apparatus and technique, and all data, are contained in the Ph.D. thesis of M. C. Beckett, Bryn Mawr College.

The ratio k_H/f_{Br_2} was determined by repeated experiments in solutions of known bromine concentration, in the absence of added bromide, when c and a are synonymous. In Table I are recorded the values of this ratio obtained under three sets of conditions. Duplication of these experiments in solutions containing a known amount of total sodium bromide (b moles/l.) permitted the evaluation of c, by substituting the appropriate value for k_H/f_{Br_2}, assuming that the amount of bromine withdrawn is small enough that the equilibrium is not appreciably disturbed. In one typical experiment, using a freshly prepared solution of bromine in 50% acetic acid, 0.03712 M in total sodium bromide (b) and 0.4630 M in $NaClO_4$, the following data were recorded: $n = 2.512 \times 10^{-5}$ mole per sec., $t = 600$ sec., $P = 78.41$ cm., $V = 0.1$ l., $x = 1.2275 \times 10^{-4}$ mole, $k_H/f_{Br_2} = 3.02$ moles $l.^{-1}$ $atm.^{-1}$ (from Table I), from which c was calculated as 0.02578 mole of free bromine per liter. The total bromine content at the conclusion of flow ($a - (x/V)$) was 0.04735 mole/l. and a was therefore 0.04858 mole/l. Substitution for a, b and c gave K_1 as 0.0162 mole/l. The results are summarized in Table II for two solutions of ionic strength 0.5. It is noted that the value of K_1 is changed very little on replacing $NaClO_4$ by a mixture of $NaClO_4$ and NaAc.

TABLE I

HENRY'S LAW CONSTANT FOR BROMINE IN 50% ACETIC ACID AT 24.9°

$NaClO_4$, mole/l.	NaAc, mole/l.	k_H/f_{Br_2} mole/l.-atm.	No. of determns.
0.5	..	3.02 ± 0.03	12
0.2	0.3	3.22 ± .03	9
..	..	3.37 ± .02	11

TABLE II

THE TRIBROMIDE DISSOCIATION CONSTANT IN 50% ACETIC ACID AT 24.9°

$NaClO_4$, mole/l.	NaAc, mole/l.	NaBr, mole/l.	K_1, mole/l.	No. of determns.
0.5	..	0.02–0.07	0.0164 ± 0.0007	14
0.2	0.3	0.02–0.04	0.0168 ± 0.0003	6

Results and Discussion

TABLE III

THE BROMINATION OF NAPHTHALENE IN 50% AQUEOUS ACETIC ACID AT 24.9°

Naphthalene 0.01477 M, KBr 0.2 M, Br_2 0.001437 M			Naphthalene 0.01631 M, NaBr 0.2 M, $HClO_4$ 0.01 M, $NaClO_4$, 0.29 M, Br_2 0.004710 M		
Time, min.	0.009976 N thiosulfate, ml.	10^2k_2, l. $mole^{-1}$ $sec.^{-1}$	Time, min.	0.02050 N thiosulfate, ml.	10^2k_2, l. $mole^{-1}$ $sec.^{-1}$
..	2.880		..	4.595	
10	2.440	1.88	10	3.540	2.75
20	2.085	1.85	20	2.760	2.78
30	1.770	1.87	30	2.180	2.78
45	1.410	1.85	40	1.745	2.75
60	1.115	1.85	50	1.390	2.78
80	0.830	1.84	60	1.125	2.78
105	.560	1.85	70	0.905	2.80
130	.385	1.85	80	.730	2.80

TABLE IV

THE BROMINATION OF NAPHTHALENE IN 50% AQUEOUS ACETIC ACID AT VARIOUS INITIAL CONCENTRATIONS OF REACTANTS

KBr 0.20 M, T 24.9°

Naphthalene, moles/l. $\times 10^3$	Br_2, moles/l. $\times 10^3$	$k_2 \times 10^2$, l. $mole^{-1}$ $sec.^{-1}$	Naphthalene, moles/l. $\times 10^3$	Br_2, moles/l. $\times 10^3$	$k_2 \times 10^2$, l. $mole^{-1}$ $sec.^{-1}$
16.86	9.366	1.98	14.04	1.953	1.86
16.03	8.898	1.96	4.438	1.905	1.98
15.50	4.612	1.88	14.77	1.437	1.85
9.718	4.523	1.96	8.386	0.9476	1.95
16.03	4.360	1.88	9.986	.8953	1.93
9.722	2.147	1.88	9.444	.8928	1.93
16.85	2.060	1.85	16.49	.8255	1.87

The Rate Expression.—Under the conditions stated above, *i.e.*, in 50% aqueous acetic acid and in the presence of an excess of bromide ion, the reaction is strictly of the second order, as shown by two examples in Table III. The value of the rate constants, obtained from the integrated form of the second-order rate equation, is not changed when the initial concentration of naphthalene and bromine are varied by factors of 4 and 10, respectively, at a constant bromide ion concentration (Table IV). There is a slight increase in rate as the ratio of naphthalene to bromine decreases, which is probably due to a small amount of dibromination.[16] Reaction was usually followed from 10% to about 80% completion and, for these, and all other runs, a 20-fold excess of bromide ion was the smallest used. Unlike bromination in glacial acetic acid, the reaction in 50% aqueous acetic acid and in the presence of an excess of bromide ion is thus of the second order, first order in bromine and first order in naphthalene. The substituting agent is therefore an entity proportional to the first power of bromine, and the observed rate law can be expressed as

$$-dx/dt = k_2(\text{naphthalene})(Br_2)_t \qquad (2)$$

where $(Br_2)_t$ stands for total bromine concentration. In order to identify the substituting agent further, the reaction was studied over a 0.1 to 0.5 M range of bromide ion concentration; sodium perchlorate was used to keep the ionic strength constant (Table V). The addition of bromide ion retards the rate considerably, because of the instantaneous complexing of free bromine, $(Br_2)_f$, to form the tribromide ion according to (3)

$$Br_3^- \rightleftarrows (Br_2)_f + Br^- \qquad (3)$$

---

(19) W. J. Jones, *J. Chem. Soc.*, **99**, 392 (1911).

The total bromine concentration, $(Br_2)_t$, determined iodometrically, is rigorously expressed as the sum of the free and complexed bromine, as well as all other bromine containing species (4)

$$(Br_2)_t = (Br_2)_f + Br_3^- + HOBr + CH_3COOBr + H_2OBr^+ + CH_3COOHBr^+ \quad (4)$$

but the concentrations of the latter are undoubtedly so small that they can be neglected,[20] and the equation reduces to (5)

$$(Br_2)_t = (Br_2)_f + Br_3^- \quad (5)$$

Combining (3) and (5) gives the relationship between the total and the free bromine (6).

$$(Br_2)_f = \frac{K_1}{(K_1 + Br^-)}(Br_2)_t \quad (6)$$

where K_1 is the equilibrium constant for (3). As stated before, the initial bromide ion concentration was large enough compared to that formed during substitution that the term $K_1/(K_1 + Br^-)$ stayed virtually constant at any one bromide ion concentration. If the substituting agent is free molecular bromine, the rate expression becomes

$$-dx/dt = k(C_{10}H_8)(Br_2)_f = kK_1(C_{10}H_8)(Br_2)_t/(K_1 + Br^-) \quad (7)$$

and, comparing (2) and (7), k_2, the observed rate constant should be

$$k_2 = \frac{kK_1}{(K_1 + Br^-)} \quad (8)$$

where k is the specific rate constant for bromination by free bromine. Figure 1 shows a plot of the observed rate constants from Table V against $K_1/(K_1 + Br^-)$. The relationship expressed in (8) is in fact obtained, and the slope of the straight line, which is equal to the specific rate constant, k, has the value 0.341 ± 0.002 l.mole^{-1} sec.$^{-1}$.

The dependence of the rate on the bromide ion concentration establishes molecular bromine uniquely as the main substituting agent, because any of the other possible species mentioned above require an additional (Br^-) and, in some cases (H^+), term in the denominator of equation 8.

TABLE V

THE DEPENDENCE OF THE RATE ON THE BROMIDE ION CONCENTRATION

Naphthalene ≃ 0.016 M, Br_2 ≃ 0.005 M, T = 24.9°

NaBr, mole/l.	$NaClO_4$, mole/l.	10^2k_2, l. mole^{-1} sec.$^{-1}$
0.10	0.40	4.95
.15	.35	3.58
.20	.30	2.78
.25	.25	2.27
.30	.20	1.96
.40	.10	1.52
.50	..	1.21

According to equation 8, for exclusive bromination by free bromine, the straight line should go through the origin. Actually, it has an intercept of (1.7 ± 0.2) × 10^{-3}, which, although only about 0.5% of the slope, is experimentally real. The existence of an intercept, as well as the numerical value of the slope, depend to some extent on the exact value for K_1, the tribromide dissociation constant. This constant was first determined by an aspiration method at 18° by Jones,[19] who reported two determinations with the values 0.019 and 0.020 mole/l. Because of the difference in temperature and ionic strength in the present work, the dissociation constant was redetermined by the same method, and a value of 0.0164 ± 0.0007 mole/l. was found. This value was used in plotting Fig. 1. The use of Jones' value for K_1 results also in a straight line, which has the same intercept, although a somewhat different slope (0.283 ± 0.003 l.mole^{-1} sec.$^{-1}$). Moreover, it is possible to use equation 8 to calculate K_1, assuming the line to go through the origin. If it is rewritten in the form $1/k_2 = (Br^-)/kK_1 + 1/k$ and if $1/k_2$ is plotted against (Br^-), a straight line of slope 154.8 ± 0.7 sec. and intercept 4.8 ± 0.2 l.$^{-1}$ mole sec. is obtained from which the value for K_1 is calculated to be 0.031 mole/l. and k, 0.21 l.mole^{-1} sec.$^{-1}$. This value for K_1 is so much in disagreement with the literature value and the present one that the assumption that there is no intercept in (8) does not seem justified, and the intercept in Fig. 1 cannot be due to an incorrect value for K_1. It is therefore experimentally real and, if it is mechanistically significant, it represents bromination by the tribromide ion, or, less likely, by HBr_3. Tribromide ion would be expected on general chemical grounds to be a very much weaker brominating agent than bromine, and the rate constant for bromination by tribromide calculated from the intercept in Fig. 1 constitutes in fact only 0.5% of the rate constant for molecular bromination.[21] A small activity has been ascribed to tribromide in the electrophilic addition of bromine to stilbene.[22]

Effect of Ionic Strength.—In the range of sodium perchlorate concentration of 0.2–0.8 M, the rate increases with ionic strength in a virtually linear manner (Table VI, Fig. 2). Such linear dependence of the rate on ionic strength is not uncommon at high salt concentration, when at least one of the reactants is a neutral molecule.[23] Positive salt effects also have been noted in bromination in less aqueous solvents.[9,24] On the basis of the Brønsted theory no prediction can be made about the direction of the change when uncharged molecules react, but the observed increase is in accord with the Hughes–Ingold theory of solvent action for a reaction in which the transition state is more highly charged than the initial state.[25] This is the case

---

[20] H. A. Liebhafsky, THIS JOURNAL, **56**, 1500 (1934); **61**, 3513 (1939); R. P. Bell and E. Gelles, *J. Chem. Soc.*, 2734 (1951).

[21] It might be argued that if Br_3^- participates in the bromination, no linear relationship of the type 8 can hold, because a term $k'(Br^-)/(K_1 + Br^-)$ would have to be added. Actually, this term is not only very small under the present conditions but is practically independent of the bromide ion concentraton. At the extreme concentration of Br^- (0.1–0.5 M) it varies from (1.5–1.6) × 10^{-3}, a difference which is within the error calculated for the intercept.

[22] P. D. Bartlett and D. S. Tarbell, THIS JOURNAL, **58**, 466 (1936). Bromination by the tribromide ion also has been observed in the very fast bromination of substituted anilines. Private communication by Professor R. P. Bell.

[23] R. P. Bell, "Acid Base Catalysis," Oxford University Press, Oxford, 1941, pp. 32–34.

[24] P. W. Robertson, R. M. Dixon, W. G. M. Goodwin, I. R. McDonald and J. F. Scaife, *J. Chem. Soc.*, 294 (1949); see also H. G. Kuivila and E. K. Easterbrook, THIS JOURNAL, **73**, 4629 (1951).

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

TABLE VI

THE DEPENDENCE OF THE RATE ON THE IONIC STRENGTH

Naphthalene $\simeq$ 0.016 M, $Br_2 \simeq$ 0.005 M, NaBr = 0.20 M

$NaClO_4$, mole/l.	μ, mole/l.	10^2k_2, l. mole^{-1} sec.$^{-1}$
..	0.2	1.91
0.1	.3	2.20
.2	.4	2.48
.3	.5	2.78
.4	.6	3.06
.5	.7	3.37
.6	.8	3.64

here, where ions are formed from neutral molecules.

Effect of Acid and Base.—With molecular bromine as substituting agent, the reaction should not be catalyzed by acids or bases, at least insofar as the formation of the substituting agent is concerned. In accord with this, the data in Table VII show that up to 0.3 M perchloric acid concentration at a constant ionic strength the rate is practically unchanged. The slight increase, which is noticeable at a 0.6 M concentration, is ascribed to an activity effect, caused by changing the sodium for the hydrogen ion. If either hypobromous acid or acetyl hypobromite were substituting agents, an inverse proportionality of the hydrogen ion concentration would be required.

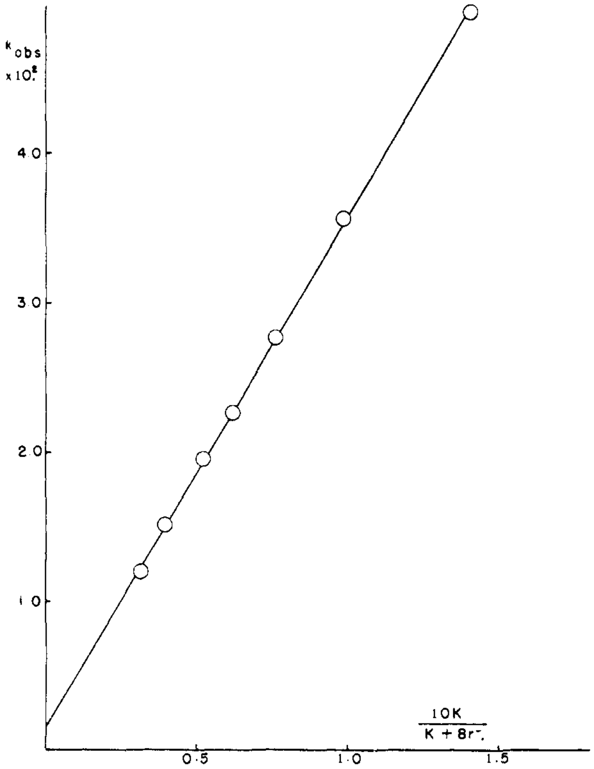

Fig. 1.—The dependence of the rate on the bromide ion concentration.

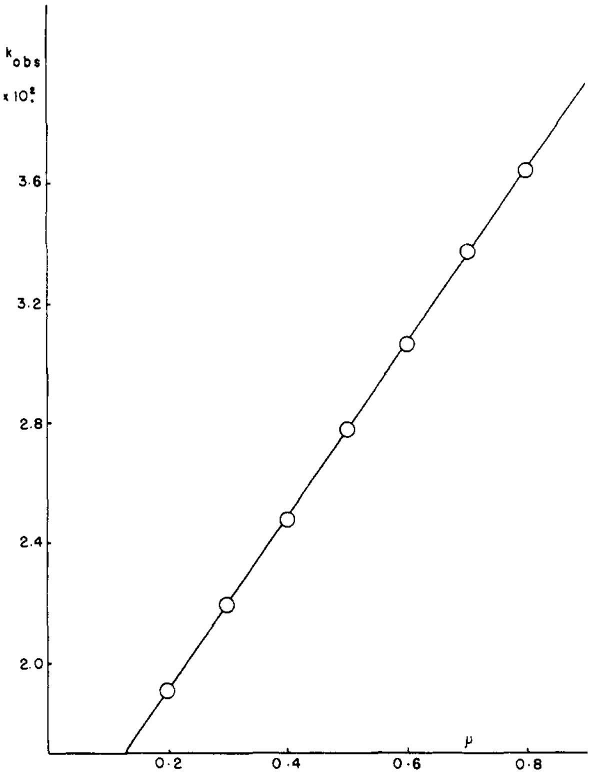

Fig. 2.—The dependence of the rate on the ionic strength.

The rate is slightly decreased by sodium acetate at a constant ionic strength, the change being somewhat more pronounced than with $HClO_4$. A comparable effect with sodium acetate has been observed in other cases.[9,24] This is not a secondary salt effect, because K_1 is practically the same in the presence (0.0168, mole/l.) and absence of sodium acetate (0.0164 mole/l.). Instead, it is more likely a primary salt effect, again because of the change produced when sodium acetate replaces sodium perchlorate, which was used to keep the ionic strength constant. Actually, both sodium acetate and sodium perchlorate increase the rate by a primary salt effect (bottom lines of Table VII), but the increase for sodium acetate is less than for sodium perchlorate. At the high salt concentrations used sodium acetate and sodium perchlorate would not be expected to have exactly the same effect on the activities of all species involved. Both the very slight effect of perchloric acid and the

TABLE VII

THE EFFECT OF PERCHLORIC ACID AND SODIUM ACETATE ON THE RATE OF BROMINATION AT 24.9°

Naphthalene $\simeq$ 0.016 M, $Br_2 \simeq$ 0.005 M, NaBr 0.20 M

$NaClO_4$, mole/l.	$HClO_4$, mole/l.	NaAc, mole/l.	10^2k_2, l. mole^{-1} sec.$^{-1}$
0.30	..	..	2.78
.29	0.01	..	2.78
.25	.05	..	2.79
.20	.10	..	2.81
.10	.20	..	2.82
..	.30	..	2.84_5
.60	..	..	3.64
..	.60	..	3.95
.20	..	0.10	2.52
.10	..	.20	2.30
..	..	.30	2.08
..	..	..	1.91
.30	..	..	2.78
..	..	.30	2.08

somewhat larger effect of sodium acetate are therefore best described as primary salt effects, rather than as indication of acid catalysis.

Effect of Temperature.—From a least square plot of the rate constants against $1/T$ at four different temperatures (Table VIII, Fig. 3), the experimental activation energy, entropy and log A were determined to be 16.8 ± 0.05 kcal., −12.1 e.u. and 10.59 ± 0.05. These are all composite values. If reference is made to the specific rate constant in (8) and the Arrhenius equation is rewritten in the form $\log k_2 = \log A/(K_1 + \text{Br}^-) + \Delta S/2.303R - (\Delta H + \Delta E)/2.303RT$, where ΔS and ΔH refer to the tribromide equilibrium, and if it is assumed that the data obtained from the measurements in water (ΔH 1.5 kcal., ΔS −0.35 e.u.)[26] will not be materially different in 50% acetic acid, the true activation energy is estimated as 15.3 kcal., the log A factor as 10.17 and the activation entropy as −14.0 e.u.[27] A decrease in activation entropy is expected in the present reaction, where ions are formed from neutral molecules, because of the "freezing" of solvent molecules in the polar transition state.[28]

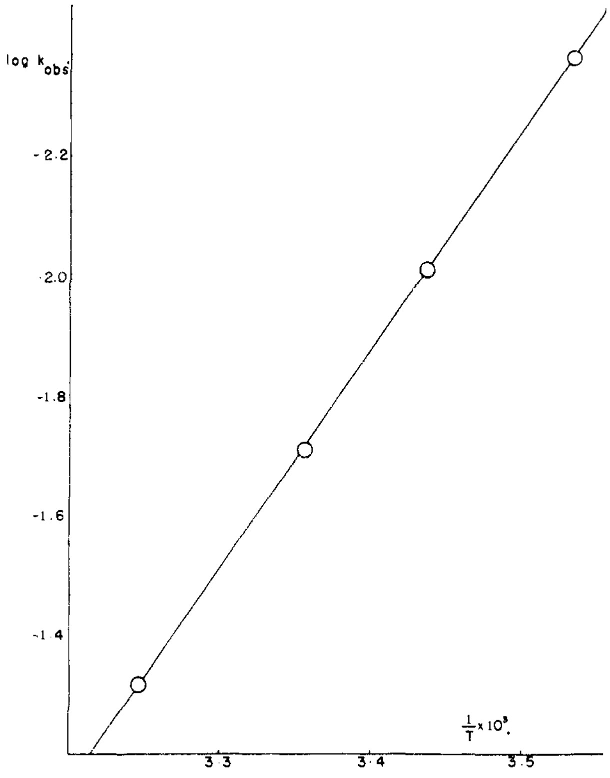

Fig. 3.—The dependence of the rate on the temperature.

TABLE VIII

THE EFFECT OF TEMPERATURE ON THE RATE OF BROMINATION

NaBr, 0.30 M; NaClO_4, 0.20 M

$C_{10}H_8 \times 10^3$, mole/l.	$Br_2 \times 10^3$, mole/l.	T, °C. ± 0.05	10^2k_2, l. mole^{-1} sec.$^{-1}$
10.59	4.142	10.00	0.435
14.61	4.762	17.90	.985
16.12	4.989	24.90[a]	1.96
16.51	4.772	34.95[a]	4.84

[a] With NaBr = 0.20 M, and no NaClO_4, $100k_2$ at 24.9 and 34.95° is 1.91 and 4.83_5, respectively, and ΔE and log A are 16.9 kcal. and 10.7.

The Mechanism.—Following the original suggestion of Robertson, it is generally agreed that high-order bromination in solvents of low dielectric constant is caused by a reaction between one molecule of bromine and an aromatic–bromine complex.[29] The additional bromine molecule is needed to break the halogen–halogen bond in the initially formed complex, and the whole process is written as (scheme A)

$\text{ArH} + \text{Br}_2 \rightleftarrows \text{ArH, Br}_2$ fast
$\text{ArH,Br}_2 + \text{Br}_2 \longrightarrow \text{ArHBr}^+ + \text{Br}_3^-$ slow scheme A
$\text{ArHBr}^+ \longrightarrow \text{ArBr} + \text{H}^+$ fast

Anything that will promote the anionization of bromine in the complex, thus replacing the bromine molecule in the second step of scheme A, will favor the first-order (in bromine) reaction. A 50% aqueous acetic acid solution with a fairly large bromide ion concentration provides these conditions, because the originally third-order (in bromine) bromination of naphthalene[2b] has been reduced to one of the first order. Neither 75% nor 90% acetic acid, in the bromination of phenol ethers[3] and methylbenzenes,[4] respectively, is sufficient to support anionization to a large extent, because both show composite orders with the second-order in bromine reaction predominating. But in 50% acetic acid phenol ethers are brominated by approximate second-order over-all kinetics in the presence of less excess of bromide ion than was used here, although the rate constants show a downward drift.[11] Also, the fourth-order over-all bromination of 1-chloronaphthalene is converted to a second-order reaction in 49% aqueous acetic acid at 52° without any added bromide.[2b] It is very likely that the large amount of water in the present reaction, rather than the bromide ions, are directly responsible for the change in order, but the latter may contribute to it by reducing the free bromine concentration and perhaps also by facilitating the formation of ions.

The present data make it inevitable that the reaction consists of an attack of one molecule of bromine on naphthalene and that the transition state is more polar than the initial state. Beyond that, one cannot distinguish between two equally plausible mechanisms. The simpler one leads to the intermediate in a straightforward bimolecular attack (scheme B)

$\text{ArH} + \text{Br}_2 \longrightarrow \text{ArHBr}^+ + \text{Br}^-$ slow scheme B
$\text{ArHBr}^+ \longrightarrow \text{ArBr} + \text{H}^+$ fast

As usual, the last step is not considered part of the rate-controlling step, assuming that the reaction,

---

[26] R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 101 (1932). Since K_1 is small compared to Br^-, the term $\log A/(K_1 + \text{Br}^-)$ was considered to be constant over the temperature range investigated.

[27] This does not take into account a possible lowering of ΔE or a change in ΔS^*, because of complexing between ArH and bromine; see, for instance, J. H. Blake and R. M. Keefer, ref. 5.

[28] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 122 ff.

[29] Ref. 2, 3, 4, 9; also, H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953); R. M. Keefer, J. H. Blake and L. J. Andrews, *ibid.*, **76**, 3062 (1954).

as iodine-catalyzed bromination of benzene, has no hydrogen isotope effect.[30] The lack of any appreciable basic catalysis by sodium acetate supports this view.[31] The other mechanism involves the preliminary formation of a complex, as in scheme A, with water acting as the electrophilic reagent in the second step instead of bromine (scheme A′)

$ArH + Br_2 \rightleftarrows ArH,Br_2$ fast scheme A′

$ArH,Br_2 + H_2O \longrightarrow ArHBr^+ + Br^-H_2O$ slow

$ArHBr^+ \longrightarrow ArBr + H^+$ fast

A third scheme (scheme C) permitted by the kinetic data is similar to scheme A′, except that the first step is slow and rate-controlling, and the second is fast. This scheme is less likely than the other two, because complex formation is usually considered to be instantaneous.

There is nothing in the present data that necessitates the postulation of a complex, as in scheme A′, but neither is there any evidence against it. The medium may be polar enough to allow a simultaneous attack of bromine and the breaking of the bromine–bromine bond. An argument in favor of an initially formed complex can be based on the reasoning that high-order bromination, according to the available evidence, most likely involves a complex, and that it is consistent to view the changes in order as a gradual process, in which the solvent or neutral salts[12,32] eventually can take the place of the second bromine molecule. The fact that the first- but not the second-order (in bromine) rate is reduced in deuterated acetic acid or 90% acetic acid[4] speaks for a fairly close participation of the solvent molecules in the transition state of the first-order reaction, although this in itself is no unique proof of the "complex" mechanism.

Acknowledgment.—The generous help afforded by a Frederick Gardner Cottrell Grant of the Research Corporation is gratefully acknowledged. We are also indebted to Professor P. W. Robertson and Dr. P. B. D. de la Mare for critically reading the manuscript and to Dr. G. Zimmerman for many helpful discussions.

---

[30] L. Melander, *Arkiv. Kemi*, **2**, 213 (1950).

[31] This observation corrects a previous statement by one of us (ref. 8, footnote 4). The increase in rate caused by NaAc in 85% acetic acid is probably a salt effect.

[32] See ref. 9, N. E. Brezhneva and S. Z. Roginsky, *Acta Physicochim. U.R.S.S.*, **12**, 209 (1940), and L. J. Andrews and R. M. Keefer, THIS JOURNAL, **78**, 4549 (1956), for the role of $ZnCl_2$, which may, however, also act by changing the nature of the substituting agent.

BRYN MAWR, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

The Reaction of Triphenylsilylpotassium with Organic Halides, a Case of Halogen–Metal Interconversion[1]

BY A. G. BROOK AND SAUL WOLFE[2]

RECEIVED AUGUST 16, 1956

Investigation of the products obtained from the reactions of triphenylsilylpotassium with a variety of organic halides indicates that as well as the normal coupling reaction, halogen–metal interconversion also occurs. The fate of the halogen–metal exchange products, whose presence in the reaction mixture was demonstrated indirectly by subsidiary experiments, depends on the order of addition of the reagents. These exchange products do not appear to contribute significantly to the over-all yield of coupling product.

Evidence for the participation of the halogen–metal interconversion reaction in the reaction of organosiliconmetallics with an organic halide has been reported recently.[3] Despite the frequent occurrence of this reaction in organic chemistry, this appears to be the only reported evidence for the occurrence of this reaction in organosilicon chemistry. Recent studies in this Laboratory on the coupling of triphenylsilylpotassium with a variety of organic halides has shown that these reactions are far from clean and the products formed seem to indicate that halogen–metal interconversion plays an important role.

Although triphenylsilylpotassium is a highly reactive organometallic reagent, the yield of coupled product from the reaction with organic halides, in our own work as well as that reported by others,[4] is surprisingly low, rarely exceeding 50%, although all the silylmetallic reagent appears to be consumed. It has generally been assumed that cleavage of the solvent, hydrolysis and incomplete formation of the silylmetallic from the starting material, hexaphenyldisilane, accounted for the fate of the remainder of the reagents and for the by-products isolated.

Since it was felt that halogen–metal exchange might account for some of the by-products isolated, we have reinvestigated the products formed between triphenylsilylpotassium and a variety of halides. In each case, unless otherwise mentioned, 0.038 mole of triphenylsilylpotassium in about 150 ml. of ether was allowed to react with 0.038 mole of halide, also in ether. The results with bromobenzene, which was most thoroughly studied, will be interpreted, and it will be shown that the other halides follow closely the same behavior.

Table I shows the products and yields obtained when triphenylsilylpotassium reacts with bromobenzene. As can be seen, except for the coupling product tetraphenylsilane, the nature and yields

---

[1] Presented in part at the 39th Conference of the Chemical Institute of Canada, Montreal, May, 1956.

[2] Dept. of Chemistry, University of Ottawa, Ontario. Holder of a Research Council of Ontario Scholarship, 1954–1955.

[3] A. G. Brook, H. Gilman and L. S. Miller, THIS JOURNAL, **75**, 4759 (1953).

[4] R. A. Benkeser and R. G. Severson, *ibid.*, **73**, 1424 (1951); R. A. Benkeser, H. Landesman and D. J. Foster, *ibid.*, **74**, 648 (1952); H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).