covered cyclohexanone, 6.8 g., 42%, of methyl ω-chlorohexanoate and 5.6 g. of non-distillable residue.

5-(Methoxycarbonyl)-pentyl with Methallyl Chloride and Cupric Sulfate.—The charge consisted of 19.6 g. of cyclohexanone, 11.5 g. of 30% hydrogen peroxide, 10 ml. of concd. sulfuric acid, 3 g. of cupric sulfate hydrate, 84 ml. of freshly redistilled methallyl chloride in 300 ml. of methanol and 41.7 g. of ferrous sulfate hydrate in 400 ml. of methanol. Methyl chlorodecenoate boiling at 146–151° (2 mm.) (n^{20}D 1.4698–1.4703) was obtained in 8.1 g. yield together with a mixture of methyl 5-hexenoate and methyl ω-methoxyhexanoate (3.0 g.) and 3.2 g. of high boiling residue.

Anal. Calcd. for $C_{11}H_{19}ClO_2$: C, 60.2; H, 8.7; Cl, 16.2; ester value, 0.456. Found: C, 59.7; H, 9.0; Cl, 17.2; ester value, 0.52.

Cyclohexanone–Hydrogen Peroxide with Butadiene in Acetic Acid.—The usual mixture of 19.6 g. of cyclohexanone and 11.5 g. of 30% hydrogen peroxide was stirred for 30 minutes and 300 ml. of acetic acid and 3 g. of cupric chloride were added. After stirring for 30 minutes at room temperature the reaction was cooled to 15°, 200 ml. of butadiene was added and the reaction cooled further to 0°. A solution of 20 g. of ferrous chloride in 200 ml. of acetic acid and 50 ml. of water was added. The mixture was added to excess water and extracted three times with chloroform. Distillation yielded, in addition to acetic acid and cyclohexanone, 8.0 g. of ω-chlorohexanoic acid, a 53% yield based on H_2O_2. The infrared spectrum matched that of an authentic sample.[4]

Cyclohexanone–Hydrogen Peroxide and Butadiene in *t*-Butyl Alcohol.—A charge of 40 g. of cyclohexanone and 24 g. of 30% hydrogen peroxide after stirring for 15 minutes was cooled to 5° and a chilled solution of 40 ml. of concd. sulfuric acid in 100 ml. of water was added. A mixture of 3 g. of cupric sulfate, 400 ml. of *t*-butyl alcohol and 340 ml. of butadiene was added at 0°. To the chilled solution was added dropwise a solution of 84 g. of ferrous sulfate hydrate in 125 ml. of water. A total of 500 ml. of gas was given off. The reaction was worked up in the usual manner to yield 50 g. of material after the chloroform was distilled off. Further distillation yielded 35 g. of cyclohexanone and 15 g. of non-distillable material. The infrared spectrum indicated it to be a carboxylic acid. However, attempts to distil the acid *in vacuo* (bath temp. 50–60°) led to its rapid decomposition with the evolution of heat. The material was not further characterized.

When the aqueous mother liquor was titrated for ferrous ion with a standard ceric sulfate solution, it was found that only 30% of the ferrous ion equivalent to the hydrogen peroxide was consumed. It is believed that the lability of the acidic products is due to unreacted peroxidic materials.

NOTE ADDED IN PROOF.—The addition of free radicals to conjugated olefins in the presence of copper salts has also been reported recently by Minisci, *et al.*, *Gazz. Chim. Ital.*, **91**, 1023, 1031 (1961).

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

The Bromination of Fluorene in Aqueous and Glacial Acetic Acid[1]

BY UN-JIN P. ZIMMERMAN[2] AND ERNST BERLINER[3]

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The bromination of fluorene by bromine in 75% aqueous acetic acid and in the presence of an excess of bromide ion has been found to have the same kinetic characteristics as the reaction in 50 and 60% aqueous acetic acid.[8,10] The reactions in glacial acetic acid, 90 and 75% aqueous acetic acid, without added bromide ion, are of an order higher than one in bromine. The separate second- and third-order rate constants in the two aqueous solvents have been evaluated, and the results are discussed in terms of the accepted bromination mechanism. In 75% acetic acid, fluorene is brominated to an extent of 97.0 ± 0.8% in the 2-position, as determined by the isotopic dilution method.

In glacial acetic acid and other solvents of low polarity the bromination of aromatic compounds is often of an order higher than one in bromine. According to the work of Robertson, de la Mare and their co-workers,[4] the reaction is best described as a composite one of the kinetic form

$$-\mathrm{d}x/\mathrm{d}t = k_2(\mathrm{ArH})(\mathrm{Br_2}) + k_3(\mathrm{ArH})(\mathrm{Br_2})^2 + k_4(\mathrm{ArH})(\mathrm{Br_2})^3 \quad (1)$$

where the contributions of each term to the total rate depend on various experimental factors. Later workers,[5] notably Keefer and Andrews,[6] have confirmed the presence of high-order terms and the general form of the rate equation, and the latter evaluated spectrophotometrically the separate constants k_2 and k_3 for bromination of various hydrocarbons in pure and in 90% aqueous acetic acid. Bradfield and co-workers[7] did the same for the reaction of phenol ethers in 75% acetic acid.

Following the observation of Robertson, *et al.*, that water and a low concentration of bromine favor low-order brominations, it was found that in 50% aqueous acetic acid, and in the presence of an excess of bromide ion, the bromination of naphthalene is strictly second order over-all, first order in each reactant.[8] The presence of bromide ion, in addition to reducing the free bromine concentration, also simplifies the kinetics, because the excess is much larger than the amount of bromide ion formed during reaction, and the latter can therefore be neglected. The occurrence of second-order kinetics under those conditions has since been confirmed for bromination of some other hydrocarbons and appears to be quite general.[9] It also holds for reaction in 60% aqueous acetic acid when bromide ion is present.[10]

It seemed of interest to find out whether in these latter reactions the increased water content, the bromide ions, or both, contribute to the lowering

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(1) Kinetics of Aromatic Halogenation. X.

(2) Taken from the Ph.D. thesis of Mrs. U. P. Zimmerman, Bryn Mawr College, June, 1961.

(3) To whom inquiries should be addressed.

(4) P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, *J. Chem. Soc.*, 276 (1943); P. B. D. de la Mare and P. W. Robertson, *ibid.*, 100 (1948); P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications, London, 1959, Chapter 9.

(5) G. Illuminati and G. Marino, *J. Am. Chem. Soc.*, **78**, 4975 (1956); S. F. Mason, *J. Chem. Soc.*, 4329 (1958); L. M. Yeddanapalli and N. S. Gnanapragasam, *J. Indian Chem. Soc.*, **36**, 745 (1959).

(6) R. M. Keefer, A. Ottenberg and L. J. Andrews, *J. Am. Chem. Soc.*, **78**, 255 (1956); R. M. Keefer and L. J. Andrews, *ibid.*, **78**, 3637 (1956).

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

(8) E. Berliner and M. C. Beckett, *J. Am. Chem. Soc.*, **79**, 1425 (1957).

(9) E. Berliner and J. C. Powers, *ibid.*, **83**, 905 (1961).

(10) E. Berliner and B. J. Landry, *J. Org. Chem.*, **27**, 1083 (1962).

of the reaction order. The reaction was therefore extended further to a less aqueous solvent, 75% (by volume) aqueous acetic acid, a solvent in which a compound of proper reactivity, fluorene, could be studied both in the presence and the absence of bromide ion. Because high-order bromination had never been demonstrated for fluorene, the reaction was also studied in 90% aqueous acetic and in glacial acetic acid, with no added bromide ion, with the intent of establishing, for a single compound, the reaction orders in these four different media, of defining the kinetic form and of determining the change in order with a change in bromine, bromide and water concentration. It was hoped to express these changes quantitatively in terms of the attendant changes in the individual rate constants.

Because of the interest in relative reactivities of polynuclear aromatic systems, the major product of bromination of fluorene was determined by the isotopic dilution method, and the partial rate factor for bromination was determined in conjunction with previous data.

Experimental

Materials.—All materials were best Reagent Grade chemicals; the sodium bromide and sodium perchlorate were dried at 110° before use. The glacial acetic acid was purified as before.[8] The solutions of aqueous acetic acid were prepared by mixing required volumes (*e.g.*, 100 ml. of water and 900 ml. of acetic acid) which had been separately thermostated at 25°. Fresh batches of the 75 and 90% acid were made frequently, and the kinetic runs in different batches were found to be reproducible. Fluorene (Distillation Products) was first chromatographed over alumina and was then crystallized from 95% ethanol, 90% acetic acid and again from ethanol. The melting points remained essentially the same, and the final material of m.p. 114.7–115.1° (cor.) was stored in a brown bottle.

Kinetic Determinations. **(A) Runs in the Presence of Bromide Ion.**—These determinations were carried out essentially as described before.[8,9] All stock solutions were made up at the temperatures of the kinetic runs. The fluorene solutions were found to be stable for only a short period—one week at the most—and fresh solutions were prepared for almost all kinetic runs. Within a single run rate constants calculated from the second-order integrated rate equation showed a downward drift as reaction progressed. This was traced to a small amount of fast reacting impurity in the fluorene, which had not been completely eliminated by the purification procedure.[11] It manifested itself in a small difference between the bromine concentration obtained from a blank and that obtained from a rapidly taken initial sample. Very good constants were obtained graphically, when it was confirmed that the initial bromine concentration calculated from the intercept was always slightly less than that obtained from the blank, although the difference was not more than 1.1% on the average. Rate constants were calculated from least-square plots; the corrected initial bromine concentration, as obtained from the intercept, was used. Averaged errors in the slopes and intercepts were 0.9 and 0.2%, respectively, and duplicate runs agreed on the average within 0.8%. It was found from blank runs that loss of bromine due to volatility was negligible. The plots expressing the dependence of k_{obs} on bromide ion concentration and temperature were also calculated by least squares, and all errors listed are probable errors obtained from these calculations. All rate constants listed in Table II are average values of at least duplicate runs, except those under (A), which are representative.

(B) Kinetic Runs in the Absence of Bromide Ion.—Reactions were usually carried out on a 10-ml. scale (20 ml. for more dilute solutions) in a 25-ml. brown bottle fitted with a glass stopper. Since it was usually desirable to have exactly equal concentrations of reactants, a blank solution of bromine was prepared, twice the desired strength. This was then diluted with the same volume of solvent, and the bromine content was determined in three different samples. A fluorene solution twice this strength was then prepared, and 5 ml. of the bromine solution was pipetted into 5 ml. of the fluorene solution at the start of the reaction; 1-ml. samples were withdrawn for analysis at suitable intervals. Five samples were taken for each run, and at least duplicate runs were conducted for each set of conditions. Where the concentrations of the reactants were not exactly equal, an average value was used. Over-all kinetic orders were then determined from an experimental curve of % reaction *versus* time, from which times for 10, 20, 30, etc. % reaction were read off, and the over-all orders were determined from the equation $n = 1 + (\log t_1/t_2)/(\log a_2/a_1)$, where the symbols t_1 and t_2 refer to times required for definite percentages of reaction in runs with initial concentrations a_1 and a_2, respectively. A typical set of data is shown in Table I.

TABLE I

SOME DATA FOR THE BROMINATION OF FLUORENE IN THE ABSENCE OF BROMIDE ION

(A) Determination of reaction orders for runs in 75% acetic acid at 25°[a]

Reactants × 10³, moles/l.	Times for % bromine reacted, min. 10	20	30	40	50%
6.460	1.7	3.9	7.2	11.6	18.2
3.167	3.7	9.3	17.1	27.8	42.5
1.122[b]	12.5	30.0	53.1	85.6	..

(B) Calculation of apparent rate constants k'_2 for runs in 75% acetic acid at 25°

n[c]	dx/dt × 10⁶, moles l.⁻¹ min.⁻¹	$(Br_2)_f$ × 10³, moles/l.	(Fluorene) × 10³, moles/l.	k_2',[d] l. mole⁻¹ sec.⁻¹	k_2',[e] l. mole⁻¹ sec.⁻¹
0.10	7.398	0.9988	1.0098	0.122	0.134
.15	6.421	.9404	0.9537	.119	.130
.20	5.629	.8802	.8976	.119	.125
.25	4.891	.8220	.8415	.118	.124
.30	4.171	.7639	.7854	.116	.121
.35	3.484	.7057	.7293	.113	.121
.40	2.857	.6475	.6732	.109	.118

[a] Values for the reaction orders, obtained from the data are shown in Table III. [b] The experimental curve for this run is shown in Fig. 1, and the rate constants k'_2 are calculated under (B). [c] The fraction of bromine reacted. [d] From the differential form of the rate equation, method A. [e] From the integrated form of the rate equation, method B.

Calculations of Rate Constants for Runs in Absence of Bromide Ion.—Two methods were used to obtain values for the apparent second-order rate constants k_2'. (A) The first is essentially the method of Bradfield, *et al.*, which involves calculating dx/dt from a time *versus* % reaction curve.[7] These authors found that the curves representing the disappearance of bromine could be reproduced by an empirical equation of the type $t = \alpha n + \beta n^2 + \gamma n^3 + \delta n^4$, where n is the fraction of bromine reacted at time t. Values of t were read off from an experimental curve, the constants α, β, etc., were evaluated and dx/dt could be calculated. In the present case four values of t at n = 0.1, 0.2, 0.3 and 0.4 were read from the smooth experimental curve, and the coefficients α, β, etc., for the four equations were evaluated from the fourth-order determinants using Cramer's rule.[12] How well the empirical relation fits the experimental curve is indicated by the half-filled circles in Fig. 1, which is typical of the time *versus* % reaction curves that were obtained. From the values of dt/dn, dx/dt can be calculated, as shown by the authors.[7] Values of dx/dt were calculated for each value of n, usually in increments of n = 0.05, and k_2' was obtained by substitution into eq. 2, using the concentration of free bromine, which was calculated for each value of n.[7] The details of all calculations and all data are

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(11) F. A. Askew, *J. Chem. Soc.*, 512 (1935); E. A. Johnson, *ibid.*, 994 (1962).

(12) I. S. Sokolnikoff and E. S. Sokolnikoff, "Higher Mathematics for Engineers and Physicists," Sec. Ed., McGraw-Hill Book Co. Inc., New York, N. Y., 1941, p. 113.

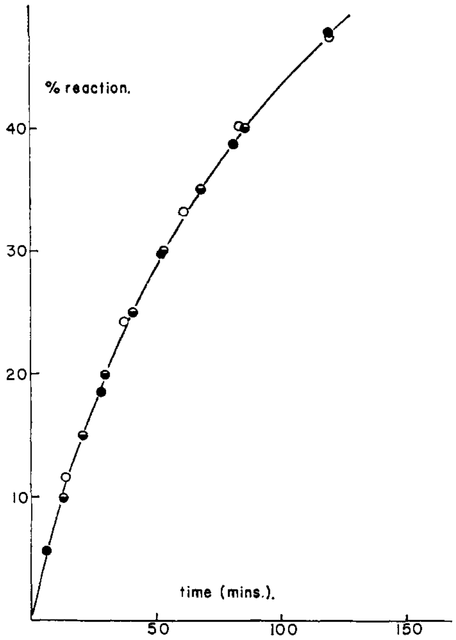

Fig. 1.—A typical % reaction *versus* time curve for the bromination of fluorene in the absence of bromide ion in 75% acetic acid. Half-empty circles represent calculated values, full and empty circles duplicate experimental points.

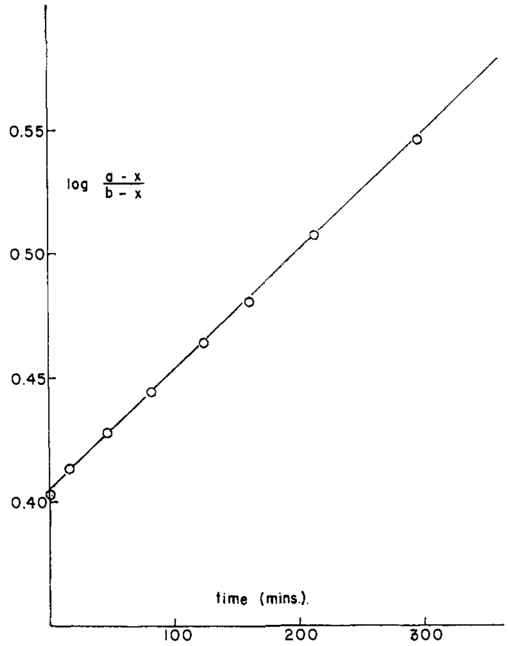

Fig. 2.—A second-order plot for the bromination of fluorene in the presence of bromide ion; fluorene 0.00225 *M*, Br_2 0.00089 *M*, Br^- 0.1 *M*, *T* 25°, slope = $0.4729 \times 10^{-3} \pm 0.5\%$, intercept = $0.4048 \pm 0.1\%$.

contained in the Ph.D. thesis of Un-Jin P. Zimmerman, Bryn Mawr College, 1961. Typical results for one set of data are also recorded in Table I.

(B) This method involved the use of the long integrated second-order rate equation of Bradfield, Jones and Orton,[13] as modified by Eaborn and Webster for runs of equal concentration of reactants and in the absence of initially added bromide ion.[14] The experimental data were obtained from the same time *versus* % reaction curve used in method A. A typical set of rate constants obtained by this method is also shown in Table I. Using both methods of calculation, the constants were evaluated (as shown in the table) for three sets of conditions in 75% and for four in 90% acetic acid, the sets differing in initial concentration of reactants. The agreement between results obtained by the two methods was satisfactory, although the two methods, both involving laborious calculations, are quite different. The deviation from the mean of the two values was on the average 3% for runs in 75%, and 9% for those in 90% acetic acid. Rate constants obtained by method B were slightly higher than those from method A. Because values obtained by method B appeared, on the whole, to be more consistent, these were used in evaluating k_2 and k_3.

The Amount of 2-Bromofluorene Formed during Bromination.—This amount was determined by the isotopic dilution method using Br^{82}, exactly as described before.[15] Runs were conducted on a 500-ml. scale in which kinetic conditions for runs in 75% acetic acid were duplicated. The solutions were 0.1 *M* in sodium bromide, 0.4 *M* in sodium perchlorate, about 0.006 *M* in fluorene and about 0.002 *M* in bromine. Inactive 2-bromofluorene (Aldrich Chemicals Co.), after three recrystallizations from benzene and 95% ethanol, m.p. 113.4–113.6° (cor.), was used as a carrier. Reactions were allowed to proceed for twelve hours, when no more test for bromine was obtained. The initial bromine concentration was obtained from two blanks and agreed with values from two samples taken rapidly from the reaction mixture and corrected to zero time (the lapse was usually 1 minute). Four independent runs were carried out. In each, the mixture of active and inactive 2-bromofluorene was usually crystallized four times before the first sample was counted. Each sample was crystallized twice more and counted after each recrystallization. In one typical run, the 4th, 5th and 6th samples contained the following % of 2-bromofluorene: 96.49 (m.p. 113.2–114.0°), 96.01 (113.3–114.0°) and 97.31 (113.1–114.0°). The average of ten values was 97.0 ± 0.8% of 2-bromofluorene.

Results and Discussion

Bromination in 75% Aqueous Acetic Acid in the Presence of Bromide Ion.—In order to study the nature of the reaction and to identify the brominating species, the same kinetic criteria were applied as in previous cases, to which reference is therefore made.[8–10] Within a single run, the reaction is of the second order over-all, and rate constants were evaluated graphically from least-square plots. One such graph is shown in Fig. 2. In Table II are listed representative data which show that the reaction is of the first order in fluorene (0.00225–0.009 *M*) and in bromine (0.0009–0.0045 *M*) at a constant bromide ion concentration (0.1 *M*). The reaction can therefore be represented by $-d(Br_2)_t/dt = k_{obs}(\text{fluorene})(Br_2)_t$, where $(Br_2)_t$ is equal to the total titratable bromine. The free bromine concentration, $(Br_2)_f$, is equal to $K(Br_2)_t/(K + Br^-)$, where *K* is the dissociation constant of the tribromide ion in 75% acetic acid.[16] Hence, if free bromine is the substituting agent, k_{obs} should decrease with an increase in bromide ion and should be equal to $kK/(K + Br^-)$, where *k* is the specific rate constant for bromination by free bromine. In Table IIB are listed rate constants at bromide ion concentrations which varied from 0.1 to 0.5 *M*

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

(14) C. Eaborn and D. E. Webster, *ibid.*, 4449 (1957).

(15) E. Berliner, F. J. Ochs and G. L. Zimmerman, *J. Org. Chem.*, **23**, 495 (1958); E. Berliner, G. L. Zimmerman and G. C. Pearson, *ibid.*, **26**, 1633 (1961).

(16) The value 0.0110 mole/l. from ref. 7 was used. For *K* in 90% acetic acid a value of 0.0073 mole/l. was estimated by extrapolation of the data of T. W. Nagakawa, L. J. Andrews and R. M. Keefer, *J. Phys. Chem.*, **61**, 1007 (1957).

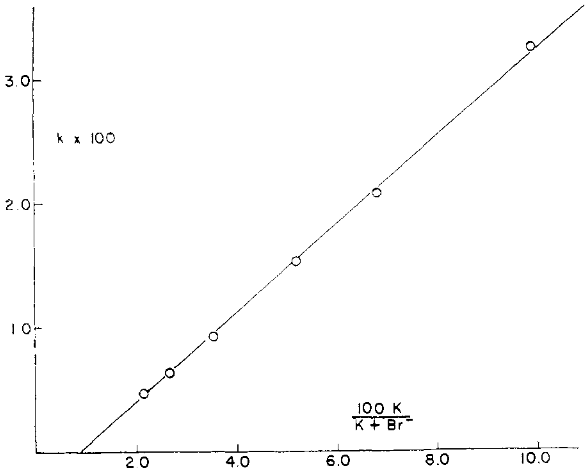

Fig. 3.—The dependence of the rate on the bromide ion concentration.

at a total salt concentration of 0.5 M, maintained with sodium perchlorate. A plot of k_{obs} against $K/(K + \mathrm{Br}^-)$ is shown in Fig. 3, from which it is evident that the postulated relationship is obtained, and that molecular bromine is the substituting agent, and not any species derived from it. The slope, k, is 0.359 ± 1% l. mole^{-1}sec.$^{-1}$ at $\mu = 0.5$. The line should go through the origin, but as in previous cases,[8-10] a small, and probably insignificant, finite intercept is obtained (−0.0033 l. mole^{-1} sec.$^{-1}$). The activation energy, obtained from measurements of k_{obs} at five temperatures (Table IIC), is 17.4 ± 0.5% kcal., log A is 10.52 ± 0.6% and ΔS^* is −12.4 e.u. These values are not directly comparable with previous ones on other hydrocarbons because of the unknown thermodynamic parameters of the tribromide ion equilibrium in 75% acetic acid. Data in Table IID show that the rate increases almost linearly with an increase in salt concentration (0.1 to 0.9 M). This, as well as the negative entropy of activation, is not unexpected for reactions in which ions are formed from neutral molecules.[17] Sodium acetate, as has been observed before,[6,8,18] appears to decrease the rate at a constant ionic strength. Actually (last three entries in Table II), both sodium acetate and sodium perchlorate increase the rate, but the former is much less effective. This is believed to be a primary salt effect. The conclusion can be drawn that bromination in 75% acetic acid in the presence of bromide ion has the same kinetic characteristics as bromination in the more aqueous solvents,[8-10] and that under these conditions the region of transition to high-order bromination has not yet been reached, if, in the presence of bromide ion, it ever is reached.[19]

TABLE II

RATE DATA FOR THE BROMINATION OF FLUORENE IN THE PRESENCE OF BROMIDE ION IN 75% ACETIC ACID[a]

(A) Dependence of rate on initial concentration of reactants; NaBr 0.1 M, T 25.0°

Fluorene × 10³, moles/l.	$\mathrm{Br_2}$ × 10³, moles/l.	k_{obs} × 100
2.250	0.8946	1.32
4.500	0.8880	1.31
4.500	1.8211	1.32
9.000	0.9705	1.35
9.000	1.5909	1.37
9.000	2.6057	1.32
9.000	3.3809	1.34
9.000	4.5872	1.39[b]

(B) Dependence of rate on bromide ion concentration; fluorene 0.0045 M, $\mathrm{Br_2} \simeq 0.001$ M, T 25.0°

NaBr, mole/l.	$\mathrm{NaClO_4}$, mole/l.	k_{obs} × 100
0.10	0.40	3.25
.15	.35	2.07
.20	.30	1.52
.30	.20	0.920
.40	.10	.631
.50	..	.468

(C) Dependence of rate on temperature; fluorene 0.0045 M, $\mathrm{Br_2} \simeq 0.001$ M, NaBr 0.40 M, $\mathrm{NaClO_4}$ 0.10 M

T, °C.	k_{obs} × 100
17.85	0.304
25.00	0.631
31.85	1.24
38.85	2.35
44.85	3.85

(D) Dependence of rate on salt concentration; fluorene 0.0045 M, $\mathrm{Br_2} \simeq 0.001$ M, NaBr 0.1 M, T 25.0°

$\mathrm{NaClO_4}$, mole/l.	k_{obs} × 100
..	1.31
0.10	1.85
.20	2.31
.30	2.74
.40	3.25
.60	4.41
.80	5.70

NaOAc, mole/l.	$\mathrm{NaClO_4}$, mole/l.	k_{obs} × 100
0.10	0.30	2.72
.20	.20	2.30
.30	.10	1.95
.40	..	1.61
..	.40	3.25
..	..	1.35

[a] All rate constants are in l. mole^{-1}sec.$^{-1}$. [b] The average of 18 values is 1.35 × 10^{-2} ± 2%.

Bromination without Added Bromide Ion. (A) The Order of the Reaction.—Rate measurements were made with equimolecular initial concentrations of reactants, and the over-all kinetic orders were obtained from an experimental curve of % reaction *versus* time. The results are shown in Table III. In glacial acetic acid the order with respect to fluorene was determined in the concentration range 0.1–0.05 M for fluorene with a constant bromine concentration of 0.01 M. It was found to be one. Therefore, bromination of fluorene in glacial acetic acid is of an order higher than two in

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(17) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Ch. VII; A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 122 ff.; R. P. Bell, "Acid Base Catalysis," Oxford University Press, Oxford, 1941, pp. 32–34.

(18) P. W. Robertson, *J. Chem. Soc.*, 1267 (1954).

(19) Second-order over-all rate constants have been obtained in the bromination of dibromophenols in 80% acetic acid in the presence of bromide ion; see E. Grovenstein, Jr., and U. V. Henderson, Jr., *J. Am. Chem. Soc.*, **78**, 569 (1956).

TABLE III

RATE DATA FOR THE BROMINATION OF FLUORENE IN THE ABSENCE OF BROMIDE ION

(A) Reaction orders

Solvent	Approximate concn. range, mole/l.	Reaction orders at % bromine reacted							
		5	10	15	20	25	30	40	50%
Acetic acid	0.1 –0.05		3.7		3.7		3.7		
	.05– .01		3.2		3.2				
	.01– .006	2.9	3.1						
90% acetic acid	0.02 –0.01		2.7		2.7		2.6	2.5	
	.01 - .006		2.6		2.7		2.7	2.6	
	.006– .003		2.6	2.6	2.6	2.7			
75% acetic acid	0.0065–0.003		2.1		2.2		2.2	2.2	2.2
	0.003 –0.001		2.2		2.1		2.1	2.1	

(B) Average values of apparent rate constants k_2'

	Av. $(Br_2)_f \times 10^3$, mole/l.	Av. k_2',[a] l. mole^{-1} sec.$^{-1}$	Av. k_2',[b] l. mole^{-1} sec.$^{-1}$
90% acetic acid	12.97	0.0228	0.0184
	6.744	.0138	.0117
	3.980	.0091	.0077
	2.133	.0059	...
75% acetic acid	4.409	.169	.166
	2.249	.143	.131
	0.823	.125	.117

(C) Rate constants for bromination in absence of bromide ion[c]

	k_2, l. mole^{-1} sec.$^{-1}$	k_3, l. mole^{-2} sec.$^{-1}$
90% acetic acid	0.0026	1.61
75% acetic acid	0.115	12.2

[a] From the integrated form of the rate equation, method B. [b] From the differential form of the rate equation, method A. [c] Only values obtained by method B were used in calculating the rate constants.

bromine, and the order decreases with a decreasing initial concentration of reactants from about 2.7 to 2. This is entirely consistent with the behavior of other compounds in the same concentration range.[4,20] In the present case, a mixed third- and fourth-order over-all reaction is indicated. If one makes the reasonable assumption that the order in fluorene stays one also in the more aqueous solvents, the results in Table III show that in 90% aqueous acetic acid a mixed first- and second-order reaction (in bromine) occurs in the investigated concentration range. In 75% acetic acid the over-all order is almost two, so that the order in bromine is almost, although not quite, one, and a second-order in bromine term is still present. The data clearly indicate and confirm that the presence of water is a strong factor in reducing the kinetic order from almost four in glacial acetic acid to almost two in 75% acetic acid.[4,21]

(B) Rate Constants for Reaction in 90% and 75% Aqueous Acetic Acid.—From the preceding results it appears then that the reaction in the two aqueous solvents, in the absence of initially added bromide, is of mixed first and second order with respect to bromine concentration, and that the rate equation has a form corresponding to (1), without the last, fourth-order term. The first term predominates in 75% acetic acid, and the second contributes appreciably in the 90% solvent. To effect a separation of the two rate constants, k_2 and k_3, from the experimental data, it was assumed, as a first approximation, that only the first term contributes, *i.e.*

$$-\,dx/dt = k_2'(\text{fluorene})(Br_2)_f \qquad (2)$$

The apparent second-order rate constants, k_2', were evaluated by two independent methods. The first, which followed essentially the procedure of Bradfield, Davies and Long,[7] made direct use of the differential form of the rate equation and involved calculating dx/dt from a time *versus* % reaction curve as described in the Experimental. The other method made use of the long integrated second-order rate equation of Bradfield, Jones and Orton,[13] as modified by Eaborn and Webster,[14] which takes into account the effect of the bromide ion, produced during reaction, on the free bromine concentration. The results of these calculations are shown in Table III. The values of k_2' decrease with a decrease in bromine concentration, and the drift, as expected, is more pronounced for reaction in 90% than in 75% acetic acid. Furthermore, k_2' varies linearly with $(Br_2)_f$. From plots of average values of k_2' against an average value of $(Br_2)_f$, k_3 and k_2 were obtained as the slope and intercept, respectively. These rate constants are also listed in Table III, and the straight-line relationship is shown in Fig. 4 for reaction in 90% acetic acid.

Conclusions.—The magnitudes of both k_2 and k_3 are increased as the polarity of the medium increases through addition of water. Quantitatively, the increase in k_2 is much greater (44) than the increase in k_3 (7.6) on going from 90% to 75% acetic acid. This was also observed in the bromination of

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(20) The very rapid bromination of phenol in pure acetic acid has been found to be first order in bromine. The low concentration range of reactants (0.004-0.001 *M*) must be in part responsible for this considerable reduction in order; see L. M. Yeddanapalli and N. S. Gnanapragasam, *J. Chem. Soc.*, 4934 (1956).

(21) See also the changes in order (and the increase in rate) in the bromination of anisole in the range 100 to 75% acetic acid; L. M. Yeddanapalli and N. S. Gnanapragasam, ref. 5.

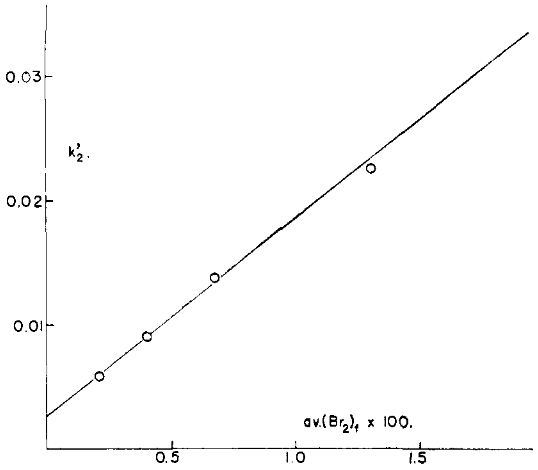

Fig. 4.—A plot of the apparent second-order rate constants k'_2 against $(Br_2)_f$ in the absence of bromide ion in 90% acetic acid.

mesitylene in 100 and 90% acetic acid.[6] The absolute increase in rate constants as the polarity of the medium increases is as expected for a reaction of this type[21]; the differential increase of k_2 indicates that the second-order over-all reaction becomes more important, and the third-order reaction less so, as the medium becomes more polar. The result is that the second-order term predominates. Because of the different degree of rate enhancement, it contributes 68% to the total reaction in 75% acetic acid, but only 12% in the 90% acid. The third-order rate constant k_3 is larger numerically than k_2, but the ratio k_3/k_2 decreases from 619 in 90% to 106 in 75% acetic acid.[22]

In the presence of bromide ion in 75% acetic acid the reaction is kinetically of the second order, with no detectable high-order term. From the results in the same solvent without added bromide ion, it appears that the water is the main factor in reducing the order. Yet, without added bromide, there is still 32% of a third-order term, which vanishes when bromide ion is present. The main reason for this is that the bromide ion acts by reducing the free bromine concentration and by making the term involving $(Br_2)_f^2$ in (1) negligibly small.[23] If this is so, then the reactions in the presence and absence of bromide ion are really kinetically, and presumably mechanistically, identical, and the decisive factor is the reduced bromine concentration. The correctness of this view is demonstrated by the identity of the rate constants in the two reactions in 75% acetic acid. If the observed rate constant in the presence of bromide ion, $k_{obs} = 1.35 \times 10^{-2}$ l. mole^{-1}sec.$^{-1}$, is corrected for bromide ion (0.1 M), the specific rate constant for reaction by free bromine becomes 0.136 l. mole^{-1}sec.$^{-1}$, as compared with 0.115 l. mole^{-1}sec.$^{-1}$ obtained in the absence of bromide ion. Since the former refers to reaction at an ionic strength of 0.1, and the latter to reaction of zero initial ionic strength, and since the ionic strength increases the rate, the agreement is good.[24] If the reactions in the absence and presence of bromide ion are identical, there must be a third-order term in the latter case also. Because of the greatly reduced free bromine concentration, which appears as a square term in the third-order over-all reaction, this term was calculated to contribute never more than 1% to the total rate, in spite of the numerically greater value of k_3 than k_2. It was therefore not only not detected but did not obscure the kinetic analysis. If the reaction in the presence of bromide ion should be truly second-order, with absolutely no third-order term, then the bromide ion must in some way alter the mechanism, in addition to reducing the free bromine concentration. This is not considered likely, and the bromide ion, after allowing for complexing with bromine, merely acts by an ionic strength effect, as other salts do.[4,6,14]

All these observations are in agreement with the postulated mechanism[4,6,8] by which first a complex is formed between bromine and the hydrocarbon in a rapid and reversible step. Because of the low polarity of the medium, this complex does not ionize readily to the ionic intermediate, but can do so

$$ArH + Br_2 \rightleftarrows ArH, Br_2 \qquad \text{fast}$$

$$ArH, Br_2 + Br_2 \longrightarrow [ArHBr]^+ + Br_3^- \qquad \text{slow}$$

$$[ArHBr]^+ \longrightarrow ArBr + H^+ \qquad \text{fast}$$

with the help of a second bromine molecule, which thus assists the ionic rupture of the Br–Br bond. In aqueous solvents, ions are more easily formed, and the greater polarity of the medium eliminates or diminishes the necessity for the second bromine molecule. The second-order over-all reaction continuously gains in importance, as reflected in the absolute and differential changes in k_2 and k_3. The water should not be pictured as taking the place of the second bromine molecule in a stoichiometric sense, because it is a much poorer electrophile than bromine. Rather, ions are formed more readily because of the more favorable medium. Because of the occurrence of low-order terms, this is to some extent, but much less, also possible in pure acetic acid.[25]

The second-order reaction, both in the presence and absence of bromide ion, could also be a straightforward bimolecular attack without the intervention of a complex, ArH,Br₂, and made possible by the increased polarity of the medium. The

$$ArH + Br_2 \longrightarrow [ArHBr]^+ + Br^- \qquad \text{slow}$$

kinetics do not distinguish between these alternatives. However, in view of the gradual change-over from high- to low-order reactions, and the simultaneous occurrence of both, the view that an initial

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(22) In the bromination of mesitylene (ref. 6), k_2 and k_3 increase about 800- and 90-fold, respectively, on going from 100 to 90% acetic acid; the ratio k_3/k_2 changes from about 5700 to about 600.

(23) A reduction of order on addition of HBr has been noted in tbe bromination of mesityfene; ref. 18.

(24) An extrapolation from k, 0.359 l. mole^{-1} sec.$^{-1}$ from μ = 0.5 to initial μ = 0, using the data in Table IID, would also result in a value close to 0.115. For a similar case in bromodesilylation, see ref. 14.

(25) A termolecular collision, or a reaction involving the dimer Br_4, are other possibilities permitted by the kinetics for the reaction which is second order in bromine; see ref. 4. In looking for possible and reasonable interpretations of the high-order terms, it is well to remember that no conclusions can be drawn from the kinetics about the structure or the existence of the suggested intermediates in the initial state or on the reaction path. The above formulations can strictly only refer to the transition state.

complex reacts with bromine or ionizes directly in the rate-determining step has the advantage of picturing the total mechanism in a continuous fashion, with the fate of the initially formed complex depending on the ease of its breakdown in a given medium. The observation that an increase in polarity of the medium through addition of certain salts increases k_2 more than k_3,[6] and that in deuterium oxide–acetic acid k_2 is reduced more than k_3,[6] lends support to this view, but it is not a sufficient proof that the bimolecular reaction proceeds through a complex. The proton loss is for all mechanisms kinetically insignificant, which is supported by the absence, or near absence, of a significant deuterium isotope effect in aromatic bromination of hydrocarbons,[26] as well as by the absence of basic catalysis.

Partial Rate Factors.—The major product in the preparative bromination of fluorene is 2-bromofluorene.[27] The exact amount, formed under the kinetic conditions in 75% acetic acid, was determined by the isotopic dilution method with Br^{82}, as described before for other compounds.[15] From four independent determinations the amount of 2-bromofluorene was found to be 97.0 ± 0.8%. This value confirms, *inter alia*, that no appreciable free-radical bromination could have intervened, because free-radical bromination is known to attack the 9-position of fluorene.[28] In order to compare the reactivity of fluorene with that of other compounds, which had been measured in 50% acetic acid, naphthalene was brominated in 75% acetic acid at a 0.1 and 0.2 M sodium bromide concentration (at $\mu = 0.5$) and the rate constants compared with those for fluorene under the same conditions. The relative rate of fluorene to naphthalene was found to have an average value of 20.9. Assuming that a difference in solvent composition does not appreciably affect relative values of the second-order rate constants, fluorene is brominated 2.49×10^6 times faster than benzene, and the partial rate factor for bromination in the 2-position of fluorene is 7.25×10^6.[29] A value of 6.33×10^6, obtained by the technique of comparing reaction times, recently has been reported for bromination in glacial acetic acid[30]; the agreement is very satisfactory. In molecular chlorination the rate ratio of fluorene to benzene is 1.1×10^5,[31] and in nitration, which is much less selective than bromination or chlorination, it is considerably less.[32] The value for fluorene falls in an expected order of reactivity, and the partial rate factors for bromination, which have so far been obtained,[8,9] parallel data for the solvolysis of arylmethylcarbinyl chlorides[33] and aryldimethylcarbinyl chlorides.[34] The considerable increase in rate of fluorene over biphenyl (a factor of 2000) is due to forced planarity in the former compound,[35] in addition to the rate-enhancing effect of the methylene group.[30,31,32,36]

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Intramolecular Nucleophilic Participation. II. Solvolysis of the 1- and 4-Carbomethoxy-9-bromofluorenes[1]

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The relative reactivities of 1- and 4-carbomethoxy-9-bromofluorenes with respect to solvolysis in aqueous ethanol and with respect to hydrolysis in aqueous acetone in the presence of silver nitrate have been determined. In both media the 1-substituted compound is less reactive than its isomer. These results serve as the basis for a discussion of the geometric requirements for effective participation by a nucleophilic *ortho* substituent in the solvolysis of a benzhydryl-type halide.

It has been shown previously that the rates of certain types of reactions at aromatic side chains are substantially enhanced when substituents which are nucleophilic in character are located *ortho* to the reaction centers.[1-3] The fact that a benzhydryl bromide bearing an *o*-carbophenoxy substit-

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[1] For the first paper in this series see A. Singh, L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **84**, 1179 (1962).

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