Calculations.—The experiment described in Table II will illustrate the methods used in calculating the new features of this work. From the saponification data of Table II it is apparent that, after saponification, a 5-ml. aliquot of the reacted solution had liberated (10.760 − 8.070) × 0.0209 = 0.0562 mmole of acid. The concentration of acid in the reaction mixture is, accordingly, 0.0112 M. The concentration of liberated acid can be equated to the combined concentrations of alcoholic solvolysis products and rearranged ester present in the solvolysis reaction mixture: [HX] = [ROH] + [R'OH] + [R'X], and the concentration of rearranged ester can then be calculated to be [R'X] = 0.0112 − (0.329) (0.0168) = 0.0057 M. The total concentration of alkyl azide is then given by difference: [RN₃] + [R'N₃] = [RX]₁ − [R'X] − [ROH] − [R'OH] = 0.0168 − 0.0057 − 0.0055 = 0.0056 M. Thus the solvolysis mixture is found to consist of 34.4% rearranged ester (R'X), 32.7% alkyl azides and 32.9% alcohols.

By the methods described in the preceding paper,[3] the ultraviolet data can be shown to require that, of the solvolysis products (alcohols and azides), 7.9% are in the γ-aryl-γ-methylallyl form: ($\%_{ROH}$ + $\%_{RN_3}$)/($\%_{R'OH}$ + $\%_{ROH}$ + $\%_{RN_3}$ + $\%_{R'N_3}$) = 0.079. This equation can be solved for the percentage of α-phenyl-γ-methylallyl azide ($\%_{RN_3}$), provided it is assumed that the ratio of allylic alcohols is unaffected by the presence of azide ion; i.e., that $\%_{ROH}$/($\%_{ROH}$ + $\%_{R'OH}$) = 0.158, the value reported in the accompanying paper. Then (32.9 × 0.158 + $\%_{RN_3}$)/(32.9 + 32.7) = 0.079, and $\%_{RN_3}$ = ± 0.0.

The Bromination of Biphenyl and Benzene in 50% Aqueous Acetic Acid[1]

BY ERNST BERLINER AND JOHN C. POWERS[2]

The kinetics of bromination of biphenyl and benzene in 50% by volume aqueous acetic acid in the presence of an excess of bromide ion has been found to have the same characteristic features as the bromination of naphthalene.[3] Relative rates of bromination of these compounds, as well as some partial rate factors, have been established.

The bromination of naphthalene by bromine in 50% by volume aqueous acetic acid, in the presence of an excess of bromide ion, is first-order in bromine and in naphthalene, and the brominating species is molecular bromine.[3] This kinetic behavior differs from bromination in glacial acetic acid or other non-polar solvents, where the order with respect to bromine is usually higher than one, although the brominating entity is the same.[4] In order to test the generality of the kinetic form observed in 50% aqueous acetic acid, as well as the suitability of the reaction for a comparison of the reactivities of different aromatic compounds with various theoretical parameters, two other compounds, biphenyl and benzene, were subjected to a similar kinetic study. The results are reported below.

Experimental

Materials.—All inorganic materials and the glacial acetic acid were as described before.[3] The purified acetic acid had a m.p. of at least 16.4°. Runs made with different batches of solvent gave identical results. One lot of acetic acid (for a series of runs with benzene) was first purified in the usual way with chromic oxide and was then treated with a small amount of bromine, followed by treatment with an excess of silver acetate and distillation. This acid melted at 16.3°, but the kinetic results did not change. Biphenyl (Distillation Products) was recrystallized three times from ethanol and melted at 69.5–70.3° (cor.). Benzene (J. T. Baker reagent grade), purified with concentrated sulfuric acid and twice distilled, boiled at 80.0° over a range of less than 0.1° and was stored in a brown bottle over sodium wire.

Kinetic Determinations.—The preparation of stock solutions and the kinetic runs in the bromination of biphenyl were carried out exactly as described previously for naphthalene.[3] All stock solutions were made up at the tempera-

tures at which runs were conducted. All runs were conducted at least in duplicate, and the data in Table II, except those under heading A, are average values of duplicate runs. Duplicate runs usually agreed within less than 2%. In the bromination of benzene, a solution of all reagents except the bromine was similarly prepared from appropriate stock solutions in a 100-ml. volumetric flask, into which the benzene had originally been either weighed out or added from a calibrated pipet. To 90 ml. of this solution was then added 10 ml. of the bromine stock solution, which also contained some of the bromide. After thorough mixing, approximately 12-ml. samples were poured carefully into eight 16–150 mm. Pyrex test-tubes which had previously been constricted at one end. The narrow portions of the tubes were carefully dried with absorbent paper and, after sealing, the tubes were placed in the thermostat. About 30 min. was allowed for the tubes to reach the reaction temperature and for the attainment of equilibrium between dissolved bromine and the bromine in the small air space above the solution. After appropriate time intervals, 10-ml. samples were withdrawn from the opened tubes with a pipet and the residual bromine determined in the usual way, using a microburet. Blank runs were conducted in the same way, except that the benzene was omitted. Sometimes a kinetic run went extremely fast, and this was usually attributed to minute amounts of carbon deposits which had formed during the sealing of the tubes; such runs were discarded. Benzene was always used in excess, and rate constants for the over-all brominations and the blank reactions were obtained from first-order plots, which were calculated by the method of least squares. The least square slopes had errors which were rarely greater than 2%. Final second-order rate constants for the bromination of benzene were calculated by subtracting the pseudo-first-order rate constants of the blank reactions from those of the over-all reactions and dividing by the excess of benzene used. The errors for both the bromination of biphenyl and of benzene, quoted in the text, are the probable errors obtained from the least square calculations.

The Blank Reaction in the Bromination of Biphenyl.—Although rate constants calculated by the integrated form of the second-order rate equation were usually good and internally consistent, discrepancies were noted when the concentration of biphenyl was reduced to about 0.002 M and the reaction became very slow. In these cases rate constants were about 30% higher than those with the concentration of biphenyl at about 0.01 M. Under these conditions the loss of bromine through a blank reaction was not negligible. It was possible to determine approximate first-order rate con-

(1) Kinetics of Aromatic Halogenation. VIII.

(2) Post-doctorate Fellow, 1958–1959.

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

(4) (a) P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, *J. Chem. Soc.*, 276 (1943); P. W. Robertson, *ibid.*, 1267 (1954); (b) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications, London, 1959, Chapter 9.

stants for the disappearance of bromine in the absence of biphenyl (and of benzene, see above). These first-order constants were considerably better when sealed tubes were used (bromination of benzene), but since the correction is small, only a rough value for the rate constant of the blank is necessary. The total loss of bromine in the bromination of biphenyl can be expressed as follows,[5] where a and b are the initial concentrations of bromine and of biphenyl respectively, and x and y are the amounts of bromine and biphenyl consumed

$$-dx/dt = k_2(a - x)(b - y) + k_1(a - x) \text{ and} \quad (1)$$

$$-dy/dt = k_2(a - x)(b - y) \quad (2)$$

Division of 1 by 2 affords

$$dx/dy = 1 + \frac{k_1}{k_2(b - y)} \quad (3)$$

Through integration and by suitable approximation one obtains from 3

$$x = y(1 + (k_1/k_2b)) = Ky, \text{ where } K = 1 + (k_1/k_2b)$$

Substitution of the above into 1 affords

$$-dx/dt = (k_2/K)(a - x)(b' - x) + k_1(a - x) \text{ where}$$
$$b' = bK$$

Integration of this expression affords the final equation

$$-\frac{k_2 t}{K} = \frac{1}{(k_1K/k_2) + b' - a} \ln \frac{a}{(k_1K/k_2) + b'}$$

$$\frac{(k_1K/k_2) + b' - x}{(a - x)}$$

$$= \frac{1}{B - a} \ln \frac{a}{B} \frac{(B - x)}{(a - x)} \quad \text{where} \quad B = \frac{k_1K}{k_2} + b'$$

In the actual calculations, the approximate value obtained from the uncorrected second-order rate equation was used for k_2 on the right side of the equation. This is not a serious approximation because the ratios k_1/k_2, the factor on which the correction depends, are very small. This ratio was determined individually for every set under which kinetic runs were studied; k_1, the rate constant for the blank reaction, was obtained from first-order plots. A typical example is listed in Table I.

TABLE I

A KINETIC RUN IN THE BROMINATION OF BIPHENYL IN 50% AQUEOUS ACETIC ACID

NaBr 0.10 M, NaClO$_4$ 0.40 M, T 34.98°

Time, min.	0.00955 N thiosulfate, ml.	10^5k_1, sec.$^{-1}$	Time, min.	0.00955 N thiosulfate, ml.	10^5k_2, 1. mole^{-1} sec.$^{-1}$	10^5k_2 (cor.),[a] 1. mole^{-1} sec.$^{-1}$
(A) Blank, Br$_2$ 0.000880 M			(B) Biphenyl 0.009996 M, Br$_2$ 0.000869 M			
0	1.842	..	0	1.820	..	..
79	1.826	(1.85)	73	1.694	1.64	1.52
169	1.823	1.02	166	1.541	1.68	1.56
257	1.801	1.46	261	1.408	1.66	1.53
364	1.796	1.16	363	1.283	1.63	1.50
462	1.774	1.36	471	1.152	1.65	1.52
568	1.756	1.40	583	1.037	1.64	1.52
685	1.747	1.29	710	0.924	1.63	1.51
789	1.725	1.38				
Av. 1.3 × 10^{-6} (from graph)			Av. 1.65			1.52

[a] $k_1/k_2 = 0.0008$, $K = 1.080$, $b' = 0.010796$, $B = 0.011\text{-}660$.

Results and Discussion

The Bromination of Biphenyl.—Because biphenyl is brominated considerably more slowly than naphthalene, all experiments, except those for the calculation of activation parameters, were conducted at 35°. The reaction shows exactly

(5) We are very much indebted to Dr. George L. Zimmerman for his invaluable help in deriving this equation.

TABLE II

THE BROMINATION OF BIPHENYL IN 50% AQUEOUS ACETIC ACID[a]

(A) Dependence of rate on concentration of reactants NaBr 0.1 M, NaClO$_4$ 0.4 M, T 34.98°

Biphenyl, mole/l.	Br$_2$, mole/l.	10^5k_2	10^5k_2 (cor.)
0.01038	0.00179	1.59	1.50
.01035	.00179	1.62	1.53
.01007	.000865	1.67	1.53
.0100	.000869	1.65	1.52
.00945	.00440	1.67	1.59
.00957	.00438	1.68	1.60
.00955	.00357	1.66	1.56
.00606	.00288	1.73	1.57
.00598	.00287	1.75	1.59
.00398	.00178	1.76	1.49
.00389	.00177	1.79	1.50
.00210	.000865	2.09	1.46
.00218	.000838	2.05	1.46

(B) Dependence of rate on bromide ion concentration Biphenyl $\simeq$ 0.0095 M, Br$_2$ $\simeq$ 0.0037 M, T 34.98°

NaBr, mole/l.	NaClO$_4$, mole/l.	10^5k_1 (cor., av.)
0.300	0.200	0.534
.250	.250	.657
.200	.300	.820
.150	.350	1.094
.100	.400	1.593
.050	.450	2.811

(C) Dependence of rate on ionic strength Biphenyl $\simeq$ 0.0095 M, Br$_2$ $\simeq$ 0.0035 M, NaBr 0.1 M, T 34.98°

NaClO$_4$, mole/l.	10^5k_2 (cor., av.)
0.00	0.865
.100	1.055
.200	1.24
.300	1.42
.400	1.59
.500	1.80
.600	2.01
.700	2.19

(D) Dependence of rate on temperature Biphenyl $\simeq$ 0.006 M, Br$_2$ $\simeq$ 0.003 M, NaBr 0.1 M, NaClO$_4$ 0.4 M

T, °C.	10^5k_2 (cor., av.)
24.91	0.583
30.00	0.993
34.98	1.58
40.00	2.65
44.99	4.14

[a] All rate constants are in 1. mole^{-1} sec.$^{-1}$.

the same kinetic characteristics as the bromination of naphthalene, and the pertinent data are summarized in Table II. It is first-order each in biphenyl (0.002 to 0.01 M) and in bromine (0.0008 to 0.004 M), and the rate decreases with an increase in added bromide ions at a constant ionic strength. This dependence is due to the formation of the tribromide ion, which has no, or very little, brominating power. As shown before,[3] the observed rate constant is related to the rate constant by free bromine, k, by the expression $k_{obs} = kK_1/(K_1 + Br^-)$, where K_1 is the dissociation constant of the tribromide ion. Hence a straight line is obtained
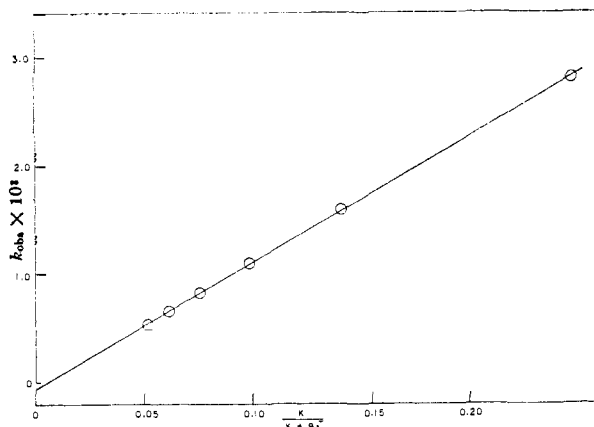
Fig. 1.—The bromination of biphenyl; the dependence of the rate on the bromide ion concentration at 34.98°; K is equal to 0.0164 mole/l.

Fig. 2.—The bromination of benzene; a typical kinetic run at 44.89°: upper line, blank; lower line, over-all reaction.

when k_{obs} at different bromide ion concentrations is plotted against $K_1/(K_1 + Br^-)$ (Fig. 1). The slope of the straight line, $1.17 \times 10^{-2} \pm 3.6 \times 10^{-5}$, is equal to the rate constant for bromination by free bromine at 35°, and, using the same argument as before,[3] free bromine is thus identified as the only substituting entity present in the system.[6] The observed activation energy for bromination of biphenyl, obtained from measurements at five temperatures, is 18.6 ± 0.13 kcal., log A is 10.38 ± 0.091 and ΔS^* is −13.0 e.u., while for bromination of naphthalene the values are 16.8 kcal., 10.59 and −12.1 e.u. The reaction is dependent also on the ionic strength, and the rate increases practically linearly with an increase in salt concentration (0.1 to 0.8 M).

The Blank Reaction in the Bromination of Biphenyl.—Because the bromination of biphenyl is relatively slow, attention had to be paid to the loss of bromine other than through bromination of biphenyl—always a bothersome and recurring problem in aromatic bromination. This loss was determined by conducting kinetic runs identical in every respect with the bromination runs, except that the hydrocarbon was omitted. It was established that bromine disappears in the blank approximately according to a first-order law. The blank is not necessarily all due to the reaction of bromine with the acetic acid; some of it is due to volatility losses or to reaction with impurities in the acetic acid. The main point is that, for a given sample of purified solvent, the bromine loss can be treated as a first-order reaction under the conditions of the kinetic runs, and hence the total bromination reaction can be treated as if the bromine reacted by a simultaneous second- and first-order reaction. The derivation of the appropriate integrated rate equation is given in the Experimental.[5] Because the blank reaction is rather slow compared to bromination, k_1, the rate constant for the blank, need not be known with great precision, and the first-order rate constants are only rough average values. The corrected rate constants were about 5–10% less than the uncorrected ones, except in

cases where the reaction was very slow. This was evident particularly in runs where the dependence of rate on concentration of reactants was tested (Table II, A), when an upward drift of rate constants with decreasing concentration of reactants was eliminated by the use of the correction. All rate constants here reported have been corrected.

The Bromination of Benzene.—The bromination of benzene in 50% aqueous acetic acid is extremely slow, and a sufficient excess of benzene was used to treat the reaction as a pseudo-first-order one. Since the blank reaction, which is similar in magnitude to the bromination itself, also follows first-order kinetics, the rate constants for bromination of benzene could be calculated in a straight forward manner. A sealed-tube technique was used, and under those conditions very good first-order plots for both the blank and the over-all reaction were obtained (Fig. 2).

The bromination of benzene (Table III) has the same characteristic features as that of naphthalene and biphenyl. It is first order in benzene (0.1 to 0.2 M) and bromine (0.0009 to 0.008 M), and the observed rate constants are proportional to $K_1/(K_1 + Br^-)$, when the bromide ion concentration is varied from 0.05 to 0.25 M. Free bromine is therefore again the substituting agent, and the rate constant for bromination by free bromine (the slope of the line)[7] is $(2.17 \pm 0.035) \times 10^{-5}$ at 45°. The observed activation parameters are $\Delta E = 19.6 \pm 0.41$ kcal., log $A = 7.97 \pm 0.29$ and $\Delta S^* = -24.1$ e.u. (Fig. 3).

Because the absolute value for bromination of benzene at 25° is important for comparisons with other hydrocarbons, particular care was exercised to obtain a reliable value. To this end, the bromination of benzene was repeated after about one year by a different investigator,[8] using new reagents and an individually differing technique. The results were the same. The uncertainty in the rate constants for the bromination of benzene is greater than that of the other two compounds, because of the

(6) The straight line should go through the origin. The small observed intercept of $(-6.09 \pm 0.015) \times 10^{-4}$ is probably insignificant and negligible.
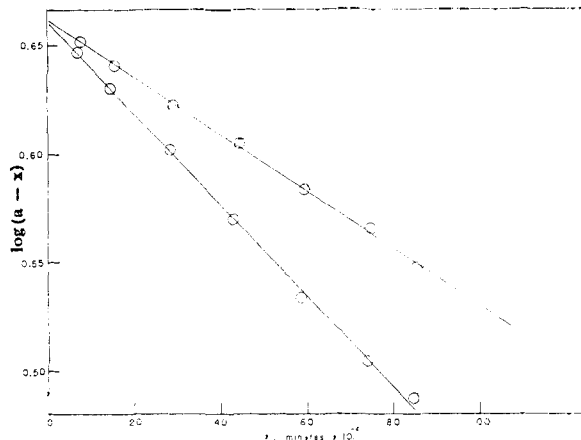
(7) The intercept is $(2.07 \pm 0.49) \times 10^{-7}$. See the comment in footnote 6.

(8) These runs were conducted by Miss Barbara J. Landry. We are very grateful to Miss Landry for carrying out these determinations as well as numerous least square calculations.
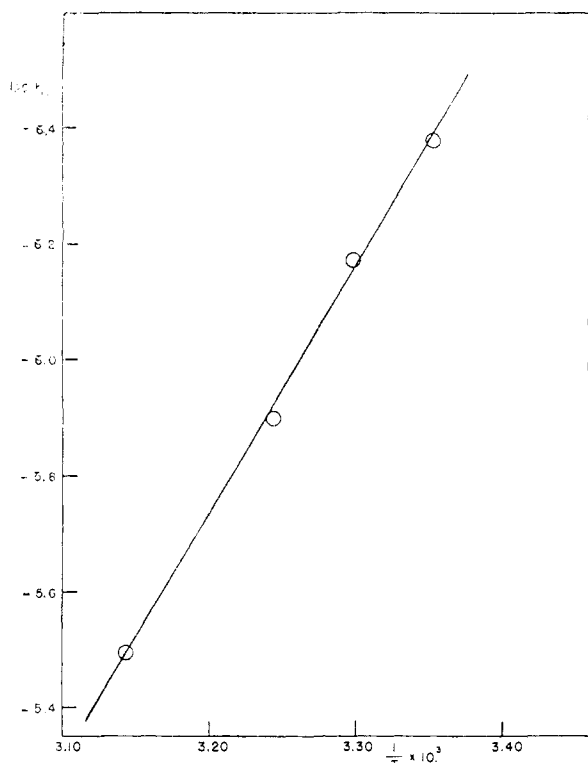
Fig. 3.—The bromination of benzene; the dependence of the rate on the temperature.

extreme slowness of the reaction and because rate constants are obtained as differences of two larger constants. Also, the blank values, and hence the rate constants for the over-all reaction, varied

TABLE III

THE BROMINATION OF BENZENE IN 50% AQUEOUS ACETIC ACID[a]

(A) Dependence of rate on concentration of reactants; NaBr 0.1 M, NaClO$_4$ 0.4 M, T 44.89°

Benzene, mole/l.	Br$_2$, mole/l.	$10^7 k_1$	$10^7 k_B$	$10^8 k_2$
0.200	0.000908	16.63	10.58	3.03
.200	.000867	17.48	11.40	3.04
.200	.00858	9.92	3.57	3.18
.200	.00863	9.95	3.62	3.17
.201	.00765	12.81	5.82	3.44[b,c]
.203	.00770	12.95	(5.82)[d]	3.46[b,c]
.0974	.00449	8.03	5.00	3.11
.0974	.00448	7.97	4.85	3.20
.0983	.00468	24.37	21.10	3.28[b,c]

(B) Dependence of rate on bromide ion concentration; benzene ≃ 0.097 M, Br$_2$ ≃ 0.0045 M, T 44.89°

NaBr, mole/l.	NaClO$_4$, mole/l.	$10^7 k_1$	$10^7 k_B$	$10^8 k_2$	$10^8 k_2$ (av.)
0.250	0.250	5.68	4.17	1.55	
.250	.250	6.95	4.40	(2.62)	1.55
.200	.300	6.10	4.22	1.93	
.200	.300	6.32	4.68	1.68	1.81
.150	.350	14.05	11.60	2.45[b,c]	
.150	.350	14.05	(11.60)[d]	2.45[b,c]	2.45
.100	.400	See last three entries in A			3.20
.050	.450	11.07	5.78	5.43	
.050	.450	11.07	5.47	5.75	5.59

(C) Dependence of rate on temperature; benzene ≃ 0.097 M, Br$_2$ ≃ 0.0044 M, NaBr 0.1 M, NaClO$_4$ 0.4 M

T, °C.	$10^7 k_1$	$10^7 k_B$	$10^8 k_2$	$10^8 k_2$ (av.)
25.00	0.803	0.427	0.386	
	.850	.410	.452	
	1.403	.979	.431[b]	
	1.510	1.073	.444[b]	
	1.381	1.002	.386[b]	0.420[g]
30.04	2.551	1.887	.675[b]	
	2.553	(1.887)[d]	.676[b]	0.676
35.11	2.458	1.275	1.21	
	2.492	1.198	1.33	1.27
44.9[e]	See last three entries in A			3.21[f]

[a] k_1 is the first-order rate constant for the over-all reaction in sec.$^{-1}$, k_B is the first-order rate constant for the blank in sec.$^{-1}$ and k_2 the second-order rate constant for the bromination of benzene in 1. mole^{-1} sec.$^{-1}$. [b] Run conducted by Miss Barbara J. Landry; see ref. 8. [c] Corrected from 45.04 to 44.89° using ΔE 19.6 kcal. [d] The same blank as in the run above was used. [e] Average temperature of runs at 44.89 and 45.04°. [f] The value for the last entry in A, not corrected for T and used for this average, is 3.33 × 10^{-6}. [g] ±0.027.

somewhat with the sample of acetic acid used,[9] but this did not seem to affect the final values for bromination of benzene. These were reproducible,

TABLE IV

RELATIVE RATES OF BROMINATION IN 50% AQUEOUS ACETIC ACID AT 25.0°[a]

	Benzene	Biphenyl	Naphthalene
k_{obs}[b]	4.20 × 10^{-7}	5.88 × 10^{-4}	5.00 × 10^{-2}
k_{rel}	1	1.40 × 10^3	1.19 × 10^5
ΔE,[c] kcal.	18.1	17.1	15.3
log A[c]	7.11	9.52	10.17
ΔS^*,[c] e.u.	−28.0	−17.0	−14.0

	Benzene	Naphthalene 2-position	Biphenyl 4-position	Naphthalene 1-position
f_x	1	1.79 × 10^5	3.94 × 10^3	1.77 × 10^5

[a] Rate constants for biphenyl and naphthalene have been corrected from 24.91 and 24.90, respectively, to 25.0°; all rate constants refer to runs 0.1 M in NaBr and 0.4 M in NaClO$_4$. [b] In 1. mole^{-1} sec.$^{-1}$. [c] These activation parameters refer to bromination by free bromine and have been calculated from the observed values by correcting for ΔH (1.5 kcal.) and ΔS (−0.35 e.u.) of the tribromide equilibrium (ref. 10), assuming that these values are the same as in water. The correction also allows for the different bromide ion concentrations used in determining the activation parameters (ref. 3). The observed values are reported in the text.

and we feel that the values can be used as a standard for setting up a scale of relative reactivities.

Relative Reactivities of Bromination.—In Table IV are listed the observed over-all rate constants for the bromination under identical conditions of benzene, biphenyl and naphthalene. Because the experimental conditions, kinetic characteristics and the substituting entity are the same for all three reactions, a direct comparison is possible. The over-all reactivities are of the same order of magnitude as those reported recently for high-order bromination in 85% aqueous acetic acid.[11] Under the kinetic conditions here employed, naphthalene is bromi-

(9) For this reason, no attempts were made to draw any conclusions about the kinetics of bromination of acetic acid itself.

(10) R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 101 (1932).

(11) S. F. Mason, *J. Chem. Soc.*, 4329 (1958). The relative rates, in the same order as in Table IV, are 1, 1.1 × 10^3 and 1.4 × 10^5. The kinetic order for the over-all reaction is 3.

nated to the extent of 1% in the β-position, as determined by the isotopic dilution method.[12] By the use of the same technique, it was found that biphenyl affords 93.9 ± 2.4% of substitution in the 4-position.[13] With this information, and the usual statistical corrections, the partial rate factors, f_x, shown in the table, can be calculated. They are similar to those estimated for bromination in glacial acetic acid.[14]

The relative order of reactivities is one which might have been expected on general chemical grounds and which also agrees qualitatively with that predicted from the order of localization energies as calculated by the molecular-orbital method.[15] It is particularly noteworthy that the

order 4-biphenyl > 2-naphthalene falls in the theoretical sequence, as it does in a variety of other reactions.[16] However, a plot of log f_x against (N_0 − N_x), the so-called reactivity numbers,[17] though qualitatively correct, is by no means linear. Four compounds, to be sure, are not a sufficient number from which to draw any conclusions, but it seems that a better correlation is obtained when these partial rate factors are plotted against some other *measured* quantity, such as the rates of solvolysis of α-arylethyl chlorides.[18] A more detailed discussion will have to await the accumulation of more data.

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(12) E. Berliner, F. J. Ochs and G. L. Zimmerman, *J. Org. Chem.*, **23**, 495 (1958).

(13) Unpublished results with G. L. Zimmerman and G. Pearson; from the senior honors thesis of Miss G. Pearson, 1959.

(14) P. B. D. de la Mare and J. H. Ridd, ref. 4b, pp. 157 and 176. The values for f_x, in the same order as in Table IV, are 1, 10³, 3 × 10² and 10⁵. Those for naphthalene utilize the data from ref. 12.

(15) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3341 ff. (1952); M. J. S. Dewar in J. W. Cook, "Progress in Organic Chemistry," Vol. II, Academic Press, Inc., New York, N. Y., 1953, p. 1.

(16) For a recent compilation of data see F. B. Deans, C. Eaborn and D. E. Webster, *J. Chem. Soc.*, 3031 (1959); see also ref. 18.

(17) M. J. S. Dewar, T. Mole and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956); also, the discussions in P. B. D. de la Mare and J. H. Ridd, ref. 4b, Chapters 13 and 17, and S. F. Mason, ref. 11.

(18) E. Berliner and N. Shieh, *J. Am. Chem. Soc.*, **79**, 3849 (1957).

Studies on the Mechanism of the Benzilic Acid Rearrangement; the Rearrangement of Alloxan (I)

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Previous reports[15,16] on the alloxanic acid rearrangement had suggested that the reaction followed a simple course of rearrangement of the monoanion of alloxan (AH₃⁻¹). It is here shown that the reaction involves a more complex dependence on pH than hitherto elucidated, which suggests rearrangements not only in the monoanion but also the dianion (AH₂⁻²) and trianion (AH⁻³) (or its equivalent). The rate law based on this complex mechanism is derived and found to be in good agreement with the rate data. Rearrangements in AH₃⁻¹ and AH₂⁻² appear to be quite similar in character but decidedly different from the corresponding reaction in AH⁻³, as judged by several kinetic criteria. For instance, general base catalysis is identified for AH⁻³ rearrangement but is absent in the cases of AH₂⁻² and AH₃⁻¹. An unusual and exceedingly strong specific catalytic effect of borate buffer is demonstrated and its intensity characterized as a function of pH. The activation parameters of the borate-catalyzed, when compared to those of the hydroxide-catalyzed, rearrangement appear to indicate a cyclic intermediate is formed between substrate and borate monoanion as a preliminary to the rate-determining migration step. A discussion of these and other data is presented which arrives at the conclusions (i) that the driving force for both hydroxide ion and general base-catalyzed benzilic acid rearrangement is derived from a "*push*" on the migrating electron pair developed by electron pressure at the seat of reaction; and (ii) that the occurrence of specific ion catalysis of the rearrangement can be correlated with the presence of a reagent (such as borate) which can develop a "*pull*" on the migrating bond at the adjacent carbonyl center in concert with the relief of the electron pressures that are responsible for the "*push*."

Introduction

The familiar transformation of α-diketones by means of base to the salts of α-hydroxy acids is known as the "benzilic acid" rearrangement and is one of the oldest[2a] and most widely studied[2b] carbon–carbon bond cleavage reactions. Specific hydroxide ion catalysis of the cleavage in the parent compound, benzil, has been carefully documented in the work of Westheimer[3] and Roberts and Urey.[4] These authors established by a variety

of rate[3] and tracer[4] studies the formation of an intermediate hydroxide ion adduct (I) of benzil. This intermediate had been isolated by Scheuing[5] and Lachman[6] and is capable of independent existence at lower temperatures in the absence of a polar medium.

The course of rearrangement proposed[3,4] as most consistent with these observations is also similar to one suggested earlier by Ingold[2b] and involved the rate-determining migration of an aryl group in the adduct I according to the indicated course resulting in II. Recently Hine and Haworth,[7] by means of rate studies in D₂O media, have eliminated the occurrence of a concerted participation of the conjugate acid with proton trans-

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(3) F. H. Westheimer, *J. Am. Chem. Soc.*, **58**, 2209 (1936).

(4) I. Roberts and H. C. Urey, *ibid.*, **60**, 880 (1938).

(5) G. Scheuing, *Ber.*, **56**, 252 (1923).

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