Kinetics of Bromination of Benzene in Water[1]

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The high-order terms in the bromination of aromatic substances in acetic acid or other solvents of low polarity can be eliminated by adding water to the acetic acid or by conducting the reaction in the presence of an excess of bromide ion. Under those conditions, the reaction becomes second order over-all and first order in bromine and in the aromatic hydrocarbon; molecular bromine is the substituting agent. Identical kinetic characteristics have been shown to prevail in 50, 60, 75, and 90% aqueous acetic acid,[3] and it remained to demonstrate that they also hold for water. That they might hold in as polar a solvent as water could be anticipated from a general consideration of the mechanism of the high- and second-order bromination,[3,4] but it had not previously been demonstrated in detail. There are some data on the aqueous brominations of nitroanisole and benzene,[5] as well as extensive data on the very fast brominations of amines and phenols,[6] but it seemed worthwhile to apply the same kinetic criteria to bromination in water that had previously been used in the bromination of various aromatic hydrocarbons in aqueous acetic acids.

In Table I are listed the relevant kinetic data for the bromination of benzene in water. Because of the low reactivity of benzene, even in water, and its low solubility, reactions were conducted at elevated temperatures in sealed tubes. The results are analogous to those obtained in the aqueous acetic acid solvents, and it is sufficient to summarize the kinetic features of the reaction. Second-order rate constants are obtained within one kinetic run. Because of the limited solubility of benzene, and the necessity of keeping the benzene in an excess with regard to bromine, the concentrations of benzene and bromine were not altered by more than factors of 2 and 3, respectively, but the rate constants are not changed by these changes in concentrations of reactants. A plot of the rate constants, obtained from runs at different bromide ion concentrations at a constant ionic strength, against the expression $K/(K + [Br^-])$, where K is the dissociation constant of the tribromide ion, is linear. The least-squares slope has a value of $(1.18 \pm 0.06) \times 10^{-3}$ l. mole^{-1} sec^{-1} at 50°.[7] This, as has been shown before, is the value for the rate constant for bromination by free bromine. Free bromine is the sole brominating agent; there is no evidence in this system for bromination by the tribromide ion.

TABLE I

THE BROMINATION OF BENZENE IN WATER[a]

A. The Dependence of Rate on Initial Concentration of Reactants[b]

Benzene, mole/l.	Bromine (approx), mole/l.	$k_{obsd} \times 10^3$
0.01092	0.0018	1.33 ± 0.05
0.01411	0.0018	1.36 ± 0.10
0.007541	0.0018	1.44 ± 0.02
0.01092	0.0037	1.40 ± 0.15
0.01092	0.0052	1.38 ± 0.02

B. The Dependence of Rate on the Bromide Ion Concentration at 50°[c]

NaBr, mole/l.	$NaClO_4$, mole/l.	$k_{obsd} \times 10^4$
0.10	0.40	4.83 ± 0.27
0.15	0.35	3.76 ± 0.12
0.20	0.30	3.33 ± 0.13
0.25	0.25	2.67 ± 0.25
0.30	0.20	1.88 ± 0.08
0.40	0.10	1.67 ± 0.07
0.50	...	1.56 ± 0.04

C. The Dependence of Rate on Temperature[d]

T, °C	$k_{obsd} \times 10^4$
40.0	1.79 ± 0.04
50.0	4.83 ± 0.27
59.8	13.3 ± 0.50

slope = $(4.58 \pm 0.09) \times 10^{+3}$, intercept = 10.87 ± 0.29

[a] All rate constants are in liters per mole per second. [b] [NaBr], 0.10 *M;* [$NaClO_4$], 0.40 *M;* *T*, 59.8°. [c] [benzene], 0.01092–0.01411 *M;* [bromine], 0.00162–0.00276 *M*. [d] [NaBr], 0.10 *M;* [$NaClO_4$], 0.40 *M;* [benzene], 0.01092 *M;* [bromine], 0.001551–0.002100 *M*.

The observed activation energy is 21.0 kcal/mole, log A is 10.87 and $\Delta S^{\ddagger}$ is −10.8 eu at 25°.[8] This value of the activation energy was used to extrapolate the individual rate constants at various bromide ion concentrations to 25°, and, from a plot of k_{obsd} against $K/(K + [Br^-])$, a value of $(8.34 \pm 0.13) \times 10^{-5}$ l. mole^{-1} sec^{-1} was obtained for bromination of benzene at 25°. This should be compared with the value of 2.74×10^{-6} for bromination of benzene in 50% acetic acid.[3,9] The rate decreases with an increase in acetic acid. When two rate constants are compared at the same bromide ion concentration, for instance at 0.1 *M*, the reaction in water is 74 times as fast as that in 50% acetic acid. However, part of that decrease is due to the fact that less free bromine is available in 50% acetic acid than in water (*K* is smaller). The comparison of the true rate constants shows that the reaction in water is 30 times as fast as that in 50% acetic acid. The activation energy for bromination of benzene in 50% acetic acid is 19.6 kcal mole^{-1}, log A is 7.97, and $\Delta S^{\ddagger}$ −24.1 eu.[9] Bromination in water therefore proceeds with a higher activation energy, and the increase in rate is entirely due to a larger entropy of activation.[10] There is ample

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(1) Kinetics of Aromatic Halogenation. XI.

(2) National Science Foundation Trainee, 1965–1966. Taken from the M.A. Thesis of F. Gaskin, Bryn Mawr College, 1967.

(3) E. Berliner and M. C. Beckett, *J. Am. Chem. Soc.*, **79**, 1425 (1957); E. Berliner and B. J. Landry, *J. Org. Chem.*, **27**, 1083 (1962); U. P. Zimmerman and E. Berliner, *J. Am. Chem. Soc.*, **84**, 3953 (1962); L. Altschuler and E. Berliner, *ibid.*, **88**, 5837 (1966).

(4) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworth and Co. (Publishers) Ltd., London, 1959, Chapter 9. P. W. Robertson, P. B. D. de la Mare, and W. T. G. Johnston, *J. Chem. Soc.*, 276 (1943).

(5) W. J. Wilson and F. G. Soper, *ibid.*, 3376 (1949).

(6) R. P. Bell and D. J. Rawlinson, *ibid.*, 63 (1961); R. P. Bell and T. Spencer, *ibid.*, 1156 (1959); R. P. Bell and E. N. Ramsden, *ibid.*, 161 (1958).

(7) The line should go through the origin. The small observed intercept, $(-6.40 \pm 4.72) \times 10^{-6}$, is probably without significance.

(8) When allowance is made for the tribromide ion equilibrium, the activation parameters for bromination by free bromine become ΔE = 19.5 kcal mole^{-1}, log A 10.15, and $\Delta S^{\ddagger}$ −14.1 eu.

(9) E. Berliner and J. C. Powers, *J. Am. Chem. Soc.*, **83**, 905 (1961).

(10) The assumption is made that $\Delta H°$ and $\Delta S°$ for the tribromide ion equilibrium are not significantly changed on going from water to 50% aqueous acetic acid. Since these values are very small compared to the activation parameters, (1.5 kcal/mole and −0.35 eu, respectively),[11] the assumption seems reasonable.

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

precedence that the decreased rate on going from water to a less polar solvent is due to a decrease in entropy, and a case has also been made that this process may be accompanied by a decrease in activation energy.[12]

Experimental Section

The kinetic determinations and all inorganic materials were as described before. The benzene was a research grade sample of the Phillips Petroleum Co. (99.91 mole%), which was redistilled several times during the investigation. All solutions were made up at the temperatures of the kinetic runs. Changes in volume were determined for each temperature and appropriate corrections were applied. Special care was taken to minimize volatility loss of benzene during the preparation of the solutions. The benzene was added to the solution containing the other reagents at room temperature from a specially calibrated pipet. The mixture was then thoroughly shaken and placed in the thermostat for several minutes to affect complete solution of benzene. After a few minutes the flask was cooled to 35°, a bromine–bromide solution was added quickly, and the solution was transferred to eight or ten test tubes. The sealed test tubes were placed in the thermostat and allowed to come to temperature. After 15 min one test tube was withdrawn for the determination of 0 time and cooled in ice, and a 10-ml sample was analyzed for bromine as usual. Reactions were allowed to go to at least 50% completion, and all runs were conducted at least in duplicate. A vpc analysis of a completed run indicated that the product consisted of 99.5% of bromobenzene.[13] Rate constants were determined from second-order plots by the least-square method. The slopes rarely had an error of more than 2.5%. Although the precision within one kinetic run was always good, duplicate runs showed greater scatter than in aqueous acetic acid, possibly because of some unavoidable loss of benzene during the preparation of the solutions.

A value of 0.072 mole l.$^{-1}$ was obtained for the equilibrium constant K at 50° by extrapolation from literature data at lower temperatures, while for 25° the value of 0.0594 from the same source was taken.[14] From the literature data, a value of 1.45 kcal mole^{-1} was obtained for ΔH°, which agrees with the earlier value of 1.5 kcal mole^{-1}.[11]

Registry No.—Benzene, 71-43-2.

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(12) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 137 ff.

(13) We thank Mr. John Raniseski for carrying out this analysis.

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Magnetic Anisotropy of the Oximido Group. Additional Proof of Greater Deshielding from Proximity of the Hydroxyl Group

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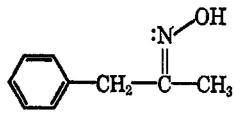
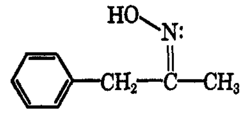
In a recent communication[2] we have reported the observation of a large difference in the geometrical dependence of the deshielding effect of the oximido group on the two sides of the functional group. For example, in 4-*t*-butylcyclohexanone oxime the difference in chemical shifts of the equatorial and axial hydrogen on a given α carbon is 1.68 ppm while on the other α carbon the difference is only 0.43 ppm, when measured in deuteriochloroform. This observation confirms the conformational dependence of chemical shifts of α hydrogens in aliphatic aldoximes proposed by Karabatsos, *et al.*[3] This conformational dependence provides a logical explanation for the known phenomenon[4] that in the nmr spectra of mixtures of isomeric *syn* and *anti* oximes of methyl ketones there is usually a significant difference in the chemical shifts of the α-methylene hydrogens in the two isomers, but little difference, if any, in the chemical shifts of the methyl groups.

Regarding the relative deshielding effects of the hydroxyl group and the unshared pair of electrons on the nitrogen of the oximido group, Karabatsos and coworkers[3] have given evidence that the largest deshielding results from the proximity of the hydroxyl group. Other investigators[4-8] have presented evidence which leads to the same conclusion. Recently, Saitô and co-workers[9-12] have come to the conclusion that the greatest deshielding effect is caused by the unshared pair of electrons on the nitrogen.

We now present additional experimental proof, from the characterization of *anti*- and *syn*-benzyl methyl ketoxime by a Beckmann rearrangement, of a greater deshielding by the proximity of the hydroxyl group of the oximido group than by the proximity of the unshared pair of electrons on the nitrogen.



anti-benzyl methyl ketoxime (I)



syn-benzyl methyl ketoxime (II)

Oxime formation of phenyl-2-propanone by standard methods in pyridine or aqueous sodium hydroxide solution[13] yielded a mixture of I and II in ratio of about 2 to 1 as analyzed by nmr. The spectrum of the mixture in carbon tetrachloride gives a single peak at τ 8.24[14] for the combined signals of the methyl groups of the two isomers, and two signals in ratio of 2:1 at τ 6.55 and 6.30, respectively, attributed to the α-methylene hydrogens of the *anti* and *syn* isomers. The signals of aromatic hydrogens overlap to give a single peak at τ 2.85. In pyridine at 60 Mc the signals of

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(14) Chemical shifts were seen to vary slightly with changes in concentration.