frequency orientation. Substitution of a methyl group in the free *ortho*-position changes this value, as would be expected so that 17% of the molecules then have the high frequency orientation. It would be expected that substitution of bulkier groups in the 6-position would increase the absorptivity of the high frequency peak until the di-*o*-*t*-butylphenol situation was achieved.

Subsequent to this work with the fundamental hydroxyl band, a few compounds were run at the first overtone of the free hydroxyl stretching band at 1.4 μ in order to get comparative data. These data in Table II confirm the conclusions drawn from Table I. The values for the per cent. high frequency form are slightly lower but are of the same order of magnitude.

This work, in addition to the data presented, points out the value of high resolution spectra in dilute solutions for detecting minor intramolecular interactions of hydroxyl groups. Similar interactions may be detectable between *t*-butyl groups and other functional groups. Such correlations are valuable in establishing molecular configurations and explaining the reactivity of the various functional groups.

Experimental

The work at 2.7 μ was carried out on a Beckman Model DK-2 Spectrophotometer using a 2x expanded scale, scanning time of 20, time constant 0.2 and sensitivity such that a slit width of 0.12 mm. was obtained at 3619 cm.$^{-1}$ (2.763 μ) (half-intensity band-width 8 cm.$^{-1}$ or 6 mμ). The work at 1.4 μ was done on a Cary Model 14 Spectrophotometer using a slit width of 0.15 mm. at 7143 cm.$^{-1}$ (1.400 μ) (half-intensity band-width 2.6 cm.$^{-1}$ or 0.53 mμ) and a recording speed of 5Å./sec. Slit widths were set with a cell filled with dry carbon tetrachloride in the reference beam. Further details on methods of calculation, cells and solvents are in the earlier paper.[7]

All compounds are believed to be 95% pure or better. While a few were commercial samples, most were prepared here.[8]

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[8] Prepared by the Naval Stores Research Division of this Research Center. The author is particularly indebted to Drs. C. E. Smith, L. J. Filar and R. A. Bankert.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY, CAMPUS STATION, SOCORRO, NEW MEXICO]

The Volume Change of Activation in the Decomposition of Aromatic Diazonium Salts

BY K. R. BROWER

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The volume changes of activation for the decomposition of various benzenediazonium fluoroborates in aqueous solution are nearly equal and surprisingly large. It is suggested that the leaving group does not move independently of its water of solvation and has in effect a large cross-sectional area. The product ratio for the decomposition of *p*-nitrobenzenediazonium ion in solutions containing bromide ion is insensitive to pressure and the involvement of a bimolecular process is therefore doubtful.

Introduction

The effects of hydrostatic pressure on the rates of many bimolecular reactions have been measured and the volume changes of activation calculated therefrom, but very few unimolecular reactions have been so treated. It has been shown that solvolyses of certain alkyl halides for which the S$_N$1 mechanism may be reliably postulated are accelerated by pressure and therefore have negative volume changes of activation.[1] This effect is ascribed to electrostriction of solvent by the polarized transition state and is analogous to the effect of pressure on the ionization constants of water and other weak acids. Measurements have also been made on the acid-catalyzed hydrolysis of formals, acetals and ethyl orthoformate which is believed to be a two step process involving equilibrium-controlled transfer of a proton followed by slow unimolecular decomposition.[2]

As an example of a simple one-stage unimolecular process uncomplicated by large changes in polarization the decomposition of aromatic diazonium salts in aqueous solution shows promise. The kinetics have been extensively investigated and except for one case which will be discussed in the next section, have been shown to be first-order with rates nearly independent of the kind and concentration of anions.[3] The effects of substituents on the rates of reaction are consistent with a carbonium-ion mechanism; for example, a *p*-nitro group greatly decreases the rate, whereas it would be expected to favor nucleophilic attack by water if such were involved.[4]

Measurement of the sign and magnitude of the volume change of activation for diazonium ion decomposition could be expected to answer at least the first and perhaps both of these two questions: whether nucleophilic attack by water occurs and whether a simple bond-breaking process results in a measurable increase in molecular volume. A negative volume change would conclusively establish the bimolecular mechanism since the reaction of a neutral molecule with an ion could only cause a slight release of electrostricted solvent,[5] and a net decrease of volume could only result from contraction along the reaction coördinate. A considerable positive volume change would tend to confirm the carbonium-ion mechanism, and its magnitude might be expected to correlate with the reactivity.

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[1] J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, **49**, 1425 (1953); H. G. David and S. D. Hamann, *ibid.*, **50**, 1188 (1954).

[2] J. Koskikallio and E. Whalley, *ibid.*, **55**, 809 (1959).

[3] H. Euler, *Ann.*, **325**, 292 (1902); J. C. Cain, *Ber.*, **38**, 2511 (1905); H. Pray, *J. Phys. Chem.*, **30**, 1417, 1477 (1926); J. E. Taylor and T. J. Feltis, THIS JOURNAL, **74**, 1331 (1952); E. A. Moelwyn-Hughes and P. Johnson, *Trans. Faraday Soc.*, **36**, 948 (1940).

[4] M. L. Crossley, R. H. Kienle and C. H. Benbrook, THIS JOURNAL, **62**, 1400 (1940).

[5] C. T. Burris and K. J. Laidler, *Trans. Faraday Soc.*, **51**, 1497 (1955).

Results and Discussion

The rates of evolution of nitrogen from aqueous solutions of variously substituted benzenediazonium fluoroborates and diazotized sulfanilic acid were measured at pressures up to 1360 atm. The volume changes of activation were calculated from the equation

$$RT(\delta \ln k/\delta P)_T = -\Delta V^*$$

in which k is the reaction rate constant and ΔV^* is the change of molar volume resulting from the transformation of one mole of reactant into activated complex. The plots of ln k *vs.* P show no systematic curvature over the range of pressure used. The results are shown in Table I which lists the volume changes of activation reduced to a standard temperature of 323° K., the reaction rate constants at normal pressure, and the temperatures actually used.

TABLE I

Compound	ΔV^* (ml.)	k (hr.$^{-1}$)	T (°C.)
$C_6H_5N_2BF_4$	10.0	0.298	29.3
p-$NO_2C_6H_4N_2BF_4$	9.4	.116	60.3
p-$CH_3C_6H_4N_2BF_4$	9.0	.49	49.4
p-$CH_3OC_6H_4N_2BF_4$[a]	(7.1)	(.0174)	71.4
p-$ClC_6H_4N_2BF_4$	10.8	.071	60.7
p- $^{-}O_3SC_6H_4N_2{}^{+}$	10.7	.263	49.9
m-$NO_2C_6H_4N_2BF_4$	9.2	.144	69.3
m-$ClC_6H_4N_2BF_4$	11.4	.117	44.7

[a] Data on this compound is unreliable owing to tar formation during decomposition.

The volume changes are substantially positive and nearly equal within the range of experimental error which is approximately ±1 ml. In view of their magnitudes it seems most unlikely that nucleophilic attack by water is involved. If one assumes that the departing diazonium salt group may be represented as a cylinder which elongates without changing its cross-sectional area, it is possible to estimate either the increase in length of the carbon–nitrogen bond or its cross-sectional area by using an assumed value for one of the parameters. Previous calculations of this nature have been based on an assumed 10% elongation of the breaking bond,[6] which is the present case gives a cross-sectional area of approximately 125 Å.^{2} Measurement of a Godfrey model,[7] which is based on van der Waals radii, shows that the leaving group would attain only half of this area even if it were completely surrounded by undistorted water molecules. Nevertheless, it has been estimated that an unshielded ion in water produces electrostriction of solvent amounting to 26 ml./mole,[8] and release of somewhat less than half that amount of water of solvation could account for the observed volume changes of activation. It is not easy to see how such solvent release could occur, however, since the center of positive charge is not destroyed in the transition state and should not even be shifted in position by more than 1 Å. If the positive charge were displaced very far toward the ring then the decomposition of diazobenzenesulfonic acid should be abnormal in consequence of the change in its electric moment. Its rate of reaction and volume change of activation are quite ordinary, however. A more satisfying explanation of the volume change is that the leaving group is in effect very large owing to the solvent cage being rigidly attached to it up to the point of transition.

It has been reported that certain bimolecular aromatic substitution reactions show a strong correlation between reactivity and volume change of activation,[9] but no such correlation is found here. Evidently the potential function for the breaking bond slopes steeply up to the transition point so that considerable differences in free energy of activation correspond to a small difference in geometry.

A kinetic study of the decomposition of *p*-nitrobenzenediazonium ion in solutions containing bromide ion indicates simultaneous operation of bimolecular and unimolecular mechanisms.[10] In brief, the ratio of the yield of *p*-bromobenzene to that of *p*-nitrophenol increases with increasing concentration of the bromide ion more rapidly than would be expected from the unimolecular mecha-

TABLE II

SUMMARY OF KINETIC DATA

Benzenediazonium fluoroborate, 29.3°

P (atm.)	1	340	612	980	1360
k (hr.$^{-1}$)	0.298	0.258	0.233	0.209	0.181

p-Toluenediazonium fluoroborate, 49.4°

P (atm.)	1	405	542	680	815	1360
k (hr.$^{-1}$)	0.494	0.447	0.425	0.396	0.376	0.323

p-Nitrobenzenediazonium fluoroborate, 60.3°

P (atm.)	1	272	678	950	1360
k (hr.$^{-1}$)	0.116	0.104	0.090	0.081	0.071

p-Methoxybenzenediazonium fluoroborate, 71.4°

P (atm.)	1	272	815	1360
k (hr.$^{-1}$	0.0174	0.0162	0.0141	0.0121

p-Chlorobenzenediazonium fluoroborate, 60.7°

P (atm.)	1	272	612	935	1360
k (hr.$^{-1}$)	0.071	0.063	0.055	0.050	0.042

p-Diazobenzenesulfonic acid, 49.4°

P (atm.)	1	136	420	817	1155	1360
k (hr.$^{-1}$)	0.263	0.236	0.226	0.190	0.168	0.163

m-Nitrobenzenediazonium fluoroborate, 69.3°

P (atm.)	1	340	680	1020	1360
k (hr.$^{-1}$)	0.144	0.137	0.113	0.102	0.091

m-Chlorobenzenediazonium fluoroborate, 44.7°

P (atm.)	1	272	545	817	1090	1360
k (hr.$^{-1}$)	0.117	0.104	0.093	0.086	0.073	0.064

N,N,N-Trimethyl-*p*-nitroanilinium chloride, 0.04 *M*, and sodium hydroxide, 51.4°

P (atm.)	1	1360	1	1360
k (l./mole hr.)	0.066	0.064	0.066	0.064
(OH^-)	0.890	0.890	0.356	0.356

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[6] A. E. Stearn and H. Eyring, *Chem. Revs.*, **29**, 509 (1941).

[7] Godfrey Molecular Models, Inc., New Brunswick, New Jersey.

[8] A. M. Couture and K. J. Laidler, *Can. J. Chem.*, **34**, 1209 (1956).

[9] K. R. Brower, THIS JOURNAL, **80**, 2105 (1958); **81**, 3504 (1959).

[10] E. S. Lewis and W. H. Hinds, *ibid.*, **74**, 304 (1952).

nism alone. The expression given for this ratio was

$$\mathrm{ArBr/ArOH} = (\mathrm{Br}^-)[k_3/k_2 + k_4(\mathrm{H_2O})/k_1 + k_3k_4(\mathrm{Br}^-)/k_1k_2]/(\mathrm{H_2O})$$

in which k_1 is the unimolecular rate constant, k_4 is the bimolecular rate constant and k_2 and k_3 are the rate constants for the combination of the carbonium ion with water and bromide ion, respectively.

If the volume changes of activation for the two mechanisms should differ by more than 1–2 ml./mole, then the product composition would vary sensibly with pressure. The values of the rate constants are such that the product ratio is much less sensitive to changes in k_3/k_2 than in k_4/k_1. The value of k_1 is known from the present work to be decreased by one-third at 1360 atm., and it might be expected that k_4 would be unaffected or even increased by pressure.

In order to shed light on the latter point, a preliminary experiment was performed on the reaction of N,N,N-trimethyl-*p*-nitroanilinium chloride with hydroxide ion which produces *p*-nitrophenol as the chief product. The reaction is bimolecular since its rate is proportional to the hydroxide ion concentration, and at 1360 atm. the rate is retarded by 4% which corresponds to a volume change of activation of 1 ml./mole. The fact that the volume change is not negative as in most bimolecular reactions is owing to the fact that it involves ions of opposite charge, and water of solvation is released as the transition state is formed.

If the volume change of activation for the bimolecular reaction of bromide ion with *p*-nitrobenzenediazonium ion were also 1 ml./mole, then the ratio of *p*-nitrobromobenzene to *p*-nitrophenol would change from 0.259 ± 0.012 at 135 atm. to 0.356 at 1360 atm. The measured ratio at the upper pressure was 0.240 ± 0.015. Any evidence of simultaneous reactions having different pressure coefficients is therefore entirely lacking.

Experimental

Kinetic Measurements.—The high pressure vessel and thermostat bath have been previously described.[9] A 2.5 ml. sample of 0.04 *M* diazonium salt solution was inclosed in a small-mouthed glass bell of 6.5 ml. capacity together with a stirrer consisting of a small piece of iron wire sealed in glass. The remaining volume was filled with mercury, and the bell was pushed up inside an inverted test tube. The mouth of the bell was pressed against the end of the tube to effect a seal, and the apparatus was re-inverted. A few ml. of mercury was added to the test tube to allow for compression of the liquid. After a period of heating under pressure the sample holder was cooled to 20°, and dissolved nitrogen was expelled from the solution in the bell by agitating the stirrer with an external magnet. The bell was removed by reversing the procedure above after tipping the test tube to equalize the internal and external mercury levels. The volume of nitrogen was then measured by filling the bell with water from a 10 ml. buret. The average deviation of duplicate measurements was 2–3%.

Solutions of N,N,N-trimethyl-*p*-nitroanilinium chloride and sodium hydroxide were treated in the manner previously described.[9] The reaction mixture was analyzed for *p*-nitrophenol spectrophotometrically after extraction with chloroform to remove *p*-nitrodimethylaniline. A 1 ml. aliquot of a solution originally 0.04 *M* in quaternary salt was diluted to 250 ml. with water and diluted further 10:1 with 0.09 *N* sodium hydroxide. The concentration was calculated from the optical density at 399 mμ with a path length of 1 cm.

Measurements of Product Composition.—The mixture resulting from the decomposition of *p*-nitrobenzenediazonium fluoroborate in a solution 1.5 *M* in bromide ion was analyzed by the method of Lewis and Hinds.[10] The reaction was carried out in a glass tube fitted with a rubber piston and having dimensions such that the piston was not completely expelled by nitrogen gas when the pressure was released.

A solution of N,N,N-trimethyl-*p*-nitroanilinium chloride, 0.04 *M*, and sodium hydroxide, 0.89 *M*, was allowed to react for 96 hr. (10 half-lives) at 51.4° and was found to contain 86% of the theoretical amount of *p*-nitrophenol. A solution of 1 g. of the quaternary salt in 10 ml. of 1 *M* sodium hydroxide was placed in a sealed tube and heated for 2.5 hr. in boiling water. Extraction of the reaction mixture with chloroform and evaporation of the extract gave 0.24 g. (31%) of *p*-nitrodimethylaniline, m.p. 163–164°, which was identified by the undepressed m.p. of a mixture with an authentic sample. An aliquot of the aqueous layer was analyzed spectrophotometrically for *p*-nitrophenol and was found to contain 61% of the theoretical amount.

Reagents.—The diazonium fluoroborates were prepared by generalizing the method of Lewis and Hinds.[10] N,N,N-Trimethyl-*p*-nitroanilinium chloride was prepared by the method of Zaki and Fahim.[11]

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[11] A. Zaki and H. Fahim, *J. Chem. Soc.*, 270 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY, STANFORD, CALIFORNIA]

Peroxides. IX. The Kinetics of the Hydrogen Evolution from the Thermal Decomposition of 1-Hydroxyalkyl Alkyl Peroxides[1]

BY LOIS J. DURHAM[2] AND HARRY S. MOSHER

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The kinetics of the thermal decomposition of 1-hydroxy-*n*-butyl *n*-butyl peroxide and 1-hydroxyisobutyl isobutyl peroxide have been studied over the temperature range of 80–110° by following the rate of hydrogen evolution as a means of elucidating the mechanism of the decomposition of these compounds and the corresponding hydroperoxides from which they were derived. α-Methylsytrene was used both as a solvent and as a trap for free-radicals. The Arrhenius energies of activation and frequency factors and the enthalpies of activation and entropies of activation were calculated from the rate data for both compounds. These data have been interpreted in terms of a concerted cyclic transitions state.

Introduction

Studies on the thermal decomposition of *n*-butyl hydroperoxide[3] led to the postulate that 1-hydroxy-*n*-butyl *n*-butyl peroxide was the intermediate which was responsible for the formation of

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[1] Previous communication, Paper VIII in this series, L. J. Durham, C. F. Wurster and H. S. Mosher, THIS JOURNAL, **80**, 332 (1958).

[2] Taken from the Ph.D. Dissertation of Lois J. Durham, Stanford University, 1959.

[3] H. S. Mosher and C. F. Wurster, THIS JOURNAL, **77**, 5451 (1955).