the exit gases being bubbled through 100 ml. of water. Ozonization was terminated when the green color of excess ozone appeared; this occurred when about 150% of the theoretical ozone had been passed in. The contents of the water trap were assayed for formaldehyde with chromotropic acid.[31] The carbon-tetrachloride solution was transferred to a round-bottomed flask, washing in the gummy ozonide with 15–25 ml. of glacial acetic acid, and refluxed for an hour with 100 ml. of water. After cooling, the CCl_4 layer was drawn off and twice re-extracted with water; the combined aqueous extracts were then assayed for formaldehyde. Most of the formaldehyde was found here rather than in the water-trap.[32]

(b) **Geronic Acid.**[33]—The aqueous and carbon tetrachloride layers were recombined and refluxed for one hour with 5 ml. of 30% hydrogen peroxide. The mixture was then made alkaline with ammonia and the carbon tetrachloride layer extracted three times with 75-ml. portions of 1% ammonia water. The combined ammoniacal extracts were concentrated under vacuum to about 300 ml., acidified to *p*H 1, and treated with a hot solution of 3.0 g. of 2,4-dinitrophenylhydrazine, 10 ml. of concd. hydrochloric acid, and 3 ml. of water in 30 ml. of glacial acetic acid. After standing at 5° overnight, the crude derivative was filtered off and leached five times at 80° with 50-ml. portions of 3% potassium bicarbonate. The geronic acid derivative was reprecipitated from the cooled, combined filtrates by acidifying to *p*H 1, and filtered off on a sintered glass funnel. It was then redissolved on the filter with a minimum quantity of glacial acetic acid and the filtrate diluted at 60° with six-fifths its volume of hot water. After cooling to 5° the precipitated derivative was filtered off, washed sparingly with 50% acetic acid and dried under vacuum. Some specimens melted as low as 130–134° and others as high as 136–138°.

(c) **α,α-Dimethylglutaric Acid.**—*trans*-VIII (7.2 g.) was ozonized in 50 ml. of carbon tetrachloride and 50 ml. of glacial acetic acid; the time of ozonization was as above. The solution of ozonide was vigorously stirred overnight with 35 ml. of 30% hydrogen peroxide and 50 ml. of 0.2 *N* sulfuric acid,[34] then, with an additional 10 ml. of Superoxol, for two hours at 100°. (The CCl_4 was allowed to escape.) The cooled solution was freed of peroxides with sodium sulfite, and concentrated on the steam-bath at aspirator pressure. The resulting damp solid was taken up in 75 ml. of 20% hydrochloric acid, and extracted with four 50-ml. portions of ether; the dried ether extract was concentrated and distilled. The fraction boiling at 110–145° (0.1 mm.) largely crystallized on standing; a small sample of the crystals, after washing with hexane, melted at 81.5–82.5°. The whole fraction (2.45 g.) was dissolved in 30 ml. of 0.5 *N* NaOH, filtered, and treated with 3.0 g. of benzylisothiourea hydrochloride in 10 ml. of water. After an hour at 5°, the crystalline solid was filtered off, dried at 80° and weighed: 2.35 g., m. p. 172–174°. Recrystallization from aqueous acetone gave microprisms, m. p. 177–178°.

Anal. Calcd. for $C_{15}H_{22}O_4N_2S$: C, 55.19; H, 6.80; N, 8.58. Found: C, 55.29; H, 6.94; N, 8.45, 8.57.

Authentic α,α-dimethylglutaric acid was prepared in the same way as similar α,α-dialkylglutaric acids.[35] The cyanoethylation of isobutyraldehyde[36] (50% aqueous KOH as catalyst, at 70°) gave a 60% yield of γ-formylisocapronitrile, b.p. 82–84° (2 mm.), $n^{25}D$ 1.4355. Alkaline hydrolysis, followed *in situ* by $KMnO_4$ oxidation, furnished in 90% yield crude dimethylglutaric acid melting at 75–79°. The benzylisothiuronium salt, after recrystallization, melted at 175–176°; mixed m.p. with the specimen from ozonolysis, 176–177°.

Anal. Found: C, 55.33; H, 7.01; N, 8.36.

Absorption Spectra.—All absorption spectra were determined in 95% ethanol using a Beckman spectrophotometer.

Acknowledgment.—The authors are indebted to Mr. Robert A. Mallory and Mr. William Häffcke for technical assistance, and to Mr. Joseph Grodsky for the microanalyses.

---

[31] D. A. MacFadyen, *J. Biol. Chem.*, **158**, 112 (1945).

[32] Yields of formaldehyde up to 5% were considered insignificant. Anomalous yields of formaldehyde up to 2.5% were obtained from negative controls by G. R. Clemo and J. M. Macdonald (*J. Chem. Soc.*, 1294 (1935)) who used no water trap. Their positive controls gave 20–32% formaldehyde. Y.-R. Naves [*Helv. Chim. Acta*, **31**, 908 (1948)], using a water-trap, obtained 49–65% yields from positive controls. In the present work 1-acetoxy-3-methylbutene-3 (E. Arundale and L. A. Mikeska, U. S. Patent 2,246,285) was used as a positive control and gave 43% formaldehyde.

[33] This procedure is a modification of that of H. H. Strain [*J. Biol. Chem.*, **102**, 144 (1933)].

[34] W. G. Young and S. L. Linden, THIS JOURNAL, **69**, 2042 (1947).

[35] H. A. Bruson and T. W. Riener, *ibid.*, **66**, 57 (1944); J. Cason, *J. Org. Chem.*, **13**, 233 (1948).

[36] French Patent 886,846 (1943); H. A. Bruson and T. W. Riener, U. S. Patent 2,353,687 (1944). The boiling point given by J. F. Walker [U. S. Patent 2,409,086 (1946)] is too high.

RARITAN, NEW JERSEY RECEIVED JANUARY 22, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

The Bimolecular Displacement of Nitrogen from *p*-Nitrobenzenediazonium Ion[1]

BY EDWARD S. LEWIS AND WILLIAM H. HINDS

In excess acidic sodium bromide solutions *p*-nitrobenzenediazonium ion reacts to give a mixture of *p*-nitrobromobenzene, *p*-nitrophenol and tar. The reaction is pseudo first-order, since the apparent first-order rate constant increases linearly with the bromide ion concentration. This behavior indicates the presence of a second-order displacement of nitrogen by bromide accompanying the recognized first-order decomposition of this diazonium salt. Such an interpretation is supported by the ratio of the yields of *p*-nitrobromobenzene and *p*-nitrophenol as a function of bromide ion concentration. Low concentrations of copper have a large effect on this reaction, but the small quantities unavoidably present could not alone account for the observed kinetics.

Introduction

The decomposition of benzenediazonium ion in dilute solution in water is a first-order reaction leading to phenol,[2] the rate of which is little influenced by the presence of other ions in moderate concentration.[3] In the presence of chloride ion appreciable yields of chlorobenzene are also produced.[2] A two-step mechanism has been proposed[4] to explain these observations. The first is a rate-determining loss of nitrogen from the diazonium ion

$$C_6H_5N_2^+ \longrightarrow C_6H_5^+ + N_2 \qquad (1)$$

This is followed by a fast reaction of the phenyl cation with water to give phenol

$$C_6H_5^+ + H_2O \longrightarrow C_6H_5OH + H^+ \qquad (2)$$

or, in the presence of chloride ion

$$C_6H_5^+ + Cl^- \longrightarrow C_6H_5Cl \qquad (3)$$

---

[1] From the Ph.D. Thesis of W. H. Hinds, Rice Institute, May, 1951. Presented in preliminary form at the Southwest Regional Meeting of the American Chemical Society, December, 1950.

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

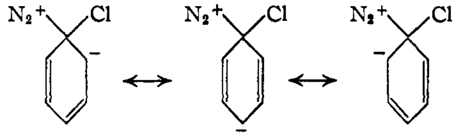
[3] H. A. H. Pray, *J. Phys. Chem.*, **30**, 1477 (1926).

[4] W. A. Waters, *J. Chem. Soc.*, 266 (1942).

However, in the presence of fairly concentrated hydrochloric acid, Blumberger,[5] and Crossley, Kienle and Benbrook[2] noted a small increase in rate. The effect of neutral salts in general appears, from the data of Pray,[3] to be small, and the rate is slightly depressed in salt solutions of high concentration. While the change in rate is small, the presence of a second-order reaction of diazonium ion with chloride ion is suggested

$$C_6H_5N_2^+ + Cl^- \longrightarrow C_6H_5Cl + N_2 \qquad (4)$$

In the transition state for all bimolecular displacements on aromatic systems, structures such as



must contribute. We are not in a position to say whether there exists an unstable intermediate of this structure.

In the case of unsubstituted benzenediazonium ion this reaction, which is presumably a normal bimolecular displacement (the S_N2 reaction of Gleave, Hughes and Ingold[6]), is not suited to a more careful study because the first-order reaction (the S_N1 reaction) obscures it except in the very concentrated solutions. We selected the *p*-nitro substituent as one of the most favorable since the first-order reaction is very slow in this case,[2] and the *p*-nitro group would be expected to facilitate the bimolecular reaction. As the displacing reagent we selected bromide ion, both because it is a more powerful nucleophilic reagent than chloride ion, and because it could give information about the possibly analogous reaction of iodide ion, which is kinetically very complicated.[7] Recently a related reaction has been studied by Pfeil,[8] who investigated the reaction of *p*-nitrobenzenediazonium ion in the presence of chloride. Pfeil was interested in the yields of *p*-nitrophenol and *p*-nitrochlorobenzene in solutions of varying chloride content. His data are of little use for our purposes because the accuracy of his analyses is partially vitiated by a questionable treatment of tar formation, and because the corresponding kinetic data do not appear.

Experimental

Materials.—*p*-Nitrobenzenediazonium fluoborate was prepared by the addition of excess cold 40% fluoboric acid to a solution of diazotized *p*-nitroaniline (m.p. 147°) in hydrochloric acid. The resulting clean, pale yellow crystalline material was washed with alcohol and then with ether. It gave 93% of the theoretical amount of nitrogen in a reaction with an equivalent amount of cuprous chloride in 3 *M* hydrochloric acid. This represents only a minimum value of the purity of the diazonium salt since some of the nitrogen is found as azo compound. Balz and Schiemann,[9] for the first preparation of this compound, found that the nitrogen content was about 5% low. It is stable for several weeks if light and moisture are excluded, and has been found a most convenient source of diazonium ion.

The sodium bromide was Merck and Co., Inc., "Reagent Grade" material; a 5 *M* solution of this substance was 1.6×10^{-6} *M* in copper. J. T. Baker "Analyzed" sodium nitrate and 48% hydrobromic acid were used. Deionized water was distilled twice in an all-glass system before use: analysis showed that it was 1.5×10^{-7} *M* in copper.

Copper was estimated by the method of Snell and Snell[10] using reduced phenolphthalein, and quantitative analyses were made by spectrophotometric determination as the dithizone complex.[11]

In the determination of yields, 200 ml. of a solution of hydrobromic acid and sodium bromide of appropriate composition and 1.00 g. of *p*-nitrobenzenediazonium fluoborate were placed in a 500-ml. Kjeldahl flask fitted with a cold finger reflux condenser. This concentration of diazonium salt is of the same order as that used in the kinetic runs. The flask was immersed in the thermostat at 75°. After sufficient time for completion of the reaction, the contents of the flask and rinsings from the condenser were subjected to steam distillation. The distillate contained virtually all of the *p*-nitrobromobenzene, m.p. 126–127°, which could be readily dried and weighed. Similar treatment of a weighed sample of pure *p*-nitrobromobenzene resulted in the recovery of 98.2%. The residue was filtered while hot, and the tarry material on the filter was extracted three times with 100-ml. portions of boiling water, and the last extract gave only a barely perceptible color with sodium hydroxide. The combined filtrate and extracts, containing the *p*-nitrophenol, was diluted with water to two liters, and a further tenfold dilution with 0.10 *M* sodium hydroxide solution was made before measuring the optical density at 450 mμ. This procedure measures the water-soluble materials which are intensely colored in basic solution, but eliminates even those components of the tar which are soluble in sodium hydroxide with coloration. Thus only *p*-nitrophenol is measured here. It was isolated from one run with a m.p. 113–114°, but the isolation procedure was far from quantitative. Analysis of known solutions of *p*-nitrophenol by this method gave results always within 5% of the calculated concentration, and the reproducibility of analyses was better than this.

The tar, while manifestly containing several components, resisted attempts at fractionation into pure substances. It contained no detectable amount of *p*-nitrophenol. Contrary to the observation of Pfeil on the reaction with chloride ion, more tar resulted from the reactions at high bromide concentrations than at lower concentrations. The quantity of tar was not accurately determined.

Kinetic Measurements.—Kinetic data on the reactions under consideration were obtained by measurement of the rate of nitrogen evolution. The reactions were conducted in a jacketed reaction vessel of about 250-ml. capacity, maintained at constant temperature (±0.02°) by circulating thermostated water through the jacket. Supersaturation of the solution by nitrogen was prevented by mounting the reaction vessel in an electrically driven shaker which was operated continuously throughout the run. The reaction vessel was connected by a length of small bore flexible tubing to a manometer and a 100-ml. gas buret thermostated by the effluent from the reaction vessel jacket. Kerosene was used as a containing fluid in both buret and manometer.

A solution of the desired acidity and bromide ion concentration was prepared by diluting the appropriate amounts of sulfuric acid or 48% hydrobromic acid and sodium bromide to 100 ml. All but about 20 ml. of this solution was poured into the reaction vessel and allowed to come to temperature before starting the run. Air was removed from this solution by passing nitrogen through it. The remainder of the bromide solution was kept in a beaker at the thermostat temperature. This was used to dissolve and transfer 0.60 to 0.80 g. of diazonium salt into the reaction vessel. A variable amount of room temperature air was unavoidably admitted with the sample. The shaker was started and five minutes was allowed for the entire system to come to thermal equilibrium before collection of gas was begun. This procedure was necessary to insure good kinetics at the beginning of the reaction, although a necessary consequence was the loss of information on the total nitrogen yield. This datum was not essential, and in any case was not available since the temperature of the gas was in doubt for several

---

[5] J. S. P. Blumberger, *Rec. trav. chim.*, **49**, 259 (1930).

[6] J. L. Gleave, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 236 (1935).

[7] W. H. Hinds, unpublished work.

[8] E. Pfeil, *Ann.*, **561**, 220 (1948).

[9] G. Balz and G. Schiemann, *Ber.*, **60**, 1187 (1927).

[10] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," 3rd ed., Vol. 2, D. Van Nostrand and Co., Inc., New York, N. Y., 1949, p. 132.

[11] *Ibid.*, p. 114.

minutes. Volume readings were made at successive intervals as close to five minutes in length as was experimentally possible. Normally the reactions were followed for a minimum of five half-lives.

First-order rate constants were computed by the method of Guggenheim,[12] in which they are obtained from the slopes of lines resulting from plotting the logarithms of successive volume increments over constant time intervals against the time. This method has the advantage of not being dependent upon an accurate final volume reading. Treatment of the data in this manner showed that the reactions conform unmistakeably to first-order kinetics. Departures from linearity often present in late stages of the reaction were attributed to side reactions, presumably those giving rise to the tarry substances. A typical plot, carried to about 80% completion, is shown in Fig. 1.

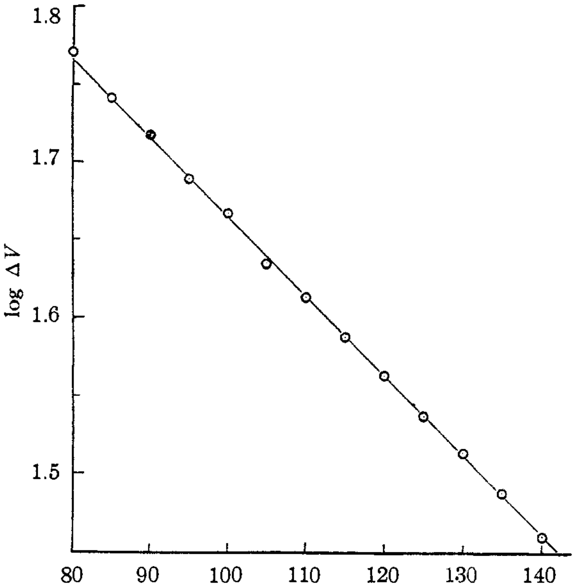


Fig. 1.—Guggenheim plot using 80-minute intervals for the decomposition of *o*-nitrobenzenediazonium fluoborate in 1 *M* H_2SO_4, 2.12 *M* NaBr, 75°.

Results and Discussion

Table I shows the apparent first-order rate constants at 75° at different bromide concentrations in solutions 1.0 *M* in sulfuric acid. These results are plotted in Fig. 2, and on the same figure is also plotted a more extensive but somewhat less reproducible series in which all solutions were 1.0 *M* in hydrobromic acid, instead of sulfuric acid.

TABLE I

VARIATION OF RATE CONSTANT WITH BROMIDE CONCENTRATION

(Br^-), moles/l.	k_{app} × 10^4 sec.$^{-1}$
0	1.65
0	1.53
1.00	1.80
2.12	1.98
4.00	2.50
6.00	2.89

Table II shows the yields of products at 75° in solutions 1.0 *M* in hydrobromic acid containing varying amounts of sodium bromide. Yields were not determined in sulfuric acid containing solutions.

Preliminary results on the rates of the reaction showed that the rate of nitrogen evolution was higher in the solutions of high bromide concentrations, but that the rate constants were very erratic. This scatter of experimental results was traced to small amounts of copper in the water used, and a run containing 10^{-2} *M* cupric sulfate was too fast to measure (half-life at 75° not more than two minutes). The concentration of copper in the water originally used was about 10^{-5} *M* and this caused a scatter of rate constants at 6 *M* bromide between 3.4 and 5 × 10^{-4} sec.$^{-1}$. These preliminary results also showed that the rate was very insensitive to acid concentration, and in the absence of bromide was depressed 6% by 2 *M* and 19% by 4 *M* sodium nitrate. The tabulated data reported above were all taken using redistilled water but the remaining scatter can probably still be attributed to unavoidable and varying traces of copper. Possible catalytic activity of other materials was not considered.

TABLE II

YIELDS OF PRODUCTS FROM DECOMPOSITION OF *p*-NITROBENZENEDIAZONIUM FLUOBORATE

Total (Br^-), moles/l.	% *p*-$NO_2C_6H_4Br$	% *p*-$NO_2C_6H_4OH$	k_3/k_2
1.5	20.4	75.4	2.3
1.5	21.0	75.6	
4.0	33.6	45.1	1.9
4.0	34.4	46.8	
6.0	38.3	27.3	2.9
6.0	40.3	30.9	
7.5	46.0	22.0	3.4
8.0	45.5	19.2	3.5

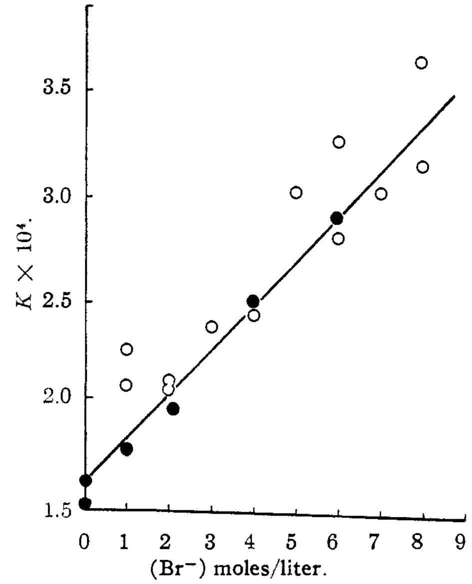


Fig. 2.—Change in apparent first-order rate constants for the decomposition of *p*-nitrobenzenediazonium ion with bromide ion. Open circles are in HBr solution, filled circles are in H_2SO_4 solution.

The following reactions were assumed

$$ArN_2^+ \xrightarrow{k_1} Ar^+ + N_2 \quad (5)$$

$$Ar^+ + H_2O \xrightarrow{k_2} ArOH + H^+ \quad (6)$$

$$Ar^+ + Br^- \xrightarrow{k_3} ArBr \quad (7)$$

---

(12) E. A. Guggenheim, *Phil. Mag.*, Ser. 7, 2, 538 (1926).

$$ArN_2^+ + Br^- \xrightarrow{k_4} ArBr + N_2 \qquad (8)$$

with the first and last slow.

On this basis the rate of nitrogen evolution is

$$d(N_2)/dt = [k_1 + k_4(Br^-)](ArN_2^+) \qquad (9)$$

and since the bromide ion is present in large excess, its concentration does not vary during a run and the first term of eq. (9) is the apparent rate constant k_{app}

$$k_{app} = k_1 + k_4(Br^-) \qquad (10)$$

Thus in Fig. 2 the intercept with the rate constant axis is k_1 and the slope is k_4. The kinetic data are thus consistent with the above formulation. The values obtained are $k_1 = 1.64 \times 10^{-4}$ sec.$^{-1}$, and $k_4 = 2.12 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$. Using the same method, k_1 and k_4 were calculated from less complete data at 65 and 85°. These data yield an energy of activation of 27.8 kcal. for reaction (5), and a much less accurate value of 37 kcal. for reaction (8). Crossley, Kienle and Benbrook report on the basis of measurements at only two temperatures a value of 29.8 kcal. for reaction (5).

An adequate fit of the yield data is a more rigorous test of this mechanism. The ratio of rate expressions for the formation of *p*-nitrophenol and *p*-nitrobromobenzene is readily integrated, leading to the expression

$$\frac{(ArBr)}{(ArOH)} = \frac{(Br^-)}{(H_2O)}\left[\frac{k_3}{k_2} + \frac{k_4}{k_1}(H_2O) + \frac{k_3k_4}{k_1k_2}(Br^-)\right] \qquad (11)$$

In Fig. 3 values of this ratio calculated from Table II are plotted against bromide concentration. The curve drawn is calculated from eq. (11) using $k_4/k_1 = 0.129$, and $k_3/k_2 = 2.8$. The value of k_4/k_1 is the one obtained from the kinetic data, and that of k_3/k_2 is the average value calculated for each point by eq. (11), and therefore represents an adjustable constant. The average values of k_3/k_2 for each bromide concentration are given in the last column of Table II.

The alternative assumption that reaction (8) does not exist does not fit the yield data as well, and is inconsistent with the kinetic data. The assumption that the phenol results from another bimolecular reaction

$$ArN_2^+ + H_2O \longrightarrow ArOH + H^+ + N_2 \qquad (12)$$

and that the aryl bromide comes only from reaction (8) gives exactly the same fit as the above alternative, and is still reasonably consistent with the kinetics, but reaction (5) is well enough established with other aryl groups to make it probable in this case also. Reaction (5) unaccompanied by reaction (7) is unlikely.

A further alternative is that the increase in rate on adding sodium bromide is due entirely to the corresponding increase in concentration of copper, resulting from the presence of traces of this metal in the sodium bromide. This can be tested by estimating the effect of changes in copper concentration. The rate expression required by this assumption is

$$d(N_2)/dt = k_1(C_6H_5N_2^+) + k_6(Cu)^n(C_6H_5N_2^+) \qquad (13)$$

from which the expression for the measured first-order rate constants is

$$k_{app} = k_1 + k_6(Cu)^n$$

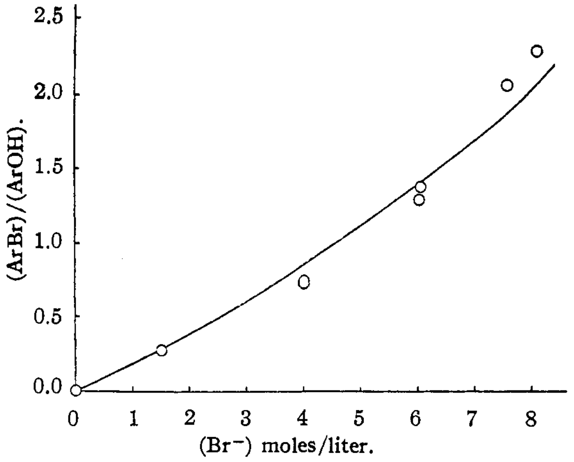


Fig. 3.—Effect of bromide ion concentration on the ratio of yields of p-$NO_2C_6H_4Br$ and p-$NO_2C_6H_4OH$.

Table III gives values of k_{app} and $k_6(Cu)^n$ with the corresponding concentrations of bromide ion and copper, based on the estimations described in the experimental section. It is assumed that the sulfuric acid contributes only a negligible amount of copper. The justification for this assumption lies in the observation that in the absence of bromide, the rate was unaltered by the substitution of nitric acid for sulfuric acid, although the reaction is still sensitive to copper under these conditions. Unless the concentrations of copper were coincidentally the same in the two acids, the concentrations must have been very small in both.

TABLE III

EFFECT OF COPPER CONCENTRATION ON THE RATE OF DECOMPOSITION OF *p*-NITROBENZENEDIAZONIUM ION

(Br^-), M/l.	$Cu^{++} \times 10^6$ M/l.	$k_{app} \times 10^4$ sec.$^{-1}$	$k_6(Cu)^n \times 10^4$ sec.$^{-1}$
0	0.15	1.6	0.0
1	0.45	1.8	0.2
6	1.8	2.7	1.1
6	12	5	3.4

From the last two runs, a value of the order, n, of the reaction in copper can be calculated, knowing that $k_6(Cu)^n$ changes by a factor of 3.1 with a change in copper concentration of a factor of 6.7. The value of n must then be 0.59. Using this value the ratio of the values of $k_6(Cu)^n$ for a change of a factor of 4 in copper concentration is 2.3. This factor of 4 appears between the second and third entries in the table, but the corresponding ratio of $k_6(Cu)^n$ is 5.5. Thus eq. (13) does not give a good fit to the kinetic results. Since an adequate fit is obtained on the assumption that bromide ion is alone responsible for the change in rate, it does not appear necessary to consider simultaneous reaction of copper and bromide, although our data cannot exclude this possibility.

It is possible that the catalysis by copper is in part simply a Sandmeyer reaction, for in solutions of high bromide ion content, the equilibrium

$$2Cu^{++} + 7Br^- \rightleftharpoons 2CuBr_2^- + Br_3^- \qquad (14)$$

is appreciably displaced to the right. The equilibrium constant for this reaction at 25° calculated from the data of Latimer[13] is 1.05×10^{-18}, and in 4 M bromide solution 0.3% of 10^{-5} M cupric ion solution is in the cuprous state. The true extent of reduction of cupric ion is probably even greater because of still more extensive complexing of the cuprous ion. Since the *p*-nitro group favors the Sandmeyer reaction with cuprous chloride greatly[14] and since reactions with bromide are faster than those with chloride, as shown by competition experiments,[15] this Sandmeyer reaction should be very fast at 75°, and might well be important even at 10^{-5} M total copper.

An alternative mechanism to the nucleophilic attack of bromide ion on carbon is the kinetically indistinguishable series

$$ArN_2^+ + Br^- \rightleftarrows Ar{-}N{=}N{-}Br \qquad (15)$$

$$ArN_2Br \longrightarrow ArBr + N_2 \qquad (16)$$

with (15) rapid and reversible, and (16) rate determining. Reactions analogous to (15) have often been written, and the small alteration of the ultraviolet absorption spectrum of *p*-nitrobenzenediazonium ion in solutions of high bromide ion concentrations may be due to the presence of covalent diazobromides.[16] There are, however, no well-established analogies to reaction (16), and there is no justification for the acceptance of this mechanism in preference to the straightforward attack of bromide ion on carbon. It is possible that the tarry materials are partly derived from the free-radical scission of the covalent diazobromide of reaction (15).

---

[13] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, pp. 53, 169, 170, 171.

[14] W. A. Cowdrey and D. S. Davies, *J. Chem. Soc.*, S48 (1949).

[15] H. H. Hodgson, *Chem. Revs.*, **40**, 251 (1947).

[16] Unpublished work of J. J. Cole, formerly of this Laboratory.

HOUSTON, TEXAS RECEIVED JUNE 2, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

The Kinetics and Stereochemistry of the Decomposition of Secondary Alkyl Chlorosulfites[1]

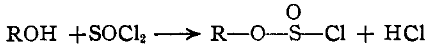
BY EDWARD S. LEWIS AND CHARLES E. BOOZER

The thermal decompositions of some secondary alkyl chlorosulfites have been studied kinetically and stereochemically with the aim of elucidating the mechanism of the formation of alkyl halides from alcohols and thionyl chloride. In dilute solution the decompositions of 2-butyl, 2-pentyl and 2-octyl chlorosulfites in dioxane are first-order reactions, yielding olefin and alkyl chloride as the principal products. The chloride has the same configuration as the alcohol from which it was derived and is only slightly racemized. When the chlorosulfite is decomposed in "isoöctane" solution or in the absence of solvent, the chloride has the opposite configuration from the alcohol.

Introduction

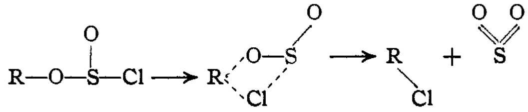
The mechanism of nucleophilic displacement reactions has been extensively studied, but much experimental evidence is lacking concerning the cases in which the product has the same stereochemical configuration as the starting material. These cases can be classified in two groups: the first contains all the cases where the stereochemical result is determined by a neighboring group effect,[2] and the second contains the remaining examples in which no participation of a neighboring group can be considered.

Some of the reactions of thionyl chloride with alcohols belong in this latter group; for example, α-phenylethanol, cholestanol, methylcyclohexylcarbinol[3,4] and various closely related compounds react under suitable conditions to give a chloride of unaltered configuration. Hughes, Ingold and co-workers[5] have proposed a mechanism for this reaction involving the intermediate formation of a chlorosulfite[6] followed by loss of sulfur dioxide from



$$ROH + SOCl_2 \longrightarrow R{-}O{-}\overset{O}{S}{-}Cl + HCl$$

the chlorosulfite and simultaneous formation of the carbon–chlorine bond at the point where the oxygen had previously been attached, presumably by way of a cyclic transition state



They call this the $S_N i$ reaction, and believe that it applies in essence to all nucleophilic displacement reactions resulting in retention of configuration not otherwise explained.

Two experimentally verifiable conditions are required by this mechanism: first, that a chlorosulfite results from the reaction of thionyl chloride and the alcohol, and, second, that this chlorosulfite decomposes by a unimolecular reaction to give a chloride with retention of configuration. It has never been shown that these conditions are met. No chlorosulfites have been prepared of any of the alcohols which give retention of configuration in the reactions with thionyl chloride, and none of the many chlorosulfites which have been prepared have given rise to chlorides of the same configuration on decomposition. No kinetic measurements on chlorosulfite decompositions have shed light on the order of this reaction. Nevertheless, the mechanism of Hughes and Ingold[5] has experimental foundation in the parallel work on the reactions of the chlorocarbonates, in which the analogous conditions have both been met.[7] It therefore seemed

---

[1] From the Masters Thesis of C. E. Boozer, The Rice Institute, May, 1951.

[2] S. Winstein and R. E. Buckles, THIS JOURNAL, **64**, 2780 (1942).

[3] J. Kenyon, A. G. Lipscomb and H. Phillips, *J. Chem. Soc.*, 415 (1930).

[4] P. A. Levene and L. A. Mikeska, *J. Biol. Chem.*, **75**, 587 (1927).

[5] W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1196 (1937).

[6] The English workers refer to these esters as chlorosulfinates. We prefer the term chlorosulfite because it carries no implication of a carbon–sulfur bond.

[7] A. H. J. Houssa and H. Phillips, *J. Chem. Soc.*, 108, 1232 (1932).