[CONTRIBUTION FROM THE ORGANIC CHEMISTRY BRANCH, CHEMISTRY DIVISION, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION]

The Reaction of *n*-Butyl Nitrate with Alkaline Hydrosulfides[1]

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The reaction of *n*-butyl nitrate with sodium hydrosulfide yields *n*-butyl alcohol, sodium nitrite, a small amount of ammonia and sulfur. With ammonium hydrosulfide, all of the nitrate nitrogen is reduced to ammonia, and four gram-atoms of sulfur are produced per mole of nitrate. Above *p*H 13, either of the hydrosulfide reagents reduces the nitrate only to nitrite ion, with the production of one gram-atom of sulfur. The reaction does not involve alkaline hydrolysis of the ester, elimination of nitric or nitrous acid, reduction to the nitrite ester, or a displacement on the α-carbon atom of the nitrate ester. The reaction is apparently second order kinetically, and is catalyzed by hydroxyl ion and by polysulfide.

Previous work on the reaction of nitrate esters with alkaline hydrosulfides has been principally concerned with cellulose nitrate, and the organic product has been shown to be regenerated cellulose.[3,4] In addition, Ryan and Coyle[5] showed that ethanolic ammonium sulfide reacted with *n*-butyl nitrate to give *n*-butyl alcohol and sulfur, together with a small quantity of an oil which was presumed to be a mercaptan. Kopp,[6] in 1847, reported that ammoniacal hydrogen sulfide reacted with ethyl nitrate to give ethyl mercaptan, but no experimental data were presented. He also reported that ethyl nitrate reacted with hydrogen sulfide to form ethyl alcohol, ammonia and sulfur.

As part of a program of studies on the chemistry of nitrate esters, the reaction with sodium and ammonium hydrosulfides was investigated from the standpoint of reaction products, stoichiometry and kinetics. *n*-Butyl nitrate was chosen as the model organic nitrate for most phases of this investigation because it offered the advantage of providing readily isolable products, as well as satisfactory solubility for study in homogeneous systems.

Experimental

Materials.—The *n*-butyl nitrate employed in this work was obtained from City Chemical Corp. and was used without further purification; $n^{24.5}_{D}$ 1.4053; $d^{24.5}$ 1.0221; M_D calcd., 29.22; M_D found, 29.18.

2-Octyl nitrate was prepared by esterification of 2-octanol.[7] The refractive index was found to be different from that reported in the literature,[7] but the boiling point, density and nitrogen analysis were in agreement. Refractive index found, $n^{20.5}_{D}$ 1.4260; lit. n^{20}_{D} 1.4299; M_D 47.66; calcd., 47.23.[8]

The sodium hydrosulfide reagent was prepared by saturating a solution of approximately 6 *N* sodium hydroxide with hydrogen sulfide gas, and had a composition approximating NaHS. The ammonium hydrosulfide solution was prepared by saturating concentrated ammonium hydroxide (15 *M*) with hydrogen sulfide, and had a composition intermediate between NH_4HS and $(NH_4)_2S$. The hydrolysis of ammonium sulfide is substantially complete, so that this solution actually contained ammonium hydrosulfide and excess ammonia. Solutions containing added polysulfide were prepared by adding sulfur to concentrated hydrosulfide solutions and allowing the mixtures to stand overnight.

Preliminary Experiments.—To develop the stoichiometry of the reactions, aqueous ethanolic solutions of *n*-butyl nitrate were mixed with an excess of concentrated (2–8 *M*) sodium or ammonium hydrosulfide solutions and allowed to stand overnight at room temperature. The solutions were then extracted with ether, the aqueous layers were decomposed with dilute hydrochloric acid, and the precipitated sulfur was collected and weighed. Four gram-atoms of sulfur were produced per mole of butyl nitrate from the ammonium hydrosulfide reagent. Varying amounts of sulfur were obtained from the sodium hydrosulfide reaction, due to the subsequent reduction of nitrite ion by hydrogen sulfide on acidification of the solution. This is discussed later.

The ether extracts were washed with water and dried over potassium carbonate, and the ether was removed by distillation. All but a trace of the organic material distilled over the range from 83 to 113° (700 mm.) and consisted of a mixture of ethanol and butanol. It was found possible to estimate the amount of butanol in the mixture, without separating it from the ethanol, by means of the refractive index. In several experiments, about 90% of the organic fragment was thus accounted for as butyl alcohol. No evidence was found for the presence of the mixed ether.

The residue, after distillation of the butyl alcohol, had a disagreeable odor, although it was not that of butyl mercaptan. This may have been due to traces of butyl sulfide, but, as it was present in amounts too small for characterization, it was not investigated further.

Reaction Rate Studies.—In the earliest rate experiments, the extent of reaction was followed by measurement of sulfide disappearance. The results of these experiments are in agreement with later ones, which were followed by analysis for polysulfide sulfur or for butyl nitrate, and all of the rate experiments described herein were followed by these latter methods.

All of the runs were conducted in 60% ethanol by volume, each run being made up by adding 40 volume per cent. total of water and aqueous reagent solutions to a volumetric flask containing absolute ethanol and the appropriate amount of *n*-butyl nitrate, and then making up to volume with absolute ethanol. The reactions were run in a thermostated bath controlled to ±0.05°, and most experiments were run at 26.9°. The time at which addition of the last reagent (usually the sulfide solution) was completed was taken as the starting time of the run. Aliquots were removed from time to time for analysis.

Analytical Procedures. A. Analysis for Sulfide.—The term sulfide is used throughout this paper to denote hydrogen sulfide, hydrosulfide ion, sulfide ion and the sulfide portion of polysulfide and hydropolysulfide ions. The ordinary iodimetric method was found to be inapplicable, due to interfering reactions of nitrite ion with sulfide[9] and with iodide[10] in acid medium, and buffering with sodium acetate[11] rendered the solution too alkaline for quantitative titration with thiosulfate.

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[1] Presented before the 122nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1952.

[2] University of Colorado, Boulder, Colo.

[3] B. Rassow and E. Dörr, *J. prakt. Chem.*, **108**, 113 (1924).

[4] T. Tomonari, *Z. Elektrochem.*, **40**, 207 (1934).

[5] H. Ryan and V. J. R. Coyle, *Proc. Roy. Irish Acad.*, **37**, 361 (1927).

[6] E. Kopp,, *Ann.*, **64**, 320 (1847).

[7] The authors are indebted to Mr. Robert Snell for this material prepared according to the procedure of R. L. Shriner and E. A. Parker, THIS JOURNAL, **55**, 766 (1933).

[8] This value was obtained by using the bond refractions given by A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, *J. Chem. Soc.*, 514 (1952). Shriner and Parker (ref. 7) give M_D (calcd.) as 47.60.

[9] L. S. Bagster, *J. Chem. Soc.*, 2631 (1928).

[10] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Tbe Macmillan Co., New York, N. Y., 1937, p. 600.

[11] A. Nadai, *Z. physik. Chem.*, **136**, 289 (1928).

A modified procedure[12] was found to give better although not completely satisfactory results. The sulfide was precipitated with ammoniacal cadmium chloride solution. The precipitate was filtered, washed with water, ethanol and ether, and decomposed with acid and an excess of standard iodine solution. The excess iodine was then titrated with standard thiosulfate. The somewhat erratic results obtained were presumably due to incomplete removal of interfering substances from the sulfide precipitate, and also to some difficulty in obtaining complete reaction of the sulfide precipitate with the acid–iodine solution.

B. **Analysis for Polysulfide.**—In view of the difficulties encountered in determining sulfide, no methods for polysulfide were considered which involved estimation by the difference between total sulfur and sulfide, or which involved iodine or thiosulfate titrations.

The method for determination of polysulfide which proved most satisfactory was a modification of the procedure of Schulek,[13] which involves the reaction

$$S_x^{=} + (x - 1)CN^- \longrightarrow S^{=} + (x - 1)CNS^-$$

and the subsequent estimation of thiocyanate. The procedure used in this investigation is given.

To a hot (almost boiling) solution of 50–60 ml. of 2% boric acid in an erlenmeyer flask was added 2 ml. of 10% sodium cyanide solution and the sample containing up to 0.01 gram-atom of polysulfide sulfur. The solution was then placed on a hot-plate and boiled until the hydrogen sulfide and hydrogen cyanide were completely removed. A negative test with lead acetate paper was satisfactory. The solution was then cooled, about 0.5 ml. of saturated ferric alum solution was added together with enough 6 *N* nitric acid to dissolve the ferric hydroxide, and the solution was then titrated with standard 0.1 *N* silver nitrate solution.

Experiments showed that *n*-butyl nitrate, nitrate ion and ammonia did not affect the accuracy of this method.

C. **Analysis for Butyl Nitrate.**—Butyl nitrate was determined polarographically after extraction from the reaction mixture with ether and thorough washing of the ether extract.[14]

D. **Analysis for Nitrite Ion.**—Attempts to determine nitrite ion in the reaction mixtures after removal of the sulfide and polysulfide by precipitation with cadmium chloride, cadmium nitrate or ammoniacal cadmium nitrate were not successful. It was not possible to obtain consistent results, apparently because of incomplete removal of sulfide and/or loss of nitrite by occlusion in the sulfide precipitate.

The method[15] adopted, while not completely satisfactory, particularly in solutions where sulfide concentration was of the order of 10 times as high as nitrite concentration, made it possible by frequent sampling to follow the reactions. Sulfide and polysulfide were precipitated by adding the sample to an excess of a smooth suspension of cadmium carbonate, *freshly prepared* by adding a slight excess of concentrated sodium carbonate solution to 25% cadmium sulfate. The precipitate was filtered and thoroughly washed with water. To the filtrate were added about 8 g. of solid sodium bicarbonate and 10 ml. of 20% potassium iodide solution. Carbon dioxide was bubbled through the solution for about 10 minutes. Then 25 ml. of 6 *N* oxygen-free sulfuric acid was added very slowly, and the liberated iodine titrated with standard thiosulfate. A few drops of starch solution, added when the solution became pale yellow, was the indicator. The value of nitrite concentration must be corrected for thiosulfate present in the sample.

E. **Analysis for Thiosulfate.**—While thiosulfate did not appear to be a product of the denitration reaction, its presence led to low values for nitrite ion concentration in some cases. The procedure used for determining thiosulfate[15] was as follows.

The sulfides and polysulfides were precipitated, filtered and washed as in the analysis for nitrite ion. The filtrate was just neutralized with dilute sulfuric acid to the phenolphthalein end-point, and titrated with standard iodine solution, or an excess of standard iodine solution was added and back-titrated with standard thiosulfate.

F. ***p*H Measurement.**—The *p*H changes during denitration were followed by the use of a Beckman Type "E" glass electrode and a normal calomel electrode, which were fitted through rubber stoppers into a three-neck round-bottom flask containing the reaction mixture.

G. **Ammonia Determination.**—Ammonia was determined by the Kjeldahl method in ammonium hydrosulfide stock solutions and in spent sodium hydrosulfide reaction mixtures.

Results and Discussion

Fate of the Organic Fragment.—In several experiments, with both sodium and ammonium hydrosulfides, butyl alcohol was found in yields of 90% or more. There was no indication of mercaptan formation.

Fate of the Nitrogen.—In the reaction of butyl nitrate with unbuffered sodium hydrosulfide, at a *p*H of 10–11, approximately 93% of the nitrogen was converted to nitrite ion, and the remaining 7% to ammonia. With ammonium hydrosulfide, nitrite ion was formed initially at a relatively rapid rate; the nitrite concentration passed through a maximum value and then fell off slowly to zero as the reaction proceeded to completion. The changes in concentration of butyl nitrate, nitrite ion and polysulfide sulfur [$(x - 1)$S of $S_x^{=}$] during this reaction are shown in Fig. 1.

Nitrite ion is reduced to ammonia by hydrosulfides below *p*H 10,[9] and the rate of reduction is apparently sensitive to changes in *p*H, being very slow at $pH > 10$. The stoichiometry of this reaction is given by

$$NO_2^- + 3HS^- + 2H_2O \longrightarrow NH_3 + 3S + 4OH^-$$

No gaseous products were found in these experiments, and no evidence could be obtained for the presence of hydrazine or hydroxylamine. It appears that butyl nitrate is initially reduced to butyl alcohol and nitrite ion, and that nitrite ion is subsequently reduced, partially or completely, to ammonia by some process which does not yield isolable intermediates.

***p*H Effects.**—In the reaction of butyl nitrate and sodium hydrosulfide, the *p*H dropped rapidly, leveled off, and then rose slightly. These changes, plotted as hydroxyl ion concentration, are shown in Fig. 2. The drop in *p*H, which could not be correlated with the extent of the reaction as measured by polysulfide formation, is believed due to the formation of polysulfide and nitrite, which are salts of stronger acids than hydrogen sulfide and are therefore less hydrolyzed.[9,16] The slight rise in *p*H occurring later is attributed to the increased basicity which results from partial reduction of nitrite ion to ammonia and hydroxyl ion.

With ammonium hydrosulfide, the *p*H variation is much less, but follows a similar pattern. The minimum point in the *p*H curve occurs approximately at the same time as the maximum in the nitrite ion concentration.

Fate of the Sulfur.—Sulfide sulfur (having an oxidation state of minus two) was found to be converted to polysulfide sulfur, or to free sulfur in those experiments where insufficient sulfide was present to keep the oxidized sulfur in solution as polysulfide. With unbuffered sodium hydrosulfide reagent, approximately 1.2 gram-atoms of poly-

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(12) R. H. Pierson and H. S. Spring, private communication.

(13) E. Schulek, *Z. anal. Chem.*, **65**, 352 (1925).

(14) The authors are indebted to Dr. J. T. Odencrantz for carrying out the butyl nitrate determinations. Details of her method are to be submitted to *Anal. Chem.*

(15) A. B. Craver, private communication.

(16) F. W. Küster, *Z. anorg. Chem.*, **44**, 431 (1905).

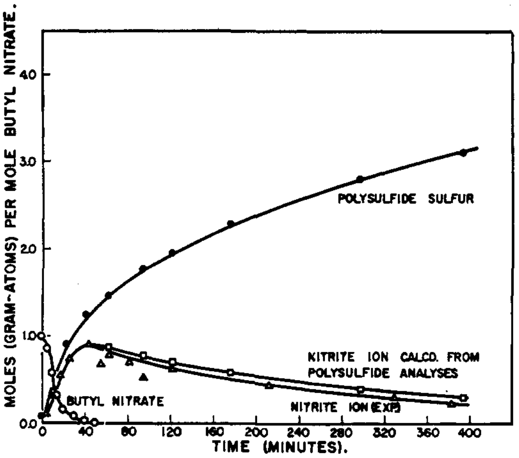

Fig. 1.—Production of polysulfide and nitrite ion in reaction of butyl nitrate with ammonium hydrosulfide.

sulfide sulfur was produced per mole of butyl nitrate. This agrees very well with the proportions of nitrite (93%) and ammonia (7%) found under the same conditions. For each mole of nitrite ion produced, one gram-atom of polysulfide sulfur should be obtained, while for each mole of ammonia, four gram-atoms should be obtained, according to the equations

$$RONO_2 + 2HS^- \longrightarrow ROH + NO_2^- + HS_2^-$$

$$RONO_2 + 8HS^- + 2H_2O \longrightarrow ROH + NH_3 + 4HS_2^- + 4OH^-$$

From the amounts of nitrite and ammonia found, one would expect to find $0.93 + (4 \times 0.07) = 1.21$ gram-atoms of polysulfide sulfur formed per mole of nitrate.

The amount of polysulfide sulfur formed in these reactions was found to be equal to the sulfide sulfur consumed, indicating that no thiosulfate or other sulfur compounds were formed as a result of the denitration reaction. Thiosulfate has been reported to be a product of the reaction of hydrogen sulfide with unbuffered solutions of alkali nitrite,[17] and of the oxidation of sulfides and polysulfides in alkaline solution either by nitrite ion or by air.[18] Old stock solutions of ammonium hydrosulfide have been shown to contain thiosulfate.[19] Analysis of some of our butyl nitrate–sodium hydrosulfide reaction mixtures after as much as four months showed little or no decrease in nitrite ion concentration, while appreciable amounts of thiosulfate were found. It therefore appears that, in these experiments, nitrite ion does not oxidize sulfides and/or polysulfides to thiosulfate.

The differences in the amounts of polysulfide sulfur produced in various denitrating solutions by reaction with butyl nitrate were shown to be due solely to the effect of *p*H on the reduction of nitrite ion, and not to any specific effect of sodium or ammonium ions or of ammonia. Thus, sodium hydrosulfide buffered to a *p*H below 10 gave four gram-atoms of polysulfide sulfur, and ammonium hydrosulfide in the presence of excess alkali yielded only slightly more than one gram-atom. At *p*H 13, no reaction occurred between sodium nitrite and sodium or ammonium hydrosulfide. Table I shows the relationship between initial *p*H and extent of the reaction.

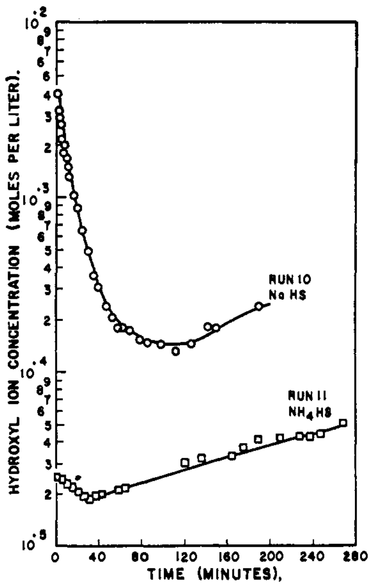

Fig. 2.—Variation of *p*H during denitration of butyl nitrate.

TABLE I

EFFECT OF *p*H ON AMOUNT OF POLYSULFIDE SULFUR FORMED IN DENITRATION REACTIONS

Reducing solution	Initial	*p*H Minimum	Final	Gram atoms polysulfide sulfur per mole butyl nitrate
NaHS	11.70	9.63	10.00	1.2
NaHS + NaOH	>13	>13	>13	1.0
NaHS + H_3BO_3	9.69	8.42	10.40	2.8
NaHS + H_3BO_3	9.04	7.37	9.80	4.0
NH_4HS	9.40	9.31	10.00	4.0
NH_4HS + NaOH	13.00	10.84	12.76	1.2

Investigation of Possible Intermediate Steps.—Nadai[11] proposed the following mechanism for the denitration of cellulose nitrate

$$RONO_2 + OH^- \longrightarrow ROH + NO_3^-$$

$$NO_3^- + 2HS^- \longrightarrow NO_2^- + HS_2^- + OH^-$$

To test this mechanism the rates of steps were investigated separately. In a solution of butyl nitrate (0.1 *M*) and sodium hydroxide (0.2 *M*) in 60% ethanol, at 26.9°, less than 10% hydrolysis had occurred in 16 days as estimated by loss of alkali. Ryan and Coyle[5] studying butyl nitrate and Baker and Easty,[20] other nitrate esters, have reported the reactions with alkali to be very slow. On the other hand, in a solution under the same conditions, but containing hydrosulfide and a little polysulfide, the reaction would be essentially complete in about four hours.

The reaction of nitrate ion with sodium hydrosulfide also was found to be extremely slow, if

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[17] D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, p. 66.

[18] I. Khmelnitzkaya and V. Verkhovskaya, *Anilinokrasochnaya Prom.*, **4**, 27 (1934); *C. A.*, **28**, 3589 (1934).

[19] R. H. Pierson and H. S. Spring, private communication.

[20] J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1193 (1952).

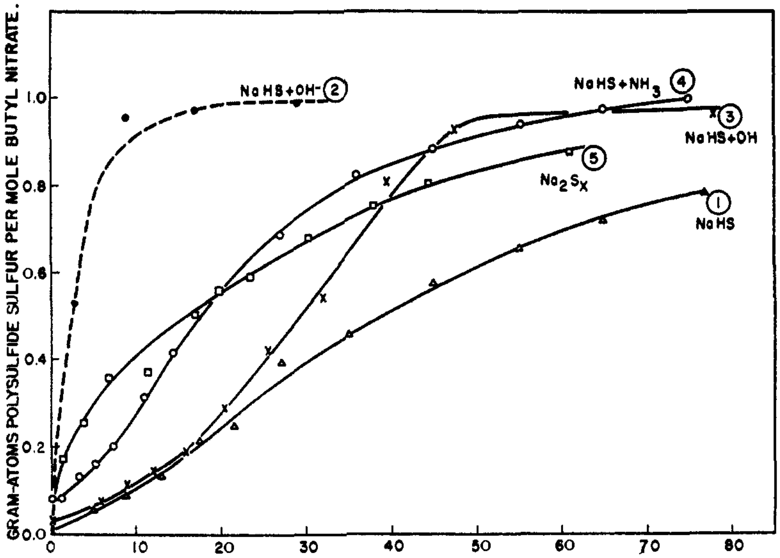

Fig. 3.—Polysulfide production in reaction of *n*-butyl nitrate with various denitrating solutions at 26.9°.

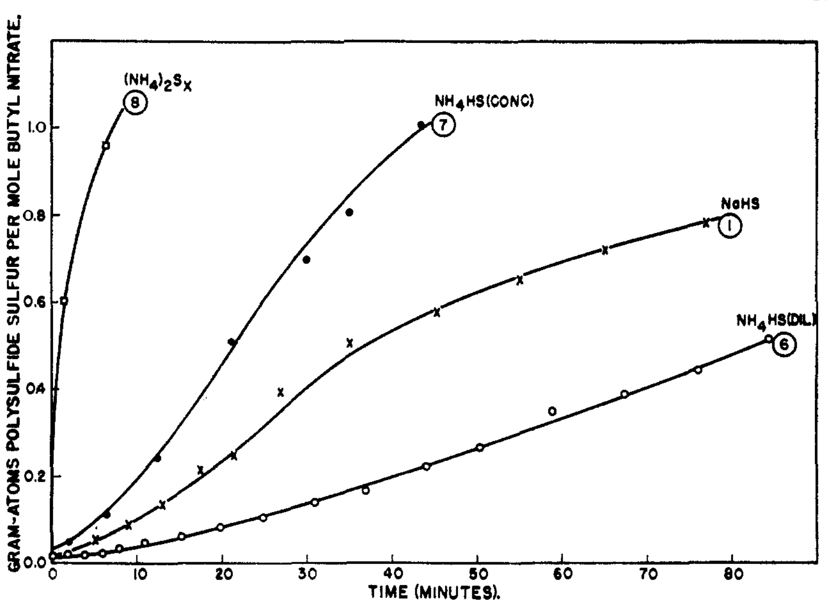

Fig. 4.—Polysulfide production in reaction of *n*-butyl nitrate (0.2 *M*) with various denitrating solutions at 26.9°.

indeed any reaction occurred. In a solution 0.2 *M* in potassium nitrate and 0.48 *M* in hydrosulfide, no reaction was apparent in two days, and only 0.2 gram-atom of sulfur was produced per mole of nitrate in seven days. Thus, the Nadai mechanism can be eliminated since both steps involved are slower than the denitration process.

Studies with *n*-butyl nitrite were made to learn whether or not this compound was an intermediate in the reduction of butyl nitrate; this was found not to be the case.

It was observed that when solutions of *n*-butyl nitrite[21] in ethanol were treated with either sodium or ammonium hydrosulfide solutions, vigorous gas evolution occurred during the addition of the first 0.4 mole of hydrosulfide per mole of butyl nitrite. The butyl nitrite was converted in excess of 90% yield to butyl alcohol. The gas consisted primarily of nitrogen and nitrogen oxides. No stoichiometric relation was established between the amounts of gases and the amounts of reactants. Since no gas evolution was observed in corresponding reactions of *n*-butyl nitrate, mechanisms involving butyl nitrite as an intermediate are eliminated from consideration.

When sodium nitrite was treated with excess ammonium hydrosulfide solution, a vigorous exothermic reaction occurred with the formation of polysulfide, as evidenced by reddening of the solution and by precipitation of sulfur upon acidification. Three gram-atoms of polysulfide sulfur were produced per mole of nitrite in the reaction. However, with sodium hydrosulfide, no evidence of reaction was apparent in four days. However, when the solution was acidified with dilute hydrochloric acid, acetic acid or carbon dioxide, varying amounts of sulfur were precipitated. These observations are in agreement with the results of Bagster,[9] who found that the reaction of nitrite ion with sulfide was acid-catalyzed, and with the observation noted elsewhere herein that nitrite ion, produced by denitration of butyl nitrate, is further reduced by hydrosulfides below *p*H 10.

Reaction Rate Studies.—Significant data on initial concentrations of reactants in the various experiments are given in Table II. The rate data are plotted in Figs. 3, 4 and 5. It will be noted that in those runs which did not have added polysulfide, the plots of polysulfide concentration against time have an S-shape. This type of curve is obtained generally under one of two conditions: (a) when the concentration of a product, rather than a reactant, is followed, the formation of an intermediate, isolable but not completely stable under the conditions of the experiment will give this type of result due to the formation and subsequent reaction of the intermediate to give the final products or (b) when one or more of the products is a reactive species, *i.e.*, when an autocatalytic reaction obtains. Possibility (a) was eliminated, despite the known formation of nitrite ion as an intermediate, by the fact that an S-shaped curve was also observed when disappearance of a reactant (butyl nitrate, Fig. 1) was followed. Hence the autocatalytic

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(21) W. A. Noyes, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 108.

TABLE II

DATA AND INITIAL CONCENTRATIONS FOR EXPERIMENTS ON THE ALKALINE HYDROSULFIDE DENITRATION OF *n*-BUTYL NITRATE IN 60 VOLUME PER CENT. ETHANOL

Run	Initial $[H_2S]$ *M*	Initial $[BuONO_2]$ *M*	Initial [Polysulfide S] *M*	Initial $[NH_3]$ *M*	Initial $[OH^-]$ *M*	Rate constant	Demonstrates effect of
1	0.45	0.20	0.003	..	..	0.0445[a,b]	....
2	.44	.20	.017	..	0.2[c]	......	Alkali
3	.18	.08	.007	..	.08[c]	......	Alkali
4	.44	.20	.017	0.15	..	......	Ammonia
5	.42	.20	.10	..	..	.0698[a]	Polysulfide
6[d]	.40	.20	.003	0.44	..	......	......
7[d]	1.20	.20	.01	1.46	..	......	......
8[d]	0.84	.20	.44	1.43	..	......	Polysulfide
9[d]	1.15	.20	.015	2[c]	..	......	......
10	0.24	.10	.002	..	..	......	......
11[d]	1.04	.20	.016	1.47	..	......	......
12	0.46	.10	.003	..	..	0.0378[a,b]	......
13	.31	.20	.10	..	..	.0726[a]	Polysulfide
14	.23	.01	.19	..	..	.447[e]	......
15	.17	.01	.14	..	..	.261[e]	......
16	.072	.005	.062	..	0.1[c]	.178[e]	......
17	.145	.005	.124	..	.1[c]	.717[e]	......
18[d,f]	.44	.20	.012	..	..	......	No polysulfide
19[d,f]	.42	.20	.008	..	.1[c]	......	Alkali in absence of polysulfide
20[d]	.00659	.10	.00425	..	.1[c]	.0115[g]	......
21[d]	.00264	.10	.00170	..	.1[c]	.0116[g]	......
22	1.147	.20	.015	..	..	......	......

[a] Second-order rate constants in liters/mole/minute, assuming that $-d[BuONO_2]/dt = k[BuONO_2][S_x^=]$. [b] These rate constants are taken from the straight portions of the plots, from 20 to 70% reaction. [c] Approximate concentrations. [d] Ammonium hydrosulfide. All other runs used sodium hydrosulfide. [e] Pseudo-first-order rate constants (butyl nitrate) in minutes^{-1}. [f] Approximately 0.75 *M* CN^- added. [g] Pseudo-first-order rate constants (sulfide) in minutes^{-1}.

nature of the reaction seems the more reasonable explanation.

In view of the drop in *p*H during the reaction, catalysis by hydrogen ion seemed possible. However, the fact that addition of alkali to the reaction mixture increased the rate many times (run 2) and did not change the shape of the curve (run 3) showed that hydrogen ion was not the catalyst. Run 4 in which ammonia was added, demonstrates that this species is not responsible for the autocatalysis.

It was demonstrated in two ways that polysulfide ion was responsible for the autocatalysis. Run 5 shows data in which a large concentration of polysulfide ion was initially present and it may be noted that the S-shape of the curve has disappeared. In another experiment (run 18) similar to run 1 except that the solution was also *ca.* 0.78 *M* in cyanide ion, about 30 hours elapsed before thiocyanate equivalent to 0.5 mole of polysulfide sulfur per mole of butyl nitrate was produced.[22]

The reaction between nitrous acid and hydrogen sulfide (or one of its conjugate bases) has also been shown to involve polysulfide catalysis or autocatalysis.[9] Bagster has suggested that the greater reactivity of polysulfide over monosulfide species is only apparent and is due to the requirement that the reducing species be bivalent negative ions and to the fact that the polysulfides are weaker bases than sulfide (see below) and thus exist in higher concentrations (are less hydrolyzed) at a given *p*H than does sulfide ion. His argument is based upon the reasoning that polysulfide is a thermodynamically poorer reducing agent than sulfide,[16] although the conclusion that it would therefore be a poorer reducing agent kinetically is of course not justifiable on *a priori* grounds. The fact that alkali increases the rate of denitration of butyl nitrate markedly in the presence of polysulfide, but not in the absence of polysulfide (Figs. 3, 5), leads to the conclusion that the bivalent anions are the active denitrating agents, but sufficient data are not available to conclude that sulfide is a faster reducing agent than is polysulfide.

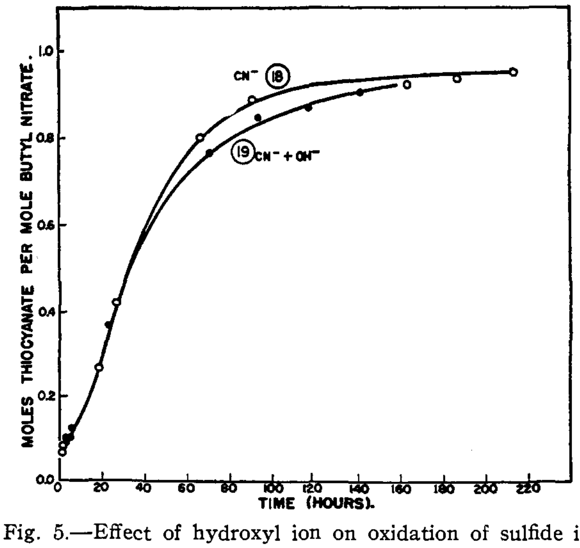

Fig. 5.—Effect of hydroxyl ion on oxidation of sulfide in denitration of butyl nitrate in the presence of cyanide ion.

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(22) See analytical procedure for polysulfide.

When rate data for runs containing only a slight excess of hydrosulfide reagent, and with no added polysulfide, were treated according to a rate law first order in butyl nitrate and first order in total sulfide concentration (as defined previously), curves were obtained whose slopes increased for a time and then became apparently constant (runs 1 and 12, Fig. 6). When the reaction mixtures contained added polysulfide, the same treatment of the data gave straight line plots (runs 5 and 13, Fig. 6). The value for *k* was somewhat higher when the ratio of polysulfide sulfur to sulfide was higher. These straight line plots maintain to 65–70% reaction.

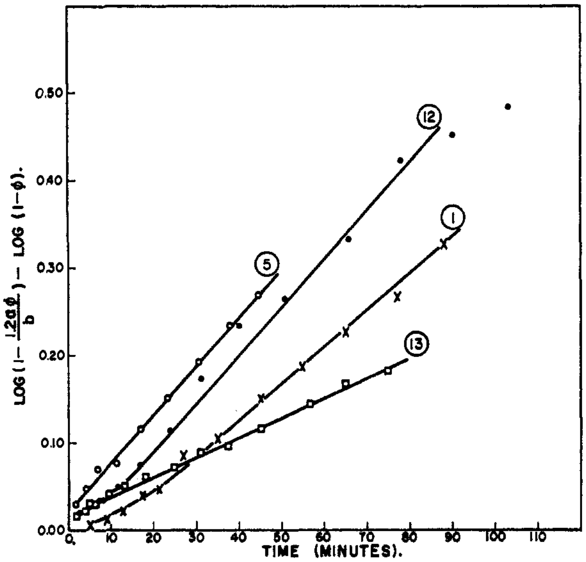

Fig. 6.—Treatment of rate data according to rate law first order in butyl nitrate and first order in total available sulfide: a, initial butyl nitrate concentration; b, initial sulfide concentration; ϕ, fraction butyl nitrate reacted.

The kinetic order of the reaction with respect to individual reactants was obtained by the isolation method. When sulfide and polysulfide were in large excess, the rate of disappearance of nitrate was found to be proportional to the nitrate concentration (Fig. 7). No simple relationship could be found between the pseudo-first-order rate constants and the sulfide or polysulfide concentrations. In the presence of added alkali, these rate constants appear to vary as the square of the sulfide concentration (runs 16 and 17), though in the absence of added alkali the agreement is not as good (runs 14 and 15).

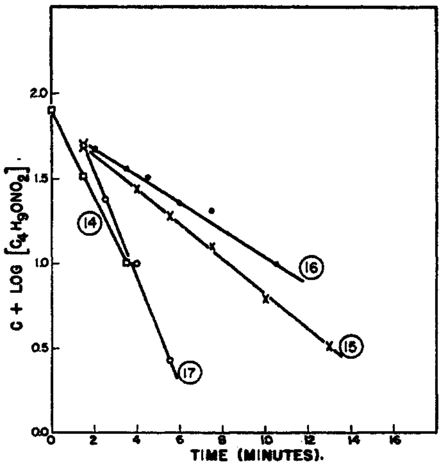

Fig. 7.—Treatment of rate data according to rate law first order in butyl nitrate (sulfide and polysulfide in large excess): $C = 3.9$ (runs 14, 15); 4.3 (runs 16, 17).

However, when butyl nitrate was in large excess, the reaction was shown to be first order with respect to sulfide (runs 20 and 21, Fig. 8). In these experiments only the first 15 or 20% of the reaction was followed, since sulfur precipitates out as the reaction proceeds further.

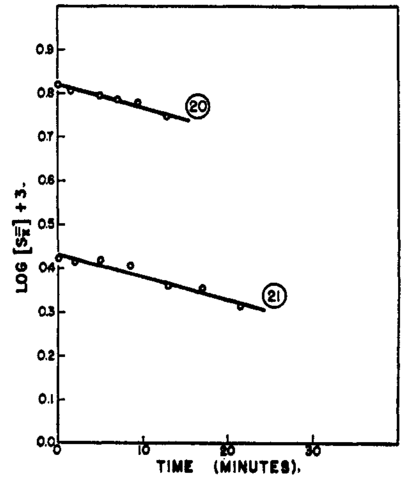

Fig. 8.—Treatment of data according to rate law first order in sulfide when butyl nitrate is in excess.

The situation is very complex in all of these reactions due to the large number of polysulfide species capable of existence in the solution, and to the various possible equilibria among these species, *viz.*

$$2S_2^= \rightleftarrows S^= + S_3^=$$
$$2S_3^= \rightleftarrows S_2^= + S_4^=, \text{ etc.}$$

as well as to the acid–base equilibria

$$HS^- + OH^- \rightleftarrows S^= + H_2O$$
$$HS_2^- + OH^- \rightleftarrows S_2^= + H_2O$$
$$HS_x^- + OH^- \rightleftarrows S_x^= + H_2O, \text{ etc.}$$

The second ionization constants for hydrogen polysulfides can be calculated from Küster's hydrolysis data.[16] While the absolute accuracy of each value may be in doubt, the trend toward higher values of K_2 for the higher polysulfides is unmistakable (Table III). It should be pointed out that solutions having compositions corresponding to di-, tri- and tetrasulfides actually contain complex equilibrium mixtures of a number of poly sulfide species.

TABLE III

Acid	Second ionization constant
H_2S[a]	1.82×10^{-14}
H_2S_2	8.48×10^{-14}
H_2S_3	4.41×10^{-13}
H_2S_4	6.35×10^{-12}

[a] N. A. Lange, "Handbook of Chemistry," 6th Edition, Handbook Publishers, Inc., Sandusky, Ohio, 1946, p. 1379, gives 1.2×10^{-15} as K_2 for H_2S.

The equilibria can be essentially "frozen" throughout the reaction by using large excesses of sulfide and polysulfide, and by adding alkali or otherwise strongly buffering the reaction mixtures. The apparent third-order kinetics found in such cases (runs 14–17) may be only apparent, and may be due to the fact that the equilibria were not "frozen" identically in these experiments.

Reaction of 2-Octyl Nitrate with Ammonium Hydrosulfide.—In 70% ethanol at 26.7°, 2-octyl nitrate reacted with ammonium hydrosulfide to produce four gram-atoms of polysulfide sulfur per mole of nitrate. The rate of polysulfide formation early in the run was much slower than in a run using *n*-butyl nitrate under identical conditions. The same autocatalytic effect was observed.

Possible Mechanisms.—The results of these experiments eliminate from consideration a number of possible reaction mechanisms. Isolation of butyl alcohol in nearly quantitative yield and the absence of nitrate ion and mercaptan indicate that the reaction does not involve displacement by the hydrosulfide reagent at the carbon atom bearing the nitrate group. Also removed from consideration are elimination processes to give olefin or aldehyde. The Nadai mechanism referred to earlier is untenable because both intermediate reactions are slower than the denitration reaction. The reaction does not proceed through the intermediate formation of butyl nitrite, since different products are obtained from the reaction of this substance with hydrosulfides.

The most reasonable mechanism appears to be one in which the rate-determining step involves attack of a sulfide or polysulfide ion, upon the nitrate group. At least two reaction paths suggest themselves, fulfilling the conditions that the rate-determining step should involve butyl nitrate and a sulfide or polysulfide ion, and that rapid subsequent steps should lead to the formation of butanol, nitrite ion and polysulfide. They are

$$\text{(a)}\quad RONO_2 + S_x^{=} \longrightarrow RO^- + NO_2S_x^- \; (x \geqq 1)$$

$$NO_2S_x^- + HS^- \text{ (or } S^{=}) \longrightarrow NO_2^- + HS_{x+1}^- \text{ (or } S_{x+1}^{=})$$

$$HS_{x+1} + HS^- \rightleftarrows HS_x^- + HS_2^-, \text{ etc.}$$

$$RO^- + HS_x^- \rightleftarrows ROH + S_x^{=}$$

$$HO^- + HS_x^- \rightleftarrows H_2O + S_x^{=}$$

$$\text{(b)}\quad RONO_2 + S_x^{=} \longrightarrow ROS_x^- + NO_2^-$$

$$ROS_x^- + HS^- \longrightarrow RO^- + HS_{x+1}^-$$

$$HS_{x+1}^- + HS^- \rightleftarrows HS_x^- + HS_2^-, \text{ etc.}$$

$$RO^- + HS_x^- \rightleftarrows ROH + S_x^{=}$$

$$HO^- + HS_x^- \rightleftarrows H_2O + S_x^{=}$$

The first mechanism suggested involves attack by sulfide or polysulfide ion upon the nitrogen atom, with either concerted or subsequent displacement of alkoxide ion, forming "polythionitrate" ion. This substance, to which no literature reference has been found, would be expected to be unstable, giving up its sulfur atoms to the reducing agent, hydrosulfide ion. The remaining steps involve acid–base transfers (presumably rapid), and the equilibria among the various polysulfide species.

The second alternative involves attack by polysulfide on the oxygen atom, displacing nitrite ion. The data presently available do not distinguish between the two mechanisms.

These mechanisms are consistent with the second-order kinetics observed if the first reaction in each case is slow and rate determining. The variation in the values for the second-order rate constant is believed due to the differences in reactivity among the various polysulfide ions and to changes in the equilibria among these species. It is not possible at this time to define a termolecular mechanism nor one involving an equilibrium reaction preceding the rate determining step which would be consistent with the apparent third-order kinetics observed in certain cases.

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The S_N Mechanism in Aromatic Compounds. V. Halogen Substituents[1]

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The activating power of halogens in a group of aromatic S_N reactions has been measured and found to be in the order I > Br > Cl > F $\simeq$ H. The results are discussed in terms of inductive (I) and tautomeric (T) effects.[3] Crudely quantitative values of the individual effects for the different halogens are obtained.

The substituent effects of halogen atoms in aromatic S_N reactions have been discussed recently[4] and it was concluded that activation by any one halogen would be similar in all positions and this has been confirmed for Cl.[5–7] It was also assumed that the permanent mesomeric (M) effects would not be large enough to reverse the order due to the total inductive (I) effects, but the results given below show this assumption to be incorrect.

In contrast with aromatic S_E reactions the halogens are classified as $-I+M$ instead of $-I+T$. The $-I$ effects include the inductomeric (I_d) as well as the permanent (I_s) effect.

The order of the I_s effect, due to electronegativity, is well known to be in the order F > Cl > Br > I and has already been discussed[8] in connection with the nucleophilic replacement of halogens.

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[2] A Scholarship awarded to R. L. Heppolette by the Universities Commission (Australia) is gratefully acknowledged.

[3] The terminology for electronic effects is that used by Ingold, *et al.*, and discussed fully by Remick, "Electronic Interpretations of Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1949.

[4] J. Miller, *Revs. Pure and Applied Chem.* (*Aust.*), **1**, 171 (1951).

[5] J. Miller, *J. Chem. Soc.*, 3550 (1952).

[6] M. Liveris, P. G. Lutz and J. Miller, *Chem. and Ind.*, 1222 (1952).

[7] J. Miller and V. A. Williams, *J. Chem. Soc.*, 1475 (1953).

[8] A. L. Beckwith, J. Miller and (in part) G. D. Leahy, *ibid.*, 2552 (1952).