[Contribution from the Department of Chemistry and Chemical Engineering of the University of Washington]

Decomposition of Nitrosyl Disulfonate Ion. I. Products and Mechanism of Color Fading in Acid Solution[1,2]

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Quantitative determination of the products of decomposition of the nitrosyl disulfonate ion in neutral and dilute acid solution showed the reaction to conform closely to the equation (1). The decomposition proceeded by two routes. One of these was first order in respect to each of the ions nitrosyl disulfonate and hydronium; the other was a degenerate branching material chain process propagated by nitrous acid. A proposed mechanism is described by equations (8) through (10).

Solution in water reversibly transforms the diamagnetic orange crystals of potassium nitrosyl disulfonate[3a-c] into a blue-violet paramagnetic solute ion,[4] from which it has been concluded that the crystal anion is the quadrivalent dimer, $[(SO_3)_2NO]_2^{=}$, of a divalent free radical solute ion, $(SO_3)_2NO^{\dot{=}}$. The salt decomposes,[3a-c,5,6] rapidly in acid, slowly in alkaline solution. In the latter case a complete examination of the products was made by Haga,[7] who found in seemingly arbitrary proportions the anions, hydroxylamine trisulfonate, hydroxylamine disulfonate, sulfate and nitrite, together with nitrous oxide and nitrogen. In no case could a stoichiometry or a mechanism be deduced. Therefore an effort is being made to establish more definitely the course of the decomposition, and the work reported here comprises the first results obtained.

Experimental

Preparation of Potassium Nitrosyl Disulfonate.—The preparation was carried out by Raschig's method,[3b] modified in respect to proportions, temperature and salting-out reagent. To prepare the salt, 0.3 *M* sodium hydroxylamine disulfonate solution was prepared at 0°. Then sodium hydroxide, two molar proportion as 5 *N* solution, was added, followed by finely powdered potassium permanganate, 0.8 equivalent proportion. After 30–40 minutes agitation the precipitate was removed by centrifuging and filtering, and solid potassium nitrate, 7 molar proportion, was added to the deep violet solution from which orange crystals then separated. After about one hour of agitation, the mixture was cooled in an ice-salt-bath. The solid was recrystallized from potassium hydroxide, 15 ml. of 1 *N* solution per g. of product. The crystals which separated after the solution was cooled in ice were washed on sintered glass with methanol, 10 ml./g. of product, and dried in a vacuum desiccator. The yield was usually about 80%.

Composition and Stability of Potassium Nitrosyl Disulfonate.—The salt prepared as described was analyzed for sulfur by decomposition of 0.5-1.0-g. portions in 100 ml. of 0.5 *N* hydrochloric acid to give solutions which were evaporated to dryness prior to re-solution and precipitation of barium sulfate. Potassium was determined on 0.5–1.0-g. samples by slow evaporation with concentrated sulfuric acid in platinum over a ring burner. The oxidizing power was determined by iodimetry. A typical analysis of the salt gave the following results:

	Found	Calcd.
Potassium	29.05	29.03
Sulfur	23.70	23.90
Oxid. equiv. weight	267.1	268.2

Solid potassium nitrosyl disulfonate prepared as described was kept indefinitely in a desiccator, and it could even be exposed to the atmosphere for several hours without undergoing the spontaneous decomposition noted by previous workers.[7] In aqueous solution the rate of decomposition depended upon the *p*H and upon the other substances present in the solution. Neutral salts were without great effect. Halides accelerated the decomposition in proportion to their ease of oxidation, but only iodide ion gave the free element. Acidic and basic salts affected the decomposition in the way predicted from the catalytic action of hydronium ions and the relative stabilization experienced in mildly basic solutions. The effect of hydronium and hydroxyl ions on the decomposition is shown in Table I, where the time recorded is that for loss of visible color from solutions of 1 g./100 ml. concentration of potassium nitrosyl disulfonate.

Table I

Effect of Hydronium and Hydroxyl Ions on Stability of Potassium Nitrosyl Disulfonate

*p*H	1.84	3.03	3.97	4.96	7.5	8.0
Decomp. time, hr.	0.25	0.42	1.92	19.2	160	500
*p*H		12.7	13.0	13.4	13.7	14.0
Decomp. time, hr.		456	312	125	105	78

Absorption Spectrum of Potassium Nitrosyl Disulfonate.—The hitherto unrecorded absorption spectrum of this salt was measured on a Beckman DU spectrophotometer. The results are plotted in Fig. 1. The molar extinction coefficient was 1690 at the 248 mμ maximum and 20.8 at the 545 mμ maximum.

Decomposition Products.—The equation for the over-all reaction was established by analysis for all of the products. The results shown in Table II support within the experimental error the over-all reaction summarized by equation (1)

$$4(SO_3)_2NO^{\dot{=}} + 7H_2O \longrightarrow 2(SO_3)_2NOH^{=} + N_2O + 4SO_4^{=} + 4H_3O^{+} \quad (1)$$

Sulfate formed was determined by the method devised by Haga[7] in which barium hydroxylamine disulfonate was solubilized by dissolved ammonium chloride.

Table II

Decomposition Products of Potassium Nitrosyl Disulfonate[a] at 25°

Reaction conditions, *p*H	Concn., mole/l.	Products $SO_4^{=}$	H^{+}	$(SO_3)_2NOH^{=}$	N_2O	N_2	NO
3.73	0.0373	3.76					
7.0-2.5	.0373		3.57	1.80			
7.0-1.8	.186				0.911		
3.78	.186				.855	0.040	trace
3.78	.186[b]				.809	.175	0.0004

[a] 3.73 millimoles of salt decomposed; all quantities given in millimoles of substance indicated. [b] Sulfamate ion present at 0.191 mole/liter.

If barium sulfate was precipitated immediately after the color disappeared 3.73 millimoles of salt gave 3.39 millimoles

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(1) Abstracted from a thesis by J. Hamoodi Murib, submitted to the Graduate School of the University of Washington in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1951.

(2) Presented at the Pacific Northwest Regional Meeting held in Seattle, Washington, June 8, 9, 1951.

(3) (a) E. Fremy, *Ann. chim. phys.*, [3] **15**, 408 (1845); (b) F. Raschig, *Ann.*, **241**, 161, 223 (1887); (c) A. Hantzsch and W. Semple, *Ber.*, **28**, 2744 (1895).

(4) R. W. Assmussen, *Z. anorg. Chem.*, **212**, 317 (1933).

(5) A. Claus, *Ann.*, **158**, 205 (1871).

(6) M. Wagner, *Z. physik. Chem.*, **19**, 680 (1896).

(7) T. Haga, *J. Chem. Soc.*, **85**, 78 (1904).

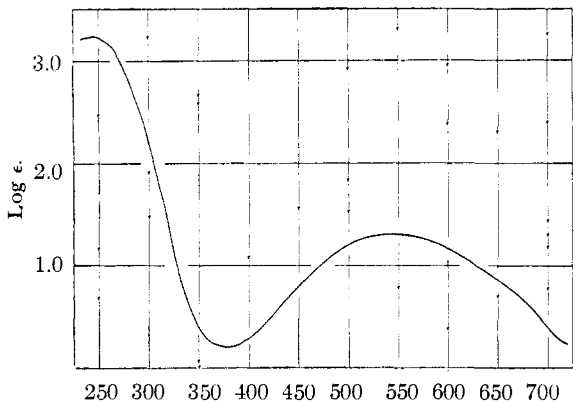

Fig. 1.—Absorption spectrum of nitrosyl disulfonate ion.

of barium sulfate, but if the solution was left standing for an hour, 3.76 millimoles of barium sulfate was obtained.

The presence of hydroxylamine disulfonate ion in the decomposition products was deduced from (a) the development of the characteristic violet-blue color of nitrosyl disulfonate ion upon oxidation with lead dioxide in potassium carbonate solution[3b,6,7] and (b) the formation, upon reduction with 3% sodium amalgam, of the amine disulfonate ion, $(SO_3)_2NH,^{=}$ which was isolated as the potassium mercury salt $K_4[(SO_3)_2N]_2Hg$.[8]

The quantitative estimation of hydroxylamine disulfonate ion was begun by hydrolysis of the decomposition mixture made 0.5 *N* in hydrochloric acid. After three days on the steam-bath, the solution was evaporated to dryness, and hydroxylamine was determined on the redissolved solids by the ferric ion oxidation method of Bray, Simpson and McKenzie.[9] The amount of hydroxylamine thus found, in relation to the amount of sulfate not precipitated as barium sulfate, gave an estimate of the quantity of hydroxylamine disulfonate ion. The procedure described by Haga[7] for the estimation of hydroxylamine trisulfonate ion failed to disclose any of that substance.

The amount of hydronium ion formed was determined by electrometric titration of an aqueous solution of the decomposed salt. The measurement was made within an hour after the color disappeared because after longer intervals the acid-catalyzed hydrolysis of hydroxylamine disulfonate ion contributed additional acidity. The *p*H was 2.63 in the solution obtained from the decomposition of 0.746 mole of salt in 200 ml. of water. Only the anions of strong acids were present, as shown by the one inflection observed at *p*H 7. The presence of a detectable quantity of nitrous acid was thus excluded.

The gaseous products were collected from reactions carried out in an inverted-V apparatus fitted with a break-off tip for a vacuum tube opener.[10] The salt was weighed into one arm and the aqueous phase was added to the other. The apparatus was evacuated; the aqueous portion was degassed by repeated freezing and melting *in vacuo*, and after final evacuation to 10^{-5} mm. pressure the tube was sealed-off from the vacuum apparatus. The liquid phase, melted and warmed to room temperature, was poured onto the solid which dissolved quickly. After the color disappeared the tube was opened to the vacuum apparatus through the vacuum tube opener. The volatile components were separated by fractional condensation in U-tubes cooled to −78.5° (solid CO_2) for water, to −183° (liquid oxygen) for nitrous oxide, and to −195° (liquid nitrogen) for nitric oxide. The gas non-condensable at liquid nitrogen temperature was collected by a Toepler pump.

Procedures for Rate Determinations.—Constant hydrogen ion concentration during the decomposition was maintained by use of acetate–acetic acid buffers. These were made in two parts; the first, solution I, was 0.045 *N* potassium acetate; the second, solution II, was 0.045 *N* potassium acetate with enough acetic acid to give the required *p*H when equal volumes of solutions I and II were mixed. To carry out an experiment potassium nitrosyl disulfonate was dissolved in 50.00 ml. of solution I where it remained stable until the decomposition was initiated by addition of 50.00 ml. of solution II. The reaction was followed by observation of 5.00-ml. aliquots removed at intervals and added to 5.00 ml. of 1 *M* potassium carbonate solution. The undecomposed nitrosyl disulfonate ion was determined by measurement of the optical density at 540 mμ on a Beckman DU spectrophotometer.

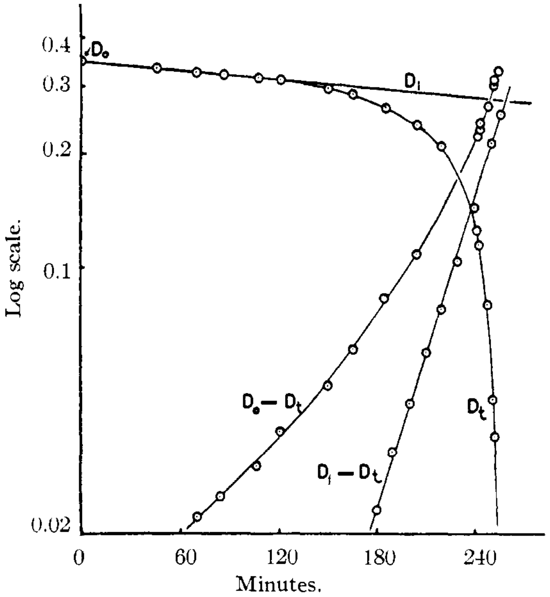

Fig. 2.—Treatment of data.

The variables examined for the effect on reaction velocity were (a) the *p*H between 1.80 and 5.00 at 0.0373 *M* initial concentration of potassium nitrosyl disulfonate (Table III), (b) the initial concentration of the decomposing salt between 0.007 and 0.065 *M* at *p*H 3.61 (Table IV), (c) the effect of potassium sulfamate as an inhibitor at concentrations between 0.00373 and 0.405 *M* with the *p*H at 3.61 and the initial concentration of nitrosyl disulfonate ion at 0.0373 *M* (Fig. 3), and (d) the effect of temperature on both the uninhibited and the inhibited reactions within the range 20–35° at *p*H 3.61, initial concentration of nitrosyl disulfonate at 0.0373 *M* and sulfamate ion at 0.207 *M*, when present (Table V, Figs. 4, 5).

Calculation of Velocity Constants.—The plot of the observed quantities D_0, the initial optical density, and D_t, the optical densities after reaction times *t*, is shown on a logarithmic scale for a typical case in Fig. 2. The early reaction was first order in respect to nitrosyl disulfonate ion, and, had the reaction continued first order, the optical densities at various times would have been values D_l, shown by the linear extension of the early reaction as illustrated in Fig. 2. The quantity log $(D_0 - D_t)$, proportional to the total amount of substance decomposed, gave the curved relation shown in the figure. This indicated that the over-all reaction did not exactly follow equation (2) for a degenerate branching chain.[11]

$$x = Ne^{\phi t};\ \ln x = \phi t + \ln N \qquad (2)$$

If the portion initially first order was assumed to continue in that way, the remainder of the substance reacted could be defined as X_c where

$$X_c = (D_0 - D_t) - (D_0 - D_l) = D_l - D_t \qquad (3)$$

The quantities log $D_l - D_t$ were related linearly to the time as required for a branching chain and as shown by the line $D_l - D_t$ in Fig. 2. Velocity constants, *k*, for the pseudo first-

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(8) E. Divers and T. Haga, *J. Chem. Soc.*, **61**, 976, 986 (1892); **69**, 1629 (1896).

(9) C. W. Bray, M. E. Simpson and A. A. McKenzie, THIS JOURNAL, **41**, 1363 (1919).

(10) A. Stock, "Hydrides of Boron and Silicon," Cornell Univ. Press, Ithaca, N. Y., 1933; R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons Inc., New York, N. Y., 1948.

(11) N. Semenoff, "Chemical Kinetics and Chain Reactions," Oxford Univ. Press, New York, N. Y., 1935, pp. 40–87, 454 ff.

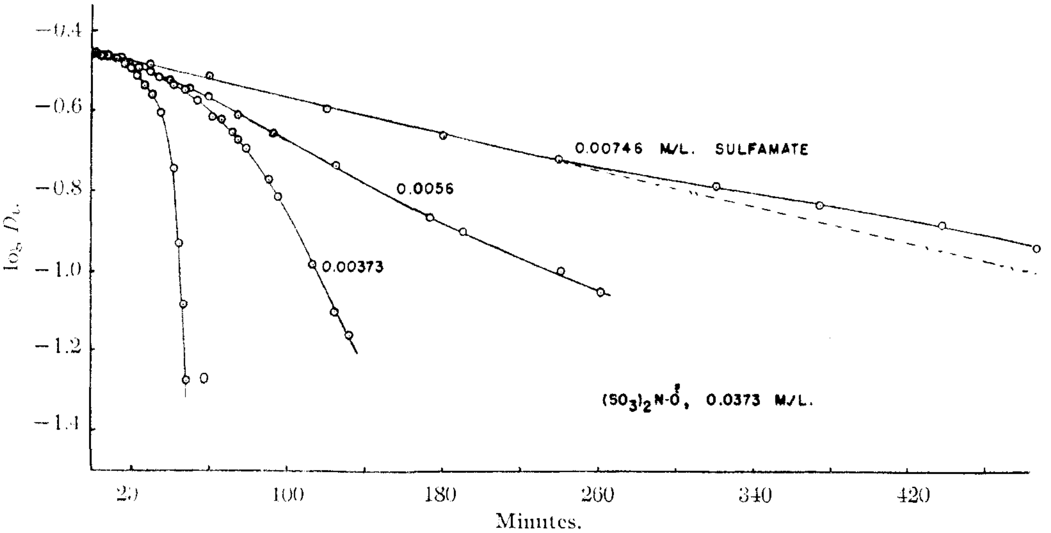

Fig. 3.—Inhibition by sulfamate ion.

order reaction with respect to nitrosyl disulfonate ion were calculated from the slopes of the lines $D_0 - D_1$, and the quantities ϕ for the branching chain were calculated from the slopes of the lines $D_1 - D_t$.

Discussion

In contrast to the findings in alkaline solution, nitrosyl disulfonate ion decomposed in acid solution to give a few products in the proportions shown by equation (1). Though the over-all reaction through which the products were obtained is obviously complex, a few conclusions can be reached on the basis of the stoichiometry and the kinetic measurements summarized in this discussion.

Kinetic measurements showed that above *p*H 3 the color disappeared by two routes (1) a reaction first order in nitrosyl disulfonate ion and hydronium ion, respectively, and (2) a degenerate branching material chain in which nitrous acid served as the chain-propagating species.

Values of the velocity constant k as recorded in Table III for the pseudo first-order reaction at constant *p*H gave a linear log k *vs.* *p*H plot. A graphical determination gave the slope 0.99, indicative of first-order participation of hydronium ions in this phase of the reaction. Confirmation of the pseudo first-order entry of nitrosyl disulfonate ion was obtained when the first-order velocity constants at *p*H 3.61 were found independent of its initial concentration as recorded in Table IV.

TABLE III

INFLUENCE OF *p*H ON k AND ϕ

*p*H	k	ϕ
1.84	1.27	....
2.80	0.0160	0.245
3.03	.0143	.196
3.25	.0110	.166
3.47	.00680	.132
3.61	.00342	.103
3.97	.00188	.0632
4.25	.000860	.0325
4.47	.000540	.0219
4.95	.000253	.0085

In the interval *p*H 2.80–4.95 ϕ varied with *p*H as shown in Table III and at *p*H 3.61 ϕ was independent of the initial concentration of nitrosyl disulfonate ion except at higher concentrations as shown in Table IV. Additional evidence of the chain character of the autocatalytic reaction was found when the temperature dependence of the chain constant was described by the equation

TABLE IV

EFFECT OF INITIAL CONCENTRATION ON k AND ϕ

Concn., mole/l.	k	ϕ
0.010	0.00359	0.1025
.015	.00325	.1020
.020	.00334	.1015
.024	.00364	.1056
.030	.00353	.1015
.031	.00355	.1010
.040	.00354	.1036
.050	.00310	.1050
.055	.00325	.1032
.060	.00337	.1158
.065	.....	.1220

$$\phi = ap^n e^{-c/T} \qquad (4)$$

where p is the pressure in a gas reaction, T is the absolute temperature; while a, n and c are constants.[12] The data in Table V determined the equation.

$$\ln \phi = 42.9 - \frac{26,800}{RT} \qquad (5)$$

TABLE V

EFFECT OF TEMPERATURE ON ϕ

T, °C.	ϕ
20.0	0.0536
22.5	.0733
25.0	.1024
30.0	.1983
35.0	.4470

The chain reaction was inhibited by sulfamate ion, $SO_3NH_2^-$, as shown in Fig. 3 where the data are plotted for runs with various amounts of sulfamate. At 25° as little sulfamate as 0.00746 mole/l. suppressed the chain initiated during the decomposition of 0.0373 mole/l. nitrosyl disulfonate, but as seen in Fig. 4 a 28-fold increase in sulfamate ion did not completely suppress the chain at 30°.[13]

The effect of temperature on both the uninhibited and the inhibited reactions is illustrated by the values for the

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[12] In solution p becomes the concentration of reactant, a quantity irrelevant in this case because as seen in Table IV, n = 0 from the absence of a concentration dependence for ϕ.

[13] At 27.6° a downward concavity was just perceptible.

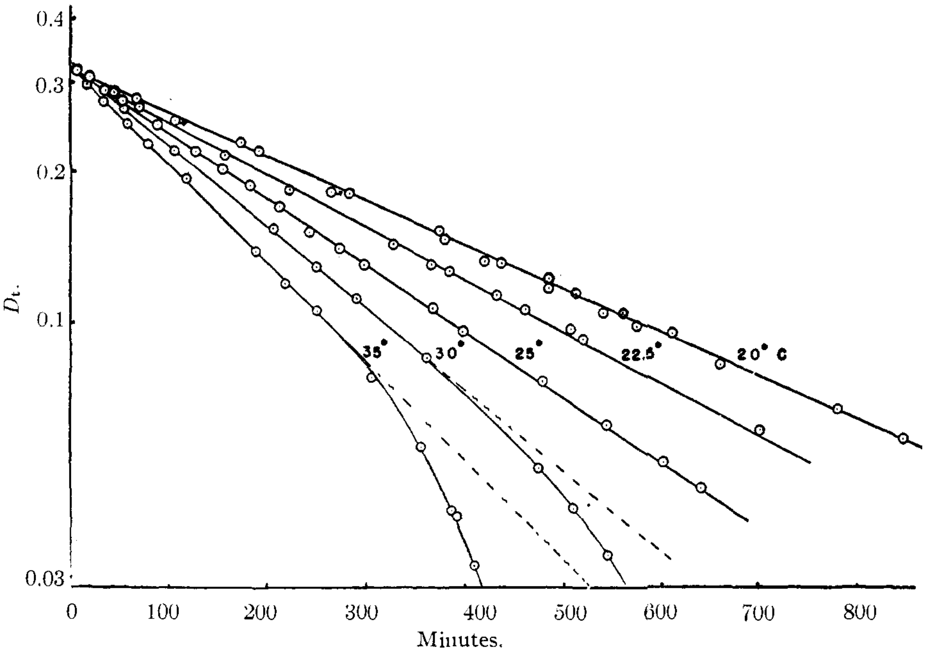

Fig. 4.—Temperature influence on inhibited reaction: $[(SO_3)_2NO^{=}]$ = 0.0373 mole/l.; $[SO_3NH_2^-]$ = 0.207 mole/l.

velocity constants k and k_i shown in Fig. 5. The values for k can be expressed by the equation

$$\ln k = 18.8 - \frac{14{,}500}{RT} \qquad (6)$$

Below 27.6° the values for k_i fit the equation[14]

$$\ln k_i = 15.5 - \frac{11{,}300}{RT} \qquad (7)$$

Identification of nitrous acid as the chain propagating species has been based upon four independent observations. (a) Haga[7] found nitrite ion as a product of decomposition in alkaline solution. (b) Sulfamate ion inhibited the chain with evolution of nitrogen[15] at the expense of nitrous oxide (*cf.* items 4 and 5, Table II). (c) Added nitrous acid greatly accelerated the decomposition of nitrosyl disulfonate ion. (d) The pH dependence of ϕ was that required for $\phi \sim [HNO_2]$ or $\phi \sim [H^+]/(K + [H^+])$ where $K = 4.60 \times 10^{-4}$, the dissociation constant for nitrous acid. The amount of sulfamate ion required for complete inhibition (20 mole %) and particularly the ratio $0.5N_2/(N_2O + 0.5N_2) = 0.097$ permit an estimate of about 10% reaction to give nitrous acid. According to this interpretation the processes described by k and k_i were identical; the quantitative differences in the interval 20–27.6° were ascribed to the primary salt effect on a reaction between ions of unlike charge. Consistent with this was the parallel diminution in activation energy.

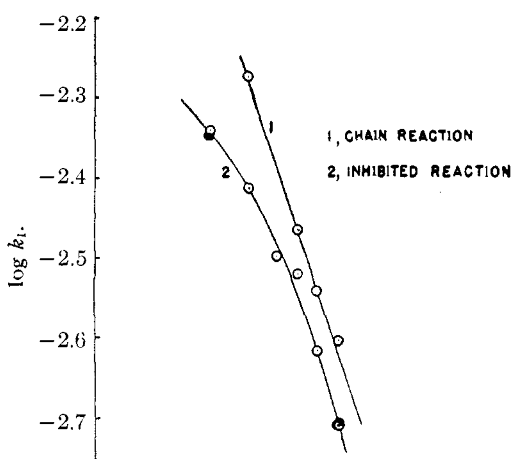

Fig. 5.—Arrhenius plot, log k *vs.* $1/T$.

The primary reaction by which color faded can be best understood if the products of the over-all reaction are classified in respect to their origin. One-half the nitrogen was found in nitrous oxide (and/or a minor fraction of nitrous acid) with the accompanying formation of sulfate and hydronium ions. The latter were formed at rates different from that of color disappearance. Early in the reaction $+\Delta[H^+]/-\Delta[(SO_3)_2NO^{=}] = 0.70$ and at 70% decoloration the ratio was 1.37. These products thus can be excluded from the primary process as can nitrous oxide, which would require for its direct formation a reaction second order in nitrosyl disulfonate ion.

In contrast the other one-half of the nitrogen was found in hydroxylamine disulfonate ion which arose by alteration of the nitrosyl disulfonate ion through the single step of adding one hydrogen atom. If the hydrogen atom be assumed to have come from the hydronium ion reactant, this transformation can be considered the primary process described by equation (8) and followed by the very rapid reaction of equation (9).

$$(SO_3)_2NO^{=} + H_3O^+ \xrightarrow{k_1} (SO_3)_2NOH^- + H_2O^{+}\cdot \qquad (8)$$

$$H_2O^{+}\cdot + H_2O \rightleftarrows H_3O^+ + HO\cdot$$

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(14) The curvature in the Arrhenius plot for k_i denotes a presently baffling complexity in the action of sulfamate ion. Not only is the chain suppressed, but an additional temperature-dependent inhibition of the pseudo first-order reaction must also occur. For present purposes this has been considered negligible below 27.6° and at the risk of over-simplification the mechanism proposed has been partly deduced on that basis.

(15) P. Baumgarten and I. Marggraff, *Ber.*, **63**, 1019 (1930).

$$(SO_3)_2NO^{=} + HO\cdot \xrightarrow{k_2} \text{intermediate} \longrightarrow \left\{\begin{array}{l} N_2O \\ HNO_2 \\ SO_4^{=} \\ H_3O \end{array}\right. \quad (9)$$

The differential rate equation should be equation (10), and with the logical supposition that $k_2 \cdot [HO\cdot] \ll k_1[H_3O^+]$ the observed reaction should be first order in respect to each of the reacting species, nitrosyl disulfonate ion and hydronium ion as was found to be the case.

$$-d[(SO_3)_2NO^{=}]/dt = [(SO_3)_2NO^{=}]\{k_1[H_3O^+] + k_2[HO\cdot]\} \quad (10)$$

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SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Studies Relating to Boron. V. Chemistry of the Dibutylboron Group[1]

BY ROBERT W. AUTEN[2] AND CHARLES A. KRAUS

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The reduction of dibutylboron chloride by means of sodium-potassium alloy in ether solution takes place in two steps. One equivalent of chloride reacts with one equivalent of metal to produce dibutylboron which is soluble in ether. On evaporation of solvent, the compound disproportionates to form tributylboron and a solid, presumably monobutylboron. With excess metal, the chloride is reduced to the boride, $MB(C_4H_9)_2$; the yield is 65%. This boride reacts with methyl iodide to yield methyldibutylboron. On treating the boride with dibutylboron chloride, there was obtained, in addition to tributylboron and monobutylboron, a small quantity of a difficulty volatile substance whose boron content corresponds to that of dibutylboron. When the metal boride reacts with one equivalent of hydrogen chloride (at −70°), there are obtained hydrogen, tributylboron and monobutylboron. With two equivalents of hydrogen chloride, the products are hydrogen and dibutylboron chloride. Similar reactions take place with triethylammonium chloride.

I. Introduction

Alkylboron halides of the type R_2BX, heretofore, have not been reduced to the free group R_2B or to the negative ion R_2B^-. However, Booth[3] has obtained evidence which indicates that such reduction may be effected by means of sodium-potassium alloy in diethyl ether. Using dibutylboron chloride, we have confirmed Booth's observation.

The reduction of dibutylboron chloride by means of sodium–potassium alloy takes place in two stages. In the first stage, the chlorine is split off quantitatively according to the equation

$$(C_4H_9)_2BCl + M = (C_4H_9)_2B + MCl \quad (1)$$

The free group, $(C_4H_9)_2B$, is soluble in ether; it doubtless exists as a polymer of unknown complexity. For the sake of brevity we shall omit any symbol indicating polymer complexity; the formulas indicate composition only. In the second stage, reaction occurs according to the equation

$$(C_4H_9)_2BCl + 2M = MB(C_4H_9)_2 + MCl \quad (2)$$

If an attempt is made to separate the product of reaction (1) by evaporation of the solvent, the product undergoes disproportionation according to equation

$$2(C_4H_9)_2B = (C_4H_9)_3B + C_4H_9{\cdot}B \quad (3)$$

Reaction (2) is not quantitative; somewhat more than 60% of the dibutylboron is converted to metal boride. The existence of the metal boride, which is soluble in ether, is established by its reaction with methyl iodide, methyldibutylboron being formed according to the equation

$$MB(C_4H_9)_2 + CH_3I = CH_3B(C_4H_9)_2 + MI \quad (4)$$

On treating the metal boride with dibutylboron chloride, the final, over-all reaction is in accord with the equation

$$(C_4H_9)_2BM + ClB(C_4H_9)_2 = (C_4H_9)_3B + C_4H_9B + MCl \quad (5)$$

Doubtless, the dibutylboron initially formed disproportionates according to equation (3). In this reaction, a small quantity of a difficultly volatile substance was obtained whose composition, on analysis, corresponded to that of $(C_4H_9)_2B$.

On treating the metal boride with excess hydrogen chloride, reaction occurs according to the equation

$$MB(C_4H_9)_2 + 2HCl = (C_4H_9)_2BCl + H_2 + MCl \quad (6)$$

On treating the boride with one equivalent, the final products conform to the over-all reaction

$$2MB(C_4H_9)_2 + 2HCl = (C_4H_9)_3B + C_4H_9B + H_2 + 2MCl \quad (7)$$

Dibutylboron chloride is initially formed and this in turn reacts with metal boride according to equation (5). The reaction of the boride with triethylammonium chloride is similar to that which hydrogen chloride. The products may be accounted for by the equation

$$2MB(C_4H_9)_2 + 2(C_2H_5)_3NHCl = (C_4H_9)_3B + C_4H_9B + 2(C_2H_5)_3N + H_2 + 2MCl \quad (8)$$

No evidence was found which indicated the formation of the hydride $(C_4H_9)_2BH$. The metal boride appears to be stable in liquid ammonia solution but reacts slowly with ammonia vapor at room temperature.

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(1) This paper is based on a portion of a thesis presented by Robert W. Auten in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1937.

(2) Anthony Fellow in Brown University, 1933–1934; University Fellow, 1935–1937.

(3) R. B. Booth, Thesis, Brown University, 1934.