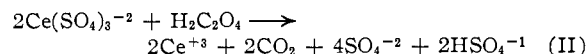
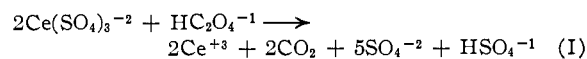


of these ions were roughly estimated from the dissociation constants of oxalic acid and bisulfate ion.⁸ Molar concentrations were converted to molalities and ionic strengths were derived from these latter values. The graph in Fig. 3 shows that the differences between $\log k$ and $\log k_0$ over the temperature range 19 to 35° are approximately the same for solutions of similar ionic strength (with respect to sulfuric acid). This same conclusion can be reached by comparing the slopes of the curves in Fig. 2. The data plotted in Figs. 2 and 3 indicate that the same species of reactants are involved in the rate-determining step, regardless of the acidity of the reaction medium.

There is considerable evidence that the cerium(IV) ion exists primarily as the trisulfato complex ion in sulfuric acid solutions. This is especially true in acid concentrations such as those employed in this work.^{6,9} It is also reasonable to assume that in these strongly acid solutions the oxalate is present mainly as oxalic acid with smaller amounts of bioxalate ion and only traces of oxalate ion. The rate-determining step must then be either (I) or (II)



Since both reactions I and II produce bisulfate ions, they might be expected to respond to a change in acid concentration. The presence of excess sulfate ions in the reaction medium would also tend to reduce the rate of the reaction. From the standpoint of the concentration of the reactants, an in-

(8) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solution," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1949, Chap. 14.

(9) (a) G. F. Smith and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 191 (1938); (b) T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 828 (1951).

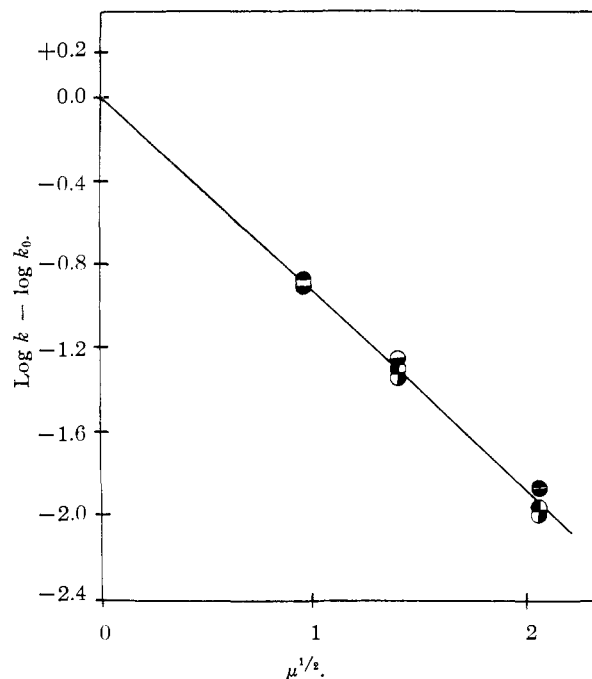


Fig. 3.—Relationship between measured second-order rate constants and ionic strength of acid medium: ●, 19°; ○, 25°; ◐, 30°; ◑, 35°.

crease in acid concentration would tend to slow down reaction I and speed up reaction II. However, as the concentration of the sulfuric acid solutions is increased from 0.5 to 2.0 M, the concentration of bioxalate ion and oxalic acid remains fairly constant. Therefore, the noted effect of the acid on the reaction rates must be due to the excess sulfate, bisulfate and hydrogen ions in solution.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING AND FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Chemical Properties of Nitrosyl Perchlorate: The Neutralization Equivalent

BY MEYER M. MARKOWITZ, JOHN E. RICCI, RICHARD J. GOLDMAN AND PAUL F. WINTERNITZ

RECEIVED MARCH 5, 1957

The quantitative preparation of nitrosyl perchlorate from dinitrogen trioxide and perchloric acid is limited by the subsequent hydrolysis of the product below a minimum acid concentration. The neutralization equivalent weight of nitrosyl perchlorate under defined conditions is $\text{NOClO}_4/2$. Some aspects of the thermal behavior of the salt are treated briefly.

Introduction

Interest in the nitric oxide molecule stems from the diversity of bond types into which the group may enter.¹⁻³ Previous studies concerning nitrosyl perchlorate (NOClO_4), as representative of a compound containing a nitric oxide cation (NO^+), have dealt with the electrolytic behavior in an-

hydrous nitromethane,⁴ the Raman spectrum in perchloric acid,⁵ the crystallographic structure,⁶ the heat of formation,⁷ and the thermal decomposition.⁸ The material to follow presents lab-

(1) C. C. Addison and J. Lewis, *Quart. Revs. (London)*, **9**, 115 (1955).
 (2) T. Moeller, *J. Chem. Educ.*, **23**, 441, 542 (1946).
 (3) E. S. Gould, D. H. Ross and W. A. Fessler in R. E. Kirk and D. F. Othmer, "Encyclopedia of Chemical Technology," Vol. 9, Interscience Encyclopedia, Inc., New York, N. Y., 1952, pp. 462-472.

(4) A. Hantzsch and K. Berger, *Z. anorg. allgem. Chem.*, **190**, 321 (1930).

(5) W. R. Angus and A. H. Leckie, *Trans. Faraday Soc.*, **31**, 958 (1935); *Proc. Roy. Soc. (London)*, **A150**, 615 (1935).

(6) L. J. Klinkenberg, *Rec. trav. chim.*, **56**, 749 (1937).

(7) K. Cruse, G. Huck and H. Moeller, *Z. anorg. Chem.*, **259**, 173 (1949); **260**, 295 (1949).

(8) K. Cruse, G. Huck and H. Moeller, *ibid.*, **259**, 159 (1949); K. Gerding and W. F. Haak, *Chem. Weekblad*, **52**, 282 (1950).

oratory investigations directed at the further elucidation of the chemical properties of nitrosyl perchlorate.

Experimental

Preparation.—Nitrosyl perchlorate was prepared by passage of dinitrogen trioxide into aqueous perchloric acid, following the method of Hofmann and Zedtwitz.⁹ The gas from 89 g. of sodium nitrite (1.3 moles), on to which 57 ml. of 70% nitric acid (0.89 mole) was added dropwise, was passed slowly into 40 ml. of 70–72% perchloric acid (0.47–0.49 mole) immersed in an ice-bath. The gas generator was contained in an ice-bath to moderate the gas flow. Drying tubes, filled with sodium nitrite and glass beads, and Drierite, respectively, were interposed between the gas generator and reaction tube in order to prevent the passage of nitric acid and water into the perchloric acid.

The precipitated nitrosyl perchlorate was suction-filtered on a fritted glass funnel, and washed with six 20-ml. portions of nitromethane which previously had been dried over anhydrous magnesium perchlorate and then vacuum distilled. The washed material was pumped down for five hours in a vacuum desiccator sealed with a fluorocarbon grease. The nitrosyl perchlorate subsequently was allowed to stand *in vacuo* over phosphorus pentoxide for five days.

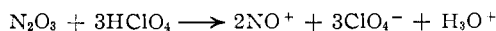
It should be noted that nitrosyl perchlorate is a strong oxidant and that suitable care must be taken in its handling; yield 18.3 g. (30% of theory on the basis of 0.48 mole of HClO₄). Preparation of nitrosyl perchlorate by the direct reaction of sodium or potassium nitrite with aqueous perchloric acid was not possible.

Analytical Methods.—Analyses for chlorine were performed by admixture of the product with anhydrous sodium carbonate in a platinum crucible, addition of water dropwise to allow for conversion to sodium perchlorate, oven-drying at 90°, and ignition over a blast lamp for decomposition of the perchlorate to chloride.¹⁰ Chlorine was then determined gravimetrically as silver chloride.

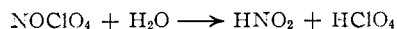
Direct determination of the nitrosyl group was afforded by suspension of the salt (0.5 g.) in concentrated sulfuric acid (100 ml.), and slow addition, accompanied by constant stirring, of excess potassium permanganate (0.2 *N*).^{11,12} The permanganate solution must be added below the surface of the acid to avoid any loss of sample by hydrolysis. The excess permanganate was titrated with acidified ferrous sulfate solution (0.2 *N*).

Anal. Calcd. for NOClO₄:Cl, 27.39; nitrosyl group, 23.17. Found: Cl, 27.28; nitrosyl group, 23.16.

Hydrolysis of Nitrosyl Perchlorate.—The low yield obtained may, in part, be traced back to the ready hydrolysis of ionic nitrosyl compounds.^{1,13} Solution of dinitrogen trioxide in strong, concentrated acids yields the nitrosyl ion.^{14,15} Thus, with perchloric acid, the following reaction must occur



As the addition of dinitrogen trioxide is continued, nitrosyl perchlorate will precipitate and the concentration of the water will rise. However, precipitation can only proceed to the point at which hydrolysis of the product ensues because of the augmenting water concentration. Hydrolysis will yield nitrous acid as per



which may, in turn, decompose according to the disproportionation reaction



Titration with sodium hydroxide of the filtrate obtained from the above-described preparation of nitrosyl perchlorate

(9) K. A. Hofmann and A. Zedtwitz, *Ber.*, **42**, 2031 (1909).

(10) K. A. Hofmann, A. Metzler and K. Hoebold, *ibid.*, **43**, 1080 (1910).

(11) G. Balz and E. Mailaender, *Z. anorg. allgem. Chem.*, **217**, 161 (1934).

(12) E. Wilke-Doerfurt and G. Balz, *ibid.*, **159**, 197 (1926).

(13) H. J. Schlesinger and A. Salathe, *THIS JOURNAL*, **45**, 1863 (1923).

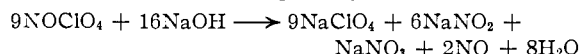
(14) R. J. Gillespie, J. Graham, E. D. Hughes, C. K. Ingold and E. R. A. Peeling, *J. Chem. Soc.*, 2504 (1950).

(15) D. J. Millen, *ibid.*, 2600 (1950).

showed that the alkali titer, expressed as equivalents of base per 1000 g. of solution, had changed from the value of 7.10 for the original perchloric acid (71.4%) to a final value of 6.18 after precipitation.

Nitrosyl perchlorate placed in 51.7% perchloric acid at 25.0° (5.14 equivalents per 1000 g. of dilute acid) decomposed until the alkali titer of the acid plus nitrosyl perchlorate decomposition products reached 5.44. These data indicate that nitrosyl perchlorate will hydrolyze in perchloric acid solutions of less than about 55% concentration.

The Neutralization Equivalent of Nitrosyl Perchlorate.—Previous studies of the alkali titers of nitrosyl compounds suggest neutralization equivalent weights dependent upon the reaction conditions which would determine the extent of the nitrous acid disproportionation reaction.^{7,16} Cruse, *et al.*,⁷ reported the reaction of nitrosyl perchlorate with 0.5 *N* sodium hydroxide to be given by



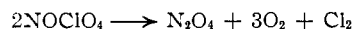
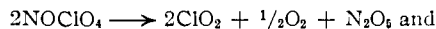
In order to determine the neutralization equivalent under conditions such that the disproportionation reaction would be minimized, a series of titrations with sodium hydroxide was carried out at 0°. 0.25–0.30 g. of nitrosyl perchlorate contained in a small vial was dropped into a flask containing 25 ml. of water and 45–50 ml. of 0.1 *N* sodium hydroxide. The flask was stoppered quickly, shaken vigorously, and allowed to stand for three minutes whereupon the contents were titrated with 0.1 *N* sulfuric acid to a phenolphthalein end-point. Of ten such determinations, an average titer corresponding to 98.82% nitrosyl perchlorate (average deviation, 2.3 parts/1000) on the basis of a neutralization equivalent weight of NOClO₄/2 was obtained. This substantiates the neutralization reaction to be



No appreciable variations in the alkali titer were found in performing the titrations at higher temperatures, *i.e.*, 25 and 30°, indicating that the neutralization reaction under the described conditions is sufficiently rapid to avoid a significant amount of interference from nitrous acid disproportionation. At 25°, the average value of six titrations was 98.54% (average deviation, 2.1 parts/1000), and at 35°, for three determinations, 98.40% (average deviation, 2.8 parts/1000). This titration method thus affords a convenient means for the analysis of nitrosyl perchlorate-containing materials.

Nitrosyl perchlorate was found to deteriorate on exposure to and handling in the open air because of the extreme hygroscopicity of the substance. This was seen in a lower alkali titer from a subsequent series of experiments at 0°. The average value for seven experiments on such a treated sample corresponded to 98.14% nitrosyl perchlorate (average deviation, 1.0 part/1000).

Thermal Behavior of Nitrosyl Perchlorate.—Nitrosyl perchlorate is thermally unstable,⁸ yielding volatile decomposition products as per the equations



It was determined in the present work that at 92°, under vacuum (3–5 mm.), weight losses of 27, 61, 94 and 100% occurred with a 0.5-g. sample after 3, 6, 9 and 12 hr., respectively. Losses at 100°, under similar conditions, were 65, 80 and 99%, after 3, 6 and 9 hr., respectively.

Unlike ammonium perchlorate and the alkali metal perchlorates,¹⁷ nitrosyl perchlorate undergoes no crystallographic transition before the onset of rapid decomposition. This was determined by thermal analyses¹⁸ of the compound (5-g. samples), performed over the range from 0 to 100° at heating rates of 5 and 10° per minute. Because nitrosyl perchlorate is isomorphous with ammonium perchlorate,⁸ it may be supposed that the normal rhombic structure of the latter is retained by nitrosyl perchlorate at least up to 100°.

Miscellaneous Reactions.—Because the nitrosyl group contains an unshared pair of electrons about the nitrogen atom,

(16) A. Perret and R. Perrot, *Compt. rend.*, **193**, 937 (1931).

(17) S. Gordon and C. Campbell, *Anal. Chem.*, **27**, 1102 (1955).

(18) For procedure see: M. M. Markowitz, J. E. Ricci and P. F. Winteritz, *THIS JOURNAL*, **77**, 3432 (1955).

attempts were made to obtain coördinate bond formation between nitrosyl perchlorate and oxygen (to yield nitronium perchlorate), boron trifluoride and dinitrogen tetroxide, respectively. Nitrosyl perchlorate was thus brought in contact with a rapid stream of gaseous oxygen at room temperature, heated with nitrosyl fluoborate, and treated with liquid dinitrogen tetroxide at 0°, all without any indications of compound formation.

Acknowledgment.—The studies reported herein

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NEW YORK 53, N. Y.

[CONTRIBUTION FROM THE BALLISTICS RESEARCH LABORATORIES]

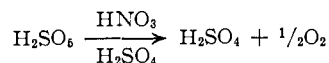
The Nitronium Ion Catalyzed Decomposition of Caro's Acid

BY LESTER P. KUHN

RECEIVED DECEMBER 26, 1956

Caro's acid in strong sulfuric acid is catalytically decomposed by small amounts of nitronium ion to yield sulfuric acid and oxygen. The kinetics of the reaction have been studied and a mechanism is presented which is compatible with the data. An unusual feature of the reaction is that both the rate and the order depend upon the strength of the sulfuric acid. Below 91% sulfuric acid the reaction is -1 order in peroxide and above 95% acid, the order in peroxide is $+1$. Throughout the entire range studied, from 85 to 98% acid the reaction is second order in nitric acid.

Aqueous solutions of Caro's acid, H_2SO_5 , are relatively unstable; the kinetics and mechanism of their decomposition recently has been reported.¹ Solutions of Caro's acid in concentrated sulfuric acid, on the other hand, are quite stable and may be stored for days at room temperature without change of peroxide titer. It has been found that the addition of a very small amount of nitric acid to such solutions produces a reaction in which oxygen is evolved and the Caro's acid is converted completely to sulfuric acid. The nitric acid is recovered unchanged. A study of the kinetics of this reaction



and a mechanism which is compatible with the data are presented in the succeeding paragraphs.

Experimental

The reaction was followed by measuring the rate of gas evolution. The gas was collected in inverted graduated cylinders over water which had previously been saturated with oxygen. The reactions were run in a 125-ml. erlenmeyer flask containing a sidearm which was connected through a gas bubbler containing concentrated sulfuric acid to the inverted cylinders. The mouth of the flask was closed with a rubber stopper which held a buret that was calibrated in 0.05 ml. The flask was held in a constant temperature bath that was constant to $\pm 0.05^\circ$. The reaction mixture was stirred with a magnetic stirrer, the motor of which was below the constant temperature bath. Two sets of stock solutions were made up, one for reactions in the more concentrated acid, and the other for the less concentrated acid region. The latter was J. T. Baker C.P. concentrated sulfuric acid, and the former was made by mixing 75 parts by volume of concentrated acid with 25 parts of 20% fuming sulfuric acid. Nitric acid stock solutions approximately 0.05 *M* were made by dissolving 98% nitric acid or potassium nitrate in each of the sulfuric acid stock solutions. The stock solutions were saturated with oxygen. In a typical run a volume of the sulfuric acid stock solution, such that after the addition of the peroxide and nitric acid stock solution the total volume would be 50 ml., was put into the reaction flask and the stirrer started. The appropriate amount, usually 0.5 to 1 ml. of 90% hydrogen peroxide was then added and the flask was stoppered and allowed to stand in the constant temperature bath for 40 minutes to allow for temperature equilibration. The reaction was started by

the addition of the nitric acid stock solution, 1 to 10 ml., from the buret. Readings of gas volumes were taken at 30-second or longer intervals, depending upon the rate. Immediately after each run two 10-ml. samples were pipetted from the reaction mixture and, after dilution with distilled water in 500-ml. volumetric flasks, titrated with standard base to give the normality of the reaction mixture. Before each run the glassware which was to come in contact with the sulfuric acid was washed with distilled water, rinsed with alcohol and dried at 130° for several hours. Every effort was made to minimize the exposure of the sulfuric acid solutions to atmospheric moisture. In those experiments in which water was required to obtain the desired acid strength, the appropriate amount of water was added prior to the peroxide.

Results and Discussion

One of the most interesting features of this reaction is the profound effect that water has on both the rate and the order of the reaction. In the region below 91% sulfuric acid the reaction is -1 order in peroxide, above 95.5% acid, the order in peroxide is $+1$, and in a very narrow region at about 93% acid the reaction is zero order in peroxide. In the regions of about 91–92.5% and 93.5–95.5% acid one observes no integral order. Over the entire range studied, from 85 to 98% acid the reaction is second order in nitric acid. The rate constants in the region below 91% acid will be called k_{-1} and those for the region above 95.5% acid will be designated as k_1 . These constants were obtained graphically from the relationships

$$k_1 = \frac{2.303 \Delta \log (1 - V_t/V_f)}{\Delta t (\text{HNO}_3)^2}$$

$$k_{-1} = \frac{\Delta(1 - V_t/V_f)^2 C_0^2}{2 \Delta t (\text{HNO}_3)^2}$$

Concentration is in moles per liter, time is in seconds, C_0 is the initial concentration of peroxide, V_t is the volume of gas given off at time t and V_f is the total volume of gas given off. Typical curves from which the k 's were calculated are shown in Fig. 1. Straight lines were generally obtained for at least 60% of the reaction. Values of k 's from runs using different initial concentrations of peroxide and nitric acid are shown in Table I. As will be shown shortly, the values of the k 's are extremely

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