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.

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[CONTRIBUTION FROM THE BALLISTICS RESEARCH LABORATORIES]

# The Nitronium Ion Catalyzed Decomposition of Caro's Acid

BY LESTER P. KUHN

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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

$$H_2SO_5 \xrightarrow[H_2SO_4]{HNO_3} H_2SO_4 + {}^1/_2O_2$$

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 ±0.05°. 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

$$k_1 = \frac{2.303\Delta \log (1 - V_t/V_f)}{\Delta t\ (HNO_3)^2}$$

$$k_{-1} = \frac{\Delta(1 - V_t/V_f)^2 C_0^2}{2\Delta t(HNO_3)^2}$$

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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[1] D. L. Ball and J. O. Edwards, THIS JOURNAL, **78**, 1125 (1956).

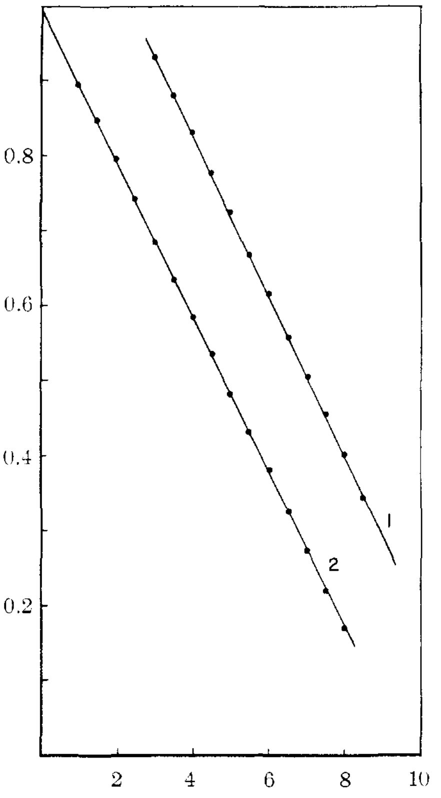

Fig. 1.—Curve 1, first-order reaction, log $(1 - V_t/V_f)$ *vs.* time, run no. 23; curve 2, −1 order reaction, $(1 - V_t/V_f)^2$ *vs.* time, run no. 11. Experimental conditions given in Table I. Curve 1 displaced along time axis.

sensitive to the amount of water present. For this reason, in order to obtain constant values for the *k*'s, it is necessary to compare runs in which the acid strength is as constant as possible. Since duplicate runs are not always of the same acidity because of the hygroscopic nature of sulfuric acid, and since varying the initial concentration of peroxide at the same time varies the acidity, it was necessary to make a great number of runs in order to get enough comparable curves to yield the data shown in Table I.

The rate of the reaction is very sensitive to the strength of the sulfuric acid, it being at a maximum at 93 to 94% acid. In Fig. 2 are plotted $k_1$ and $k_{-1}$ as a function of the acid strength. The addition of water increases $k_1$ and decreases $k_{-1}$. The effect of the addition of potassium or ammonium bisulfate is qualitatively the same as that of water.

Some miscellaneous experiments were performed which have a bearing on the reaction mechanism. Substitution of potassium nitrite for potassium nitrate as the catalyst, or substitution of potassium persulfate for hydrogen peroxide as the source of Caro's acid produces no change in the course of the reaction or its kinetics. To determine whether free radicals are intermediates in the reaction, a run was made in the presence of *m*-dinitrobenzene (nitrobenzene was nitrated under our reaction conditions, and thus could not be used). No change in the yield of oxygen or the kinetics was observed.

TABLE I

RATE CONSTANTS, $k_1$ AND $k_{-1}$, FOR THE DECOMPOSITION OF CARO'S ACID AT VARIOUS ACID STRENGTHS; $T$ = 303.0°K.

| No. | Acid. $N$ | (N)[a] | (P)[b] | $k_1$ |
|---|---|---|---|---|
| 4 | 36.50 | 0.01 | 0.21 | 30.8 |
| 12 | 36.47 | .01 | .42 | 32.4 |
| 14 | 36.48 | .005 | .42 | 31.5 |
| 10 | 36.40 | .01 | .42 | 36.0 |
| 13 | 36.36 | .01 | .21 | 38.1 |
| 23 | 35.93 | .005 | .42 | 156.8 |
| 24 | 35.91 | .005 | .21 | 165.6 |
| | | | | $k_{-1}$ |
| 5 | 32.75 | 0.0015 | 0.420 | 17.9 |
| 11 | 32.76 | .0030 | .435 | 17.7 |
| 6 | 32.70 | .0045 | .437 | 16.5 |
| 8 | 32.90 | .0030 | .372 | 20.6 |
| 9 | 32.86 | .0030 | .704 | 19.3 |
| 16 | 32.90 | .0030 | 1.070 | 20.7 |

[a] Initial concentration of nitric acid in moles/l. [b] Initial concentration of peroxide in moles/l.

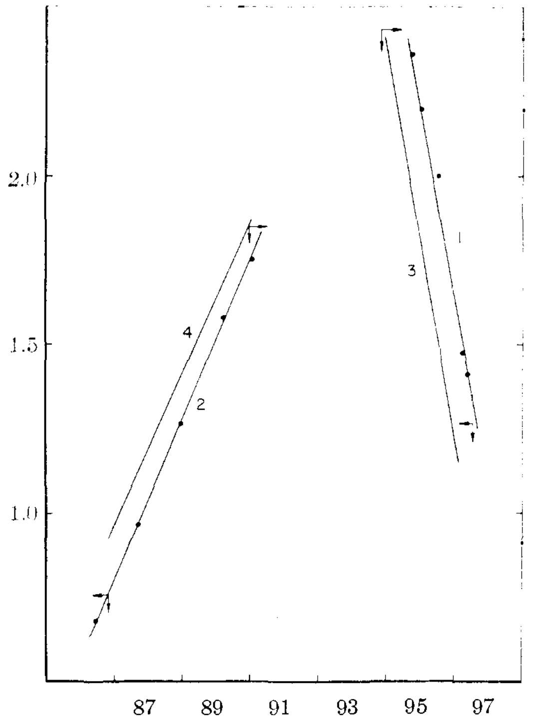

Fig. 2.—(1) log $k_1$; (2) log $k_{-1}$; (3) 4 log $(HSO_4^-)/(H_2SO_4)$; (4) 2 + 2 log $(H_2SO_4)/(HSO_4^-)$; each *vs.* % $H_2SO_4$.

In another run the reaction mixture was irradiated with ultraviolet light from a mercury vapor lamp. Again no effect was observed, indicating that free radicals are probably not involved. To determine whether the reaction of hydrogen peroxide or potassium persulfate with the solvent to yield Caro's acid is kinetically important, several runs were made in which solutions of either of these were allowed to stand 18 hours before the addition of the nitric acid. The results were identical with those in which the nitric acid was added after 30 minutes.

The following reasonable mechanism is compatible with the experimental data. The following reversible equilibria are rapidly established

$$H_2O_2 + 2H_2SO_4 \overset{K_1}{\rightleftarrows} H_3O^+ + HSO_4^- + H_2SO_5$$

$$H_2SO_5 + HSO_4^- \overset{K_2}{\rightleftarrows} HSO_5^- + H_2SO_4$$

$$HSO_5^- + NO_2^+ \overset{K_3}{\rightleftarrows} HSO_5NO_2$$

$$HSO_5NO_5 + HSO_4^- \overset{K_4}{\rightleftarrows} SO_5NO_2^- + H_2SO_4$$

$$H_2SO_4 + H_2SO_5 \overset{K_5}{\rightleftarrows} H_2O + H_2S_2O_8$$

$$HNO_3 + 2H_2SO_4 \overset{K_6}{\rightleftarrows} NO_2^+ + H_3O^+ + 2HSO_4^-$$

$$H_2O + H_2SO_4 \overset{K_7}{\rightleftarrows} H_3O^+ + HSO_4^-$$

The first equilibrium represents the formation of Caro's acid from the reaction between hydrogen peroxide and sulfuric acid.[2] The fact that identical kinetics are observed when either hydrogen peroxide or potassium persulfate are used gives further support to this equilibrium. The product of the third equilibrium is the mixed anhydride of nitric and Caro's acids. Although this anhydride has never been reported its existence is not unreasonable. Peracids have a strong tendency to form mixed anhydrides with ordinary acids, *e.g.*, acetyl peroxide, benzoyl peroxide and peroxydisulfuric acid, $H_2S_2O_8$. The other equilibria require no comment.

The total amount of nitric acid present in all forms will be designated by $N$ and the total amount of peroxide will be designated by $P$.

$$(N) = (HNO_3) + (NO_2^+) + (NO_2HSO_5) + (NO_2SO_5^-) \tag{1}$$

$$P) = (H_2SO_5) + (HSO_5^-) + (NO_2HSO_5) + (NO_2SO_5^-) + (H_2S_2O_8) \tag{2}$$

Since the measurements were made under conditions such that $(P)/(N)$ is in the range of 25 to 500

$$(NO_2HSO_5) + (NO_2SO_5^-) << (H_2SO_5) + (HSO_5^-) + (H_2S_2O_8)$$

and eq. 2 can be replaced by

$$(P) = (H_2SO_5) + (HSO_5^-) + (H_2S_2O_8) \tag{3}$$

From the above equilibria and eq. 1 and 3 the following relationships can be derived

$$(NO_2^+) = \frac{K_6K_7Z(N)}{K_6K_7Z + K_7(H_3O^+)X^2Z + K_2K_3K_6X^2(H_3O^+)(P)(1 + K_4X)} \tag{4}$$

$$(NO_2SO_5^-) = \frac{K_2K_3K_4K_6X^3(H_3O^+)(N)(P)}{K_6K_7Z + K_7(H_3O^+)X^2Z + K_2K_3K_6X^2(H_3O^+)(P)(1 + K_4X)} \tag{5}$$

Where $X = (HSO_4^-)/(H_2SO_4)$ and $Z = K_2X(H_2O) + (H_2O) + K_5(H_2SO_4)$.

The reaction proceeds in two steps

$$NO_2 + NO_2SO_5^- \xrightarrow{\text{slow}} NO^+ + NO_2^+ + SO_4^{--} + O_2$$

$$NO^+ + HSO_5^- \xrightarrow{\text{fast}} NO_2^+ + HSO_4^-$$

The rate of the reaction is given by the equation

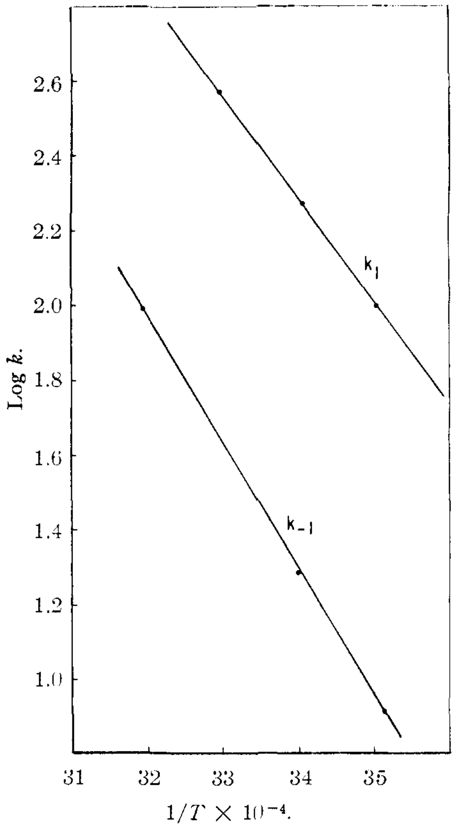

Fig. 3.—Temperature dependence of $k_1$ and $k_{-1}$. The acid concentrations were 95.8% acid for $k_1$ and 88.9% for $k_{-1}$.

$$r = k(NO_2^+)(NO_2SO_5^-) = \frac{kK_2K_3K_4K_6^2X^3Z(H_3O^+)PN^2}{[K_6K_7Z + K_7ZX^2(H_3O^+) + K_2K_3K_6(P)X^2(H_3O^+)(1 + K_4X)]^2} \tag{6}$$

Since peroxy acids are weaker than the corresponding non-peroxidic acids, $K_2$ and $K_4$ must be smaller than one. We shall assume then that $K_4X << 1$ and that $K_5(H_2SO_4) >> (H_2O) + K_2X(H_2O)$. The first assumption means that $(NO_2SO_5^-) << (NO_2SO_5H)$ and the second assumption means that the peroxide is predominantly in the form of $H_2S_2O_8$ in the acid range we have used. Therefore $Z = K_5(H_2SO_4)$.

Since addition of water increases $X$ and decreases $Z$ at acid strength greater than 95% the first term in the denominator of eq. 6 is much larger than the second and third terms and the equation reduces to

$$r = kK_2K_3K_4X^3(H_3O^+)PN^2/K_5K_7^2(H_2SO_4)$$

Since $(H_3O^+)$ is approximately equal to $(HSO_4^-)$ this may be written as

$$r = kK_2K_3K_4PN^2X^4/K_5K_7^2 \tag{7}$$

At acid strength below 91% acid the last term in the denominator of eq. 6 becomes large compared to the first two terms and the equation reduces to

$$r = kK_4N^2Z/K_2K_3(P)X(H_3O^+) = kK_4K_5N^2/K_2K_3PX^2 \tag{8}$$

According to eq. 7 the reaction in strong acid is second order in nitric acid and first order in peroxide whereas in more dilute acid eq. 8 requires that the reaction be second order in nitric acid and −1

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(2) N. V. Sidgwick, "The Chemical Elements and their Compounds," Oxford Press, New York, N. Y., 1950, p. 939.

order in peroxide in agreement with the experimental data. The experimentally determined rate constants $k_1$ and $k_{-1}$ are related to the constants given in eq. 7 and 8 by the equations

$$k_1 = kK_2K_3K_4X^4/K_5K_7^2 \quad (9)$$

$$k_{-1} = kK_4K_5/K_2K_3X^2 \quad (10)$$

which show that log $k_1$ should be proportional to 4 log $X$ and that $k_{-1}$ should be proportional to 2 log $1/X$. The value of $(HSO_4^-)/(H_2SO_4)$, which we designate by $X$, has been related to the Hammett acidity function, $H_0$, by the equation[3]

$$H_0 = -8.36 + \log (HSO_4^-)/(H_2SO_4)$$

Values of 4 log $X$ and 2 log $1/X$ as a function of % sulfuric acid were calculated from Brand's data and are shown in Fig. 2. The slopes of these lines are $-0.58$ and $+0.23$ while the slopes of the log $k_1$ *vs.* % sulfuric acid and log $k_{-1}$ *vs.* % sulfuric acid are $-0.59$ and $+0.24$.

The good agreement is further evidence for the proposed mechanism. The nitrosonium ion, $NO^+$, which is formed in the rate-determining step, is rapidly oxidized to $NO_2^+$ by a persulfate ion. Since potassium nitrite yields the nitrosonium ion in sulfuric acid, it is just as effective a catalyst as potassium nitrate or nitric acid.

The temperature dependence of $k_1$ and $k_{-1}$ is shown in Fig. 3, the former being determined in 95.8% sulfuric acid and the latter in 88.9% acid. From the slopes of these lines the activation energy of $k_1$ is 13.3 kcal. per mole, and of $k_{-1}$ 15.3. Since $K_3$ and $X$ have negative temperature coefficients and since these appear in the numerator in the equation for $k_1$ and in the denominator for $k_{-1}$, the temperature dependence and hence the activation energy of $k_1$ would be expected to be lower than that of $k_{-1}$.

The rate-determining step shown above is probably a sequence of steps which may be formulated as

$$NO_2^+ + SO_5NO_2^- \longrightarrow O_2N\text{-}O\text{-}O\text{-}SO_2\text{-}ONO_2$$

$$O_2N\text{-}O\text{-}O\text{-}SO_2\text{-}ONO_2 \longrightarrow NO_3^+ + SO_4^{--} + NO_2^+$$

$$NO_3^+ \longrightarrow NO^+ + O_2$$

ABERDEEN PROVING GROUND, MD.

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[3] J. C. D. Brand, *J. Chem. Soc.*, 1002 (1950).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CLARKSON COLLEGE OF TECHNOLOGY]

# The Ionization of Sulfuric Acid[1]

BY MILTON KERKER

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The method of Sherrill and Noyes, based on conductance and transference number, has been used to calculate the ionization of sulfuric acid at 18 and 50° from data in the literature and to extend the results at 25° to higher concentrations. The results have been compared with those obtained by other methods. The effect of the nature of the counterion on the equivalent conductance of sulfate and hydrogen ion has been examined. The equivalent conductance of bisulfate ion has been calculated at 18, 25 and 50°.

The ionization of sulfuric acid has been studied by electromotive force,[2] colorimetry,[3,4] kinetics,[5] Raman spectra[6-8] and a combination of conductance and transference number.[9] Sherrill and Noyes employed transference number as well as conductance data because of the unavailability of the equivalent conductance of the bisulfate ion. Assuming the first hydrogen is completely ionized, they developed the equations

$$\alpha = (\Lambda + \Lambda T - \Lambda_H)/(\Lambda_H + \Lambda_{SO_4}) \quad (1)$$

$$\Lambda_{HSO_4} = (\Lambda - \Lambda T - \alpha\Lambda_{SO_4})/(1 - \alpha) \quad (2)$$

where

$\alpha$ fraction of $HSO_4^-$ dissociated
$\Lambda$ equivalent conductance of $H_2SO_4$
$\Lambda_H$ equivalent conductance of $H^+$ in the $H_2SO_4$
$\Lambda_{SO_4}$ equivalent conductance of $SO_4^=$ in the $H_2SO_4$
$\Lambda_{HSO_4}$ equivalent conductance of $HSO_4^-$ in the $H_2SO_4$
$T$ stoichiometric transference number

In solving the above equation, Sherrill and Noyes used values of $\Lambda_H$ and $\Lambda_{SO_4}$ obtained from the conductance and transference number of hydrochloric acid and potassium sulfate at the ionic strength prevailing in the sulfuric acid solution under consideration. However, they did recognize that this "ionic strength principle" could not be justified theoretically. Since the ionic strength in the sulfuric acid is given by $m(1 + 2\alpha)$, eq. 1 had to be solved by a series of successive approximations.

The results of Sherrill and Noyes are confined to 25° because of the limited data for $T$ available at that time.[10] In this paper we extend their calculations to 18 and 50° using data which have since appeared in the literature. We have also carried the 25° calculations to higher concentrations.

The stoichiometric transference number, $T$, which appears in the above equations is related to the individual ionic transference number,[11] $t$, by

$$T = t_H - t_{HSO_4} \quad (3)$$

where

$$t_H = c_H\Lambda_H/c\Lambda \quad (4)$$

$$t_{HSO_4} = c_{HSO_4}\Lambda_{HSO_4}/c\Lambda \quad (5)$$

and $c_H$, $c_{HSO_4}$ and $c$ are the normalities of $H^+$, $HSO_4^-$ and $H_2SO_4$, respectively. In the Hittorf

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[1] This work has been supported by the Atomic Energy Commission, Contract No. AT (30-1)-1801.

[2] (a) W. J. Hamer, THIS JOURNAL, **56**, 860 (1934); (b) C. W. Davies, H. W. Jones and C. B. Monk, *Trans. Faraday Soc.*, **48**, 921 (1952).

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