molecules of trifluoroacetic acid. Thus, the $CF_3 \cdot COO^-$ ion in trifluoroacetic acid is not easily available for the termination step, while the same ion in hydrocarbon surroundings may easily recombine with its gegenion.

In conclusion, we would like to point out that trifluoroacetic molecules behave like different species in different surroundings (the same applies, of course, to many other systems). The molecules of trifluoroacetic acid in trifluoroacetic acid surrounding are probably highly associated and are strong proton donors, because the equilibrium

$$(CF_3 \cdot COOH)_{n-1} \rightleftarrows (CF_3 \cdot COOH)_n \cdot CF_3 \cdot COO^- + H^+$$

is shifted to the right by the stabilizing effect of trifluoroacetic acid on the CF_3COO^- ion. On the other hand, the same molecules in other surroundings are weaker proton donors, because the respective ion is poorly stabilized. For example, addition of trifluoroacetic to styrene produces simultaneously a polymer and a low molecular weight ester. A closer inspection demonstrated that the polymer results from the interaction of styrene with bulk trifluoroacetic acid (*i.e.*, with the mass introduced before it was dispersed completely), while the low molecular weight ester results from the interaction of the dispersed acid with styrene. For this reason, in the experiments described previously, trifluoroacetic acid was added to styrene in the form of its solution in ethylbenzene.

Experiments in which styrene was added to trifluoroacetic acid in form of small and large droplets showed that the size of the droplets did not affect the per cent. of conversion or the molecular weight of the product (see Table III). This means that the time of growth of a polymeric ion is much shorter than the time needed for dispersion of even small droplets.

TABLE III

ADDING STYRENE TO TRIFLUOROACETIC ACID AND VARYING THE SIZE OF DROPLETS ($T = 0°$).

No. of drops per cc.	% conversion	Molecular weight
95	89	16,700
30	87	16,000
14	88	16,000
stream	96	17,600

The inorganic chemist is well aware of the fact that a description of a system as, *e.g.*, "Ferric ion," is inadequate for its characterization, since the solvation shell changes profoundly its chemical property. For example, the exchange reaction between radioactive ferric and non-radioactive ferrous exhibits not only a different rate when different anions are present in the system, but sometimes proceeds by entirely different mechanism. We hope that this paper will demonstrate that the solvation shell is equally important in the realm of organic chemistry, and explain why A + B is not always equal to B + A.

SYRACUSE, NEW YORK

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY]

The Kinetics and Mechanism of the Decomposition of Caro's Acid. I

BY DONALD L. BALL AND JOHN O. EDWARDS

RECEIVED SEPTEMBER 26, 1955

The kinetics and mechanism of the aqueous decomposition of Caro's acid has been investigated. Both titration and kinetic data indicate that the second ionization constant is about 4×10^{-10}. Both spontaneous and catalytic paths for decomposition were observed; however, the latter path can be eliminated by addition of EDTA. The rate of spontaneous decomposition is second order in peroxide concentration and the *p*H dependence indicates the presence of one proton along with two divalent anions in the activated complex. The temperature dependences of the rates at high and low *p*H values allow the calculation of ionization and activation parameters.

Introduction

The chemistry of peroxymonosulfuric acid (Caro's acid) is less well-understood than the chemistries of the two related compounds, peroxydisulfuric acid and hydrogen peroxide. Caro's acid is highly reactive; in aqueous solution around neutrality it decomposes rapidly. It readily oxidizes many inorganic reagents and it attacks most organic compounds. Pure, stable[1] salts of Caro's acid have never been prepared.

Although the structure of Caro's acid has never been elucidated conclusively,[2] it is generally accepted that it consists of a central sulfur atom that is surrounded tetrahedrally by a perhydroxyl group, a hydroxyl group and two oxygen atoms. The acid is dibasic; one proton is highly acidic and the second is weakly acidic.

The present study concerns the kinetics and mechanism of the spontaneous decomposition of Caro's acid to give oxygen and sulfate ion. In addition, the second ionization constant of Caro's acid has been measured by means of both *p*H titration data and kinetic data.

Experimental

Preparation.—Caro's acid was customarily prepared by the reaction of 90% hydrogen peroxide and chlorosulfonic acid at a temperature between −40 and −50°.[3] The liquid product consists of an upper layer (about one-third of the total volume) and a lower layer. It was reported[3] that Caro's acid is a crystalline solid melting at 45°; however, large amounts of sulfate were present as an impurity in our preparations. Investigations[4] revealed that the upper layer contains chlorine, sulfuric acid, small amounts of Caro's acid, and some unreacted chlorosulfonic acid; this layer was discarded. The bottom layer contains Caro's acid, sulfuric acid and hydrogen chloride. The product was purified further by the vacuum removal of the by-product,

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[1] (a) T. S. Price, *J. Chem. Soc.*, **89**, 54 (1906); (b) **91**, 536 (1907); (c) "The Per-acids and Their Salts," Longmans, Green and Co., London, 1912, p. 53.

[2] A. Simon and G. Kratzsch, *Z. anorg. Chem.*, **242**, 369 (1939).

[3] J. D'Ans and W. Friederich, *Ber.*, **43**, 1880 (1910).

[4] A. Alexio, unpublished experiments at Brown University.

hydrogen chloride. The final product is a sirup-like liquid, which is roughly half Caro's acid and half sulfuric acid; it is about seven molar in peroxide. It slowly evolves oxygen at room temperature and must be stored at Dry Ice temperature. Even at this low temperature, none of our product crystallized. Caro's acid was also prepared in an impure form by the cautious distillation of sulfur trioxide from oleum onto 90% hydrogen peroxide.[5] The hydrolysis of peroxydisulfate ion[6] was not a convenient preparation since the product was only one molar in Caro's acid and seven molar in sulfate ion.

Materials.—Distilled water was used throughout. The 90% hydrogen peroxide used in the preparation of Caro's acid was donated by the BECCO Division of the Food Machinery and Chemical Corporation. No further concentration of this reagent was considered necessary. The chlorosulfonic acid (Eastman Kodak practical) was purified by distillation immediately before use. The buffer constituents were potassium dihydrogen phosphate (B. and A. reagent and Mallinckrodt analytical reagent), potassium carbonate (B. and A. reagent), sodium bicarbonate (B. and A. reagent), and sodium hydroxide (B. and A. reagent and reagent special and Mallinckrodt analytical reagent). No further purification was undertaken as a rule. The disodium salt of ethylenediaminetetraacetic acid was a Versenes, Inc., product. Solutions of sodium thiosulfate, potassium permanganate and ceric ammonium sulfate were prepared and standardized using customary procedures.

Analytical Methods.—The *p*H readings were obtained on a Beckman Model G *p*H meter. Other than at 0° the *p*H data were reproducible to ±0.02 *p*H unit. *p*H readings at 0° for the runs buffered by carbonate were approximated by extrapolation using values obtained at 10 and 20°. The concentration of Caro's acid was determined iodometrically in acid solution using standard thiosulfate. Hydrogen peroxide oxidizes iodide ion very slowly compared with the Caro's acid oxidation. No interference with the Caro's acid analysis was observed in the presence of relatively small amounts of hydrogen peroxide (less than 10% of the total peroxide). The oxidation of iodide ion by hydrogen peroxide is catalyzed by molybdate ion; in the presence of molybdate, the iodometric analysis determines the total concentration of hydrogen peroxide and Caro's acid. The concentration of hydrogen peroxide was determined by titration with either standard potassium permanganate solution or standard ceric ammonium sulfate solution. Only negligible amounts of peroxydisulfuric acid (less than 1% of the total peroxide) were ever present.

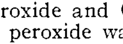
Procedure.—The kinetic runs were conducted in either phosphate (*p*H 6.04 through 8.37) or carbonate (*p*H 9.26 through 11.65) buffer. The initial concentration of Caro's acid was around 0.02 *M*. A high buffer concentration (total phosphate of 0.75 *M* and total carbonate of 0.30 *M*) was required to maintain a reasonably constant *p*H during the reaction since the product HSO_4^- of the decomposition is a much stronger acid than the reactant HSO_5^-.

The reaction vessels were 250-ml. volumetric flasks. These were cleaned between runs by rinsing with fuming nitric acid or aqua regia and subsequent steaming for several hours. Solutions were thermostated during the runs by means of a constant temperature water-bath controlled by a mercury regulator-thyratron circuit. A temperature precision of ±0.01° was maintained. At 0° an ice-bath in a large Dewar flask was employed to maintain constant temperature. Unless otherwise specified, the runs may be assumed to be at 25°.

Five-ml. aliquots were withdrawn from the reaction vessel at appropriate intervals and diluted with an excess of 0.1 *N* sulfuric acid to stop the reaction.

Experimental Results

Structure and Acidity.—As stated previously, it is generally agreed that Caro's acid has the form



$$HO\overset{O}{\underset{O}{S}}OOH$$

This structure is consistent with the observation that one proton is strongly ionized while the second is weakly ionized; roughly speaking, one is a sulfuric acid proton and the other is a hydrogen peroxide proton.

Since an estimate of the second ionization constant was necessary for the interpretation of the rate data, *p*H titrations of Caro's acid solutions were made. In some, the decomposition took place so rapidly that the data were uninterpretable; however, six titrations gave interpretable results. All six titrations (including that of a sample made from sulfur trioxide) gave a value of 9.4 ± 0.1 for pK_2 of Caro's acid. In view of the difficulties (poor end-point and decomposition), it should be noted that this value may be somewhat in error. The value is, however, quite reasonable for a hydrogen peroxide in which one of the protons has been replaced by a strongly electronegative group. Surprisingly enough, the value is significantly larger (lower ionization constant) than is found for organic peroxyacids such as peroxyacetic acid.[7]

After the completion of our *p*H titrations, it came to our attention that similar experiments were carried out at the laboratories of the BECCO Division of the Food Machinery and Chemical Corporation.[8] These experiments clearly demonstrated that HSO_5^- is a weak acid, but they were not sufficiently detailed to permit an estimate of pK_2.

The charge on the Caro's acid species which exists in the *p*H range from 6 to 8 can also be determined. If the peroxide exists as HSO_5^- (as would be expected) the ratio of protons to active oxygen atoms should be one; this ratio may be obtained from *p*H titration and iodometric titration data. Two samples of solution were analyzed and the average results are: weak acid, 0.0016 *M;* active oxygens, 0.0019 *M*. The results are consistent with the structure given since the ratio is nearly one. The discrepancy presumably can be traced to the following difficulties: (a) decomposition of Caro's acid in the course of the *p*H titration, (b) the presence of some other peroxide as an impurity, and (c) the difficulty in specifying the second end-point. Both of the first two sources of error would tend to make the observed ratio of weak protons to active oxygens less than one, as was observed.

Preliminary Kinetic Runs.—As the first kinetic experiments showed that the rate of decomposition of Caro's acid was not completely reproducible, a series of runs with three samples of phosphate were conducted in an attempt to find the source of the non-reproducibility. Two samples of reagent Baker and Adamson and one sample of analytical reagent Mallinckrodt potassium dihydrogen phosphate were used in preparing buffer solutions; henceforth these will be referred to as phosphates I, II and III. The sample of phosphate used in the buffer had a marked effect on the kinetics of the decomposition; both the magnitude of the rate constants and the rate dependence on *p*H were influenced. In no case, however, did the rate seem to be affected by the sample of distilled water, sodium hydroxide, or Caro's acid.

The decomposition appeared to be first order in the Caro's acid concentration. Plots of the logarithm of this concentration against time were linear with slopes that were independent of the initial concentration of Caro's acid. The dependences of the first-order rate constants, k'_H, on *p*H for the three phosphates are presented in Fig. 1.

With phosphate I, rate runs were conducted at *p*H values

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(5) H. Ahrle, *J. prakt. Chem.*, **79**, 129 (1909).

(6) T. S. Price and J. A. N. Friend, *J. Chem. Soc.*, **85**, 1526 (1904).

(7) A. J. Everett and G. J. Minkoff, *Trans. Faraday Soc.*, **49**, 410 (1953).

(8) E. S. Shanley, private communication, 1955.

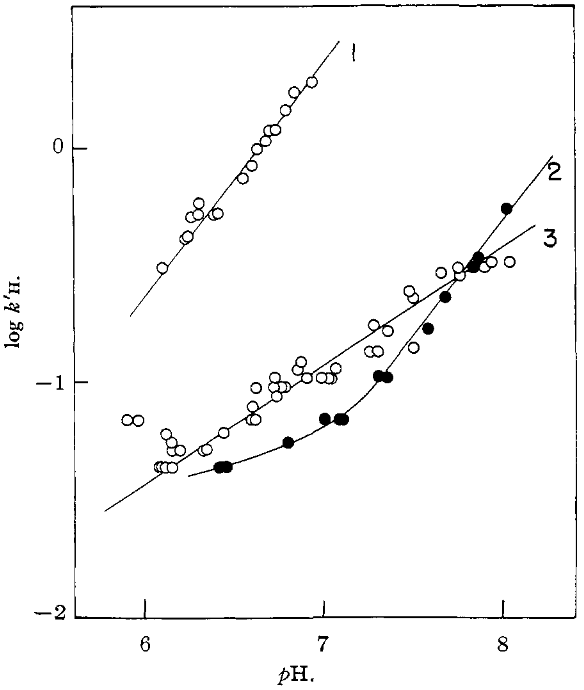


Fig. 1.—The pH dependence of the first-order rate constant, k'_H, min.$^{-1}$, obtained in unmodified phosphate buffer. Results for phosphates I, II and III are given by curves 1, 2 and 3, respectively.

between 6 and 7. As may be seen in Fig. 1, it was found that the decomposition was first order in the concentration of hydroxyl ion over this pH range.

The other B. and A. sample, phosphate II, was used for runs buffered in the pH interval between 6.4 and 8.1. Figure 1 shows that the decomposition is roughly first order in the hydroxyl ion concentration at the higher end of the pH interval; at the lower end the order in hydroxyl ion concentration tends toward a value less than one.

In the case of phosphate III, the decomposition appears to be about one-half order in the hydroxyl ion concentration throughout the entire range of pH (from 5.9 to 8.1) studied. The relatively large scatter in the data does not allow definite conclusions, however.

Several attempts to obtain reproducible rates by recrystallization of the phosphate were undertaken; little success was obtained. However, the rate of the decomposition is reduced and reproducible results are obtained when small amounts of the powerful sequestering agent, ethylenediaminetetraacetic acid (EDTA), are added to the buffer solutions.

It is necessary to conclude that the decomposition of Caro's acid is catalyzed by trace impurities present principally in the potassium dihydrogen phosphate. As the amount of phosphate used in all of the buffers was constant, the results obtained and presented in Fig. 1 are comparable. With any one buffer sample the rate was reasonably reproducible as well. From the pH dependences, it seems probable that more than one catalyst is present.

A survey has been made of the possible catalytic effect of various substances. Several effective catalysts have been found; molybdate ion and cobaltous ion are particularly active. Cobaltous ion at a concentration of 10^{-8} M noticeably increases the rate of the decomposition of Caro's acid. The effect of catalysts on the decomposition will be the subject of a later communication.

Spontaneous Decomposition.—The rate of the decomposition of Caro's acid is reduced in the presence of EDTA. Three to eight drops of a saturated solution of the disodium salt of EDTA were added to 100 ml. of buffer; reproducible results were obtained regardless of the sample of potassium dihydrogen phosphate used in the buffer. It appears that the trace amounts of catalyst originally present in the phosphate are rendered catalytically ineffective by complex formation with EDTA. EDTA was likewise added to runs at pH values above 9.2, where carbonate buffer was used. The resulting rates of decomposition represent, in all probability, the spontaneous uncatalyzed decomposition of Caro's acid. As the rate was found to be unaffected when a wad of glass wool was placed in the reaction vessel, the spontaneous decomposition is not a heterogeneous reaction.

The concentration of Caro's acid determined analytically represents the total amount present in all degrees of dissociation ($[H_2SO_5]_T = [HSO_5^-] + [SO_5^=]$). The decomposition is second order in the total concentration of Caro's acid; sample second-order rate plots are given in Fig. 2. In general the kinetic runs extended over one to two half-lives. The apparent rate constants, k_H, are given by the slopes of the plots.

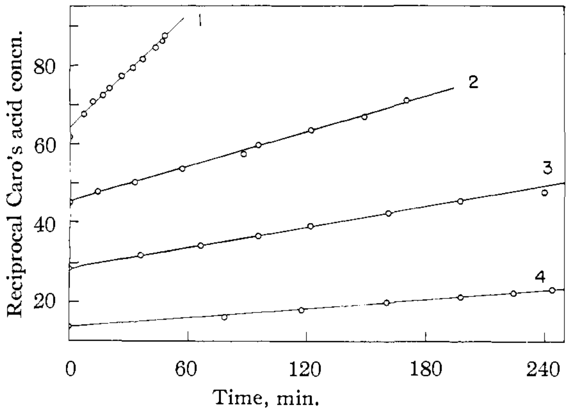


Fig. 2.—Second-order plots of the decomposition in the presence of ethylenediaminetetraacetic acid. Reactions buffered at pH values 7.84, 7.44, 7.19 and 6.78 are given by curves 1, 2, 3 and 4, respectively.

In Fig. 3, log k_H is plotted as a function of pH. The limiting slopes of the plot indicate that the dependence on the concentration of hydrogen ion is first order in the basic extreme and inverse first order in the acidic extreme. k_H may be written as $k_b \cdot [H^+]$ and $k_a/[H^+]$ in the respective extremes. Between the limits, the maximum value of k_H is found at pH 9.31. The significance of the maximum and the basis for the smooth curve that is drawn between the linear extremes in Fig. 3 will be discussed below.

In addition to the runs at 25°, more limited data were obtained at other temperatures; the average values for k_a and k_b are given in Tables I and II. In compiling the average at 25° for k_a, only runs at pH values between 6.4 and 8.0 were used. The buffering by phosphate was less effective beyond this range; also results from the region of pH where deviations from the limiting slopes are apparent must be excluded. For the latter reason, the average for k_b was compiled excluding runs buffered below a pH of 10.56. Runs at other temperatures were buffered at pH values selected to avoid the factors mentioned above.

TABLE I

T, °C.	k_a [(sec.)$^{-1}$]
0.0	$(1.3 \pm 0.1) \times 10^{-11}$
20.1	$(1.22 \pm .05) \times 10^{-10}$
25.0	$(1.90 \pm .10) \times 10^{-10}$
33.2	$(4.67 \pm .08) \times 10^{-10}$

TABLE II

T, °C.	k_b [(moles/l.)$^{-2}$ (sec.)$^{-1}$]
0.0	$(2.3 \pm 0.2) \times 10^8$
25.0	$(8.0 \pm .3) \times 10^8$
33.0	$(1.12 \pm .07) \times 10^9$
40.0	$(1.58 \pm .13) \times 10^9$

The apparent Arrhenius activation energies associated with k_a and k_b are 18 and 8 kcal./mole, respectively. The maximum error in these values is estimated to be ±0.5 kcal./mole.

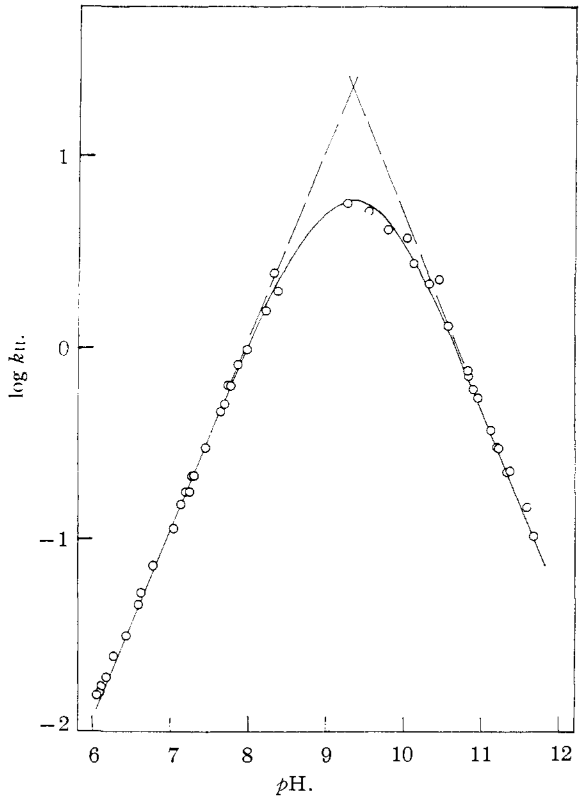


Fig. 3.—The pH dependence of the second-order rate constant, k_H (moles/liter)$^{-1}$ min.$^{-1}$, obtained in the presence of ethylenediaminetetraacetic acid.

It should be noted that the ionic strength of the solutions varied from 1.1 to 2.3 as the pH increased from 6 to 8. In the runs buffered by carbonate at pH values above 9.2, the ionic strengths of the solutions were all between 1.0 and 1.3. In dilute ionic solutions, the primary salt effect on the decomposition is undoubtedly sizable, but no evaluation of it is possible from the present data. At the high ionic strengths necessary for this study, the primary salt effect is less severe as a rule, but specific ion effects are prevalent. In order to see whether the changes in ionic strength seriously influenced the rate, the following check was made. To two solutions buffered at 6.54 and 6.61, enough potassium sulfate was added to increase the ionic strength by 2.4 and 1.2 units, respectively. The observed k_a values for these two runs were 2.30×10^{-10} and 2.46×10^{-10}, respectively. The difference from 1.90×10^{-10} is probably real; however, it is not a large enough rate difference to obscure variations in rate resulting from pH changes, etc.

Reaction with Hydrogen Peroxide.—Hydrogen peroxide was always present as an impurity in our samples of Caro's acid; it is also formed by the hydrolysis of Caro's acid when the latter is dissolved in the buffer solution. The hydrolysis is undoubtedly acid catalyzed and, although the reaction is slow at the pH values of the kinetic studies, localized regions of high acidity result in the formation of some hydrogen peroxide during the time of mixing.

It was observed during the runs in unaltered phosphate buffer that the decomposition was initially more rapid than the first-order behavior discussed above predicts. In addition there was a concomitant disappearance of the hydrogen peroxide originally present. However, the initially rapid rate was not observed in phosphate buffer when EDTA was present; so, a catalytic reaction between Caro's acid and hydrogen peroxide is indicated.

In carbonate buffer at pH values above 10, a rapid reaction between Caro's acid and hydrogen peroxide is indicated even when EDTA is present. Presumably the reaction is non-catalytic. Customarily the solutions of Caro's acid in carbonate buffer were allowed to stand at pH of about 11.6 until the hydrogen peroxide had all reacted. Subsequently, the pH was adjusted to the desired value by the addition of a solution of bicarbonate ion.

Discussion

The decomposition of Caro's acid in aqueous solution proceeds by at least two paths. As that part of the decomposition which results from trace metal catalysis will be the subject of a later communication, only the mechanism of the spontaneous decomposition will be discussed here.

In the pH range from 6 to 8 where Caro's acid exists principally as HSO_5^-, the rate law is

$$-\frac{d[HSO_5^-]}{dt} = k_a[HSO_5^-]^2/[H^+]$$

In the pH range from 10.5 to 11.7 where Caro's acid exists principally as $SO_5^=$, the rate law is

$$-\frac{d[SO_5^=]}{dt} = k_b[SO_5^=]^2[H^+]$$

Both rate laws imply a transition state whose constitution is $(HSO_5 \cdot SO_5 \cdot xH_2O)^{-3}$. The fact that the maximum rate (second order) falls at a pH value equal to the pK_2 value (about 9.4) of Caro's acid indicates that both rate laws can be attributed to the same mechanism. Remembering that the analytically determined concentration is the sum of the concentrations of the mononegative and dinegative forms, the total rate law for the entire range of pH studied is

$$-\frac{d[H_2SO_5]_T}{dt} = \frac{k[H^+][H_2SO_5]_T^2}{K_2(1 + [H^+]/K_2)^2}$$

where K_2 is the second ionization constant of Caro's acid. It follows that, in the low and high limits of pH, k_a and k_b equal kK_2 and k/K_2, respectively.

The postulated mechanism is

$$HSO_5^- + H_2O \rightleftarrows SO_5^= + H_3O^+ \qquad \text{I}$$

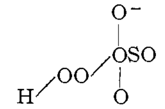
$$HSO_5^- + SO_5^= \longrightarrow \ddagger \longrightarrow HSO_6^- + SO_4^= \qquad \text{II}$$

$$HSO_6^- + OH^- \longrightarrow H_2O + SO_4^= + O_2 \qquad \text{III}$$

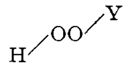
where step II is the rate-determining step and $\ddagger$ symbolizes the activated complex. On the acid side of the maximum, one HSO_5^- loses a proton; on the basic side, one $SO_5^=$ gains a proton. Since such protonic equilibria can be established rapidly, the first step (either direction) of the proposed mechanism seems to be reasonable.

Step II is believed to be the nucleophilic attack of $SO_5^=$ on the peroxide oxygen (one not attached to the sulfur) of HSO_5^-. As a result of the unsymmetrical nature of its peroxide link, the mononegative anion of Caro's acid is very reactive to strongly nucleophilic particles such as I^-, Br^-,[9] SCN^-,[9] and thiophenol.[9] Although there are no data available, the dinegative anion $SO_5^=$ is probably strongly nucleophilic; the hydroperoxide ion is known to be.[10] For these reasons, the nucleophilic attack of $SO_5^=$ on HSO_5^- seems appropriate for the rate-determining step.

The product of step II, HSO_6^-, is thought to have the structure



While such a compound might seem unlikely even as a kinetic intermediate, it is quite analogous to compounds of the type



where Y is Cl, Br, I or IO_2; such compounds appear to be intermediates in various reactions of hydrogen peroxide.[11] In all of the above cases, as in the Caro's acid decomposition, oxygen and HY are formed.

From the activation energy data, it is possible to calculate certain useful parameters; it is to be recalled, however, that the data refer to high ionic strengths and that these parameters are not the true thermodynamic values. Irrespective of mechanism, the heat of reaction for

$$HSO_5^- + H_2O \rightleftarrows SO_5^= + H_3O^+$$

is one-half of the difference between the two activation energies. From the definitions of k_a and k_b, the definition of the Arrhenius activation energy, and the van't Hoff isochore, it follows that

$$-\frac{\mathrm{d}\ln k_a}{\mathrm{d}(1/T)} = (E_a + \Delta H^0)/R$$

$$-\frac{\mathrm{d}\ln k_b}{\mathrm{d}(1/T)} = (E_a - \Delta H^0)/R$$

The calculated values for the heat of ionization and the entropy of ionization are 5,000 ± 500 cal./mole and −25.8 ± 1.7 e.u./mole. These values refer to a standard state of one mole/liter at 25°; they compare favorably with those found for similar ionizations.[12]

From the value of k at 25° and the standard enthalpy of activation ($E_a - RT$), one can calculate the entropy of activation. The values for k, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the rate-determining step of the mechanism are 0.392 [(moles/liter)$^{-1}$ (sec.)$^{-1}$], 13,000 ± 500 − RT cal./mole, and −20.1 ± 1.7 e.u./mole. The entropy value is reasonable for a reaction of two ions of such charges.[13]

It is somewhat surprising that the spontaneous decomposition of Caro's acid does not appear to proceed by a free radical mechanism. Both the order in Caro's acid and the lack of interaction with hydrogen peroxide in acid solution suggests that free radicals are not involved in the decomposition.

Acknowledgment.—This research was sponsored in part by the Office of Ordnance Research, U. S. Army. The authors are also grateful to the BECCO Division of Food Machinery and Chemical Corporation for their generous donations of concentrated hydrogen peroxide.

PROVIDENCE, R. I.

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(9) R. Carlson and J. Girard, unpublished experiments at Brown University.

(10) K. B. Wiberg, THIS JOURNAL, **75**, 3961 (1953); **77**, 2519 (1955).

(11) J. O. Edwards and A. J. Deyrup, unpublished data.

(12) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 123.

(13) Ref. 12, p. 132.