# PEROXYSULFURIC ACID AND PEROXYFORMIC ACID. EQUILIBRIUM AND FORMATION RATE

## By J. M. Monger and Otto Redlich

Shell Development Company, Emeryville, California

Received December 2, 1955

The rates of formation of monoperoxysulfuric acid from hydrogen peroxide and sulfuric acid as well as the corresponding equilibria have been determined. Similar measurements have been carried out on peroxyformic acid. If the sulfuric acid concentration is increased from 5 to 12 M, the initial rate of reaction with hydrogen peroxide increases by a factor 120,000. It is concluded that hydrogen peroxide reacts only with the undissociated sulfuric acid, not with its ions. Equilibrium concentrations, half-conversion times and initial formation rates are given for various conditions.

Hydrogen peroxide reactions are often highly susceptible to catalysis. Oxidation with a peroxyacid as an intermediate is a quite well known type of application of hydrogen peroxide.

Numerous organic acids have been successfully used as peroxide catalysts.<sup>1</sup> It seems to be strange that sulfuric acid, as a rule, is not a suitable catalyst, in view of the fact that monoperoxysulfuric acid (persulfuric acid) is known to be quite reactive and also under certain conditions readily formed from sulfuric acid and hydrogen peroxide. A study of the equilibrium and formation of peroxysulfuric acid appeared therefore to be desirable. A parallel investigation of peroxyformic acid (performic acid) illuminated the behavior of peroxysulfuric acid by contrast.

## **Experimental Details**

The reaction solutions were prepared by mixing aqueous solutions of acid and hydrogen peroxide of suitable concentrations so that the heat evolved was reduced to a minimum. The reaction was stopped by fifty-fold or higher dilution. Peroxyformic acid samples were at the same time quenched to ice temperature.

The samples were analyzed for hydrogen peroxide and peroxyacid according to one of the procedures suggested by Rius and Zulueta,<sup>2</sup> namely, titration of hydrogen peroxide by 0.1 N KMnO<sub>4</sub>, addition ot a drop of 10% KI solution, and titration of peracid with 0.05 N Na<sub>2</sub>SO<sub>3</sub> to the starchiodine end-point. In view of the small peroxyacid concentrations this procedure was more accurate than the titration of two separate samples, generally preferred by Rius and Zulueta.

In the analysis of peroxyformic acid mixtures the first titration was carried out at ice temperature. A second end point was determined after twice the titration time and the small difference was assumed to be equal to the loss of peroxyacid during the permanganate titration. The solution was then heated shortly to speed the hydrolysis of the peroxyacid, the liberated hydrogen peroxide was titrated with permanganate and any small remainder of peroxyacid was found by means of sulfite. **Peroxysulfuric Acid.**—The initial concentrations of the

**Peroxysulfuric Acid.**—The initial concentrations of the reactants and the final concentration of peroxysulfuric acid in moles/liter are given in Table I. For the kinetic calculations the small losses of total peroxide found were corrected for by a proportionate increase in the concentrations of hydrogen peroxide and peroxysulfuric acid. The concentrations  $c_1$  of  $H_2SO_4$  and  $c_4$  of  $H_2O$  were calculated from the analytical results for the concentrations.

One would expect that the quotient of the equilibrium concentrations (Table I)

$$K' = c_3 c_4 / c_1 c_2 \tag{1}$$

furnishes only a very crude estimate of the equilibrium constant K. This estimate can be slightly improved by introducing an approximate value for the ratio  $\gamma_4/\gamma_2$  of the ac-

(2) A. Rius and C. Zulueta, Anal. real. soc. espan. fis. y quim., 443, 923 (1948).

tivity coefficients of  $H_2O$  and  $H_2O_2$ . We assume that this ratio is independent of the presence of  $H_2SO_4$  and  $H_2SO_6$  and depends only on the ratio of the concentrations  $c_4/c_2$ . Then we can estimate  $\gamma_4/\gamma_2$  from the data for the binary system.<sup>3</sup> In the "adjusted equilibrium quotient" (Table I, Fig. 1)

$$L = K' \gamma_4 / \gamma_2 \tag{2}$$

the variation with  $c_2$ , clearly noticeable in K', is practically eliminated. The dependence of L on the total acid concentration indicates that  $H_2SO_6$  is an appreciably weaker acid than  $H_2SO_4$ . Extrapolation furnishes the estimates  $K = 0.1 (25^\circ)$  and  $K = 0.2 (75^\circ)$  for the equilibrium constant.

It is obvious to try a representation of the rate measurements by means of a bimolecular rate constant  $k_1$ . Eliminating the constant of the back reaction

$$k_2 = k_1 / K' \tag{3}$$

by means of smoothed values of K', we obtain indeed satisfactory agreement for each individual run. But the values of the rate "constant"  $k_1$  (Table I, Fig. 2) at 25° increase from 0.18  $\times$  10<sup>-6</sup> to 8700  $\times$  10<sup>-6</sup> l./mole minute when the acid concentration increases from 5.0 to 12.0 moles/l. The initial rate (at a constant hydrogen peroxide concentration of 1 mole/l.) increases therefore by a factor of 120,000 in the same range of acid concentration.

As far as we know, no similar concentration dependence of a reaction rate has been reported before. Yet the explanation is quite simple. The only quantity in sulfuric acid solutions which changes about as rapidly as the observed rate is the concentration of the undissociated acid.

In the concentration range of our measurements, unfortunately, there is not enough undissociated acid present to be detected by the determination of Raman intensities.<sup>4</sup> But the activity of the acid may be taken as a very crude measure of the concentration of the undissociated acid. The ratio of the activities of solutions containing 12 and 5 moles/1. can be estimated<sup>5</sup> to be about 240,000. For theoretical reasons and from results for nitric and perchloric acid<sup>6</sup> we should expect that the activity coefficient of the undissociated acid increases considerably with increasing concentration. For this reason, the concentration ratio of the undissociated acid should be considerably lower than 240,-000. The observed ratio 120,000 of the reaction rates, therefore, may be interpreted as the concentration ratio.

The very high value of the temperature coefficient of the reaction rate obviously reflects the increase of the concentration of the undissociated acid.

At constant acid concentration, the bimolecular apparent rate constant  $k_1$  is proportional to the initial hydrogen peroxide concentration. (Figure 2: The position of the broken line has been estimated from the total of the observed points.) We have not tried to represent the observations by a trimolecular rate law, though this probably would be possible.

Several ions (nickel, cadmium, fluoride, mercuric, tungstate) double the rate, if present at concentrations of 0.003 to 0.01 moles/l. without causing noticeable decomposition of hydrogen peroxide (measurements with 5 M H<sub>2</sub>SO<sub>4</sub>,

(3) G. Scatchard, G. M. Kavanagh and L. B. Ticknor, J. Am. Chem. Soc., 74, 3715 (1952).

(4) L. F. Maranville, Thesis, University of Chicago, 1949. Personal communication by Professor T. F. Young.

(5) Landolt-Börnstein, Tables, 3rd Suppl., p. 2145 (1936).

(6) G. C. Hood, O. Redlich and C. A. Reilly, J. Chem. Phys., 22, 2067 (1954).

<sup>(1)</sup> Cf. D. Swern, Chem. Revs., 45, 1 (1949).

|                                |                                                                                    |              |          | TABLE             | I        |       |      |                   |
|--------------------------------|------------------------------------------------------------------------------------|--------------|----------|-------------------|----------|-------|------|-------------------|
|                                |                                                                                    |              | F        | EROXYSULFU        | RIC ACID |       |      |                   |
|                                | Initial concn., Final concn. H <sub>2</sub> SO <sub>5</sub> ,<br>moles/l. moles/l. |              |          |                   |          |       |      |                   |
| H <sub>1</sub> SO <sub>4</sub> | H2Ó2                                                                               | H₂O          | Analysis | Cor. <sup>a</sup> | Y4/ Y20  | K'    | L    | $10^{6}k_{1}^{c}$ |
|                                |                                                                                    |              |          | At 25             | 0        |       |      |                   |
| 5.00                           | 1.012                                                                              | 40.0         |          | $0.01^{d}$        | 2.80     | 0.09  | 0.27 | 0.18              |
| 5.00                           | 5.03                                                                               | 34.8         |          | . 09 <sup>d</sup> | 2.37     | .13   | . 31 |                   |
| 5.00                           | 5.03                                                                               | 34.8         |          | $.08^{d}$         | 2.37     | . 12  | .28  | 0.34              |
| 5.00                           | 9.90                                                                               | 28.2         |          | . 30 <sup>d</sup> | 1.88     | . 19  | .36  | 1.8               |
| 8.00                           | 1.98                                                                               | 27.8         | 0.138    | . 138             | 2.63     | . 27  | .71  | 21                |
| 9.28                           | 0.705                                                                              | 28.1         |          |                   | 2.80     |       |      | 94                |
| 9.65                           | 0.986                                                                              | 30.0         | 0.140    | 0.146             | 2.79     | 0.554 | 1.54 | 97                |
| 10.1 <b>2</b>                  | 5.16                                                                               | 20.8         | 1.59     | 1.67              | 2.33     | 1.20  | 2.80 | 1220              |
| 12.0                           | 1.00                                                                               | 19.8         | 0,518    | 0.566             | 2.82     | 2.32  | 6.54 | 8700              |
| 15.0                           | 1.00                                                                               | 11. <b>2</b> | av."     | .72               | 2.83     | 3.4   | 9.6  |                   |
| 15.0                           | 1.00                                                                               | 11.2         | av."     | .71               | 2.83     | 3.3   | 9.4  |                   |
|                                |                                                                                    |              |          | At 75             | 0        |       |      |                   |
| 4.85                           | 0.911                                                                              | 39.0         | 0.016    | 0.019             | 2.81     | 0.17  | 0.49 | 97                |
| 4.85                           | 4.82                                                                               | 33.7         | . 131    | . 133             | 2.38     | . 20  | . 48 | 430               |
| 4.85                           | 9.59                                                                               | 27.4         | . 391    | . 395             | 1.89     | .27   | . 51 | 1400              |
| 9.75                           | 4.52                                                                               | <b>20</b> .0 | 1.23     | 1.24              | 2.33     | .93   | 2.71 |                   |
|                                |                                                                                    |              |          |                   |          |       |      |                   |

<sup>a</sup> Corrected for decomposition by assuming loss of  $H_2O_2$  and  $H_2SO_5$  proportional to their concentrations. <sup>b</sup> Calculated solely on basis of  $H_2O_2$  and  $H_2O$  by assuming acid to have no effect. <sup>c</sup> Based on correlated values of K' and corrected  $H_2SO_5$  values. <sup>d</sup> Values obtained after several days or weeks, extrapolated to infinite time. <sup>e</sup> The values of  $H_2SO_4$ , K', etc., are the averages of several samples. Small uncertainties exist due to diperoxysulfuric acid formation.



Fig. 1.—Adjusted equilibrium quotient of peroxysulfuric acid.

1 M H<sub>2</sub>O<sub>2</sub> at 75°). At higher concentrations these ions catalyze the decomposition to a considerable extent.



Fig. 2.—Rate of formation of peroxysulfuric acid.

Increase of the sulfate concentration of 5 M H<sub>2</sub>SO<sub>4</sub> by saturation with ammonium, zinc and magnesium sulfates increases the formation rate of peroxysulfuric acid, as expected, but also causes fairly rapid decomposition.

**Peroxyformic Acid.**—The observations on the formation of peroxyformic acid are given in Table II in a similar manner as before. The concentration quotient K' (Fig. 3) and the specific reaction rate  $k_1$  (Fig. 4) vary moderately with the concentrations of the reactants and the temperature. The agreement of the present results with previous work' is reasonably good in view of the different conditions.

### TABLE II

#### PEROXYFORMIC ACID

| Initial | eonen me                      | les/l.           | Final<br>HCOOOF   | concn.<br>L. moles/l.            |      |       |
|---------|-------------------------------|------------------|-------------------|----------------------------------|------|-------|
| HCOOH   | H <sub>2</sub> O <sub>2</sub> | H <sub>2</sub> O | Analysis          | Cor.4                            | K'   | 103kı |
|         |                               | At 25°           | ' without         | $H_2SO_4$                        |      |       |
| 1.16    | 0.30                          | 52.1             | 0.0036            | 0.0036                           | 0.56 |       |
| 5.03    | 1.00                          | 43.7             | . 060             | .061                             | . 57 | 0.23  |
| 10.0    | 1.00                          | 33.3             | .188              | .188                             | . 79 | 0.48  |
|         |                               | At 25° v         | with $0.1 A$      | $I H_2 SO_4$                     |      |       |
| 1.00    | 1.02                          | 51.8             | $0.010^{b}$       | 0.010                            | 0.52 | 0.24  |
| 1.00    | 5.02                          | 46.4             | . 69              | .70                              | .71  | . 66  |
| 5.00    | 1.00                          | 43.5             | $.068^{b}$        | .068                             | . 65 | .46   |
| 5.00    | 4.92                          | 38.3             | 3.52              | 3.86                             | .71  | . 80  |
| 10.0    | 1.02                          | 33.0             | 0.201             | 0.207                            | .87  | .77   |
| 19.5    | 5.12                          | 6.6              | 3.65              | 3.80                             | 1.9  | 7.6   |
|         |                               | At 25° v         | with 0.5 <i>I</i> | M H <sub>2</sub> SO <sub>4</sub> |      |       |
| 4.86    | 0.986                         | 42.2             | 0.080             | 0.080                            | 0.78 | 1.75  |
| 10.0    | 1.00                          | 31.8             | . 232             | .235                             | 1.00 | 2.8   |
|         |                               | At 75'           | ° without         | $H_2SO_4$                        |      |       |
| 5,00    | 1.00                          | 43.8             | $0.050^{b}$       | 0.050                            | 0.47 | 5.4   |
|         |                               | At 75°           | with 0.1 /        | $M H_2 SO_4$                     |      |       |
|         |                               |                  | 0 00 th           | 0.004                            | 0 00 | 10.0  |

5.00 1.00 43.8  $0.064^{b}$  0.064 0.60 12.3 <sup>a</sup> Corrected for decomposition by assuming losses of H<sub>2</sub>O<sub>2</sub> and HCOOOH are proportional to their concentrations. <sup>b</sup> Extrapolated.

(7) (a) J. d'Ans and W. Frey, Z. anorg. Chem., 84, 160 (1913);
(b) W. H. Hatcher and G. W. Holden, Trans. Roy. Soc. Canada, 21, 237 (1927).



The equilibrium constant, K = 0.5 at 25°, decreases slightly with increasing temperature (cf. Fig. 3).

The apparent bimolecular rate constant  $k_1$  varies less with the hydrogen peroxide concentration than the rate constant for peroxysulfuric acid. The catalytic effect of sulfuric acid (Fig. 5) and of a few other acids and salts has been previously reported by d'Ans and Frey.<sup>7a</sup> No new catalyst has been found.



Fig. 5.—Effect of sulfuric acid on the rate of formation of peroxyformic acid.

#### Discussion

The formation of peroxyformic acid shows no surprising features. This result supports the conclusion that the seemingly anomalous behavior of sulfuric acid is due to its dissociation.

A reaction mechanism should explain the fact that the ions of sulfuric acid do not react with hydrogen peroxide. It should explain the higher than first order in hydrogen peroxide. Finally it should explain the influence of catalysts, especially the differences in the catalytic effect on the formation of the two peroxyacids. On the basis of the present results, we are not able to propose a satisfactory mechanism.

The usefulness of a peroxyacid as an intermediate under given conditions may be characterized by its equilibrium concentration and by the time required for reaching one half of this concentration or by the initial formation rate. Results calculated for a few sets of conditions are given in Table III. It is seen that the characteristic quantities for performic acid do not depend very much on the concentrations of the reactants. For a reasonably rapid formation of peroxysulfuric acid, high acid concentration is indispensable.

|                     |                             | CALCULATED EQUILIBRIUM CONCENTRATIONS AND HALF-CONVERSION TIMES |                                  |                                                                 |                                            |                                   |                                                     |                                            |
|---------------------|-----------------------------|-----------------------------------------------------------------|----------------------------------|-----------------------------------------------------------------|--------------------------------------------|-----------------------------------|-----------------------------------------------------|--------------------------------------------|
| Temp.,<br>°C.       | Initial<br>acid,<br>mole/l. | Initial<br>H2O2,<br>mole/l.                                     | Equilibrium<br>H2SOs,<br>mole/l. | H <sub>2</sub> SO <sub>4</sub><br>Time<br>for 50%<br>conversion | Initial<br>formation rate,<br>mole/l. min. | Equilibrium<br>HCOOOH,<br>mole/l. | HCOOH <sup>a</sup><br>Time<br>for 50%<br>conversion | Initial<br>formation rate,<br>mole/l. min. |
| <b>25</b>           | 12                          | 1                                                               | 0.597                            | 3.2 min.                                                        | 0.10                                       |                                   |                                                     |                                            |
| <b>25</b>           | 10                          | 1                                                               | . 167                            | 1 <b>25</b> min.                                                | 0.001                                      | 0.207                             | 19 min.                                             | 0.0077                                     |
| <b>25</b>           | <b>5</b>                    | 1                                                               | .015                             | 8.0 days                                                        | $0.9 \times 10^{-6}$                       | . 068                             | 22 min.                                             | . 0023                                     |
| <b>25</b>           | <b>5</b>                    | 5                                                               | . 097                            | 3.3 days                                                        | $8.5 	imes 10^{-6}$                        | . 386                             | 14 min.                                             | .020                                       |
| <b>25</b>           | 5                           | 10                                                              | . 415                            | 1.4 days                                                        | $0.09 	imes 10^{-3}$                       |                                   |                                                     |                                            |
| <b>25</b>           | 1                           | 1                                                               |                                  |                                                                 |                                            | .010                              | 30 min.                                             | .00024                                     |
| <b>25</b>           | 1                           | 5                                                               |                                  |                                                                 |                                            | . 070                             | 15 min.                                             | .0033                                      |
| 75                  | 5                           | 1                                                               | . 019                            | 29 min.                                                         | $0.5 \times 10^{-3}$                       | .064                              | 45 sec.                                             | .062                                       |
| 75                  | 5                           | 5                                                               | . 135                            | 10.4 min.                                                       | 0.011                                      |                                   |                                                     |                                            |
| 75                  | <b>5</b>                    | 10                                                              | . 394                            | 3.9 min.                                                        | 0.072                                      |                                   |                                                     |                                            |
| <sup>a</sup> Contai | ning 0.1                    | $M H_2 SO_4$ as                                                 | catalyst.                        |                                                                 |                                            |                                   |                                                     |                                            |

TABLE III CALCULATED EQUILIBRIUM CONCENTRATIONS AND HALF-CONVERSION TIMES