

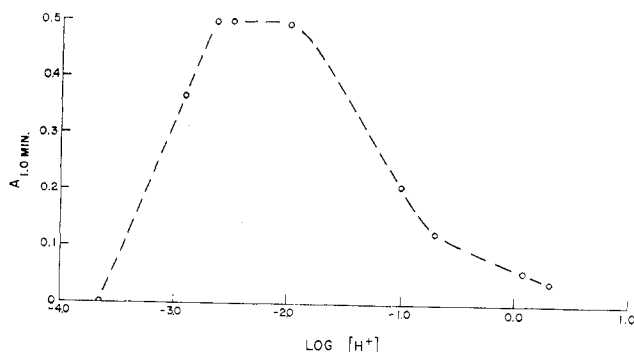


Figure 1.—Formation of chlorine dioxide as a function of the hydrogen ion concentration;  $[\text{ClO}_2^-]_0 = 7.2 \times 10^{-3} M$ ,  $[\text{Cl}^-]_0 = 0$ ; temperature  $25 \pm 0.5^\circ$ ; ionic strength  $2.0 M$ .  $A_{1.0 \text{ min}}$  is absorbance at  $3585 \text{ \AA}$  after 1 min.

$7.2 \times 10^{-3} M$  sodium chlorite solution, after the reaction has proceeded for 1 min ( $A_{1 \text{ min}}$ ), is plotted as a function of the log of the hydrogen ion concentration. The absorbance of the solution, which is proportional to the concentration of chlorine dioxide, increases markedly as the hydrogen ion concentration decreases and reaches a maximum at pH 2.0–2.7 and then decreases rapidly to zero as the hydrogen ion concentration is further decreased. Buser and Hanisch<sup>8</sup> and White, Taylor, and Vincent<sup>12</sup> noted a similar maximum

near pH 2 in the formation of chlorine dioxide from buffered solutions.

The initial rate of formation of chlorine dioxide appears to correspond to the relative amounts of chlorite ion and chlorous acid present;<sup>8</sup> *i.e.*, the maximum production of chlorine dioxide occurs approximately at the  $pK_a$  of chlorous acid<sup>23</sup> ( $pK_a = 2.31$ ). These observations suggest a third term in the rate law which involves the reaction of chlorite ion and chlorous acid to form an intermediate of the composition  $[\text{HClO}_2 \cdot \text{ClO}_2^-]$ . The observations here suggest that the intermediate produces chlorine dioxide more rapidly in the low acid region than does either the first or the second term of the rate law.

More detailed studies must be carried out in order to understand completely the mechanism of the disproportionation of chlorous acid at low hydrogen ion concentrations. Necessarily, only kinetic and stoichiometric studies in buffered solutions should be performed which make the studies somewhat more complicated since most common organic buffers are oxidized by chlorine(III) and chlorine(IV) solutions.<sup>21</sup>

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(23) F. Tachiki, *Nippon Kagaku Zasshi*, **65**, 346 (1944).

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## The Kinetics and Mechanism of the Oxidation of Water by Silver(II) in Concentrated Nitric Acid Solution

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The kinetics of the oxidation of water by silver(II) in  $2.00$ – $6.18 M$   $\text{HNO}_3$  has been studied between  $298.15$  and  $308.15^\circ\text{K}$  under a variety of conditions. Studies at  $[\text{Ag(II)}] > 1 \times 10^{-4} M$  show that the reaction is second order in  $[\text{Ag(II)}]$  and the observed rate law is

$$-d[\text{Ag(II)}]/dt = \frac{k_a[\text{Ag(II)}]^2}{k_b + k_d[\text{Ag(I)}][\text{H}^+]^2} = k_{II}[\text{Ag(II)}]^2$$

At  $6.13$ – $6.17 M$   $\text{HNO}_3$  and  $10^4[\text{AgO}]_0 = 8.33$ – $8.50 M$ ,  $k_{II} = 1.78 M^{-1} \text{sec}^{-1}$  at  $298.15^\circ\text{K}$ . The enthalpy of activation for  $k_{II}$  under these concentration conditions is  $23.0 \pm 0.4 \text{ kcal/mole}$ . The proposed mechanism (reactions 1–5) conforms to the observed rate law. The notation  $[\text{Ag(II)}]$  has been used in place of  $[\text{AgNO}_3^+]$  for simplicity. Studies at  $[\text{Ag(II)}] < 1 \times 10^{-4} M$  show that there is a first-order reaction with the rate law

$$-d[\text{Ag(II)}]/dt = \left\{ \frac{k_e + k_t[\text{Ag(I)}]}{(k_r + k_s[\text{Ag(I)}])(k_m + k_n[\text{H}^+]^2)} \right\} [\text{Ag(II)}] = k_I[\text{Ag(II)}]$$

At the same temperature and concentration conditions  $k_{II}$  was reported  $k_I = (2.38 \pm 0.10) \times 10^{-4} \text{ sec}^{-1}$ . The enthalpy of activation,  $\Delta H_I^\ddagger$ , for  $k_I$  is  $22.3 \pm 0.9 \text{ kcal/mole}$ . The mechanism proposed (reactions 8–15) involves a free-radical reaction.

### Introduction

Our interest in silver(II) chemistry came as a result of an investigation of the silver(I)-catalyzed oxidation of oxalate by peroxodisulfate,<sup>1</sup> where it was postulated that silver(I) undergoes a one-electron oxidation by peroxodisulfate to silver(II).

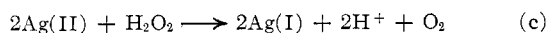
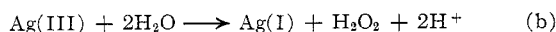
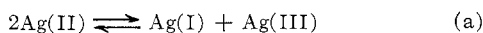
Since silver(II) is a  $d^9$ -electron system, it is paramagnetic. This has been confirmed by Noyes, Pitzer, and Dunn<sup>2</sup> by magnetic susceptibility measurements on silver(II)–nitric acid solutions. More recently, the electron paramagnetic resonance spectra of frozen acid

(1) A. J. Kalb and T. L. Allen, *J. Am. Chem. Soc.*, **86**, 5107 (1964).

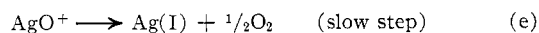
(2) A. A. Noyes, K. S. Pitzer, and C. L. Dunn, *ibid.*, **57**, 1229 (1935).

solutions of silver(II) and several solid silver(II) compounds were measured by McMillan and Smaller.<sup>3</sup>

The reduction of silver(II) by water in concentrated nitric acid solution was previously studied by Noyes and his coworkers.<sup>4,5</sup> They postulated the following mechanism to account for the observed second-order dependence in silver(II)



Kirwin, *et al.*,<sup>6</sup> investigated this reduction reaction in perchloric acid medium spectrophotometrically and proposed a mechanism involving step a followed by



Reactions in different acid media such as perchloric, phosphoric, and sulfuric acids were investigated by Rechnitz and Zamochnick.<sup>7-9</sup> They also postulated a rapid preequilibrium (step a) but stated that the subsequent step involved the reaction of silver(III) with solvent giving silver(I) and oxygen as the final products.

We have investigated the kinetics of silver(II) reduction by water in concentrated nitric acid solutions and the results are presented here.

### Experimental Section

**Materials.**—Silver(II) oxide from Ames Chemical Works, Inc. (Glens Falls, N. Y.), Lot No. 4965, was used to prepare the silver(II)–nitric acid solution. Baker and Adamson reagent grade sodium nitrate, 70% perchloric acid, 70% nitric acid, silver nitrate crystals, and Fisher Certified reagent grade cerium(IV) ammonium nitrate were used without further purification. Gases were Matheson Hi-Pure nitrogen and Liquid Carbonic Industrial oxygen. Distilled water was purified further by passing through an ion-exchange apparatus, Model 306-4, purchased from Caw Engineering Co., Palo Alto, Calif. The standard stock solutions were prepared with deionized distilled water.

**Methods and Measurements.**—Since silver(II) solutions were slowly reduced by the solvent, it was necessary to prepare the solution immediately prior to a kinetic run by dissolving the required amount of silver(II) oxide in 250 ml of thermally pre-equilibrated nitric acid solution. The kinetic runs were conducted in a Pyrex glass reaction vessel placed in the water thermostat maintained at a constant temperature ( $\pm 0.02^\circ$ ). The reaction was followed by periodically pipetting the solution into a spectrophotometer cell for optical density measurement at 390 m $\mu$  with the Cary 14 recording spectrophotometer. The spectrophotometer cells used were Beckman 1-, 5-, and 10-cm silica cells. The Cary 14 cell compartment was maintained at the reaction temperature by circulating water from a thermostat.

Preliminary results showed that nitrogen and oxygen do not affect the rate of reaction. Photochemical effects can also be ignored. The reaction conducted in a reaction vessel painted black did not show any significant difference from experiments in the presence of light. Kirwin<sup>6</sup> reported that light from a spectrophotometer has no effect on the reaction.

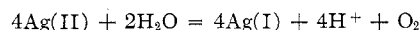
From emf and solubility measurements, Noyes and his coworkers<sup>10</sup> have established that silver(II) exists mainly in complex form with nitrate, and the average number of nitrates per silver(II) in the complex is 1.2 (from solubility data) or 1.6 (from emf data). The absorption spectrum of a silver(II)–6.17 M  $\text{HNO}_3$  solution has a single absorption peak at 390 m $\mu$ , which is due mainly to the silver(II)–nitrate complex species since silver(I) and nitric acid do not absorb at this wavelength.

The extinction coefficient of a silver(II)–6.17 M  $\text{HNO}_3$  solution can be calculated if the concentration of silver(II)–nitrate in solution is determinable. This may be done by measuring the oxidizing power of this species with a justifiable assumption that the  $[\text{Ag(III)}]$  in solution is extremely small as compared to the divalent silver. This will be justified later to be correct. The optical density of a cold silver(II)–6.17 M  $\text{HNO}_3$  solution was measured and the concentration of the divalent silver was determined by reaction with standard cerium(III) solution. Potentiometric titration of the resulting cerium(IV) with standard ferrous sulfate solution led to the silver(II) concentration. Triplicate measurements gave an extinction coefficient of  $2860 \pm 50 \text{ M}^{-1} \text{ cm}^{-1}$  for the silver(II)–6.17 M  $\text{HNO}_3$  solution.

Gryder and Dundon<sup>11</sup> have obtained a value of  $2530 \pm 50 \text{ M}^{-1} \text{ cm}^{-1}$  at 394 m $\mu$  for silver(II) in 6.18 and 4.66 M  $\text{HNO}_3$ . However, in 8.82 M  $\text{HNO}_3$ , a higher value of  $3400 \text{ M}^{-1} \text{ cm}^{-1}$  was obtained. They also found that the Beer–Lambert law was obeyed and the extinction coefficients at high and low silver(I) concentrations were the same in all cases.

### Results

**A. Second-Order Reaction.**—The over-all reaction of silver(II) by water was given by Noyes, Coryell, Stitt, and Kossiakoff<sup>5</sup> as



Unless otherwise specified, the notation  $\text{Ag(II)}$  is used to designate the silver(II)–nitrate species for simplicity.

At silver(II) concentrations higher than  $1 \times 10^{-4} \text{ M}$  the kinetics observed in this work were second order in silver(II), and graphs of reciprocal optical density *vs.* time were linear. Accordingly, the observed rate law is

$$-d[\text{Ag(II)}]/dt = k_{\text{II}}[\text{Ag(II)}]^2 \quad (\text{A-1})$$

However, at  $[\text{Ag(II)}] < 1 \times 10^{-4} \text{ M}$ , a deviation from second-order kinetics occurred. Mathematical treatment showed that there was an independent reaction path at low  $[\text{Ag(II)}]$  which was first order in  $[\text{Ag(II)}]$ . This will be reported in detail in section B. Studies at  $[\text{Ag(II)}]$  higher than  $1 \times 10^{-4} \text{ M}$  are described below.

**Silver(I) Dependence.**—The effect of silver(I) on the rate was studied using appropriate amounts of silver(I) nitrate to vary the  $[\text{Ag(I)}]$  over a 12-fold range (Table I). The linearity of the  $k_{\text{II}}^{-1}$  *vs.*  $[\text{Ag}^+]_0$  plot (Figure 1) depicts the inverse first-order dependence of rate on  $[\text{Ag}^+]$ . Accordingly, the observed rate law may be represented as

$$-d[\text{Ag(II)}]/dt = \frac{k_a[\text{Ag(II)}]^2}{k_b + k_c[\text{Ag(I)}]} \quad (\text{A-2})$$

where  $k_a$ ,  $k_b$ , and  $k_c$  are constants.

**Hydrogen Ion Dependence.**—The variation of  $[\text{H}^+]$  was carried out using the appropriate amount of  $\text{LiNO}_3$  or  $\text{NaNO}_3$  in place of  $\text{HNO}_3$  to maintain the ionic

(3) J. A. McMillan and B. Smaller, *J. Chem. Phys.*, **35**, 1698 (1961).

(4) A. A. Noyes, J. L. Hoard, and K. S. Pitzer, *J. Am. Chem. Soc.*, **57**, 1221 (1935).

(5) A. A. Noyes, C. D. Coryell, F. Stitt, and A. Kossiakoff, *ibid.*, **59**, 1316 (1937).

(6) J. B. Kirwin, F. D. Peat, P. J. Proll, and L. H. Sutcliffe, *J. Phys. Chem.*, **67**, 1617 (1963).

(7) G. A. Rechnitz and S. B. Zamochnick, *Talanta*, **11**, 713 (1964).

(8) G. A. Rechnitz and S. B. Zamochnick, *ibid.*, **12**, 479 (1965).

(9) G. A. Rechnitz and S. B. Zamochnick, *ibid.*, **11**, 1645 (1964).

(10) A. A. Noyes, D. DeVault, C. D. Coryell, and T. J. Deahl, *J. Am. Chem. Soc.*, **59**, 1326 (1937).

(11) R. W. Dundon and J. W. Gryder, *Inorg. Chem.*, **5**, 986 (1966).

TABLE I  
EFFECT OF SILVER(I) ON THE SECOND-ORDER REACTION<sup>a</sup>

| $10^3[\text{Ag(I)}]_0, M$ | $10^4[\text{Ag(II)}]_0, M$ | $k_{II}, M^{-1} \text{ sec}^{-1}{}^b$ |
|---------------------------|----------------------------|---------------------------------------|
| 0.85                      | 4.52                       | 3.92 <sup>c</sup>                     |
| 1.31                      | 4.70                       | 2.72 <sup>c</sup>                     |
| 2.80                      | 5.65                       | 1.28                                  |
| 5.34                      | 5.00                       | 0.70                                  |
| 7.84                      | 4.70                       | 0.51                                  |
| 10.3                      | 5.39                       | 0.40                                  |

<sup>a</sup> At 35.0° and 6.18 *M* HNO<sub>3</sub>. <sup>b</sup> As defined in eq A-1. <sup>c</sup> Average of two runs.

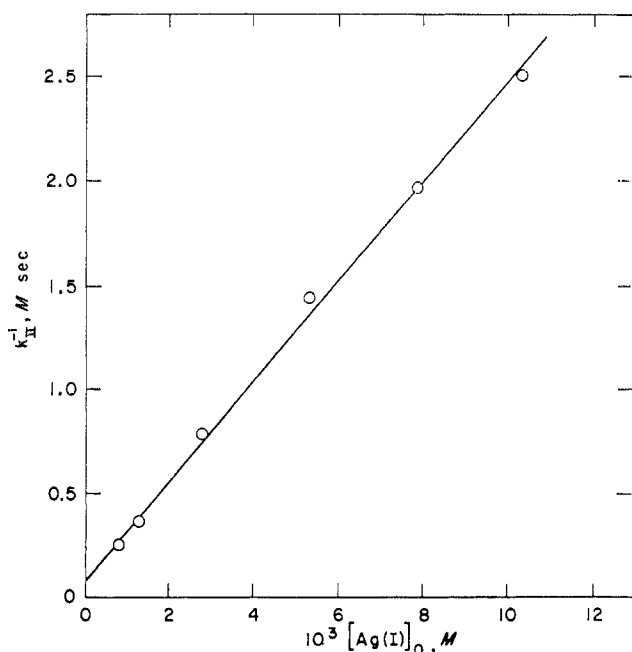


Figure 1.—Plot of reciprocal  $k_{II}$  against  $[\text{Ag(I)}]_0$  at 35° and 6.18 *M* HNO<sub>3</sub>.

strength and the nitrate concentration constant. The rate increases markedly as the  $[\text{H}^+]$  decreases (Table II). The linearity of the  $k_{II}^{-1}$  vs.  $[\text{Ag(I)}]_{\text{av}}[\text{H}^+]^2$  plot (Figure 2) leads to the observed rate law

$$\frac{-d[\text{Ag(II)}]}{dt} = \frac{k_a[\text{Ag(II)}]^2}{k_b + k_d[\text{Ag(I)}][\text{H}^+]^2} = k_{II}[\text{Ag(II)}]^2 \quad (\text{A-3})$$

TABLE II

HYDROGEN ION EFFECT ON THE SECOND-ORDER REACTION<sup>a</sup>

| $10^4[\text{Ag(I)}]_0, M$ | $10^4[\text{Ag(II)}]_0, M$ | $[\text{HNO}_3], M$ | $[\text{NaNO}_3], M$ | $k_{II}, M^{-1} \text{ sec}^{-1}{}^b$ |
|---------------------------|----------------------------|---------------------|----------------------|---------------------------------------|
| 3.68                      | 4.67                       | 6.13                | ...                  | 1.75                                  |
| 3.64                      | 4.67                       | 6.13                | ...                  | 1.81                                  |
| 5.88                      | 2.18                       | 4.10                | 2.08                 | 3.03 <sup>c</sup>                     |
| 4.92                      | 3.33                       | 4.10                | 2.08                 | 3.29                                  |
| 5.51                      | 2.69                       | 3.50                | 2.68                 | 4.66                                  |
| 8.18                      | 1.63                       | 3.18                | 3.00                 | 5.00 <sup>c</sup>                     |
| 5.40                      | 2.69                       | 3.18                | 3.00                 | 5.18                                  |
| 6.69                      | 1.45                       | 2.00                | 4.18                 | 10.2                                  |

<sup>a</sup> At 25.0°,  $\mu = 6.18 M$ , and  $[\text{NO}_3^-] = 6.18 M$ . <sup>b</sup> As defined in eq A-1. <sup>c</sup> LiNO<sub>3</sub> used instead of NaNO<sub>3</sub>.

Since silver(I) is a product of the reaction, it increases during an experiment. Therefore, the average value of  $[\text{Ag(I)}]$  for each experiment was estimated by averaging the initial and final silver(I) concentration. A plot of  $1/k_{II}$  vs.  $[\text{HNO}_3]^2$  yields a reasonable straight line for

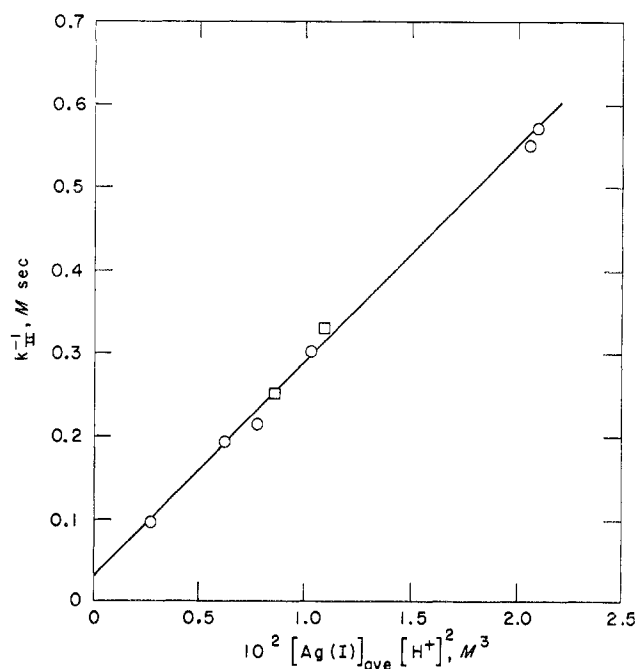


Figure 2.—Plot of reciprocal  $k_{II}$  vs.  $[\text{Ag(I)}]_{\text{av}}[\text{H}^+]^2$  at 25° and  $\mu = 6.18 M$ : open circles, sodium nitrate; squares, lithium nitrate.

points at lower values of  $[\text{HNO}_3]^2$ , but the determinations at  $[\text{HNO}_3] = 6.13 M$  are somewhat off the line. It is felt that a rate law involving a denominator which is  $[\text{HNO}_3]^2$  is not as consistent with the experimental data as one containing  $[\text{Ag(I)}]_{\text{av}}[\text{HNO}_3]^2$ .

**Nitrate Dependence.**—Kirwin and his coworkers<sup>6</sup> have shown that upon introduction of 0.3 *M* HNO<sub>3</sub> into a solution of 3 *M* HClO<sub>4</sub> containing silver(II) the intense silver(II)-nitrate peak at 390 *mμ* appears and the 475-*mμ* peak due to the silver (II)-perchlorate complex disappears. Appropriate amounts of HClO<sub>4</sub> were used in place of HNO<sub>3</sub> to maintain ionic strength and  $[\text{H}^+]$  constant to study the effect of nitrate on rate. The rate appears to decrease very slightly as nitrate increases (Table III), and within the limits of experimental error the rate of reaction is invariant to  $[\text{NO}_3^-]$  changes.

TABLE III

EFFECT OF NITRATE ON THE SECOND-ORDER REACTION<sup>a</sup>

| $[\text{HNO}_3], M$ | $[\text{HClO}_4], M$ | $k_{II}, M^{-1} \text{ sec}^{-1}{}^b$ |
|---------------------|----------------------|---------------------------------------|
| 6.13                | ...                  | 1.75                                  |
| 6.13                | ...                  | 1.81                                  |
| 5.10                | 1.03                 | 1.72                                  |
| 4.60                | 1.54                 | 2.01                                  |
| 4.60                | 1.54                 | 2.20                                  |
| 4.08                | 2.05                 | 2.15                                  |

<sup>a</sup> At 25°,  $[\text{Ag(II)}]_0 = (3.50-4.67) \times 10^{-4} M$  and  $[\text{Ag(I)}]_0 \sim 4.6 \times 10^{-4} M$ . <sup>b</sup> As defined in eq A-1.

**B. First-Order Reaction.**—Studies at silver(II)-nitrate concentrations less than  $1 \times 10^{-4} M$  were conducted. The disappearance of  $\text{AgNO}_3^+$  obeys first-order kinetics. Accordingly, the observed rate law is

$$-d[\text{AgNO}_3^+]/dt = k_I[\text{AgNO}_3^+] \quad (\text{B-1})$$

Under similar experimental conditions the results are reproducible (Table IV) and the average  $k_I$  for these four experiments is  $(2.38 \pm 0.10) \times 10^{-4} \text{ sec}^{-1}$ .

TABLE IV  
FIRST-ORDER RATE CONSTANT<sup>a</sup>

| $10^4[\text{Ag(I)}]_0, M$ | $10^4[\text{AgNO}_3^+]_0, M$ | $10^4k_I, \text{ sec}^{-1}{}^b$ |
|---------------------------|------------------------------|---------------------------------|
| 1.37                      | 0.927                        | 2.39                            |
| 1.25                      | 1.07                         | 2.37                            |
| 1.32                      | 0.840                        | 2.11                            |
| 1.02                      | 0.682                        | 2.51                            |

<sup>a</sup> At 25°,  $[\text{HNO}_3] = 6.17 M$ , and  $10^4[\text{AgO}]_0 \sim 1.70\text{--}2.30 M$ .

<sup>b</sup> As defined in eq B-1.

**Silver(I) Dependence.**—The rate is somewhat depressed by  $[\text{Ag(I)}]$ . Varying the  $[\text{Ag(I)}]$  from  $2.2 \times 10^{-4}$  to  $0.05 M$  the effect of  $[\text{Ag(I)}]$  on the first-order reaction was studied at 35° (Table V). The relationship between  $k_I^{-1}$  and  $[\text{Ag(I)}]_0$  may be best represented in Figure 3. It is readily observed that at low  $[\text{Ag(I)}]$  the rate is inversely proportional to  $[\text{Ag(I)}]$  and at high  $[\text{Ag(I)}]$  a saturation point is reached evidenced from the flat portion of the curve in Figure 3. Accordingly, the observed rate law may be expressed by the functional form

$$R = \frac{-d[\text{AgNO}_3^+]}{dt} = \frac{k_o + k_f[\text{Ag(I)}]}{k_g + k_h[\text{Ag(I)}]} [\text{AgNO}_3^+] = k_I[\text{AgNO}_3^+] \quad (\text{B-2})$$

TABLE V

EFFECT OF SILVER(I) ON THE FIRST-ORDER REACTION<sup>a</sup>

| $10^4[\text{Ag(I)}]_0, M$ | $10^4[\text{AgNO}_3^+]_0, M$ | $10^4k_I, \text{ sec}^{-1}{}^b$ | $10^4[\text{Ag(I)}]_0, M$ | $10^4[\text{AgNO}_3^+]_0, M$ | $10^4k_I, \text{ sec}^{-1}{}^b$ |
|---------------------------|------------------------------|---------------------------------|---------------------------|------------------------------|---------------------------------|
| 2.20                      | 0.685                        | 8.27                            | 31.0                      | 0.736                        | 3.64                            |
| 6.07                      | 0.700                        | 6.13                            | 41.0                      | 0.804                        | 3.62                            |
| 11.2                      | 0.545                        | 4.56                            | 76.0                      | 0.577                        | 2.81                            |
| 13.7                      | 0.402                        | 5.00                            | 76.1                      | 0.622                        | 2.97                            |
| 16.0                      | 0.755                        | 3.92                            | 101                       | 0.700                        | 3.18                            |
| 21.1                      | 0.689                        | 3.16                            | 301                       | 0.742                        | 2.79                            |
| 26.2                      | 0.671                        | 2.99                            | 501                       | 0.830                        | 3.18                            |

<sup>a</sup> At 35.0°,  $[\text{HNO}_3] = 6.18 M$ , and  $10^4[\text{AgO}]_0 = 1.62\text{--}1.84 M$ .

<sup>b</sup> As defined in eq B-1.

The two limiting cases are obtained under different conditions. When  $[\text{Ag(I)}]$  is low,  $k_f[\text{Ag(I)}] < k_o$  must hold and (B-2) becomes

$$R = \frac{k_o}{k_g + k_h[\text{Ag(I)}]} [\text{AgNO}_3^+] \quad (\text{B-3})$$

At high  $[\text{Ag(I)}]$ ,  $k_f[\text{Ag(I)}] > k_o$  and  $k_h[\text{Ag(I)}] > k_g$  must hold so that (B-2) becomes

$$R = k_f[\text{AgNO}_3^+] / k_h \quad (\text{B-4})$$

**Hydrogen Ion Dependence.**—In  $[\text{Ag(I)}]$  approximately constant at  $\sim 7.5 \times 10^{-4} M$ , the effect of  $[\text{H}^+]$  on the rate was studied at 25° over a threefold range (Table VI). The inverse second-order dependence in  $[\text{H}^+]$  as shown in Figure 4, a  $k_I^{-1}$  vs.  $[\text{H}^+]^2$  plot, may be expressed by the observed rate law

$$R = \left\{ \frac{k_o + k_f[\text{Ag(I)}]}{(k_r + k_s[\text{Ag(I)}])(k_m + k_n[\text{H}^+]^2)} \right\} [\text{AgNO}_3^+] \quad (\text{B-5})$$

At constant  $[\text{Ag(I)}]$ , (B-5) reduces to

$$R = \frac{k_j}{k_m' + k_n'[\text{H}^+]^2} [\text{AgNO}_3^+] \quad (\text{B-6})$$

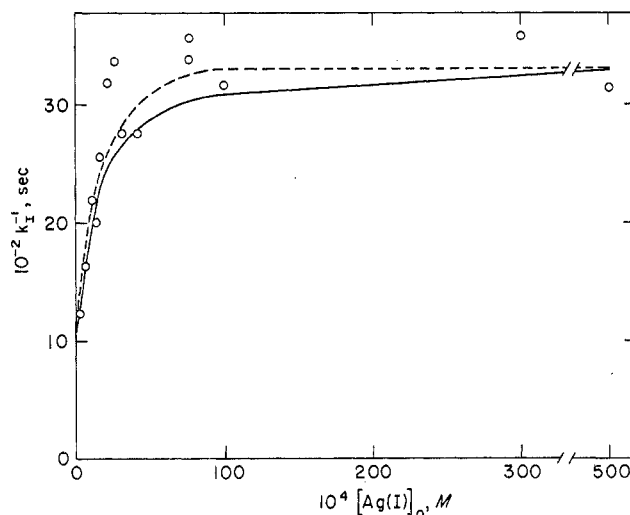


Figure 3.—Plot of reciprocal  $k_I$  vs.  $[\text{Ag(I)}]_0$  at 35° and  $6.18 M$  HNO<sub>3</sub>: dashed line, experimental curve; solid line, calculated using eq 19.

TABLE VI

EFFECT OF HYDROGEN ION ON THE FIRST-ORDER REACTION<sup>a</sup>

| $10^4[\text{Ag(I)}]_0, M$ | $10^4[\text{AgNO}_3^+]_0, M$ | $[\text{HNO}_3], M$ | $[\text{NaNO}_3], M$ | $10^4k_I, \text{ sec}^{-1}{}^b$ |
|---------------------------|------------------------------|---------------------|----------------------|---------------------------------|
| 7.37                      | 0.818                        | 6.13                | ...                  | 1.34                            |
| 7.34                      | 0.636                        | 4.10                | 2.08                 | 2.23                            |
| 7.42                      | 0.786                        | 3.50                | 2.68                 | 3.16                            |
| 7.30                      | 0.665                        | 3.18                | 3.00                 | 3.34                            |
| 7.61                      | 0.612                        | 2.50                | 3.68                 | 4.34                            |
| 7.30                      | 0.770                        | 2.00                | 4.18                 | 6.40                            |
| 7.50                      | 0.571                        | 9.25                | ...                  | 1.23 <sup>c</sup>               |

<sup>a</sup> At 25°,  $[\text{NO}_3^-]$  and  $\mu \sim 6.18 M$ , and  $[\text{AgO}]_0 \sim 8 \times 10^{-4} M$ .

<sup>b</sup> As defined in eq B-1. <sup>c</sup>  $[\text{NO}_3^-]$  and  $\mu = 9.25 M$ .

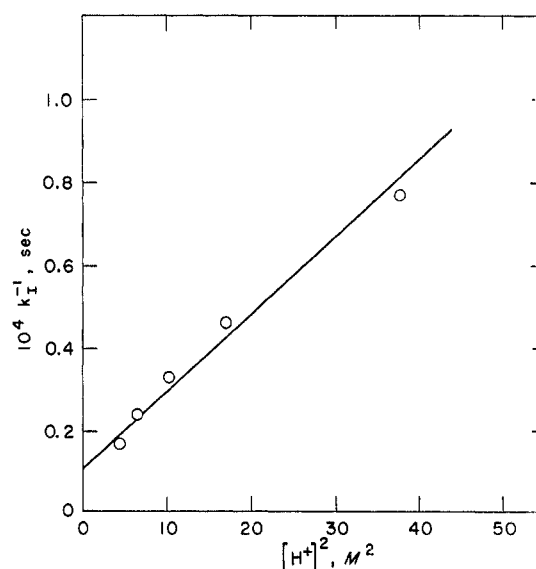


Figure 4.—Plot of reciprocal  $k_I$  vs.  $[\text{H}^+]^2$  at 25° and  $\mu = 6.18 M$ .

where  $k_j = k_o + k_f[\text{Ag(I)}]$ ,  $k_m' = k_m(k_r + k_s[\text{Ag(I)}])$ , and  $k_n' = k_n(k_r + k_s[\text{Ag(I)}])$ . At constant  $[\text{H}^+]$ , (B-5) becomes (B-2) with  $k_g = k_r(k_m + k_n[\text{H}^+]^2)$  and  $k_h = k_s(k_m + k_n[\text{H}^+]^2)$ .

**Nitrate Dependence.**—The effect of nitrate on rate was studied and within the limits of experimental error the rate is invariant to  $[\text{NO}_3^-]$  changes (Table VII).

TABLE VII

EFFECT OF NITRATE ON THE FIRST-ORDER REACTION<sup>a</sup>

| $10^4[\text{Ag(I)}]_0$ ,<br><i>M</i> | $10^4[\text{AgNO}_3]_0$ ,<br><i>M</i> | $[\text{HNO}_3]$ ,<br><i>M</i> | $[\text{HClO}_4]$ ,<br><i>M</i> | $10^4k_1$ ,<br>$\text{sec}^{-1}$ <sup>b</sup> |
|--------------------------------------|---------------------------------------|--------------------------------|---------------------------------|-----------------------------------------------|
| 7.32                                 | 0.700                                 | 4.08                           | 2.05                            | 1.41                                          |
| 7.56                                 | 0.580                                 | 4.60                           | 1.54                            | 1.38                                          |
| 7.67                                 | 0.685                                 | 4.60                           | 1.54                            | 1.50                                          |
| 7.48                                 | 0.665                                 | 5.10                           | 1.03                            | 1.39                                          |
| 7.30                                 | 0.818                                 | 6.13                           | ...                             | 1.34                                          |

<sup>a</sup> At 25° and  $[\text{H}^+] = 6.13$  *M*. <sup>b</sup> As defined in eq B-1.

**C. Temperature Dependence.**—Table VIII shows the effect of temperature on  $k_{\text{II}}$  and  $k_{\text{I}}$ . The activation energies  $\Delta H_{\text{II}}^\ddagger$  and  $\Delta H_{\text{I}}^\ddagger$  calculated from  $\log(k_{\text{II}}/T)$  and  $\log(k_{\text{I}}/T)$  vs.  $1/T$  plots are  $23.0 \pm 0.4$  and  $22.3 \pm 0.9$  kcal/mole, respectively.

TABLE VIII  
TEMPERATURE DEPENDENCE

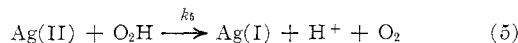
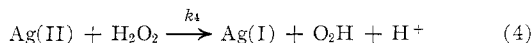
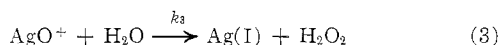
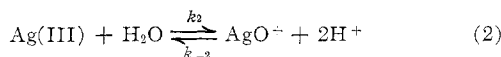
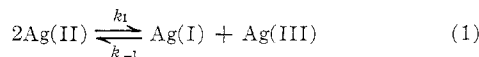
| Temp, °K | $k_{\text{II}}$ , $M^{-1} \text{sec}^{-1}$ <sup>a,c</sup> | $10^4k_{\text{I}}$ , $\text{sec}^{-1}$ <sup>b,c</sup> |
|----------|-----------------------------------------------------------|-------------------------------------------------------|
| 298.15   | 1.78                                                      | $2.38 \pm 0.10$                                       |
| 303.15   | 3.46                                                      | $4.01 \pm 0.15$                                       |
| 308.15   | 6.50                                                      | 8.27                                                  |

<sup>a</sup> At 6.13–6.17 *M*  $\text{HNO}_3$  and  $10^4[\text{AgO}]_0 = 8.33$ –8.50 *M*.<sup>b</sup> At 6.17 *M*  $\text{HNO}_3$  and  $10^4[\text{AgO}]_0 = 1.7$ –2.83 *M*. <sup>c</sup> As defined in eq A-1 ( $k_{\text{II}}$ ) and B-1 ( $k_{\text{I}}$ ).

## Discussion

### A. Mechanism of the Second-Order Reaction.—

A reasonable mechanism is postulated as



Applying the usual steady-state approximation to  $[\text{Ag(III)}]$ ,  $[\text{AgO}^+]$ ,  $[\text{H}_2\text{O}_2]$ , and  $[\text{O}_2\text{H}]$  with the assumption  $k_{-2}[\text{H}^+]^2 \gg k_3'$  and writing  $k_i'$  for  $k_i[\text{H}_2\text{O}]$ , the derived rate law is

$$\frac{-d[\text{Ag(II)}]}{dt} = \frac{4k_1k_2'k_3'[\text{Ag(II)}]^2}{k_2'k_3' + (k_{-2}k_{-1})[\text{Ag(I)}][\text{H}^+]^2} \quad (6)$$

The above rate law (6) has the same form as the experimental rate law (A-3). For simplicity,  $\text{Ag(II)}$  is used in the mechanism proposed instead of  $\text{AgNO}_3^+$ .

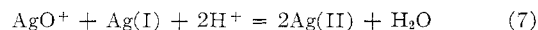
Direct isotopic exchange reactions between silver(I) and silver(II) have been studied.<sup>12,13</sup> Gordon and Wahl have observed the rate is second order in silver(II) and bimolecular reaction 1 is proposed. Magnetic susceptibility<sup>2</sup> and emf<sup>10</sup> measurements as well as epr<sup>3</sup> work indicate that, of the higher oxidation states of silver, the +2 oxidation state is the predominant state in solution. It is conceivable that silver(III) in solution is highly solvated and would most likely exist as  $\text{AgO}^+$ . It has been found that salts of oxygenated trivalent

silver precipitate when acid solutions of silver in its higher oxidation states are diluted.<sup>4,14</sup>

The oxidation of hydrogen peroxide by  $\text{Ag(II)}$  has been observed to be rapid.<sup>4</sup> This reaction has been studied by the authors using a Gibson–Durrum stopped-flow spectrophotometer (Durrum Instrument Corp., Palo Alto, Calif.). The second-order rate constant of approximately  $1 \times 10^{-3}$  *M*  $\text{Ag(II)}$  and  $0.5 \times 10^{-3}$  *M*  $\text{H}_2\text{O}_2$  in 3 *M*  $\text{HNO}_3$ –0.05 *M*  $\text{AgNO}_3$  at 23° has been measured to be  $(11.0 \pm 0.3) \times 10^6$   $M^{-1} \text{sec}^{-1}$ . Kirwin and his coworkers<sup>6</sup> were unable to detect hydrogen peroxide in their kinetic investigation. However, we have observed that the reaction is fast and therefore hydrogen peroxide will not accumulate to a sufficiently high concentration to permit its detection. The mechanism proposed by Kirwin and his coworkers<sup>6</sup> seems questionable since the production of 0.5 mol of oxygen in the rate-determining step (e) does not seem likely.

Some rate constants and constant ratios have been evaluated. From Figure 1, the graph relating  $k_{\text{II}}^{-1}$  vs.  $[\text{Ag(I)}]_0$  at 35°, the following are obtained:  $k_{\text{I}}(35^\circ) = 2.93$   $M^{-1} \text{sec}^{-1}$  and  $k_{-1}k_{-2}/k_1k_2'k_3'(35^\circ) = 25$   $M^{-2} \text{sec}$  in 6.18 *M*  $\text{HNO}_3$ . From Figure 2, the  $k_{\text{II}}^{-1}$  vs.  $[\text{Ag(I)}]_{\text{av}} \cdot [\text{H}^+]^2$  plot leads to  $k_{-1}k_{-2}/k_1k_2'k_3'(25^\circ) = 102$   $M^{-2} \text{sec}$ . Perhaps, the smaller value of the constant ratio at 35° may suggest that the forward reactions in (1) and (2) must be enhanced when temperature is increased.

Using the free energy data of Latimer for reaction 7,  $K(25^\circ) = 4.6 \times 10^3$  is estimated. Assuming the above



value of  $K$  is applicable to the present experimental conditions  $\{[\text{H}^+] = 6.17$  *M*,  $[\text{Ag(I)}] = 5 \times 10^{-4}$  *M*, and  $[\text{Ag(II)}] = 4 \times 10^{-4}$  *M*\}, the fraction of  $[\text{AgO}^+]$  has been estimated to be 0.03% of  $[\text{Ag(II)}]$ , a very small amount, indeed.

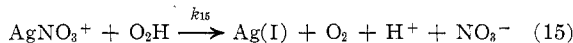
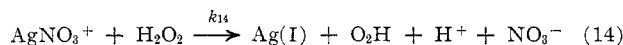
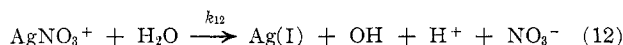
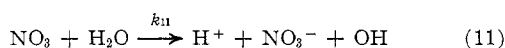
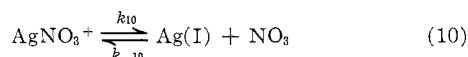
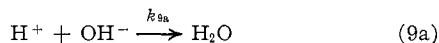
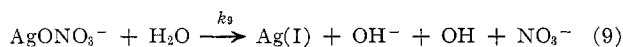
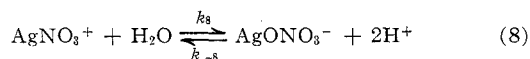
The activation energy for this reaction in 6.18 *M*  $\text{HNO}_3$  is  $\Delta H_{\text{II}}^\ddagger = 23.0 \pm 0.4$  kcal/mole, and Noyes<sup>5</sup> estimated the Arrhenius activation energy at 3.3 and 6.1 *M* nitric acid as  $26.5 \pm 2$  and  $31.0 \pm 1.4$  kcal/mole, respectively. Since  $\Delta H^\ddagger = E_a - RT$ , at 25° a difference of 0.6 kcal/mole is involved and one can compare the two results. The Arrhenius activation energies in other acid media have also been reported: in perchloric acid,  $E_a = 11.67$  and  $11 \pm 2$  kcal/mole;<sup>6</sup> in phosphoric acid,  $E_a = 11.5$  kcal/mole.<sup>8</sup> Comparison between the systems shows that  $E_a$  in nitric acid is twice those in perchloric and phosphoric acids. Rechnitz and Zamochnik<sup>8</sup> suggested that in perchloric, phosphoric, and sulfuric acids there must be a rapid equilibrium between the anionic ligands and the silver(II)–anion complexes to supply free silver(II) for the reaction. They came to this conclusion on the basis that identical values of  $E_a \sim 11$  kcal/mole for the three systems ( $\text{HClO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ ) are obtained and also on the basis of the similarities in observed kinetics. If this represents a less energetic path, it is puzzling that reaction in nitric acid would choose a higher energy route unless the reaction species

(12) B. M. Gordon and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 273 (1958).(13) M. Bruno and V. Santoro, *Ric. Sci., Suppl.*, **26**, 3072 (1956); *Chem. Abstr.*, **51**, 6295h (1957).(14) D. M. Yost, *J. Am. Chem. Soc.*, **48**, 152 (1926).

is AgNO<sub>3</sub><sup>+</sup> which we have indicated previously in the discussion.

It is difficult to predict what would happen when ClO<sub>4</sub><sup>-</sup> is used in place of NO<sub>3</sub><sup>-</sup> to study the nitrate effect on rate. At this high acid concentration, the activity coefficients of all of the species in solution vary and it is possible that the actual nitrate effect may be canceled by the perchlorate effect.

**B. Mechanism of the First-Order Reaction.**—A multistep mechanism is proposed to explain the first-order kinetics

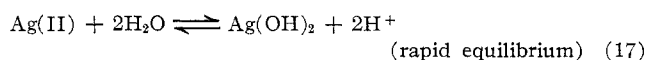


Applying the steady-state approximation to AgONO<sub>3</sub><sup>-</sup>, OH, NO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and O<sub>2</sub>H and writing  $k_i'$  for  $k_i[\text{H}_2\text{O}]$ , the derived rate law is

$$\frac{-d[\text{AgNO}_3^+]}{dt} = \left\{ \frac{2k_9'k_{11}'(k_8' + k_{10} + k_{12}') + 2k_9'k_{-10}(k_8' + k_{12}')[\text{Ag(I)}]}{(k_{11}' + k_{-10}[\text{Ag(I)}])(k_9' + k_{-8}[\text{H}^+]^2)} \right\} \times [\text{AgNO}_3^+] \quad (16)$$

The derived rate law (16) has the same form as the experimental rate law (B-5). In order to obtain eq 16, this inequality must be assumed: (the numerator terms inside the braces of eq 16)  $\gg \{2k_{-8}[\text{H}^+]^2(k_{10}k_{11}' + k_{12}'k_{11}' + k_{12}'k_{-10}[\text{Ag(I)}])\}$ . It is difficult to justify this assumption since it requires knowing all the  $k$ 's, which is impossible. Nonetheless, eq 16 conforms to (B-5) and may be reduced to (B-2) if  $[\text{H}^+]$  is constant and to (B-6) if  $[\text{Ag(I)}]$  is constant satisfying the observed kinetics under different conditions.

Gordon and Wahl<sup>12</sup> have suggested the rapid equilibrium reaction 17, involving Ag(OH)<sub>2</sub> formation, to explain the large inverse dependence of rate on  $[\text{H}^+]$ .



However, it is highly unlikely for the hydroxide complex to exist in strong acid solution. Furthermore, Noyes<sup>10</sup> reported that no hydroxide complexes of silver(II) are formed in strong acid medium. Perhaps, the fact that some silver migrated to the anode during electrolysis of a concentrated silver nitrate solution may suggest the existence of the oxynitrate anion of silver.<sup>15</sup>

(15) H. C. P. Weber, *Trans. Am. Electrochem. Soc.*, **32**, 85 (1917); *Chem. Abstr.*, **12**, 27 (1918).

Reactions involving strong oxidizing cations which may proceed *via* free-radical mechanisms have been proposed.<sup>16</sup> Since silver(II) is a strong oxidizing agent, it is conceivable to proceed *via* free-radical intermediates such as OH, NO<sub>3</sub>, and O<sub>2</sub>H. The dimerization rate of OH to give H<sub>2</sub>O<sub>2</sub> which is fast and on the order of 10<sup>10</sup> M<sup>-1</sup> sec<sup>-1</sup> was reported by Rabani and Matheson.<sup>17</sup>

The nitrate radical has been postulated as a reactive intermediate by Gryder and his coworkers<sup>11,18,19</sup> in Ce(IV)-Ti(I) and Ag(II)-Ti(I) electron-transfer reactions in nitric acid solutions. The existence of NO<sub>3</sub> radical in aqueous solutions has been confirmed by Martin, *et al.*<sup>20,21</sup> They obtained the flash absorption spectrum of the NO<sub>3</sub> radical in 6 M nitric acid solution. It is conceivable that the OH radical could react with nitrate to form the NO<sub>3</sub> radical but Daniels<sup>22</sup> has shown that the hydroxyl radical is not the precursor of the NO<sub>3</sub> radical, suggesting that reaction 11 is unidirectional.

Some rate constants and constant ratios may be evaluated from the experimental results. At constant  $[\text{H}^+] = 6.18 \text{ M}$  an expression may be obtained relating  $k_1^{-1}$  to  $[\text{Ag}^+]$ .

$$k_1^{-1} = \frac{(k_{11} + k_{-10}[\text{Ag(I)}])(k_9' + k_{-8}[\text{H}^+]^2)}{2k_9'k_{11}'(k_8' + k_{10}' + k_{12}') + 2k_9'k_{-10}(k_8' + k_{12}')[\text{Ag(I)}]} \quad (18)$$

Equation 18 has essentially the same functional form as (B-2) at 6.18 M H<sup>+</sup>.

An empirical equation has been obtained for the  $k_1^{-1}$  vs.  $[\text{Ag(I)}]$  plot (Figure 3)

$$k_1^{-1} = \frac{7.62 \times 10^2(1 + 4.13 \times 10^3[\text{Ag(I)}])}{(1 + 9.5 \times 10^2[\text{Ag(I)}])} \quad (19)$$

The solid line in Figure 3 represents the calculated plot and it agrees reasonably well with the experimental points. The constant ratio evaluated at 35.0° is  $k_{-10}/k_{11}' = 4.13 \times 10^3 \text{ M}^{-1}$ . From published results<sup>20</sup> the rate constant of Ce(III) + NO<sub>3</sub> → Ce(IV) + NO<sub>3</sub><sup>-</sup> at 35° is calculated to be 1.82 × 10<sup>6</sup> M<sup>-1</sup> sec<sup>-1</sup>. Since the Ag(I)-Ag(II) couple (-1.98 v) is more negative than the Ce(III)-Ce(IV) couple (-1.6 v), Ag(II) is a far more powerful oxidizing agent than Ce(IV). It may be assumed therefore that  $k_{-10} \sim 1 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$  and  $k_{11}' = 2.4 \times 10^2 \text{ sec}^{-1}$  ( $k_{11} = 4.3 \text{ M}^{-1} \text{ sec}^{-1}$  since  $[\text{H}_2\text{O}] = 55.5 \text{ M}$ ) are estimated. The value of  $k_{11}$  is much smaller than the rate constant for the acetic acid and NO<sub>3</sub> reaction which is 2.3 × 10<sup>2</sup> M<sup>-1</sup> sec<sup>-1</sup> at 23°. This is consistent with the suggestion that oxidation of water by NO<sub>3</sub> is slow and that added solutes consume the NO<sub>3</sub> radical more efficiently than H<sub>2</sub>O.<sup>20</sup>

**Acknowledgment.**—The financial assistance of a research grant from the National Science Foundation is gratefully acknowledged.

(16) N. Uri, *Chem. Rev.*, **50**, 375 (1952).

(17) J. Rabani and M. S. Matheson, *J. Am. Chem. Soc.*, **86**, 3175 (1964).

(18) J. W. Gryder and R. W. Dundon, *ibid.*, **88**, 275 (1966).

(19) M. K. Dorfman and J. W. Gryder, *Inorg. Chem.*, **1**, 799 (1962).

(20) T. W. Martin, R. E. Rummel, and R. C. Gross, *J. Am. Chem. Soc.*, **86**, 2595 (1964).

(21) T. W. Martin, A. Henshall, and R. C. Gross, *ibid.*, **85**, 113 (1963).

(22) M. Daniels, *J. Phys. Chem.*, **70**, 3022 (1966).