# Hydroxyl Radical Kinetics by Kinetic Spectroscopy. III. Reactions

with H_2O_2 in the Range 300-458°K[1,2]

by N. R. Greiner

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544
(Received July 10, 1967)

Gas-phase reactions of OH radicals in the presence of H_2O_2 and various amounts of Ar were studied in the region 300-458°K by flash photolysis-kinetic spectroscopy. The results were interpreted in terms of the reaction

$$OH + H_2O_2 \longrightarrow H_2O + HO_2$$
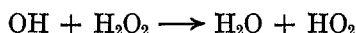
($\log k_2 = 11.39 \pm 0.05 + \frac{1}{2} \log T - 1200/2.303RT$ cc mole^{-1} sec^{-1}), and a reaction second order in [OH] ($k = 3.9 \pm 1.5 \times 10^{13}$ cc mole^{-1} sec^{-1}) observed only at 300°K. An unsuccessful search was made for an absorption spectrum of HO_2 in the region 2500–10,000 Å, with the region 3000-4000 Å studied under resolution comparable to 300°K Doppler widths. There is evidence that at least one of the products of the reaction is vibrationally excited.

Introduction

Reactions of OH radicals are of considerable interest in connection with combustion, air pollution, and atmospheric chemistry. Both the photolysis[3] and pyrolysis[4] of H_2O_2 vapor yield OH radicals by reaction

$$H_2O_2 \xrightarrow{h\nu \text{ or } \Delta} 2OH \tag{1}$$

1 and are therefore attractive sources of OH for gas kinetics studies. However, reaction 2 may compete with the reactions of interest and complicate the kinetics.[3,5]

$$OH + H_2O_2 \rightarrow H_2O + HO_2 + 29 \text{ kcal} \tag{2}$$
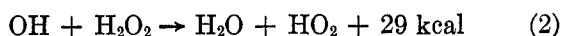
The fate of the OH radical in systems containing only H_2O_2, and sometimes an inert gas (Ar), was studied by the flash photolysis-kinetic spectroscopy method.[5] The results show that reaction 2 is quite fast (collision yield $= 3 \times 10^{-3}$ at 300°K) and has a low activation energy (1.2 kcal mole^{-1}).

Experimental Section

The apparatus has been described.[5] The cell was washed with H_2O and HNO_3 and then aged in contact with 30% H_2O_2 solution for a few days.[6] The rate of the dark decomposition of H_2O_2 vapor at 1.00 torr was then checked and found to be $\sim$10% hr^{-1}. In all experiments the H_2O_2 vapor was in contact with the cell for 15 min or less before photolysis. After H_2O_2 had been photolyzed in the cell for some time, the rate of the dark reaction was found to be only a few per cent per hour.

The H_2O_2 was prepared from "98%" H_2O_2 solution

(FMC Corp.) by pumping away $\sim^3/_4$ of a sample. Vapor pressure measurements indicated that the resulting solution was >99% H_2O_2 (mole fraction basis).

The experimental procedure was as follows. H_2O_2 was admitted to the cell and the H_2O_2 pressure was adjusted to 1.00 torr with the circulation pump running. Any Ar to be added was added immediately afterward and the total pressure was adjusted as desired. The mixture was stirred for 10 min before photolysis. A total of eight flashes was needed to provide the proper background density on the plate. The methods for analyzing the data[3,5] and for obtaining an [OH] calibration[5] have been described. We found that 25×10^{-3} torr of OH was generated per flash. Further support for the calibration was provided by comparing the observed OH 3064-Å band oscillator strength (8.7×10^{-4} as calculated from our data) with literature values (8×10^{-4} recommended).[7]

A study of [OH] at short delay times (4 to 20 μsec) showed that the e^{-1} time of the effective photolytic

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) A preliminary version of this paper was presented at the 153rd National Meeting of the American Chemical Society under the title, "Hydroxyl Radical Reactions Involved in the Flash Photolysis of Hydrogen Peroxide."

(3) N. R. Greiner, *J. Chem. Phys.*, **45**, 99 (1966); **46**, 2450 (1967).

(4) D. E. Hoare, *Proc. Roy. Soc.* (London), **A291**, 73 (1966).

(5) N. R. Greiner, *J. Chem. Phys.*, **46**, 2795 (1967).

(6) W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, "Hydrogen Peroxide," Reinhold Publishing Corp., New York, N. Y., 1955, p 171.

(7) D. M. Golden, F. P. Del Greco, and F. Kaufman, *J. Chem. Phys.*, **39**, 3034 (1963).

light pulse was ~5 μsec. The e^{-1} time of the spectroscopic flash at 3064 Å was measured with a photomultiplier and oscilloscope and was found to be ~7 μsec.

Elevated temperatures were attained by reducing the amount of thermal ballast gas mixed with the H_2O_2. The temperature rise due to the photolysis (ΔT) is given by

$$\Delta T = (h\nu - D)AC_v^{-1} \qquad (3)$$

where $h\nu$ is the energy per einstein of the light absorbed, D is the dissociation energy of the HO–OH bond (51 kcal),[8] A is the mole fraction of the gas photolyzed, and C_v is the average constant volume molar heat capacity of the gases in the system. The advantage of this method of heating is that no decomposition of H_2O_2 by pyrolysis occurs before or during flash photolysis, even in the high temperature runs. The dark decomposition during the flash is negligible because the gas stays hot only for a few milliseconds, and the homogeneous rate of H_2O_2 decomposition is quite slow even at these temperatures. This can be contrasted with the rate of decomposition that would be due to the heterogeneous reaction if the cell itself were heated to 450°K.

Rate constants (k) were determined by using the equation, $k = -d \ln [OH]/[\text{reactant}]dt$, and OH rotational temperatures (T_{rot}) were obtained in the manner described earlier.[3,5] As in the previous study,[5] the weaker lines were usually used for k and T_{rot} measurements to minimize the correction for slit function effects.

The observed absorption of any rotational line is affected by two sources of error: the usual effect of plate graininess (random) and the effect of variations in the rotational distribution due to thermal effects (systematic). These experiments were especially subject to the latter effect because of the small amounts of inert thermal ballast gas used at times. A further refinement of the data analysis was made to minimize or check both of these sources of error.

To determine T_{rot}, $\ln (I_{abs}/S_J)$ is plotted vs. E_K, where I_{abs} is the observed intensity of absorption in arbitrary units, S_J is the line strength, and E_K is the rotational energy of the lower electronic level corresponding to the absorption line. The expression for I_{abs} can be written[9]

$$\ln \left(\frac{I_{abs}}{S_J}\right) = \ln [OH] + \ln 2\nu -$$

$$\ln Q_r - E_K(kT_{rot})^{-1} \qquad (4)$$

where ν is the frequency of the absorption line, Q_r is the rotational partition function, and k is the Boltzmann constant. The slope of the plot is $-(kT_{rot})^{-1}$, and the intercept is $\ln [OH] + \ln 2\nu - \ln Q_r +$ an arbitrary constant (because I_{abs} is in arbitrary units).

For a small range of ν and constant temperature, $\ln 2\nu$ and $\ln Q_r$ are both constant, so $\ln 2\nu - \ln Q_r$ can be combined with the arbitrary constant. The sum of these constants is then defined by the [OH] calibration. When T_{rot} is not constant, Q_r can be approximated by T_{rot} (again, in arbitrary units).[10] When the amount of inert gas ballast was kept constant, the observed T_{rot} did not vary by more than ±5.5%. This variation was not considered significant, so T_{rot} was regarded as a constant, under these circumstances, in the data analysis. This method then served as a check on possible temperature fluctuations and reduced chance fluctuations due to plate graininess by combining the data from the many lines used on the T_{rot} plot.

A computer was used as an aid in processing the large amount of plate data. It printed the quantities $\ln (I_{abs}/S_J)$ and E_K in tabular form for each line. The precision of the method can be seen by noting the scatter of points about the lines for the $\ln [OH]$ vs. t plots in Figure 1.

Results

Absorption spectra of the entire OH 3064-Å band were recorded at several (at least six) delay times after the photolytic flash and were analyzed in the above manner. Figure 1 shows plots of $\ln [OH]$ vs. time for three H_2O_2 pressures: 0.25, 0.50, and 1.00 torr (measured at room temperature) with no Ar added. The observed rate constants were, respectively, 1.42 × 10^{12}, 1.52 × 10^{12}, and 1.27 × 10^{12} cc mole^{-1} sec^{-1}, which agree within the usual ±10%. The linearity of the $\ln [OH]$ plots and the observation that the OH disappearance rate is proportional to $[H_2O_2]$ show that the observed reaction is first order in both [OH] and $[H_2O_2]$, as would be expected from reaction 2.

The values of T_{rot} observed in the 1.00-torr H_2O_2 experiments are also plotted in Figure 1. Since the actual yield of OH per flash was proportional to $[H_2O_2]$, the OH spectra from the 0.25- and 0.50-torr H_2O_2 runs were weaker than those from 1.00-torr H_2O_2 runs and were not as suitable for measuring T_{rot}, but they did show that T_{rot} was within the range of T_{rot} observed in the 1.00-torr H_2O_2 runs. There is no evident trend in changes of T_{rot} with time (Figure 1). The average value is 458 ± 25°K, the standard deviation being ±5.5%. Photolysis decomposed 1.25% of the H_2O_2. If 1850 Å is considered a representative wavelength, the expected temperature rise is, according to eq 3

$$\Delta T = (154 \text{ kcal} - 51 \text{ kcal}) \times$$

$$0.0125/8.4 \text{ cal } °K^{-1} = 150°K$$

The observed temperature rise was 158 ± 25°K.

(8) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 826.

(9) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, 2nd ed, D. Van Nostrand Co., New York, N. Y., 1950, p 127.

(10) N. Davidson, "Statistical Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 123–125.
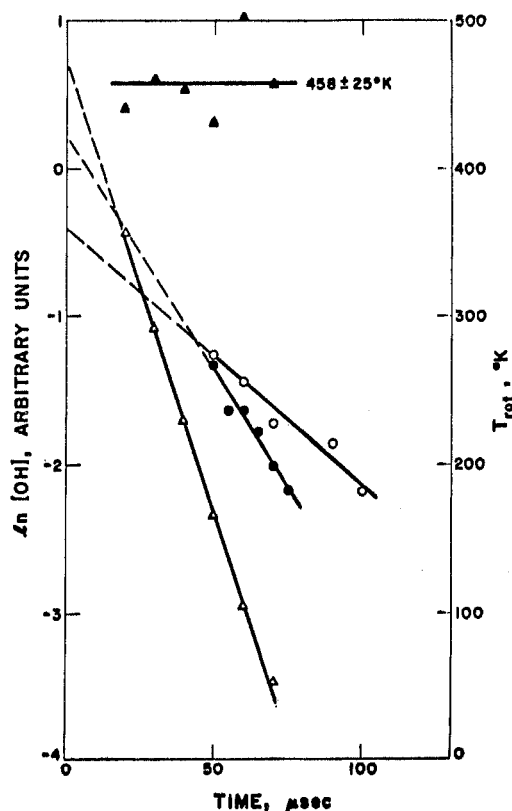
Figure 1. Plot of ln [OH] and T_{rot} at various times after the photolysis flash; ln [OH] in the presence of O, 0.25 torr of H_2O_2, •, 0.50 torr of H_2O_2, and △, 1.00 torr of H_2O_2; ▲, T_{rot} in the presence of 1.00 torr of H_2O_2.

Figure 2. Plots of ln [OH] (O) and T_{rot} (●) at various time delays in a 1.00 torr of H_2O_2 + 100 torr of Ar mixture.

Since the exothermicity of reaction 2 is 29 kcal mole^{-1}, C_v of H_2O_2 is 8.4 cal mole^{-1} $°K^{-1}$, and the ratio of [OH]$_{tot}$ to [H_2O_2] is 0.025, an additional temperature rise of as much as $29 \times 10^3 \times 0.025/8.4 = 86°K$ due to reaction 2 might be expected. No such temperature rise was observed, which implies that the excess energy of the reaction is stored in an energy mode not in equilibrium with the rest of the gas. Because vibrational relaxation is known to be slow at low pressures, the energy is probably in the form of vibration, very likely in the newly formed H_2O molecule.

By adding 100 torr of Ar to 1.00 torr of H_2O_2, ΔT was reduced to ~4°K. Results from a study under these conditions are shown in Figure 2. The observed T_{rot} was 303 ± 7°K. The kinetics of OH disappearance indicate concurrent reactions, one of which is first order in [OH], and one of which is second order in [OH]. An estimate of the second-order rate constant was obtained by multiplying [OH]$_t^{-1}$ by the difference between the actual slope of the ln [OH] vs. t plot and the extrapolated value of the slope from the low [OH] region, where contributions from the second-order reaction were insignificant. This analysis gave a second-order rate constant $k_6 = 3.9 \pm 1.5 \times 10^{13}$ cc mole^{-1} sec^{-1}. The rate constant for reaction 5 has been recently shown
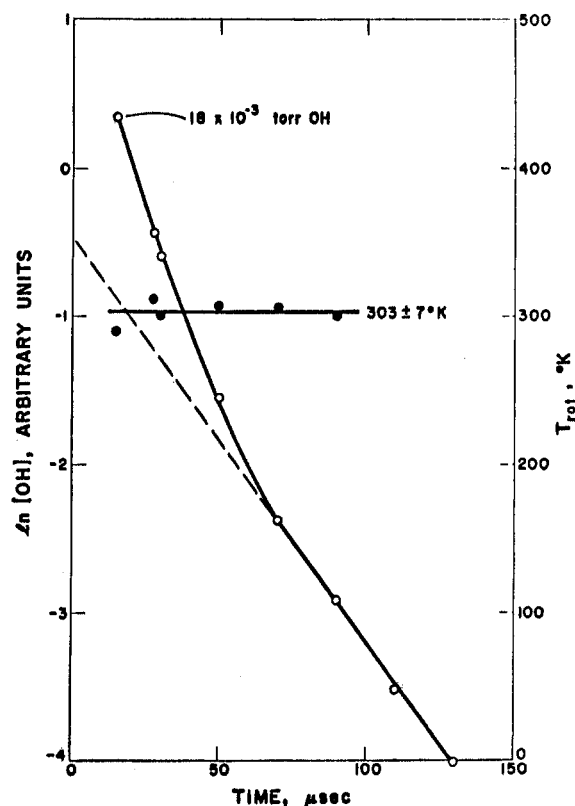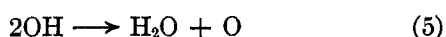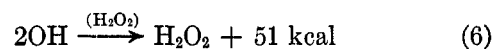
$$2OH \longrightarrow H_2O + O \quad (5)$$

to be $1.55 \pm 0.12 \times 10^{12}$ cc mole^{-1} sec^{-1} at 300°K, which is ~$1/20$ as high as the k observed here.[11] It is plausible that H_2O_2 serves as an efficient third body for the recombination of OH as in reaction 6.

$$2OH \xrightarrow{(H_2O_2)} H_2O_2 + 51 \text{ kcal} \quad (6)$$

Experiments with OH generated from H_2O photolysis in the presence of 100 torr of Ar showed a disappearance rate in agreement with the literature value for k_5, so Ar probably is not important in the second-order reaction. That the second-order reaction was not observed at the higher temperatures suggests that the temperature coefficient of the rate constant is negative. The first-order rate constant, k_2, was 5.67×10^{11} cc mole^{-1} sec^{-1} at 303°K.

Two other sets of experiments were run with intermediate amounts of Ar added (5 and 2 torr). The values for T_{rot} confirmed the values of ΔT calculated from C_v and ΔT for 1.00 torr of H_2O_2 alone.

The results of all the determinations of k_2 at the various temperatures are summarized in the Arrhenius plot, Figure 3. The line drawn through the data corresponds to the rate expression

$$\log k_2 = 11.39 \pm 0.05 +$$

$$1/2 \log T - 1200/2.303RT \quad (7)$$

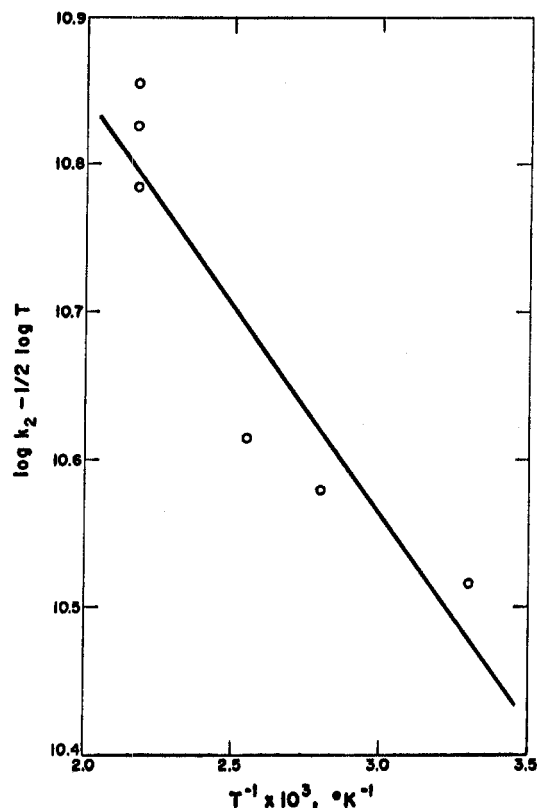(11) G. Dixon-Lewis, W. E. Wilson, and A. A. Westenberg, J. Chem. Phys., 44, 2877 (1966).

Figure 3. Arrhenius plot for the OH + H₂O₂ reaction.

The activation energy, 1.2 kcal, is low compared to other reported values for abstraction reactions involving OH.[12] However, kinetic parameters for OH reactions reported in the literature have been subject to (often drastic) change, and there is some hope that many of these reactions will be studied by more direct methods in the near future. Theoretical discussion and correlations of these parameters should be postponed until the experimental realities are more certain.

An attempt was made to photograph an absorption spectrum of the product HO_2 from reaction 2. The rate of disappearance of HO_2 by the reaction

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad (8)$$
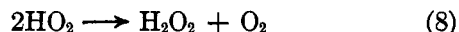
can be calculated from the data of Foner and Hudson.[13] The time of $[HO_2]_{max}$, t_{max}, can then be determined with the aid of the present data. A number of spectra were recorded at t_{max} ($\sim$50 μsec), but no absorption due to HO_2 was evident. The region 2500 Å (onset of H_2O_2 absorption) to 10,000 Å was examined with a Hilger medium quartz spectrograph. The region 3000–4000 Å was examined more closely using a Czerny-Turner spectrograph having a resolving power of 300,000. The region 3000–4000 Å was chosen because the SH molecule, which is isoelectronic with HO_2, absorbs in this region.[14] If HO_2 exhibits a discrete spectrum (sharp rotational lines) in this region as does OH, the oscillator strength must be lower than that of OH by almost two orders of magnitude, because the OH absorption

spectrum was observable with as little as 2.5×10^{-4} torr of OH, while $[HO_2]_{max}$ should have been 2.5×10^{-2} torr.

Discussion

The collision yield for reaction 2 is $\sim$3 $\times$ 10^{-3} at 300°K and $\sim$5 $\times$ 10^{-3} at 450°K. While the collision yield at 300°K is quite large, there is very little increase in the rate constant with increasing temperature because of the low activation energy. Using eq 7, we can see if reaction 2 will compete with other OH reactions under various conditions.

The rate constant for reaction 9[5,11] is $\sim$1 $\times$ 10^{11} cc

$$CO + OH \longrightarrow CO_2 + H \qquad (9)$$
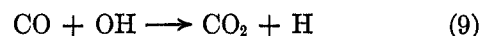
mole^{-1} sec^{-1} at 300°K, which is $\sim$0.16 times as fast as reaction 2 at that temperature. At 798°K, k_9/k_2 was found to be $\sim$0.10.[4] The difference in the two activation energies would then be $\sim$0.5 kcal, which implies that E_{act} for reaction 9 is $\sim$0.7 kcal mole^{-1}. This value supports the low value, 0.6 ± 0.3 kcal mole^{-1}, derived from a recent analysis of data on reaction 9.[11] It is seen that reaction 2 can compete with reaction 9 at 300°K and above, and the competition becomes slightly stronger at higher temperatures.

If 5 kcal mole^{-1} is taken as the activation energy of reaction 10,[5] and if k_{10} is taken as 5.3 $\times$ 10^9 cc mole^{-1}

$$OH + CH_4 \longrightarrow H_2O + CH_3 \qquad (10)$$
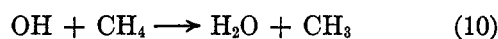
sec^{-1} at 300°K,[3] then k_{10} would be 8.3 $\times$ 10^{11} at 673°K, 1.6 $\times$ 10^{12} at 798°K, and 2.6 $\times$ 10^{12} at 923°K, while k_2 would be 2.5 $\times$ 10^{12}, 3.1 $\times$ 10^{12}, and 3.7 $\times$ 10^{12} at those respective temperatures. If we arbitrarily say that competition occurs between two reactions when the rates are equal, then competition would occur between reactions 2 and 10 when $[H_2O_2]/[CH_4]$ is 9 $\times$ 10^{-3} at 300°K, 3 $\times$ 10^{-1} at 673°K, 5 $\times$ 10^{-1} at 798°K, and 7 $\times$ 10^{-1} at 923°K. The treatment of reaction 11 is similar to that of reaction 10.[5,11] The above discussion shows that when mixtures of CO, CH₄, or H₂ with

$$H_2 + OH \longrightarrow H_2O + H \qquad (11)$$
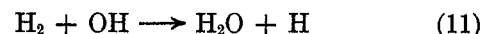
H_2O_2 are pyrolyzed at temperatures in the range 400–650°, considerable fractions of the OH are consumed in reaction 2, producing HO_2 radicals (see also ref 11). Although such systems can provide useful data, the results probably cannot be precisely interpreted in terms of a few simple reactions. For example, Arrhenius plots of the rate constant ratios obtained in the pyrolysis system are not entirely consistent with re-

(12) R. M. Fristrom and A. A. Westenberg, "Flame Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, Chapter XIV.
(13) S. N. Foner and R. L. Hudson, Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p 34.
(14) R. W. B. Pearse and A. G. Gaydon, "The Identification of Molecular Spectra," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1963, p 267.

cently measured values obtained at room temperature.[5,11]

It is concluded that reaction 2 can compete favorably with other reactions of OH in systems of various compositions and at various temperatures. This study provides a basis for quantitatively evaluating the con-

tributions of reaction 2 to the over-all scheme. The current body of data[13] on the H_2O_2 system suggests that a clean source of HO_2 radicals at high concentration could be obtained in a stream of hot H_2O_2 vapor at a point downstream from the region where reaction 2 is going to completion.

Ligand Substitution Reactions of Hexacyanoferrate(III) and

Azide Induced by Flash Photolysis[1]

by Donald J. Kenney, Guido G. Clinckemaillie,[2] and
Brother Cyril Leo Michiels

Department of Chemistry, University of Detroit, Detroit, Michigan 48221   (Received July 10, 1967)

Aqueous potassium hexacyanoferrate(III) does not react with sodium azide even upon prolonged standing in a well-lighted room. However, when irradiated strongly with sunlight or a tungsten filament lamp, the yellow solution turns purple because of the formation of azidopentacyanoferrate(III). Since the purple color disappears rather quickly due to the re-formation of hexacyanoferrate(III), reaction rates were measured after flash photolysis. The results indicate that this bleaching of the purple azidopentacyanoferrate(III) by cyanide ions proceeds by an S_N2 mechanism. Azide concentration and pH also have a dramatic influence on reaction rates, while ionic strength does not. The thousandfold increase in ligand substitution rate upon flashing suggests a photoexcited-state mechanism.

Introduction

Because of its stability, rates of hydrolysis or photohydrolysis have not previously been measured for solutions of hexacyanoferrate(III). However, Jaselskis has shown[3,4] that if aquopentacyanoferrate(III) can once be formed *in situ* or by synthesis, it will give a characteristic color with sodium azide.

$$Fe(CN)_5H_2O^{2-} + N_3^- \rightleftharpoons Fe(CN)_5N_3^{3-} + H_2O \quad (1)$$
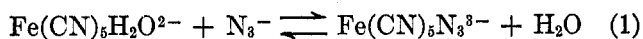
Jaselskis generally oxidized $Fe(CN)_5H_2O^{3-}$ or $Fe(CN)_5NH_3^{3-}$ with hydrogen peroxide in the presence of azide to produce the color. The $Fe(CN_6)^{4-}$ and $Fe(CN_6)^{3-}$ ions will not yield the azide color under the same conditions. One could conclude from this that normally the aquation reaction 2 is slow while the reverse is quite rapid compared with reaction 1.

$$Fe(CN)_6^{3-} + H_2O \rightleftharpoons Fe(CN)_5H_2O^{2-} + CN^- \quad (2)$$
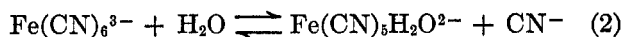
The current investigation shows that $Fe(CN)_6^{3-}$ will react directly with azide under the influence of flash photolysis. Although the development of the purple

$Fe(CN)_5N_3^{3-}$ complex with absorption maximum at 560 mμ is moderately fast, the reaction rate can be measured with an oscilloscope.

It is also shown that as a competing reaction, $Fe(CN)_5N_3^{3-}$ is decomposed by cyanide ions at a measurable rate in the dark. Reaction 3 has a first order dependence upon azidopentacyanoferrate(III) and also cyanide concentration and is reversible to a certain extent when the iron complexes are in a photoexcited state.

$$Fe^*(CN)_5N_3^{3-} + CN^- \rightleftharpoons Fe^*(CN)_6^{3-} + N_3^- \quad (3)$$
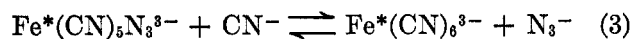
Experimental Section

Reagents. The following reagents were used without further purification: sodium cyanide, sodium car-

(1) This work was presented in part at the 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967.

(2) Based in part on a dissertation submitted by G. G. Clinckemaillie to the Graduate School of the University of Detroit, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) B. Jaselskis and J. C. Edwards, *Anal. Chem.,* **32,** 381 (1960).

(4) B. Jaselskis, *J. Am. Chem. Soc.,* **83,** 1082 (1961).