[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF QUEENSLAND, AUSTRALIA, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO, BUFFALO, NEW YORK]

The Oxidation of Thiocyanate Ion by Hydrogen Peroxide. I. The *p*H-Independent Reaction

BY I. R. WILSON AND G. M. HARRIS

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The products of the reaction between hydrogen peroxide and thiocyanate ion in the range $4 < pH < 12$ are sulfate, cyanate, ammonia and carbonate. The reaction is first order in each of the reactants and independent of the hydrogen ion concentration within the specified range. The rate constant in acetate buffer at ionic strength 0.27 is given by the expression $k = 4.0 \times 10^9 \exp(-15{,}500/RT)$ l. mole^{-1} min.$^{-1}$ within the temperature range 20–50°. The rate-determining step appears to be direct electrophilic reaction of molecular hydrogen peroxide with thiocyanate ion.

Oxidation of thiocyanate ion to sulfate by various reagents has received attention[1] as an analytical method under conditions when the customary procedures are unsuitable. Such oxidation processes could also provide a convenient method for the homogeneous precipitation of barium sulfate. The stoichiometry and kinetics of the oxidation by hydrogen peroxide have received very little attention. An outline of these is given in the present paper, and observations made of the acidity independent reaction are reported in detail. A subsequent paper[2] will examine more closely the acid-catalyzed reaction.

In a very early kinetic study, Kastle and Smith[3] established that the reaction is approximately of third order for reaction mixtures containing $10^{-2}M$ thiocyanic acid and $3 \times 10^{-2}M$ hydrogen peroxide. On re-examination, their figures suggest that the reaction under these conditions was acid-catalyzed, one unit of the observed order being due to this. In other experiments starting with approximately neutral solution, their results appear to indicate a second order reaction which is much slower. Schuster[4] examined the possibility of using oxidation by hydrogen peroxide in analysis of mixtures of cyanide and thiocyanate ions. He showed that there was quantitative oxidation of thiocyanate ion to sulfate in 0.5 *N* potassium hydroxide solution. The work was carried out with a very large excess of hydrogen peroxide (20–40 times the thiocyanate concentration). Under these conditions, 48–55% of the nitrogen was recovered as ammonia, and this figure decreased as the alkali concentration was increased. In dilute acid (0.0–0.1 *N*) a similar proportion of the nitrogen was recovered as ammonia and there was less at higher acid concentrations. Formation of nitrate ion was demonstrated in alkaline solutions, and observation that more than one mole of alkali reacted per mole of thiocyanate was attributed to this cause.

Recently Sant[5] and Csányi and Solymosi[6] have studied the rate of reaction in sulfuric acid and have shown it to be measurable.

Experimental

(a) **Reagents.**—Two samples of hydrogen peroxide were used in this work. Most measurements were made with a high-purity unstabilized sample of 98% material donated by the Becco Chemical Division of Food Mach. & Chem. Corporation. A sample of analytical grade 30% material was also used and was stated by the manufacturers (Laporte Chemicals (Australia) Pty. Ltd.) to contain as the only stabilizer 30 mg./l. of benzoic acid.

Potassium thiocyanate was of analytical grade. The rate of reaction was not changed when the solution was passed through a cation exchange resin (IR-120) column in the potassium form immediately before use. This is taken to indicate that the concentration of polyvalent cations in the original material was low enough to have negligible effect on rates. The sodium hydroxide used in the buffers and for rate measurements was of A.R. grade, purified as recommended by Kolczynski, Roth and Shanley.[7] All other materials used were of analytical reagent grade.

The laboratory distilled water was purified either by passage through a mixed-bed ion exchange resin column or by redistillation from alkaline permanganate. The stability of hydrogen peroxide solutions and reproducibility of reaction rates was satisfactory after either treatment. Some early inconsistencies were attributed to inadequate cleaning of reaction vessels, which disappeared on adoption of a cleaning procedure involving treatment with a mixture of concentrated sulfuric and nitric acids, thorough rinsing with distilled water, treatment with steam generated from distilled water and rinsing while hot with redistilled water.

(b) **Rate Measurements.**—Hydrogen peroxide concentrations were determined iodometrically[8] using ammonium molybdate as catalyst. Thiocyanate ion concentrations were determined by silver titration, using either the Volhard method[9] or potentiometric titration with a silver or platinum electrode. Cyanide determinations were made by the Liebig method[10] using the turbidimetric end-point in presence of iodide ion and ammonia.

It was also found possible to estimate the ammonia and cyanate formed during the reaction at least approximately. The rate of the peroxide-thiocyanate reaction is very slow in alkaline solution (see below), as also is cyanate hydrolysis.[11] Thus, distillation of reaction mixture aliquots rendered 1 *N* in NaOH in a micro-Kjeldahl apparatus gave direct determinations of the ammonia concentration. In acidic solution (1 *N* HCl), the main reaction product is cyanide, so that cyanate formation is slight. Also, hydrolysis of cyanate to ammonia is rapid in acid solution, so that addition of alkali and Kjeldahl distillation of these samples yielded values for (cyanate) + (ammonia). In tests of this analytical procedure, it was found that samples of pure aqueous potassium cyanate were over 98% hydrolyzed by 5 minutes digestion in 1 *N* HCl at room temperature. Similar treatment of cyanide or thiocyanate solutions resulted in less than 2% hydrolysis. Cyanide does hydrolyze readily once the solution is made alkaline, but this difficulty may be

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(1) *E.g.*, F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1911, p. 340.

(2) G. M. Harris and I. R. Wilson, manuscript in preparation.

(3) J. H. Kastle and C. R. Smith, *Am. Chem. J.*, **32**, 376 (1904).

(4) F. Schuster, *Z. anorg. allgem. Chem.*, **186**, 253 (1930).

(5) B. R. Sant, *Naturwissenschaften*, **44**, 180 (1957).

(6) L. Csányi and F. Solymosi, *Magyar Kém. Folyoérat*, **62**, 356 (1956).

(7) J. R. Kolczynski, E. M. Roth and E. S. Shanley, THIS JOURNAL, **79**, 531 (1957).

(8) A. I. Vogel, "Quantitative Inorganic Analysis," 2nd Ed., Longmans Green, London, 1951, p. 348.

(9) Ref. 8, p. 258.

(10) Ref. 8, p. 263.

(11) M. B. Jensen, *Acta Chem. Scand.*, **12**, 1657 (1958).

eliminated by bubbling air through the acidic samples before the Kjeldahl treatment.

Rate constants were calculated from integrated rate expressions whenever possible. Because of the desire to avoid excessive contribution from possible side reactions, most rates were measured with reactant concentrations close to the stoichiometric ratio. Widequist's method[12] proved convenient under these conditions, using graphical application of

$$kt = \frac{1}{d - x} - \frac{1}{d} + \frac{s^2}{3}\left(\frac{1}{(d - x)^3} - \frac{1}{d^3}\right) + \dots$$

where the initial concentrations are

$$(H_2O_2) = (d + s)$$
$$p(SCN) = (d - s)$$

and p is the stoichiometric ratio. The rate constants are given as specific rates of reaction of thiocyanate ion, since, as will be seen below, the products of reaction, and hence the stoichiometric ratio, depend upon reaction conditions. This ratio was determined by iodometric measurement of hydrogen peroxide concentrations, with confirmatory analyses for thiocyanate and sulfate.

Results and Discussion

(a) **Stoichiometry.**—The work of Schuster[4] showed clearly that the reaction in alkaline solutions and with excess hydrogen peroxide is rather complex. Kastle and Smith[3] assumed that the reaction proceeds according to

$$3H_2O_2 + SCN^- \longrightarrow HSO_4^- + HCN + 2H_2O \quad (a)$$

This is approximately true for the reaction in perchloric acid solution[2] but not for the "pH-independent" reaction. Some stoichiometry tests were run at 30° in acetate or phosphate buffers at several pH's between 4 and 8. The ratio of peroxide to thiocyanate consumption was very close to 4 in each case. All oxidized sulfur appeared as sulfate, and all product nitrogen as either ammonium or cyanate ion, the proportions of the latter two varying with pH and time of reaction. It is clear that the stoichiometry of the "pH-independent" reaction corresponds to

$$4H_2O_2 + SCN^- \longrightarrow HSO_4^- + HOCN + 3H_2O \quad (b)$$
$$HOCN + 2H_2O \longrightarrow NH_4^+ + HCO_3^- \quad (c)$$

The rate of (c) becomes very low at high pH.[11] The presence of cyanate was confirmed by the quantitative analyses and by a qualitative test with cupric ion and benzidine,[13] carried out after removal of thiocyanate by formation of the copper pyridine thiocyanate complex[14] and extraction with bromobenzene.

At pH 4.7, reaction c is relatively rapid. In an experiment at this pH and 30°, cyanate and ammonia concentrations were determined at a series of reaction times shorter than that necessary for complete oxidation of the thiocyanate present, with the result:

Time (min.)	8	39	46	117	158	216
$(OCN^-) \times 10^3$ *M*:	0.12	0.80	1.44	1.72	....	1.16
$(NH_4^+) \times 10^3$ *M*:	0.18	0.26	1.24	2.40	3.06	3.92

The concentrations of products found after 8 min. roughly indicate the extent of reaction during analysis and thus the systematic error of the procedure. The apparent rate of cyanate hydrolysis is consistent with Jensen's data.[11]

At high ratios of peroxide/thiocyanate, the peroxide consumption was found to be definitely in excess of the requirements of reactions b and c. It was observed in these experiments that gas, presumable oxygen, was evolved, whence it may be concluded that peroxide decomposition is the cause of the discrepancy mentioned. Also, during reactions at pH 4.7, it was observed that small amounts of cyanide (*ca.* $10^{-4}M$) appeared, probably as a result of a slight contribution from reaction a to the over-all stoichiometry at this pH.

(b) **Rate Data.**—The second order rate constants for the reaction at 29.8° were determined at several different hydrogen ion concentrations with the ionic strength fixed by means of $NaClO_4$. Acetate, phosphate and ammonium buffers were utilized, along with dilute NaOH, to cover the range $4 < p\text{H} < 13$. Between pH's 4 and 12, the rate constant remained unchanged at $(3.1 \pm 0.3) \times 10^{-2}$ l. mole^{-1} min.$^{-1}$. Above pH 12, this constant fell off sharply, having a value of only 6.9×10^{-3} in 0.1 *N* NaOH. This reduction in rate occurs in the region where the equilibrium

$$H_2O_2 + OH^- \rightleftharpoons HO_2^- + H_2O$$

is leading to appreciable concentrations of the HO_2^- ion.[15] A similar reduction in rate of oxidation by peroxide in moderately alkaline solutions has been reported by Mader[16] in the case of sulfite ion. It seems probable that the HO_2^- ion is substantially lower in reactivity than H_2O_2 for this type of reaction. It is therefore concluded that the rate determining step of the peroxide-thiocyanate reaction involves electrophilic substitution by hydrogen peroxide, and hence the order to reactivity to be expected is $H_3O_2^+ > H_2O_2 > HO_2^-$, as observed. An alternative formulation of the pH-independent reaction involving HSCN and HO_2^- would require an improbably high value of the specific rate (of the order of 2×10^9 l. mole^{-1} min.$^{-1}$ at pH 7 using literature values for dissociation constants of HSCN[17] and H_2O_2[15]).

The rate of the reaction was found to be practically independent of acetate or phosphate buffer concentration at constant ionic strength. In contrast, borax buffering resulted in a large apparent increase in the rate as given by hydrogen peroxide consumption. The increase was not linear in borax concentration. It cannot be due to peroxide decomposition since the rate constant for this was measured to be only 3.4×10^{-4} min.$^{-1}$ at 29.8° in 0.05 *M* borax. The cause of the rate increase is probably the formation of peroxyborate, which would calculate as peroxide under the present circumstances. The occurrence of such species has been demonstrated.[18]

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(13) F. J. Welcher, "Organic Analytical Reagents," Vol. II, D. Van Nostrand Co., New York, N. Y., 1947, p. 318.

(14) Ref. 13, Vol. III, p. 36.

(15) From data available, *K* for this reaction may be calculated to be 180–190 at 25°. M. G. Evans and N. Uri, *Trans. Faraday Soc.*, **45**, 224 (1949); S. S. Muhammed and T. N. Rao, *J. Chem. Soc.*, 1077 (1957); B. E. Conway, "Electrochemical Data," Elsevier, London, 1952, p. **187**.

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(17) T. Suzuki and H. Hagisawa, *C. A.*, **43**, 2074g (1949).

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Rates at three temperatures were measured in acetate buffer ($pH = 4.7$) at ionic strength 0.27, with the following results: 19.81°, $k = 0.012$ l. mole^{-1} min.$^{-1}$; 29.8°, $k = 0.030$; 49.87°, $k = 0.143$. This temperature variation corresponds to $k = 4.0 \times 10^9 \exp(-15500/RT)$ in the range 20 – 50°.

Effect of Oxygen on Reaction Rate at *p*H 4.6.—Two identical reaction mixtures were prepared using acetate buffer. A stream of nitrogen, saturated with water at the thermostat temperature (30°), was bubbled through one solution for an hour before addition of the hydrogen peroxide and throughout the reaction. A stream of oxygen was used similarly for the other. The reaction rates and stoichiometry were followed by titration for H_2O_2 and thiocyanate ion. No effect due to oxygen was observed.

Polymerization of Acrylonitrile.—Initiation of polymerization of vinyl monomers has been used as a mechanistic criterion and was attempted in this system. Polyacrylonitrile was precipitated in reacting solutions but was not detected when one reactant was omitted. The phenomenon was not sensitive to oxygen concentration. The solutions were prepared to contain 1.5% *v/v* acrylonitrile, acetate buffer (*p*H 4.6); H_2O_2 (0.06 *M*) and thiocyanate ion (0.02 *M*).

Tracer Experiment with C^{14}-Cyanide.—Evidence for the manner of participation of cyanide in the reaction was sought by examining the isotopic content of carbonate formed in the reaction when run in the presence of C^{14}-labelled potassium cyanide. The experiment was conducted at 30° at *p*H 4.6.

The initial concentrations used were hydrogen peroxide, 0.06 *M*; potassium thiocyanate, 0.02 *M*; potassium cyanide, 0.02 *M*; acetate buffer, 0.2 *N* in total acetate. Aliquots were taken during the reaction and the carbonate precipitated as barium carbonate and counted as thin samples using an established technique.[19] A sample of enriched carbonate was prepared to establish the activity corresponding to complete rapid conversion of cyanide to carbonate. The method used was oxidation by hydrogen peroxide in faintly alkaline solution. The results are given in the table. There is considerable scatter in them but they indicate clearly that there is no rapid equilibrium set up between thiocyanate and cyanide ions—in agreement with the findings of earlier workers.[20] They also demonstrate that most of the reaction which forms carbonate in presence of acetate buffers does not involve the intermediate formation of cyanide ion, since only about 10% of the carbonate formed in the reaction contains carbon derived from cyanide ion.

Specific Activity of Carbonate from Reaction in Presence of C^{14}-cyanide at *p*H 4.6.—

Reaction time (min.)	6.4	14	31.5	90	151	400
Specific activity (c.p.m. mg.$^{-1}$)	128	120	137	192	124	112
Carbonate by direct oxidation of cyanide	1432 c.p.m. mg.$^{-1}$					

There is, however, some path by means of which a small fraction of cyanide carbon is incorporated into product carbonate.

Mechanism.—The rate-determining reaction is most likely

$$H_2O_2 + SCN^- \longrightarrow HOSCN + OH^-$$

followed by a series of fast oxidation and/or hydrolysis reactions leading to the final products. The carbon-14 experiment and the slow relative rate of hydrolysis and oxidation of cyanide ion (less than 1% of the thiocyanate reaction at *p*H 4.6[21]) eliminate mechanisms in which cyanide appears as a major intermediate. Some additional experiments showed that the thiocyanate oxidation was independent of the presence of Fe(II) and Ni(II in low concentrations (10^{-6} and $10^{-5}M$ were used) in acetate buffer. This experiment together with the observed insensitivity of the reaction to oxygen appear to eliminate a free radial mechanism.[22] The vinyl polymerization observed is probably of the ionic type[23] and may be ruled out as a free radical indication in the present case. Further discussion of the mechanism of reaction will be deferred until consideration of the acid-catalyzed process.[2]

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