

activity coefficients of these salts over a wide range of solute concentrations near 0°. Dr. R. A. Robinson³ has pointed out that in our calculations an error in *sign* was made for the term

$$\int_0^M \Delta_j d \log M$$

in the Scatchard⁴ modification of the Lewis-Randall⁵ equation relating the freezing point depression to the activity coefficient, at a given concentration of electrolyte. The recalculated values are given in Table I.

TABLE I
VALUES OF THE ACTIVITY COEFFICIENT, γ' , FOR THE ALKALINE EARTH AND MAGNESIUM PERCHLORATES

Molality	Lim. Law	Ba(ClO ₄) ₂	Sr(ClO ₄) ₂	Ca(ClO ₄) ₂	Mg-(ClO ₄) ₂
0.001	0.910	0.897	0.900	0.900	0.901
.002	.841	.864	.871	.869	.869
.005	.760	.805	.815	.814	.814
.01	.678	.751	.763	.763	.764
.02	.577	.689	.706	.706	.707
.05	.420	.602	.630	.633	.633
.1	.293	.541	.580	.587	.587
.2	.176	.489	.543	.554	.567
.3	.119	.463	.526	.551	.575
.4	.086	.449	.534	.561	.598
.5	.064	.441	.542	.579	.630
.6		.438	.555	.603	.668
.7		.437	.572	.633	.713
.8		.438	.594	.668	.767
.9		.442	.619	.710	.828
1.0		.449	.648	.763	.898

(3) Private communication from University of Malaya, Singapore.

(4) Scatchard, Jones and Prentiss, *THIS JOURNAL*, **54**, 2676 (1932).

(5) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 286.

DEPARTMENT OF CHEMISTRY
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Ferric-Catalyzed Hydrogen Peroxide Decomposition: Effect of Nitrate Ion

BY SIGFRED PETERSON¹

The ferric-catalyzed hydrogen peroxide decomposition in nitrate solution shows deviations from first order kinetics which have been explained by Andersen² in terms of a non-chain mechanism involving atomic oxygen. It appears necessary, however, to use a chain mechanism as first proposed by Haber and Weiss³ to explain the rapid evolution of oxygen when the iron is first added as ferrous,³ the effect of ferric ion on the ferrous reaction,^{4,5} the promotion of both ferrous and ferric reactions by cupric ion,⁵ the oxidation of organic compounds,⁶

(1) The experiments reported in this paper were performed at the University of California under the direction of the late Prof. William C. Bray.

(2) V. S. Andersen, *Acta Chem. Scand.*, **2**, 1 (1948); **4**, 914 (1950).

(3) F. Haber and J. Weiss, *Proc. Roy. Soc. (London)*, **A147**, 332 (1934).

(4) C. W. Humphrey and J. Weiss, *Nature*, **163**, 691 (1919).

(5) W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, *ibid.*, **163**, 692 (1949).

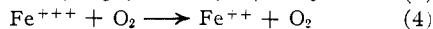
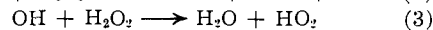
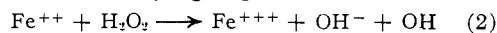
(6) J. H. Merz and W. A. Waters, *J. Chem. Soc.*, S15 (1949); I. M. Kolthoff and A. I. Medalia, *THIS JOURNAL*, **71**, 3777, 3784 (1949).

the hydroxylation of aromatic compounds⁷ and the initiation of polymerization⁸ by ferrous-peroxide solutions and the inhibition by acetanilide⁹ of the decomposition.

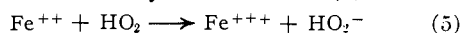
The mechanism evolved by several investigators^{3,4,5} consists of the chain initiating step



and three chain carrying steps



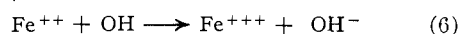
with the chain ended by the reverse of (1)



The species O₂⁻ and HO₂⁻ are presumed to be in rapid equilibrium with their conjugate acids. Application of steady state considerations to these equations gives the first order rate equation of Bertalan¹⁰

$$-d(\text{H}_2\text{O}_2)/dt = k(\text{Fe}^{+++})(\text{H}_2\text{O}_2)/(\text{H}^+)$$

Barb, Baxendale, George and Hargrave⁵ suggest that the additional chain termination becomes im-



portant with diminishing peroxide/iron ratio and increases the order of reaction with respect to peroxide as found by Andersen.

During the investigation of the inhibition of this reaction by acetanilide,⁹ deviations from first order decomposition were observed in some of the experiments without inhibitor. These experiments have been analyzed in terms of Andersen's equation

$$\log \frac{a}{x} + A \left(\frac{1}{x} - \frac{1}{a} \right) = Bt$$

in which a and x represent the concentration of hydrogen peroxide at the start of the experiment and time t , respectively. Table I gives pertinent data and the values of A and B obtained from graphs of $(\log \frac{a}{x}) / (\frac{1}{x} - \frac{1}{a})$ versus $t / (\frac{1}{x} - \frac{1}{a})$. The materials used are described in the previous paper⁹; the experimental technique did not differ significantly from that of Andersen.

TABLE I

a ^a	(Fe ⁺⁺⁺) ^a	(H ⁺) ^a	(ClO ₄ ⁻) ^a	(NO ₃ ⁻) ^a	A ^a	B ^b (min. ⁻¹)
0.077	0.019	0.040	1.78 ^b	0.000	0.0004	0.0182
.085	.061	.133	0.317	.000	.0008	.0214
.442	.066 ^c	.28	.47	.000	-.001	.0079
.425	.102	.22	.53	.000	.0005	.0208
.212	.31	.66	1.58	.000	.0002	.0266
.059	.12	.18	0.18	.37	.022	.034
.059	.12	.18	.18	.37	.025	.038
.059	.11	.36	.36	.34	.025	.018
.059	.11	.36	.36	.34	.037	.022

^a Moles/l. ^b NaClO₄ added. ^c 24°. Other experiments at 25°.

The uncertainties in A in Table I are of the order of magnitude of the value for the first five experi-

(7) H. Loebel, G. Stein and J. Weiss, *J. Chem. Soc.*, 2074 (1949); J. H. Merz and W. A. Waters, *ibid.*, 2427 (1949).

(8) J. H. Baxendale, M. G. Evans and G. S. Park, *Trans. Faraday Soc.*, **42**, 155 (1946); A. I. Medalia and I. M. Kolthoff, *J. Polymer Sci.*, **4**, 377 (1949).

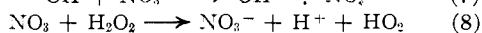
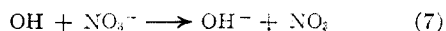
(9) W. C. Bray and S. Peterson, *THIS JOURNAL*, **72**, 1401 (1950).

(10) J. van Bertalan, *Z. physik. Chem.*, **95**, 328 (1920).

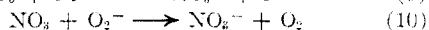
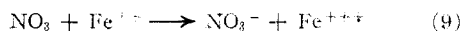
ments and about one-tenth the value in the other experiments.

Table I shows that the deviation from first order (as measured by A) over a wide variety of conditions is negligible if the only anion is perchlorate. However, when the ferric is added as nitrate, the deviations become quite significant. The variety of conditions in the experiments with nitrate present is not great enough to lead to conclusions as to the nitrate dependence of A, but combination with Andersen's results shows that the nitrate dependence is not simple. The peroxide/iron ratio is even less in these experiments than in Andersen's.

The reactions



suggested by Taube and Bray¹¹ to account for the effect of nitrate on the reaction between ozone and hydrogen peroxide will not by themselves account for a decrease in the hydrogen peroxide decomposition rate since they neither start nor stop reaction chains. However, the chain termination processes



appear to be plausible substitutes for reaction (6). A reaction of NO_3 with hydroxyl radicals is improbable since the products would include the highly endothermic atomic oxygen or its conjugate acid. Since in Andersen's work both the acid and iron were used as nitrates and A is proportional to the ferric concentration, reaction (10) which is diminished by acid is probably a factor in the nitrate effect.

Application of steady state considerations to the scheme including reactions (7), (8) and (9) or (10) but not (6) leads to a complex rate equation which for zero nitrate concentration reduces to the simple Bertalan equation. It might be remarked that the combination of reactions (7) and (9) amounts to a nitrate catalysis of the chain ending process (6).

(11) H. Taube and W. C. Bray, *THIS JOURNAL*, **62**, 3357 (1940).

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Ethylenimine by Flash Distillation¹

BY WILSON A. REEVES, GEORGE L. DRAKE, JR., AND
CARROLL L. HOFFFAUR

Since Gabriel in 1888² first successfully prepared ethylenimine by treating 2-bromoethylamine hydrobromide with silver oxide in water, several other methods for its production have been proposed. Such methods include reaction of 2-haloethylamine hydrohalides with sodium or potassium hydroxide in water³ and treating 2-aminoethyl hydrogen sulfate with sodium hydroxide.⁴ The

(1) Contribution from one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Gabriel, *Ber.*, **21**, 1049 (1888).

(3) Gabriel, *ibid.*, **21**, 2065 (1888); Gabriel and Stelzner, *ibid.*, **28**, 2929 (1895); Knorr and Meyer, *ibid.*, **38**, 3130 (1905); U. S. Patent 2,212,145 (1940).

(4) Wenker, *THIS JOURNAL*, **57**, 2328 (1935).

latter method is usually used since 2-aminoethyl hydrogen sulfate can be conveniently made from ethanalamine and sulfuric acid by the method of Wenker⁴ or by a modification of this method by Leighton and others.⁵

The usual method of converting 2-aminoethyl hydrogen sulfate to ethylenimine is to mix it with an excess of aqueous sodium hydroxide solution and distill.^{4,6} Yields of 37% ethylenimine which have been reported⁶ appear to be the highest heretofore attained.

The present investigation of this reaction indicated that the rate at which the neutralized 2-aminoethyl hydrogen sulfate is heated in contact with excess base critically controls not only the yield but also the purity of the product. Where the rate of heating was such that the neutralized sulfate in contact with the base was virtually instantaneously raised from room temperature to a temperature above the boiling point of the imine, the product was volatilized as rapidly as it was formed and could be isolated in yields as high as 83% from the water which distilled with it.

Experimental

A 5-liter, 3-neck flask containing 100 ml. of 14% sodium hydroxide solution and fitted with a dropping funnel, a stirrer and a condenser arranged for distillation was heated in a 115-volt a.c., 1200-watt, 5-liter size metal safety heater until distillation was proceeding at a rapid rate. Then 420 g. of 2-aminoethyl hydrogen sulfate dissolved in a cool alkali solution made from 250 g. of sodium hydroxide and 1800 ml. of water was added to the distillation flask through the dropping funnel at a rate such that the amount of liquid in the flask remained about constant. The superheated distillate which came over at about 110° was collected in a second 5-liter, 3-neck flask which was partially immersed in an ice-salt-bath and which was fitted with an upright ice-water condenser.

After the distillation was complete, the receiving flask was fitted with two upright ice-water condensers to provide adequate cooling and a mechanical stirrer. The imine was salted out by adding 1200 g. of solid sodium hydroxide to the distillate through one of the condensers. While salting out, the temperature of the distillate was not allowed to rise much above room temperature. The ethylenimine, which was separated with a separatory funnel weighed 107 g. and boiled at 56°. Redistilled ethylenimine also boils at 56°. The yield obtained by this flash distillation procedure was 83% based on the 2-aminoethyl hydrogen sulfate.

(5) Leighton and Perkins, *THIS JOURNAL*, **69**, 1540 (1947).

(6) "Organic Syntheses," Vol. 30, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 38-40.

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Mannich Bases Derived from a Hantzsch Pyridine Synthesis Product

BY ARTHUR P. PHILLIPS

In an earlier paper¹ a series of products was reported which had been made for testing for possible physiological activity. The compounds were prepared through the Hantzsch pyridine synthesis and resulted in substances bearing a basic amino or quaternary ammonium salt group on the 4-phenyl substituent. Other routes were sought to introduce basic salt-forming groups into the same general ring system involved. Use of the Mannich reaction on a phenolic Hantzsch synthesis product

(1) A. P. Phillips, *THIS JOURNAL*, **71**, 4003 (1949).