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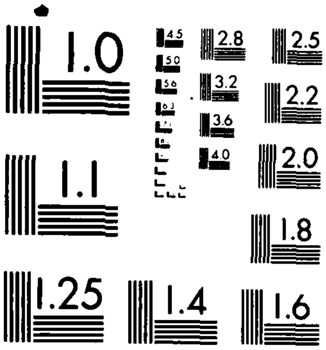

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pH Dependent Interactions Between Aqueous Iodide Ion and Selected Oxidizers

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NAVAL RESEARCH LABORATORY
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Pseudo-first order rate constants for the reaction between the oxidizers peroxydisulfate, peroxide, percarbonate, and perborate ions and aqueous iodide have been measured at pH 1, 4, 7, 9. Reactions were more rapid under acid conditions, and for the latter three test oxidizers, did not occur at all at pH 9. This fact has important implications for reactions to occur in seawater (pH ~8.3). Observed rate constants ranged from some 6.5 × 10^{-4}/sec^{-1} (peroxydisulfate at pH 1), to no reaction at high pH for some anions.

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CONTENTS

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pH DEPENDENT INTERACTIONS BETWEEN AQUEOUS IODIDE ION AND SELECTED OXIDIZERS

I. INTRODUCTION

Decontamination (decon) of Naval elements may require application of chemically active aqueous solutions. These solutions would oxidize/hydrolyze chemical and/or biological warfare (CW/BW) materials on impacted surfaces in times of conflict. In this context, aqueous hypochlorite ion is a chemically active decon material of choice (Block and Davis,1985; Hoffman and Spiner, 1962; Fielding, et al., 1967, 1968). Also, hypochlorite is kinetically active, reacting rapidly with an oxidizable/hydrolyzable substrate. This reactivity is easily followed in the laboratory by iodometry: hypochlorite interacts instantly with iodide ion. However, a kinetically rapid decon reaction may not be best for all possible situations.

An earlier report (Pellenbarg, 1985) showed that peroxygen based decon candidates such as peroxydisulfate and hydrogen peroxide reacted more slowly than did hypochlorite ion with iodide as a reducing agent. Such materials may be longer acting than is the kinetically reactive hypochlorite ion. Hypochlorite reacts effectively, but very rapidly; a slower decon reaction, based on peroxygen reagents, may prove useful in the field setting.

This report examines in detail the reactivity with iodide of a series peroxygen compounds offered as potential supplements/replacements for hypochlorite. The reactions were followed iodometrically at several pH, and in general are more rapid under acidic conditions than basic. However, the results clearly show that none of the materials tested were as kinetically reactive as hypochlorite.

II. EXPERIMENTAL

Stock solutions (0.1 N) of the candidate oxidizers (Table 1) were made up in distilled water. All tests were run in inorganic salt buffer solutions (Table 1) at pH 1, 4, 7, or 9 (nominal), and the progress of the reactions monitored by iodometric titration. Thus, multiple 25 ml aliquots of buffer were placed in separate 100 mL polycarbonate beakers, and combined with 1 mL of 20% wt/wt potassium iodide in distilled water. At the start of a test sequence, 0.5 mL of oxidizer

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solution was placed in each beaker. Periodically over the next several hours, aliquots of the test solutions were titrated with 0.0375 N thiosulfate solution (Fisher) to assay the amount of iodine liberated by the test oxidizer as a function of time. Once an oxidizer has been released to solution, it will react stoichiometrically with iodide, as in (1) and (2) below using hypochlorite ion as the example oxidizer. The liberated iodine can be titrated with thiosulfate.

$$OCl^- + 2H^+ + 2I^- \longrightarrow Cl^- + H_2O + I_2 \quad (1)$$

$$2S_2O_3^= + I_2 \longrightarrow S_4O_6^= + 2I^- \quad (2)$$

Titrations were run by lowering the pH of the test aliquot to ~2.0 with 2N H_2SO_4 in distilled water (1 or more drops as a function of initial pH in a test sequence), then titrating the solution to a pale straw color with 0.0375 N thiosulfate. Starch solution (2-3 drops), was added to give a dark blue solution which was titrated to a clear, colorless endpoint with additional thiosulfate. The total volume of thiosulfate used for the titration of each test aliquot is reported later (Tables 3-6). Blanks (25 ml distilled water plus necessary reagents) consumed no thiosulfaste, consistantly indicating low to zero background oxidants in the house distilled water. Precision of the titrations is approximately ±1%, based on multiple titrations during the test sequence.

III. RESULTS AND DISCUSSION

In aqueous solution, most peroxygen compounds appear to release the active hydroperoxide ion (HO_2^-) or H_2O_2 as an oxidant at a pH-dependent rate (Cotton and Wilkinson, 1976). Thus, the parent peroxygen anion decomposes in solution to give hydroperoxide and/or hydrogen peroxide as the actual oxidant. These species are excellent oxidants, in acid or basic systems, as indicated by the following data:

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O \qquad E_0 = 1.77V \quad (3)$$

$$HO_2^- + H_2O + 2e \longrightarrow 3OH^- \qquad E_0 = 0.87V \quad (4)$$

and for this test sequence involving iodide oxidation:

$$2I^- \longrightarrow I_2 + 2e^- \qquad E_0 = 0.54V \quad (5)$$

It is postulated that active oxidant (hydroperoxide or hydrogen peroxide)is slowly released with this oxidizer then rapidly interacting with iodide ion in solution or vice versa. The data clearly show that the oxidizer release process, or the oxidation step, or both, is heavily pH dependent. All tested peroxygen materials reacted much more rapidly with iodide under acidic conditions than under basic conditions. Indeed, the reaction monitored in this test sequence is

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O \qquad (6)$$

which is pH sensitive [K_H for $H_2O_2 \rightarrow H^+ + HO_2^-$ is 2.4×10^{-12} (Latimer and Hildebrand, 1951]. However, only peroxydisulfate reacted at all with iodide at pH 9. This fact hints that materials which actually release hydroperoxide anion prior to oxidative attack on a substrate may prove to be less useful for decontamination at the pH of seawater (~8.2 - 8.3). It is imperative that this possibility be investigated with selected oxidizers and appropriate simulants, a task beyond the scope of the current test. Note, however, that aqueous peroxydisulfate appears potentially useful as an oxidizer at even the pH of natural seawater.

The data listed in Tables 3-6 allow an initial estimate of the pH dependent rate constants for the interaction of the candidate oxidizers and iodide ion. These rate constants are listed in Table 2, and are at this point assumed to be constants for first-order, or pseudo first-order, reactions (see Laidler, 1965).

For first-order reactions, where A → products,

$$-d[A]/dt = k[A] \qquad (7)$$

which can be integrated to give

$$k = 1/t \ln a_o/a_o-x \qquad (8)$$

where a_o is the initial concentration of reactant, and x is the concentration in moles/unit volume at time t. However, if, as in the current study, one wishes to follow the appearance of a <u>product</u> (iodide as assayed by thiosulfate), the following equation pertains:

$$k = 1/t \ln \{[\text{thio}]_t/[\text{peroxygen}]_o\} \qquad (9)$$

where $[\text{thio}]_t$ is equivalent to the concentration of iodine liberated up to time t, and $[\text{peroxygen}]_o$ is the concentration of the oxidant at the start of the experiment. There is a one to one stochiometric ratio between iodine released from iodide, and thiosulfate needed to titrate the iodine [see equation (2) earlier]. Thus, if one plots $\ln \{[\text{thio}]_t/[\text{peroxygen}]_o\}$ versus t, an approximate straight line should result for the presumed pseudo-first order reactions. The slope of this line is equivalent to -d[A]/dt, and is the observed pseudo-first order rate constant. Table 2 lists the pH dependant rate constants for the reactions studied, which are presented graphically in Figures 1-4. The rate constants given are at best only estimates, however. The reactions lost gaseous iodine after approximately 60 minutes, as evidenced by an iodine odor in the head space over the reaction fluid. However, two important points are seen from the data in hand:

(1). Peroxydisulfate reacts at all pH studied.

(2). Perborate and percarbonate are salts with "hydrogen peroxide of crystallization" (see formulae listed in Table 1). These salts appear to release this hydrogen peroxide once in solution, but the peroxide reacts more rapidly than does diluted, reagent hydrogen peroxide, as shown by the relative rate constants. In fact, these two peroxygen salts appear to react roughly an order of magnitude faster than hydroperoxide from reagent hydrogen peroxide. (Note that in this sequence of tests diluted hydrogen peroxide was 0.001 M, while the peroxide salts were 0.0001 M.) This fact, coupled with the potentially greater stability of the solid peroxide salts as opposed to liquid hydrogen peroxide, has important implications for decontamination operations. In any case, the initial work reported here must now focus on defining what may influence the observed differences in the observed rate constants, as well as more carefully define those constants, especially over the first 15 minutes of the reaction sequence.

IV. CONCLUSIONS

1). Reactions between hydrogen peroxide and iodide are highly pH dependent. These materials react very slowly, or not at all, at pH ≈9.

2). Perborate and percarbonate are peroxides of crystallization salts, and release peroxide ion as oxidant when dissolved. Like peroxide itself, these salts react slowly, or not at all, at pH ≈9.

3). Peroxydisulfate reacts with iodide at all pH studied. This reactivity may be due to the non-release of peroxide as the oxidant in the peroxydisulfate system.

4). The pH dependent reactions observed in the report have significant implications for decon operations based in seawater.

V. RECOMMENDATIONS

This study has identified potential pH dependence on oxidation reactions/reagents for decontamination which are significant to the Navy. Needed now are data which:

1). Compare decon efficacy of the candidates studied against actual chemical warfare agents and biological warfare toxins, in fresh and seawater matrices, as a function of pH.

2). Examine in detail solution decomposition kinetics/mechanisms for candidate decon materials discussed here to make such chemistry more effective for decon applications. Study the influence of the ionic composition of seawater on this process.

3). Investigate the corrosivity of solutions of the candidate decon materials in fresh and seawater.

4). Examine the stability of the bulk solid oxidizers (excepting the liquid hydrogen peroxide), in environmentally significant conditions as functions of temperature and humidity.

VI. ACKNOWLEDGMENTS

The author wishes to thank the Naval Sea Systems Command, especially NAVSEASYSCOM Code 05R16, for partial support of this project.

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Table 1

A. Oxidants Examined

Name	Formula	Formula weight	test concentration (M)
hydrogen peroxide	H_2O_2	18	5×10^{-3}
sodium peroxydisulfate	$Na_2S_2O_8$	238	2×10^{-4}
sodium percarbonate	$2Na_2CO_3 \cdot 3H_2O_2$	268	9.3×10^{-4}
sodium perborate	$NaBO_3 \cdot 4H_2O$	154	1.9×10^{-4}

B. Buffers Used

pH	Buffer salt	Concentration
1	mix of KCl/HCl	0.05 M total salts
4	potassium hydrogen phthalate ($KC_8H_5O_4$)	0.05 M
7	mix of K_2HPO_4/NaH_2PO_4	5.5 g total salts/liter
9	$Na_2B_4O_7 \cdot 10H_2O$	0.01 M

Table 2 - Rate Constants as a Function of pH

Oxidizer	conc initial (M)	pH 1	pH 4	pH 7	pH 9
Sodium peroxydisulfate $Na_2S_2O_8$ f.w. = 238	2×10^{-4}	6.5×10^{-4}*	2.3×10^{-4}	1.2×10^{-4}	1.0×10^{-4}
Hydrogen peroxide H_2O_2 f.w. = 18	5×10^{-3}	9.1×10^{-5}	2.7×10^{-5}	1.6×10^{-5}	n.r.
Sodium percarbonate $2Na_2CO_3 \cdot 3H_2O_2$ f.w. = 268	9.3×10^{-4}	1.9×10^{-4}	1.2×10^{-4}	0.4×10^{-4}	n.r.
Sodium perborate $NaBO_3 \cdot 4H_2O$ f.w. = 154	1.9×10^{-4}	1.1×10^{-4}	1.4×10^{-4}	0.4×10^{-4}	n.r.

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*Units for all rate constants are sec^{-1}

n.r. = no reaction

Table 3 - Data for Sodium Peroxydisulfate

Time(min)	(sec)	titer (mL)	moles thio used	ln moles $\frac{[\text{thio}]}{[\text{oxidizer}]}$
A. pH 1				
15	900	0.80	15.2 x 10^{-6}	-2.59
45	2700	1.64	31.2	-1.87
75	4500	2.16	41.0	-1.60
120	7200	2.80	53.2	-1.34
285	17100	4.56	86.6	-0.85
450	27000	6.20	117.8	-0.54
B. pH 4				
15	900	0.25	4.7 x 10^{-6}	-3.76
30	1800	0.68	12.9	-2.76
45	2700	0.90	17.1	-2.47
60	3600	1.20	22.8	-2.19
90	5400	1.70	32.3	-1.84
120	7200	2.20	41.8	-1.58
165	9900	2.65	50.4	-1.39
C. pH 7				
15	900	0.24	4.5 x 10^{-6}	-3.80
30	1800	0.54	10.3	-2.98
45	2700	0.78	14.8	-2.62
150	9000	2.11	40.1	-1.62
240	14400	3.12	59.3	-1.23
300	18000	3.54	67.3	-1.10
360	21600	4.21	80.0	-0.93
D. pH 9				
15	900	0.09	1.7 x 10^{-6}	-4.78
30	1800	0.21	4.0	-3.93
60	3600	0.35	6.6	-3.43
105	6300	0.55	10.5	-2.96
165	9900	1.43	27.2	-2.01
420	25200	1.98	37.6	-1.69

Table 4 - Data for Hydrogen Peroxide

A. pH 1

Time(min)	(sec)	titer (mL)	moles thio used	ln moles $\frac{[\text{thio}]}{[\text{oxidizer}]}$
15	900	0.64	12.2×10^{-6}	-6.02
45	2700	1.17	22.2	-5.42
90	5400	1.45	27.2	-5.22
150	9000	1.59	30.2	-5.11
240	14400	1.55	29.4	-5.13
420	25200	1.57	29.8	-5.12

B. pH 4

15	900	0.22	4.1×10^{-6}	-7.11
30	1800	0.39	7.3	-6.53
60	3600	0.68	12.7	-5.97
105	6300	0.96	18.0	-5.63
300	18000	1.48	27.7	-5.20
450		1.41	26.4	

C. pH 7

15	900	0.05	0.9×10^{-6}	-8.57
45	2700	0.10	1.9	-7.87
105	6300	0.11	2.1	-7.78
225	13500	0.08	1.5	-8.10
420	25200	0.11	2.1	-7.78

D. pH 9

No reaction

Table 5 - Data for Sodium Perborate

A. pH 1

Time(min)	(sec)	titer (mL)	moles thio used	ln moles $\frac{[\text{thio}]}{[\text{oxidizer}]}$
15	900	0.61	11.6×10^{-6}	-2.80
30	1800	0.92	17.5	-2.39
45	2700	1.14	21.7	-2.17
75	4500	1.35	25.7	-2.01
135	8100	1.56	29.6	-1.86

B. pH 4

15	900	0.23	4.4×10^{-6}	-3.77
30	1800	0.40	7.6	-3.22
45	2700	0.51	9.7	-2.98
75	4500	0.79	15.0	-2.54
120	7200	1.03	19.6	-2.28
210	12600	1.45	27.6	-1.93

C. pH 7

15	900	0.04	0.8×10^{-6}	-5.53
45	2700	0.06	1.1	-5.12
210	12600	0.09	1.7	-4.72
390	23400	0.12	2.3	-4.42

D. pH 9

No reaction

Table 6 - Data for Sodium Percarbonate

A. pH 1

Time(min)	(sec)	titer (mL)	moles thio used	ln moles $\frac{[\text{thio}]}{[\text{oxidizer}]}$
15	900	0.80	15.2×10^{-6}	-4.11
30	1800	1.41	26.8	-3.55
45	2700	1.49	28.3	-3.49
75	4500	1.78	33.8	-3.31

B. pH 4

15	900	0.33	6.3×10^{-6}	-4.99
30	1800	0.50	9.5	-4.58
90	5400	1.12	21.3	-3.78
150	9000	1.97	37.9	-3.21
240	14400	1.61	30.6	-3.41

C. pH 7

15	900	7.4	0.6×10^{-6}	-7.39
90	5400	0.03	1.3	-6.55
240	14400	0.06	1.1	-6.70

D. pH 9

No reaction

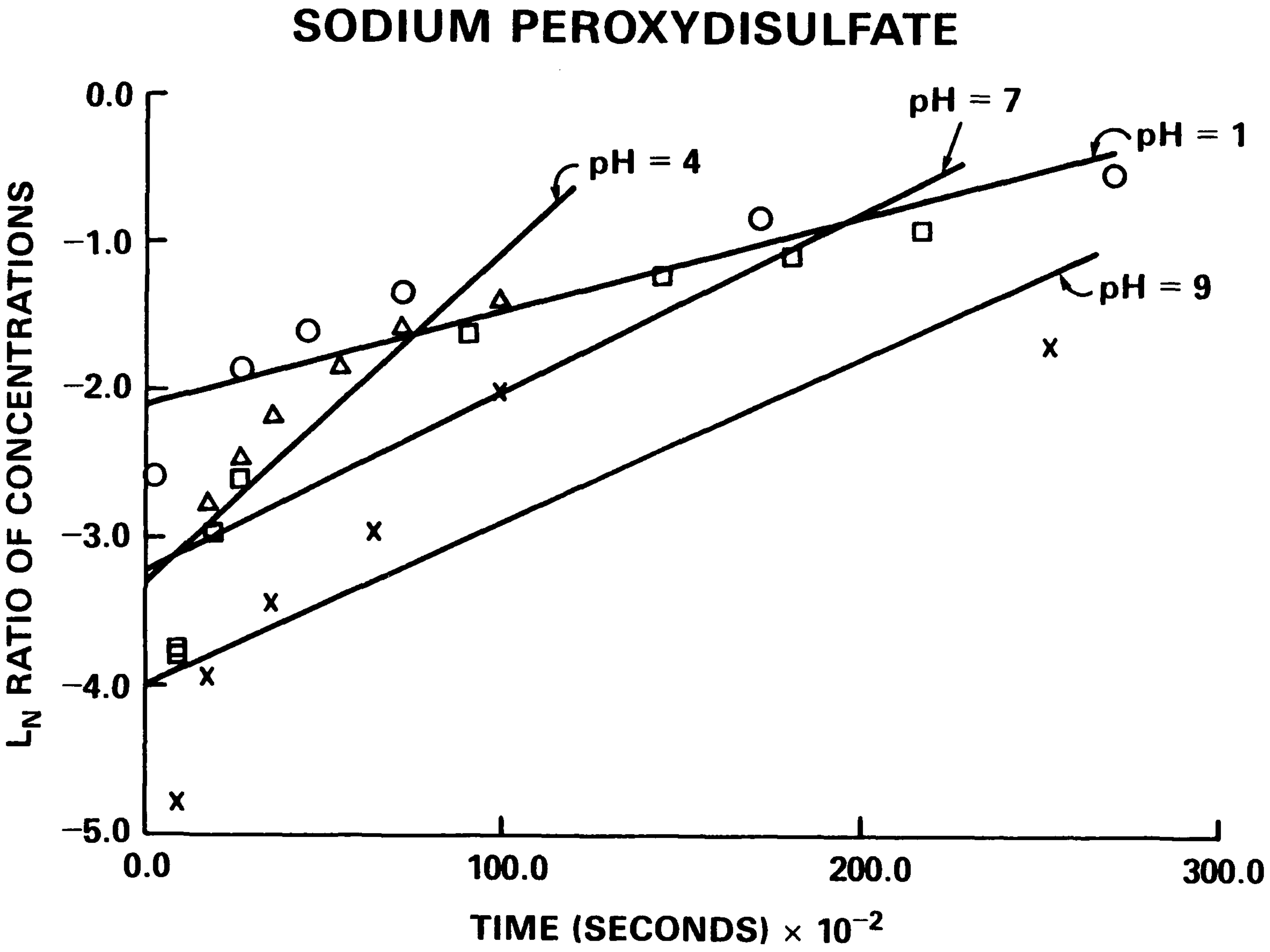

Fig. 1 — Least squares fit of pseudo-first order kinetic data for sodium peroxydisulfate as a function of pH.

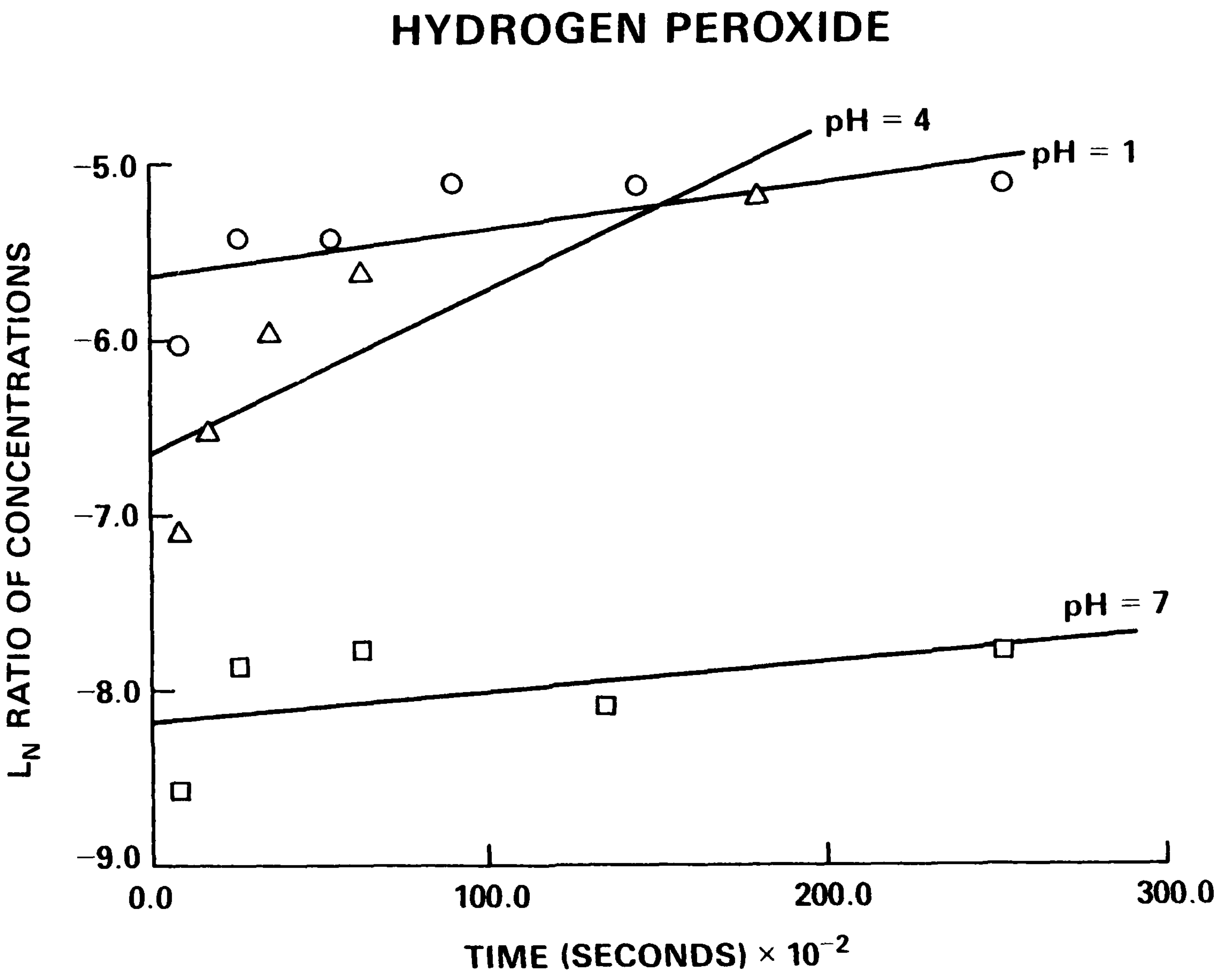

Fig. 2 — Least squares fit of pseudo-first order kinetic data for hydrogen peroxide as a function of pH.

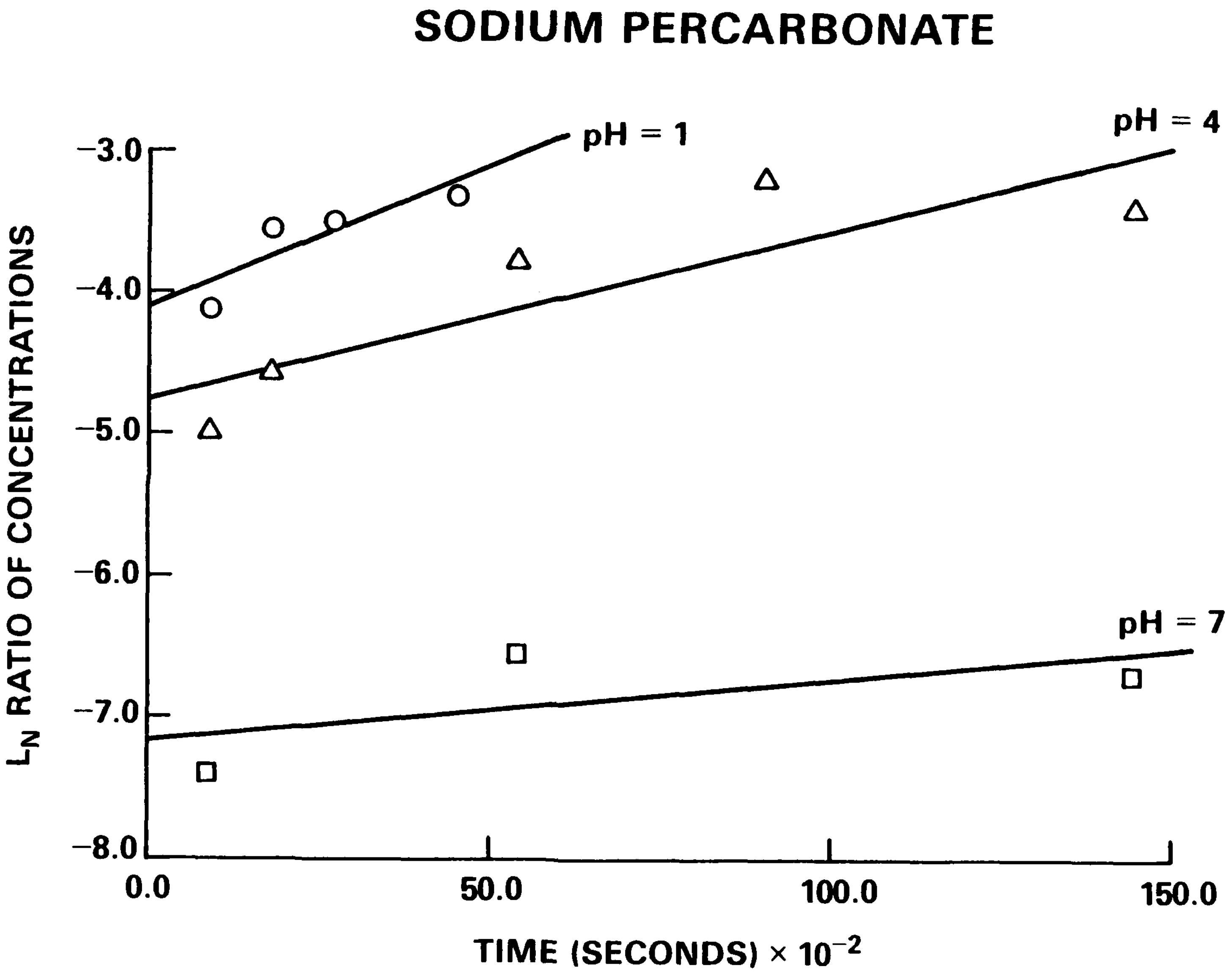

Fig. 3 — Least squares fit of pseudo-first order kinetic data for sodium percarbonate as a function of pH.

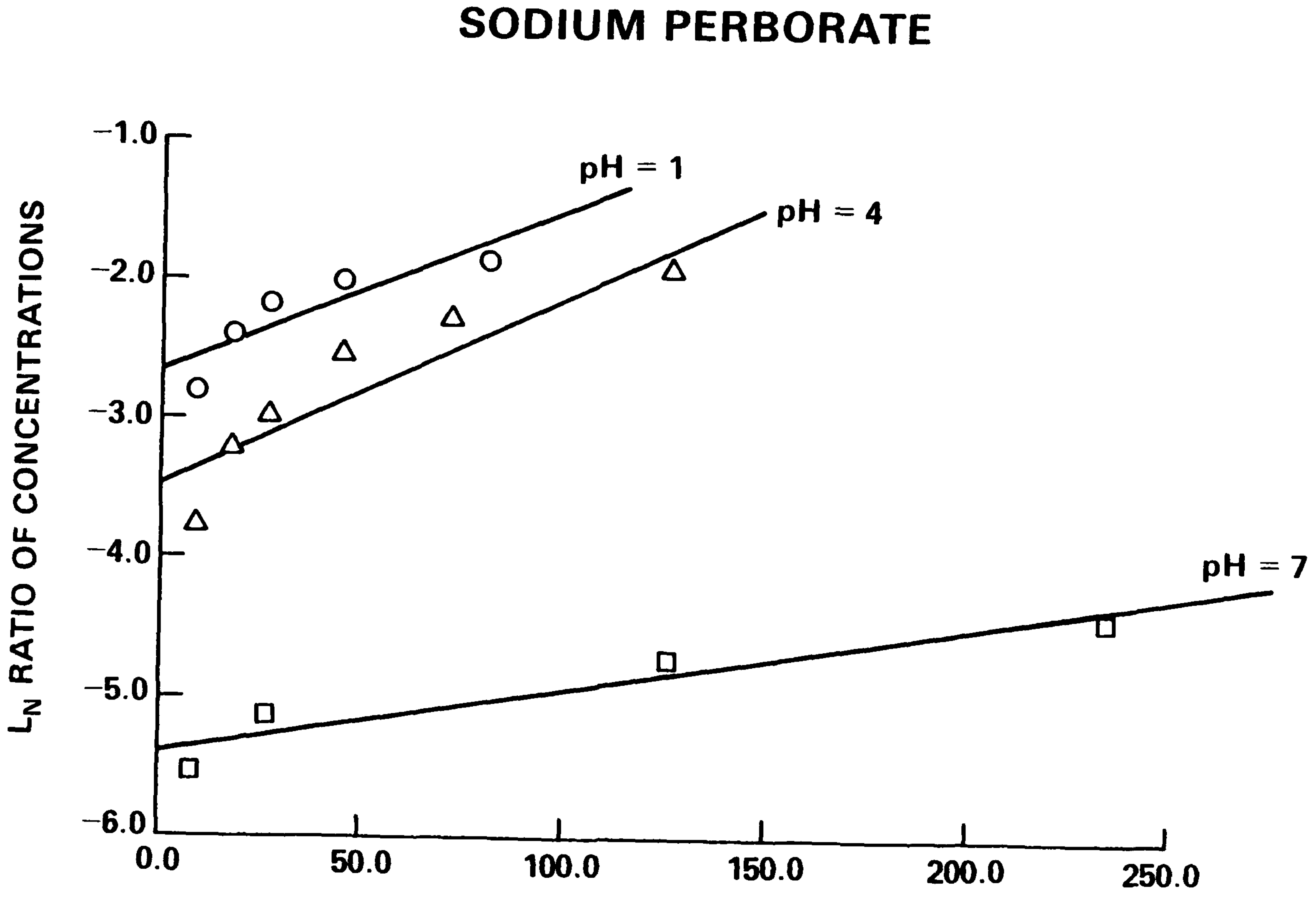

Fig. 4 — Least squares fit of pseudo-first order kinetic data for sodium perborate as a function of pH.