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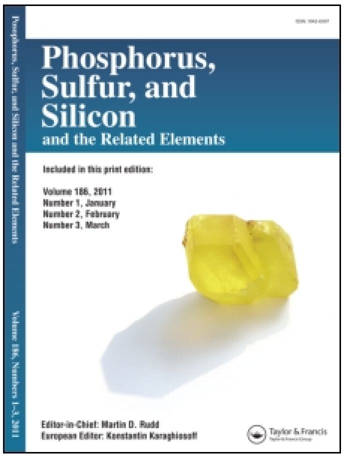

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Chemistry of Organophosphonate Scale Inhibitors, Part 4: Stability of Amino-*tris*-(Methylene Phosphonate) Towards Degradation by Oxidizing Biocides

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Chemistry of Organophosphonate Scale Inhibitors, Part 4: Stability of Amino-*tris*-(Methylene Phosphonate) Towards Degradation by Oxidizing Biocides

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*Organic additives are broadly used in water-treatment applications such as mineral scale, corrosion inhibitors, and dispersing agents. Phosphonates find extensive use as inhibitors for the formation of sparingly soluble salts such as calcium carbonates, phosphates, calcium sulfates, and others, commonly formed in open recirculating cooling systems. In such systems, biocides also are added to control microbiological growth. Some of these biocides are strong oxidants (e.g., ClO^-, BrO^-, etc.) and affect other water treatment chemicals that are sensitive to oxidative degradation. This study reports the effect of a hypobromite-based biocide towards the triphosphonate amino-*tris*-*(methylene phosphonate) (AMP). AMP reacts rapidly with the biocide at room temperature. AMP degradation continues, but it slowly reaches a plateau after 1000 min. Even after 50 h of reaction time, only 20% of the AMP has decomposed. AMP reacts with the biocide to give orthophosphate much more rapidly at 43°C than at 25°C due to faster kinetics of decomposition.*

Keywords Additives; amino-*tris*-(methylene phosphonate); degradation; oxidizing biocides; phosphonate; scale inhibitors;

INTRODUCTION

Industrial cooling-water systems face several operational challenges. Of those, the ones related to the formation of sparingly soluble salts are common and troublesome.[1–3] Water is the universal cooling medium

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used for industrial cooling because of its cost-effectiveness and its high heat capacity.[4,5] Cost considerations impose water recycling and reuse. However, this may result in the supersaturation of dissolved species until a critical point of "scaling," leading to the precipitation, and ultimately, deposition of mineral salts. Several species are associated with mineral-scale deposits (depending on water chemistry). Such undesirable deposition issues can be avoided with the careful application of chemical water treatment approaches.[6–11]

Organophosphorus compounds, usually referred to as organic phosphates or phosphonates, are an integral part of a chemical water-treatment program.[12–15] They function as scale inhibitors by adsorbing onto crystal surfaces of insoluble salts, thus preventing further crystal growth.[16–19]

Phosphonates usually contain multiple phosphonate groups (R-PO_3H_2, R = organic chain) most commonly found in their deprotonated form, due to the particular pH range of operation (virtually all open recirculating cooling-water systems operate at pH's in the range 7.0–9.8). These additives perform scale inhibition in minute (ppm) quantities and usually work synergistically with dispersant polymers. Aminomethylene phosphonates in particular are used extensively in cooling water-treatment programs,[20] oilfied applications,[21–26] and corrosion control.[27–31] Amino-*tris*(methylene phosphonate) (AMP) is one of the most common aminomethylene phosphonates and a very effective scale inhibitor.[32] Schematic structures of some aminomethylene phosphonate scale inhibitors are shown in Figure 1.

A drawback of certain scale inhibitors, such as HEDP (Hydroxyethylydene-1,1-diphosphonate), AMP, as well as other aminomethylene phosphonates is their sensitivity to oxidizing microbiocides, such as chlorine or bromine-based biocides (necessary to control microbiological growth).[33,34] Orthophosphate (PO_4^{3-}), one of the degradation products, can cause calcium phosphate scale deposition in high-hardness-process waters. Knowledge of this susceptibility to oxidizers may help water system operators on decisions regarding which phosphonate additive to apply, at what dosage level, and for how long.

In this article, we present results on the oxidative degradation of AMP by a hypobromite-based biocide at two temperatures, 25°C and 43°C.

RESULTS AND DISCUSSION

Two different temperatures are tested, 25°C and 43°C, and results are summarized in Tables I and II and shown in Figures 2 and 3.

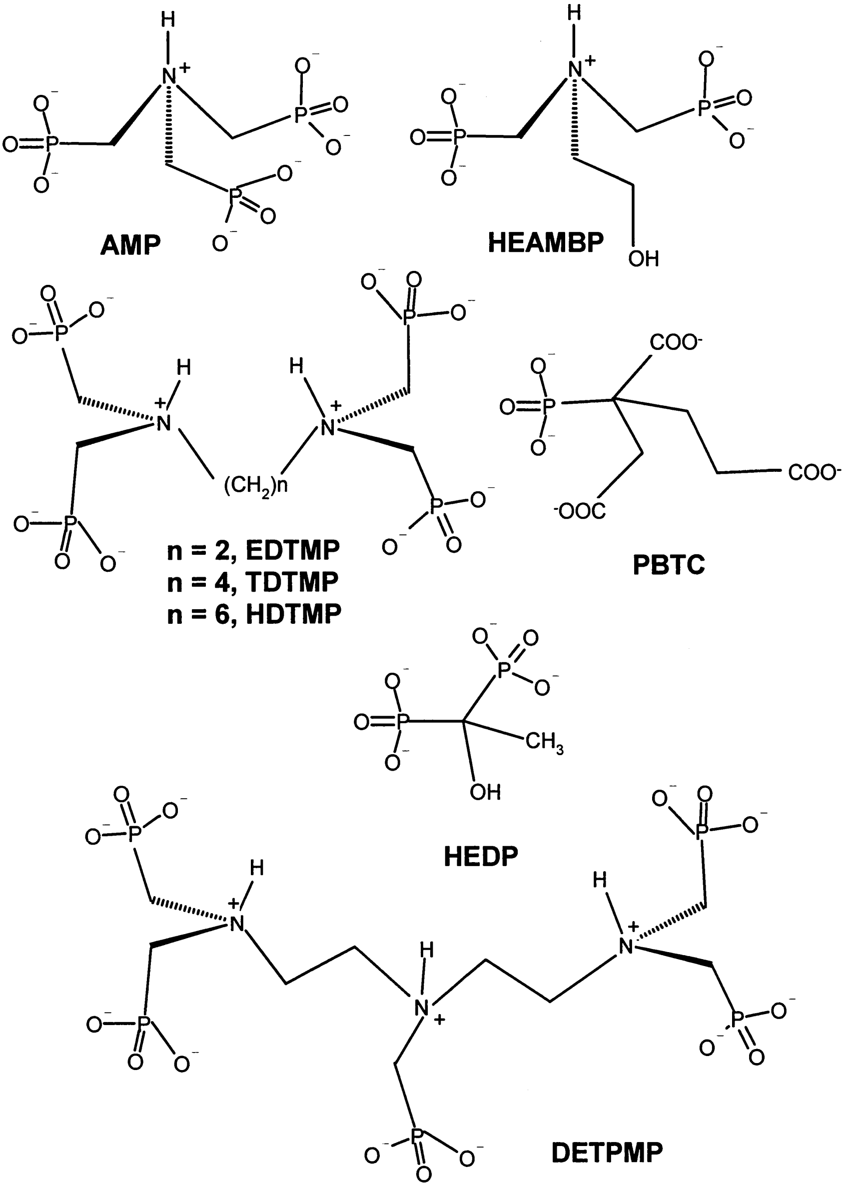

FIGURE 1 Chemical structures of some organophosphonate scale inhibitors. Abbreviations are as follows: HEABMP: 2-hydroxyethyl-amino-*bis* (methylenephosphonate), EDTMP: ethylene-diamine-*tetrakis*(methylenephosphonate), TDTMP: tetramethylenediamine-*tetrakis*-(methylenephosphonate), HDTMP: hexamethylenediamine-*tetrakis*(methylenephosphonate), and DETPMP: diethylenetriamine-*pentakis*(methylenephosphonate).

TABLE I Oxidative Decomposition of AMP at 25°C

Time (min)	o-PO$_4^{3-}$ (ppm)	Total Phosphorus (ppm)	Organic Phosphorus (ppm)	Free Halogen (ppm)	Total Halogen (ppm)	% Degradation of AMP
0	1.46	19.6	18.14			7
10	1.86	19.4	17.54			10
30	1.84	18.9	17.06			12
45	2.08	19.3	17.22	7.5	8.25	12
75	2.32	19.5	17.18			12
120	2.44	18.8	16.36			16
210	2.68	18.7	16.02			18
300	2.90	18.8	15.90			18
1350				2.75	2.75	
1740				2.0	2.25	
2760				1.25	1.25	
2820	3.70	20.9	17.2			19

The biocide is added in relatively large excess in order to “stress” the system in oxidant. It should be noted that in industrial cooling systems a residual of 0.5 to 1.0 ppm biocide is *maintained* at all times. However, overdose upsets are common phenomena and this is the reason why an exaggerated biocide dosage is selected in our studies.

AMP reacts with the biocide at room temperature immediately, producing ~1.5 ppm orthophosphate. AMP degradation continues rapidly, but it slowly reaches a plateau after 1000 min. Even after 50 h of reaction time, only 20% of AMP has decomposed. AMP reacts with the

TABLE II Oxidative Decomposition of AMP at 43°C

Time (min)	o-PO$_4^{3-}$ (ppm)	Total Phosphorus (ppm)	Organic Phosphorus (ppm)	Free Halogen (ppm)	Total Halogen (ppm)	% Degradation of AMP
0	1.44	19.0	17.56	13	12.25	7
10	3.44	18.8	15.36	11.25	10.5	17
30	3.44	18.8	15.36	8	9	17
45	3.00	21.0	18	7.25	8.75	15
75	3.93	18.9	14.97	6.5	6.5	20
120	4.0	19.3	15.3	5.5	6.5	20
240	4.22	19.1	14.88	4.75	5	21
360	4.50	19.1	14.6	3.25	4.25	23
1320	4.70	18.7	14	0.75	0.75	24
3060	4.80	19.2	14.4	0.50	0.50	24

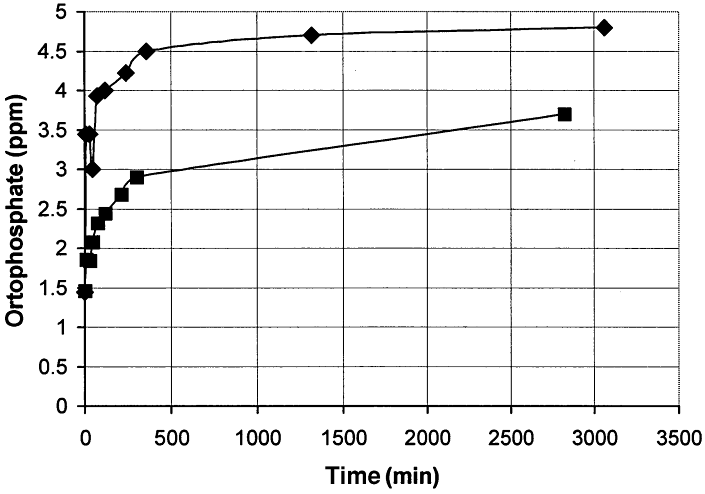

FIGURE 2 Reversion of AMP to orthophosphate as a function of time. Squares represent measurements at 25°C, whereas rhombs represent measurements at 43°C.

biocide to give an orthophosphate much more rapidly at 43°C than at 25°C due to faster kinetics of decomposition. An examination of Figure 3 reveals that organic phosphonate consumption is consistent with biocide consumption and orthophosphate production.

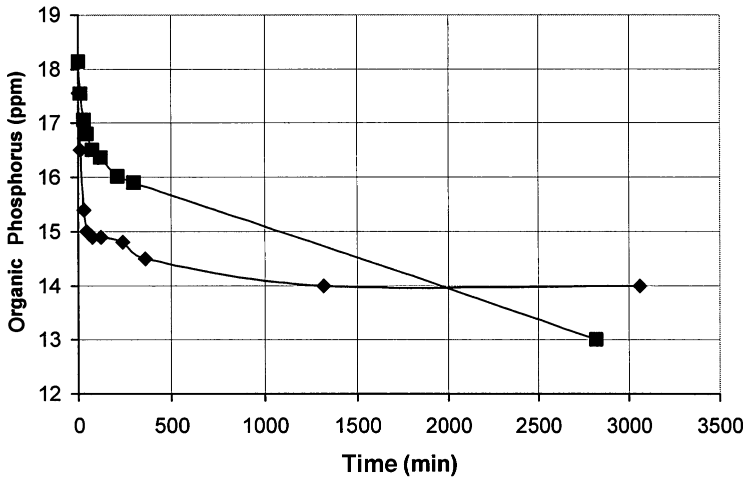

FIGURE 3 Degradation of AMP as a function of time. Squares represent measurements at 25°C, whereas rhombs represent measurements at 43°C.

Nowack and Stone have reported the degradation of AMP in the presence of O_2 and Mn^{2+}.[35,36] They proposed a radical mechanism that leads to the production of orthophosphate and iminobis(methylenephosphonate), that is similar to AMP but without the third methylenephosphonate arm.

The C—P bond has been considered to be very stable towards hydrolytic cleavage as well as oxidative and thermal decomposition.[37,38] On the other hand, rapid radical-based dephosphorylation of organophosphonates has been observed during biodegradation by *Escherichia coli*.[39] The results reported here agree with literarature examples that C—P bonds of aminopolyphosphonates are susceptible to rapid oxidative cleavage in the presence of oxidative biocides. Orthophosphate in our experiments is produced *only* by the C—P bond cleavage. We cannot draw direct conclusions about the cleavage of the C—N bond, because we did not measure possible byproducts of this reaction. However, the results based on organic phosphorus measurement shown in Figure 3 offer some useful clues. If only one C—N bond was cleaved (but not a C—P bond), the possible product would have been one methyl phosphonate molecule and one amino-bis-(methylenphosphonate) molecule. In the case of the cleavage of two C—N bonds (but not of any C—P bonds), the possible products would have been two methyl phosphonate molecules and one amino-methylenphosphonate molecule. Finally, if all three C—N bonds are broken (with no C—P bond rupture), the possible products would have been three methyl phosphonate molecules and one ammonia (most likely ammonium) molecule. In all three scenarios mentioned, the products are organic phosphonates that possess a P—C bond. Therefore, analytical measurements of an organic phosphate would have shown an unchanged level of organic phosphate since $t = 0$, *i.e.,* 20 ppm. However, the fact that organic phosphate measurements are dropping with time, together with the fact that orthophosphate is also produced, is convincing evidence that the C—P bond is ruptured.

At this point we cannot rule out a scission of the C—P bond without a rupture of the C—N bond. In such a case, orthophosphate and trimethylamine would have been the possible products. Trimethylamine detection experiments were not performed at this time.

We recently reported on the effects of a variety of oxidizing biocides on 2-phosphonobutane-1,2,4-tricarboxylate (PBTC).[40] PBTC is virtually immune to oxidative decomposition under the conditions tested. This property makes PBTC a commonly used phosphonate for scale-growth control in cooling-water applications.

Johnson and colleagues have reported on the decomposition of HEDP by ClO^-.[41] In general, HEDP is more sensitive to oxidation than AMP. This, however, cannot be rationalized based on the structures of the two

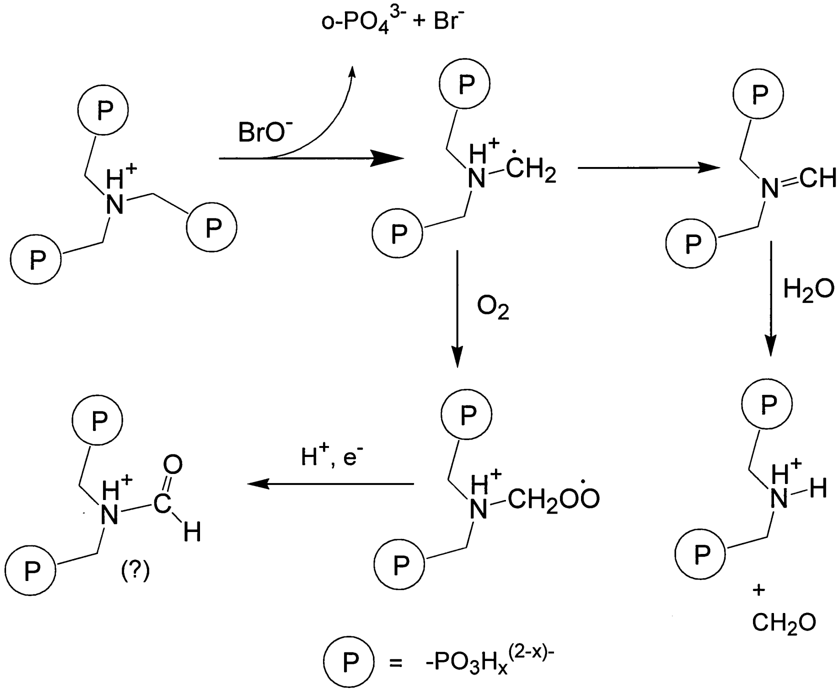

FIGURE 4 Possible oxidative degradation pathways for AMP in the presence of BrO^-.

phosphonates because they present profound structural differences (see Figure 1).

Taking into account the results described herein and others reported in the literature, possible degradation pathways of AMP can be proposed. These are shown schematically in Figure 4.

CONCLUSIONS/PERSPECTIVES

The principal conclusions of the present study can be summarized in that AMP is susceptible to the biocide tested herein. In addition, AMP is not degraded completely, but only to a ~20% level (at 25°C) and up to a ~25% level (at 43°C).

Published work on the environmental degradation behavior of AMP reported that, from results of several discontinuous and semicontinuous model tests, no evidence for biodegradability of AMP could be obtained.[42] More recent studies showed that AMP is transformed both in aerobically incubated natural and synthetic aqueous media and soils to degradation products. In the presence of microorganisms, AMP is slowly degraded to aminomethylene-monophosphonate. It was also concluded that AMP does not undergo significant degradation within the retention times of waste waters in sewage plants.[43,44] However, in surface waters a fast and quantitative abiotic degradation is expected, yielding the biodegradable aminomethylene-monophosphonate.

It is obvious that the quest for the "ideal" scale inhibitor is an ongoing endeavor. Prevention of inhibitor precipitation, coupled with control of its oxidative degradation, will allow for a better and more economical control of a chemical water-treatment program.

EXPERIMENTAL SECTION

Materials

Deionized water was used for all experiments. Materials were obtained from commercial sources. AMP (in acid form, 50% in water) was obtained from Solutia UK, Newport, United Kingdom, and was used as received with no further purification in order to better simulate conditions in real cooling-water systems. The hypobromite-based biocide is a proprietary product from the Nalco Company, Naperville IL, USA and was used as received.[45]

Phosphonate Stability Protocol

The following procedure is employed to study the decomposition chemistry of AMP by the biocide. A solution (500 mL) is prepared that contains Ca^{2+} (400 ppm as $CaCO_3$), Mg^{2+} (200 ppm as $CaCO_3$), HCO_3^- (300 ppm as $CaCO_3$), and AMP (20 ppm as actives). This solution is placed in a glass beaker and the pH is adjusted to 8.0. Then, an amount of biocide (7.5 mL of a 1000 ppm solution) is added with concomitant pH increase to ~8.6. This corresponds to 15 ppm biocide expressed as "ppm Cl_2." The pH finally is adjusted to 9.0 by the addition of a diluted, NaOH solution. The final solution is maintained under continuous stirring at ambient temperature. Samples (30 mL) are withdrawn at time intervals as follows: t = 0, 10 min, 30 min, 45 min, 75 min, 2 h, 3.5 h, 5 h, 22.5 h, 29 h, and 46 h. Sufficient quantity of the sample is withdrawn and used to test for residual free and total halogen by an established procedure.[46] The remainder is quenched with ascorbic acid (to deactivate remaining halogen by chemical reduction) and is analyzed for orthophosphate by the phosphomolybdate spectrophotometric method.[47]

This procedure is repeated, except that the reaction container is maintained at a constant temperature of 43°C in a thermostated water bath. Similar sampling procedures are employed.

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