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Silver ion-Quinalphos complexes: Kinetics and NMR Studies

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Abstract

Kinetics Studies have been carried out for the interaction between quinalphos and Ag^+ at pH 4.0, 7.0 and 10.0 and temperature 25°C. Kinetics data show that Ag^+ facilitated the hydrolysis of quinalphos, as the observed rate constants increased by adding silver ion. The extent of catalysis was greatly dependent on pH, as K_{obs} was found to increase with increasing pH.

In the second part of this research, Nuclear Magnetic Resonance (NMR) is the used instrument to investigate Ag^+ - quinalphos complexes. ^1H and ^{31}P NMR of quinlaphos (Q), ^1H of 2-hydroxyquinoxaline (HQ), and ^{31}P of O,O-diethyl phosphorothioic acid (PA) were recorded. ^1H and ^{31}P NMR results were consistent with the interpretation that binding between Ag^+ and quinalphos occurs primarily through two positions S and N.

Keywords: Kinetics, quinalphos, ^1H and ^{31}P NMR

I. Introduction

Due to the importance of hydrolysis of organophosphorus compounds, effect of metal ions on their degradation has been studied extensively [1-8]. Monovalent metal ions can catalyze the hydrolysis of organophosphate compounds containing sulfur. Satchell [7] reported that the hydrolysis of diethylthioethyl phosphate was catalyzed by Ag^+ and attributed this to the binding affinity of Ag^+ to the S atom. Monovalent silver ion is a type b metal; it is commonly found to be associated with both sulfur and nitrogen centres in a variety of ligands. Shen et al. [9] have studied the interaction between Ag^+ and human serum albumin (HSA) by using Raman Spectroscopy. Their results show that Ag^+ coordinates N as well as S atoms in HSA.

Other metal ions have the ability to accelerate the hydrolysis of OP compounds. As an example, in a very recent publication, we have reported that Hg^{2+} catalyzed the hydrolysis of Q at different pH values. In the same work, electrospray ionization mass spectrometry (ESI-MS) data support the idea that the catalysis is due to the coordination between Hg^{2+} and Q via S atom [10]. In another work, Wan and Wong have shown that presence of Hg^{2+} increased the hydrolysis rates of parathion methyl, Malathion, Fenitrothion, and Fenthion [5]. However, Hg^{2+} was found to have little effect on the hydrolysis of dichlorvos [5], as it does not contain a sulfur atom in its structure and it is postulated that catalysis by Hg^{2+} is associated with its strong affinity for S-containing ligands. In another study, we have investigated the hydrolysis of Q at high pH values (pH 11.8 – 13.6), but in the absence of metal ions. Activation parameters, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ were also determined [11].

Sulfur as well as nitrogen atoms in Q are available for binding transition and type b metal ions. As Ag^+ has affinity toward sulfur and nitrogen binding sites, it was chosen for investigation in this work.

II. Material and Methods

Quinalphos (Q), $C_{12}H_{15}N_2O_3PS$, 99.8 % and its hydrolysis product (2-hydroxyquinoxaline, HQ, $C_8H_6N_2O$, 99 %) were obtained from Crescent Chemicals, U.S.A. Both were of highest purity available and were used without further purification. A sample of the second product (O,O-diethyl phosphorothioic acid, PA) was prepared as described by Pieda [12]. The stock solutions of Q, HQ, and PA were prepared as described in ref 10. The purities of Q, HQ, and PA were verified by ESI-MS and nuclear magnetic resonance (NMR, 500 MHz).

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A. 1,4-Dioxane

1,4-Dioxane was purified by reflux over anhydrous stannous chloride for at least 5 hours followed by distillation to remove peroxide [13].

Silver nitrate

Silver nitrate ($AgNO_3$, Aldrich) solution (1.00 x 10^{-4} mol L^{-1}) was prepared by dissolving $AgNO_3$ (0.0170 g) in 1.00 L of DDW in a volumetric flask.

B. Kinetic Experiments

Experiments were performed in duplicate in clear glass vials (28 x 95 mm) sealed with Teflon-lined screw caps. Reaction solutions (25 mL) were continuously shaken using a shaker bath (Precision Scientific Company, Model 25) set at 100 oscillations / min, at 25oC. Reaction rate constants (k_{obs}) were determined in the absence (control) and presence of 0.1 mmol L^{-1} of Ag^+ at different pH values, 4.0, 7.0, and 10.0. The progress of the reactions was determined by following disappearance of Q as well as appearance of HQ product, using HPLC with UV-Visible detector. For quantitation, peak areas were measured using a wavelength of 240 nm. Details of HPLC technique can be found in ref. 14.

C. NMR Analysis

NMR experiments were performed on Q and its hydrolysis products (HQ and PA) in the absence and presence of the Ag^+ by using a Bruker 500 MHz NMR spectrometer. Both ^1H and ^{31}P NMR of Q, ^{31}P NMR of PA, and ^1H NMR of HQ were recorded in the absence and presence of different concentrations of Ag^+. Solutions of silver nitrate were prepared by dissolving $AgNO_3$ (Aldrich) in D_2O. All the NMR experiments were performed at 25ºC. It should be noted that due to the high concentrations of Ag^+, pH was not adjusted; pH of the Ag^+ solutions was ~ 4.

For the NMR analysis, in a 3 mL glass vial, 0.1 mL of Ag^+ solutions was added to 0.5 mL of Q, HQ, or PA stock solutions. In the absence of metal ion, 0.1 mL of D_2O was added to 0.5 mL of each stock solution in order to keep the experiments under the same conditions and to use it (D_2O) to lock the samples as well. Each mixture was then transferred immediately to an NMR tube using micropipette. The stock solutions of Q, HQ, and PA were prepared in dioxane with a concentration of 3.38 x 10^{-2}, 1.37 x 10^{-2}, and 3.38 x 10^{-2} mol L-1, respectively. The various combinations of Ag^+ and Q, HQ, or PA concentrations are recorded in the Tables 1 and 2. In the measurements of ^{31}P, a capillary tube containing H_3PO_4 (70 %) was placed into the NMR sample tube to use as reference. Thus ^{31}P chemical shifts were referenced to H_3PO_4 peak at 0.0 ppm, whereas, ^1H chemical shifts were referenced to the dioxane peak at 4.37 ppm. In this work, changes in the ^1H and ^{31}P chemical shifts of Q induced by the presence of various concentrations of Ag^+ were of our interest.

Table 1 Concentration of Q, HQ, and Ag^+ in each NMR tube

NMR tube No.	$[Ag^+]$ x 10^3 mol L^{-1}	[Q] x 10^2 mol L^{-1}	NMR tube No.	$[Ag^+]$ x 10^3 mol L^{-1}	[HQ] x 10^2 mol L^{-1}
0	0.00	2.82	0	0.00	1.14
1	0.88	2.82	1	0.35	1.14
2	4.42	2.82	2	1.77	1.14
3	21.7	2.82	3	8.64	1.14
4	108	2.82	4	43.3	1.14
5	542	2.82	5	217	1.14
6	1080	2.82	6	433	1.14
7	2170	2.82	7	867	1.14

Note that 2.17 mol L^{-1} is the maximum concentration of Ag^+ was used due to solubility limitation

Table 2 Concentration of PA and Ag^+ in each NMR tube

NMR tube Number	$[Ag^+]$ x 10^3 mol L^{-1}	[PA] x 10^2 mol L^{-1}
0	0.00	2.82
1	0.88	2.82
2	4.42	2.82
3	21.7	2.82
4	108	2.82
5	244	2.82
6	542	2.82
7	1080	2.82
8	2170	2.82

III. Results and Discussion

A. Kinetics Results

Hydrolysis of quinalphos was studied in the presence of the monovalent ion (Ag^+) at temperature 25°C and pHs 4.0, 7.0, and 10.0. A typical plot for the hydrolysis of Q in the presence of Ag^+ is illustrated in Figure 1. Kinetic results for the hydrolysis of Q in the absence of any metal ion are 6.75 ± 0.11 x $10^{-8,}$ 9.50 ± 0.17 x 10^{-8}, 17.6 ± 0.0 x 10^{-8} s^{-1} at pH 4.0, 7.0, and 10.0, respectively. It is clear that Ag^+ facilitated the hydrolysis of Q, as illustrated in Table 3. It is seen that the observed rate constants with added Ag^+ increased with increasing the pH. The error in k_{obs} values is expressed as the average deviation of two independent measurements.

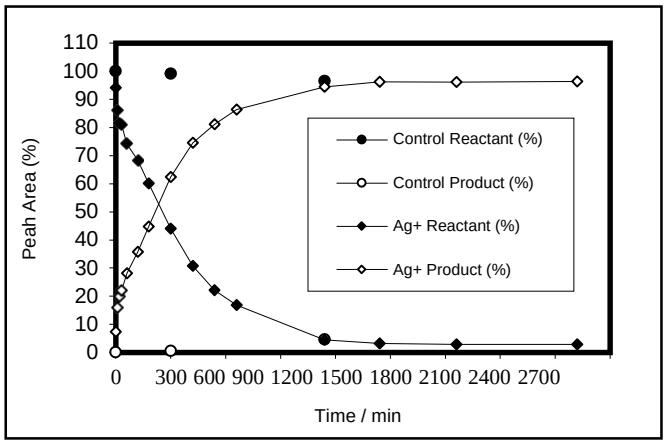


Figure 1 Typical plot showing effect of Ag^+ on the hydrolysis of quinalphos in unbuffered solution at pH 7.0

Table 3 Kinetic data for the hydrolysis of quinalphos in the presence of Ag^+ (1.0 x 10^{-4} mol L^{-1}) at 25°C

pH	kobs (dis) x 103, s-1	kobs (app.) x 103, s-1	kobs (avg) x 103, s-1
4.0	0.022 ± 0.000	0.021 ± 0.000	0.021 ± 0.000
7.0	0.038 ± 0.005	0.042 ± 0.004	0.040 ± 0.002
10.0	0.302 ± 0.000	0.300 ± 0.000	0.301 ± 0.000

k_{obs} (dis) = First order rate constant (disappearance of quinalphos, Q)
k_{obs} (app.) = First order rate constant (appearance of the product, HQ)
k_{obs} (avg) = Average first order rate constant

B. Effect of pH

Figures 1 and 2 and table 3 show clearly that Ag^+ catalyzed the hydrolysis of quinalphos at 25°C and pHs 4.0, 7.0, and 10.0. In addition, figure 2 illustrates also that hydrolysis of Q in the presence of Ag^+ is pH dependent. Thus, K_{obs} was found to increase with increasing pH (Figure 2 and Table 3). This is in agreement with our previous published results (in the case of Cu^{2+}); the observed rate constant increased with increasing pH [8]. Smolen and Stone [4] also found that rate constant increased with increasing pH during hydrolysis of parathion-methyl in the presence of Cu^{2+}. However, the opposite is true with Hg^{2+}, K_{obs} decreased with increasing pH [10]. Ag^+ exists as a full protonated aquo complex throughout the entire pH range. Increased rates at high pHs are a consequence of the greater nucleophilicity of OH^- compared to H_2O.

Table 3 show also that in the presence of Ag^+ the rate constant for the formation of HQ product is almost equal to that for the disappearance of Q. This correspondence between loss of Q and formation of HQ indicates that in the presence of Ag^+ the nucleophilic attack occurs at the phosphorus centre. In other words, any attack at the aliphatic carbon that would yield a different product is negligible.

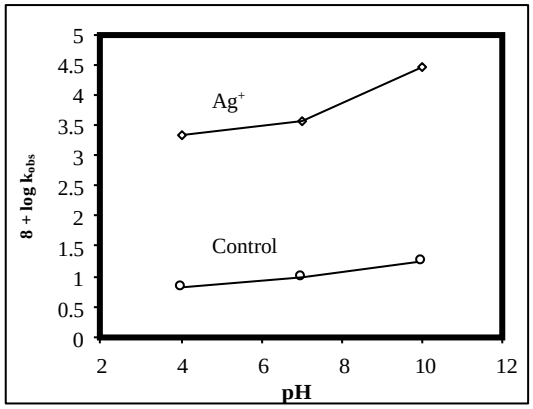


Figure 2 Effect of pH on catalysis of the hydrolysis of quinalphos (appearance of HQ)

C. NMR Results

The kinetic data show that quinalphos hydrolytic degradation is catalyzed by Ag^+. As the enhancement in the hydrolysis rates could be related to the interaction between the Ag^+ and the Q, NMR technique was chosen to investigate the possibilities of complexation between Q and Ag^+. In order to find out whether the coordination occur through N or S atom in Q, ^1H and ^{31}P NMR experiments were carried out to demonstrate the position of the interaction by recording ^1H of HQ as well as ^{31}P of O,O-diethyl phosphorothioic acid, PA.

The ^1H signal assignments, chemical shifts, and changes in chemical shift that arise from addition of Ag^+ to quinalphos are listed in Table 4 and illustrated in Figure 3. These clearly show that the ^1H signals are shifted upfield in the presence of Ag^+. In the presence of high concentrations of Ag^+ (ratio $[Ag^+]$ / [Q] > 0.77) the peaks are assigned to the hydrolysis products (HQ and PA); i.e. under these

conditions the quinalphos underwent complete hydrolysis. These data are omitted from Table 4.

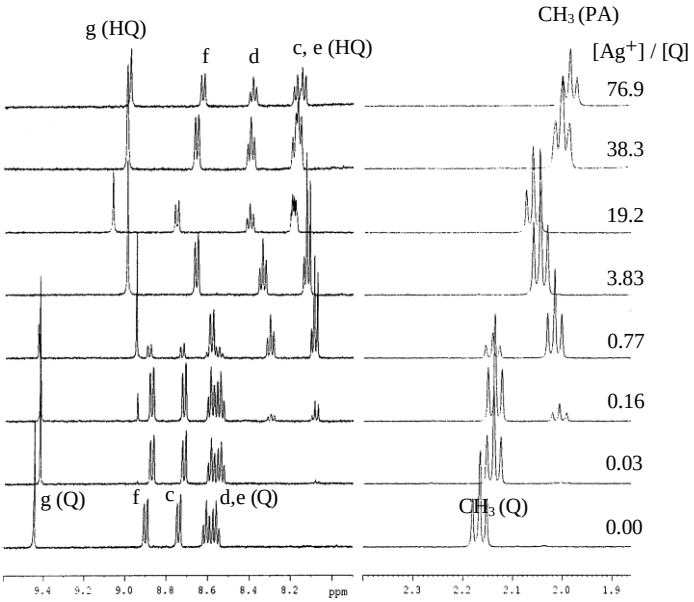


Figure 3 ^{1}H NMR spectra showing the chemical shift of quinalphos peaks in the presence

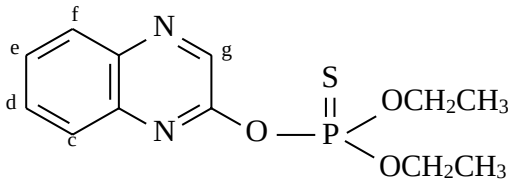


Table 4 ^{1}H NMR chemical shifts of quinalphos peaks in the absence and presence of various concentrations of Ag^{+}. [Q] = 2.82 x 10^{-2} mol L^{-1}

Exp. No.	[Ag] x 10^3 M	[Ag^+] / [Q]	δ of CH_3	Δδ	δ of $^1H^g$	Δδ	δ of $^1H^f$	Δδ
0	0.00	-	2.17	-	9.45	-	8.89	-
1	0.88	0.03	2.14	0.03	9.43	0.02	8.87	0.02
2	4.42	0.16	2.14	0.03	9.43	0.02	8.87	0.02
3	21.7	0.77	2.14	0.03	9.43	0.02	8.88	0.01

Table 4 Continued

Exp. No.	[Ag^+] x 10^3 M	[Ag^+] / [Q]	δ of $^1H^c$	Δδ	δ of $^1H^d$	Δδ	δ of $^1H^e$	Δδ
0	0.00	-	8.73	-	8.61	-	8.56	-
1	0.88	0.03	8.71	0.02	8.59	0.02	8.54	0.20
2	4.42	0.16	8.71	0.02	8.60	0.01	8.55	0.01
3	21.7	0.77	8.72	0.01	8.60	0.01	8.55	0.01

Table 4 and Figures 3 show that both the aliphatic (^{1}H of CH_3) and the aromatic peaks are shifted upfield. This shifting of the aliphatic and aromatic peaks could be in accord with Ag^{+} binding to both the S and N atoms.

Phosphorus-31 spectra of Q in the presence of various concentrations of Ag^{+} are illustrated in Figure 4. ^{31}P resonance shifts progressively to higher field with increasing Ag^{+} concentration (Table 5 Figure 5). Table 5 includes ^{31}P chemical shifts of Q (from [Ag^+] / [Q] ratio of 0.03 to 0.77) and of PA ([Ag^+] / [Q] > 0.03). At [Ag^+] / [Q] ratio > 0.77 the peak found in the spectra (Figure 4) belongs to the PA product because all quinalphos was hydrolyzed by high concentrations of Ag^{+} as shown also in Table 5.

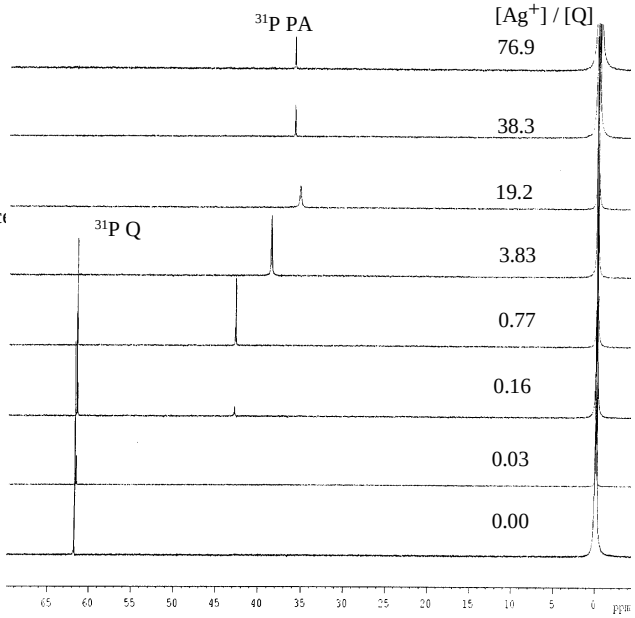


Figure 4 ^{31}P NMR spectra showing the chemical shift of quinalphos peak in the presence of various concentrations of Ag^{+} (after 1 h)

Table 5 ^{31}P NMR chemical shifts of quinalphos peak in the absence and presence of various concentrations of Ag^{+}. [Q] = 2.82 x 10^{-2} mol L^{-1}

Exp. No.	[Ag^+] x 10^3 M	[Ag] / [Q]	δ of ^{31}P	Δδ	(δ) of ^{31}P (PA product)
0	0.00	-	61.81	-	-
1	0.88	0.03	61.66	0.15	-
2	4.42	0.16	61.61	0.20	43.03
3	21.7	0.77	61.52	0.29	42.93
4	108	3.83	-	-	38.79
5	542	19.2	-	-	35.42
6	1080	38.8	-	-	36.08
7	2170	76.9	-	-	36.14

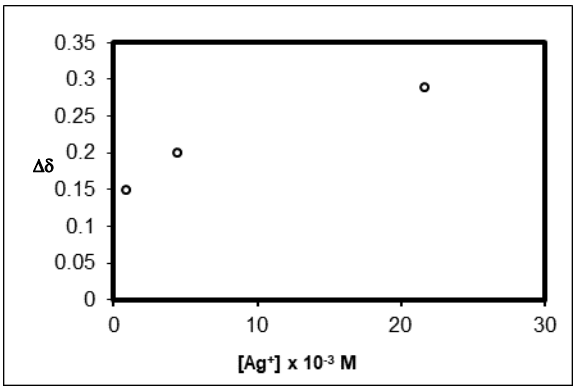


Figure 5 Effect of various concentrations of Ag^+ on the chemical shifts of the ^{31}P of quinalphos

Table 5 and Figures 4 and 5 show that as the concentration of Ag^+ increased, δ ^{31}P shifted more upfield. This probably indicates that Ag^+ binds to quinalphos *via* the S atom as well.

To confirm that Ag^+ binds to N in the substrate, ^1H NMR measurements were also conducted with HQ product in the absence and presence of different concentrations of Ag^+. ^1H peaks shifted downfield in the experiments 3 and 4 and then from experiment 5 to 7 the peaks shifted slightly upfield (Figure 6 and Table 6).

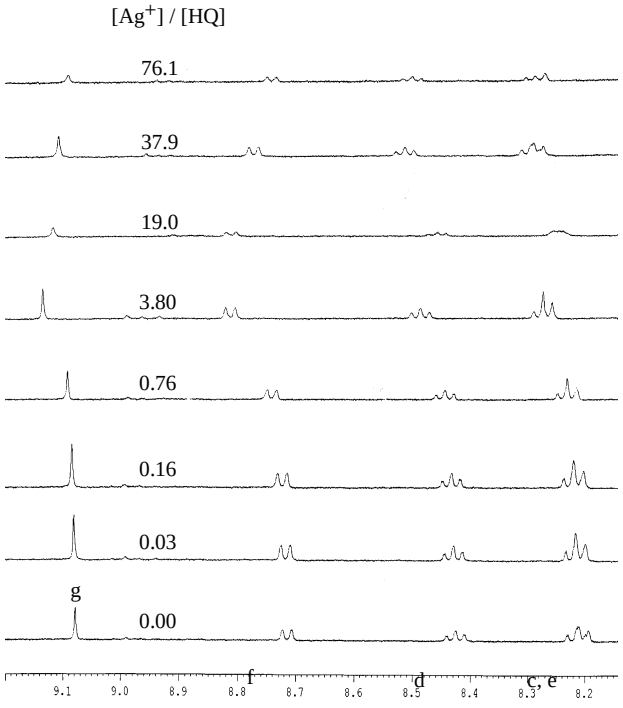


Figure 6 ^1H NMR spectra showing the chemical shift of 2-hydroxyquinoxaline peaks in the presence of various concentrations of Ag^+

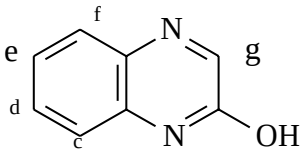


Table 6 ^1H NMR chemical shifts of 2-hydroxyquinoxaline peaks in the absence and presence of various concentrations of Ag^+. [HQ] = 1.14 x 10^{-2} mol L^{-1}

Exp. No.	[Ag^+] x 10^3 M	[Ag] / [HQ]	δ of H^g	Δδ	δ of H^f	Δδ
0	0.00	-	9.08	-	8.71	-
1	0.35	0.03	9.08	0.00	8.71	0.00
2	1.77	0.16	9.08	0.00	8.72	-0.01
3	8.64	0.76	9.09	-0.01	8.73	-0.02
4	43.3	3.80	9.14	-0.06	8.81	-0.10
5	217	19.0	9.12	-0.04	8.80	-0.09
6	433	37.9	9.11	-0.03	8.76	-0.05
7	867	76.1	9.08	0.00	8.73	-0.02

Table 6 Continued

Exp. No.	[Ag^+] x 10^3 M	[Ag] / [HQ]	δ of H^d	Δδ	δ of $H^{e,c}$	Δδ
0	0.00	-	8.43	-	8.21	-
1	0.35	0.03	8.43	0.00	8.21	0.00
2	1.77	0.16	8.44	-0.01	8.22	-0.01
3	8.64	0.76	8.45	-0.02	8.23	-0.02
4	43.3	3.80	8.49	-0.06	8.27	-0.06
5	217	19.0	8.46	-0.03	8.25	-0.04
6	433	37.9	8.51	-0.08	8.29	-0.08
7	867	76.1	8.50	-0.07	8.28	-0.07

NMR spectra of the second product, PA (Figure 7) show clearly how Ag^+ has the ability to shift the ^{31}P peak upfield, from 64.33 in the absence of metal ions to 37.24 ppm in the presence of the highest concentration of Ag^+ ([Ag^+] / [PA] ratio of 76.9).

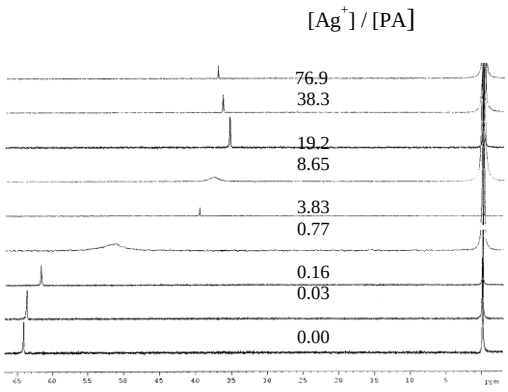


Figure 7 ^{31}P NMR spectra showing the chemical shift of O,O-diethyl phosphorothioc acid peak in the presence of various concentrations of Ag^+

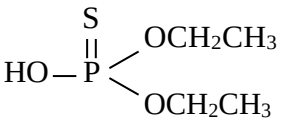


Table 7 ^{31}P NMR chemical shifts of O,O-diethyl phosphorothioic acid peak in the absence and presence of various concentrations of Ag^+ [PA] = 2.82 x 10^{-2} mol L^{-1}

Exp. No.	[Ag^+] x 10^3 M	[Ag^+] / [PA]	δ of ^{31}P	Δδ
0	0.00	-	64.33	-
1	0.88	0.03	63.93	0.40
2	4.42	0.16	61.88	2.45
3	21.7	0.77	51.44	12.89
4	108	3.83	39.69	24.64
5	244	8.65	37.90	26.43
6	542	19.2	35.41	28.92
7	1080	38.3	36.50	27.83
8	2170	76.9	37.24	27.09

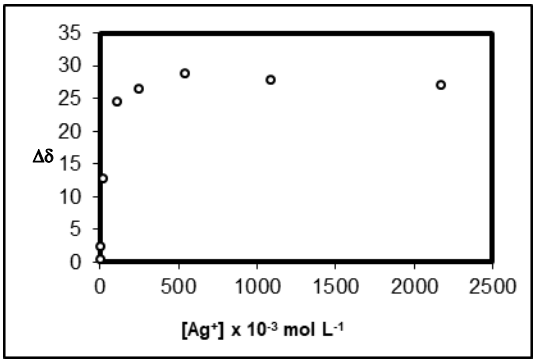


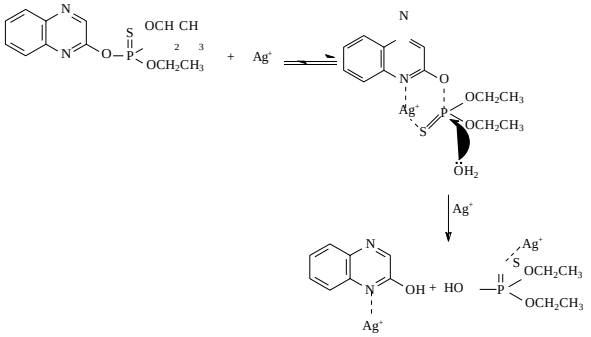
Figure 8 Effect of various concentrations of Ag^+ on the chemical shifts of the ^{31}P of O,O-diethyl phosphorothioic acid.

As shown in Table 7 and Figure 8, the significant change (~ 27.5 ppm) that attends complexation with Ag^+ in the chemical shift indicates clearly that Ag^+ binds to the PA through the S atom.

In fact, hydrolysis of Q was observed in the presence of Ag^+ (Figures 1, 2, and 3), which alone indicates that there is some kind of interaction between silver ion and the substrate. As supporting evidence, the aromatic ^{1}H peaks shifted somewhat upfield. As expected, ^{31}P shifts to a greater extent than ^{1}H CH_3 shifts. The unusual behaviour in the shifts of the ^{1}H peaks of HQ could indicate that Ag^+ binds to both N atoms in the molecule, as all the ^{1}H peaks are affected by presence of Ag^+ (see Table 6). Silver ion causes large ^{31}P NMR shifts in the upfield direction (Figures 7 and 8). The data obtained from ^{1}H NMR of Q and HQ and ^{31}P of Q and PA showed evidence of that Ag^+ binds strongly to Q through both N as well as S atoms. This is probably the underlying reason for Ag^+-catalyzed quinalphos hydrolysis.

Previous studies have shown that temperature [15,16], pH [15,17], and solvent [15] can affect the chemical shift of ^{1}H and ^{31}P. In the present study, all the NMR spectra were recorded at 25.0^{o}C and aqueous dioxane (83 % dioxane) is the solvent was used. On the other hand, in order to keep the metal ions in solution the pH was not adjusted to higher value, it was found to be ~ 4 for Ag^+ solutions. As the pH is similar in the presence of various concentrations of Ag^+, effect of pH on the ^{1}H and ^{31}P chemical shifts would be negligible.

In the present study, the NMR data has shown evidence that Ag^+ has the ability to bind to the quinalphos molecule through the S and N atoms. This leads to a hypothesis that a six membered chelate ring is formed as a transition state in the reaction as depicted in Scheme 1; this is similar to a suggestion first made (without direct evidence) by Mortland and Raman [3]. In this scheme, water is shown to be the nucleophile. In basic solutions the nucleophile would be OH^-, and it is also possible that the water or hydroxide could be coordinated to the metal ion catalyst. Note also that in Scheme 1, Ag^+ is shown as equally strongly coordinated to N and to S, i.e. Ag^+ has been placed equidistant from N and S, as Ag^+ has been shown to bind strongly to both moieties of quinalphos. It was stated in the experimental section that the pH could not be adjusted in the NMR experiments; that is due to the high concentrations of metal ions. Because the pH is low, the coordinated water molecules will not be deprotonated.



Scheme 1. Representative transition state for the Ag^+-catalyzed hydrolysis of quinalphos depicting the hypothetical formation of a six membered ring.

It is clear from the Scheme that catalysis of the hydrolysis of quinalphos is associated with the formation of a six membered ring involving interaction between Ag^+ and the possible binding sites within quinalphos. This bidentate chelation in scheme 1 increases the electrophilicity of the phosphorus centre and therefore facilitate the nucleophilic attack.

VI. Conclusion

Kinetics data for the interaction between quinalphos and Ag^+ at pHs 4.0, 7.0, and 10.0 and temperature 25^{o}C show clearly that Ag^+ significantly increased the hydrolysis reaction rates. Rate constant was found to increase with increasing pH.

^{1}H and ^{31}P NMR of Q, ^{1}H of HQ, and ^{31}P of PA were recorded in the presence of various concentrations of Ag^+ in order to figure out the coordination site between silver ion and Q. ^{1}H and ^{31}P NMR results show evidence of that Ag^+ binds strongly to both sites (N and S), as proved by ^{1}H of HQ, and ^{31}P of PA. This leads to the hypothesis that Ag^+ form a six membered ring with the parent compound (Q) in the transition state. This kind of complexation facilitates nucleophilic attack, enhancing hydrolysis rates.

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