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MnO2 and TiO2 Catalyzed the Hydrolysis of Quinalphos

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ABSTRACT

Hydrolysis of the organophosphorothioate ester, quinalphos (Q, O,O-diethyl O-quinoxaline-2-yl phosphorothioate) was investigated in the absence and presence of either MnO2 or TiO2 (heterogeneous catalysis) at 25oC and pH 4.0, 7.0, and 10.0. The hydrolysis products were 2-hydroxyquinoxaline (HQ) and O,O-diethyl phosphorothioic acid (PA). Hydrolysis of quinalphos was studied by determining the disappearance of Q as well as appearance of HQ product using HPLC with UV detection. At these pH values, MnO2 was found to exert a significant catalytic effect. TiO2 also facilitated the hydrolysis of Q, but only to a small extent..

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INTRODUCTION

Hydrolysis of organophosphorus (OP) compounds can be either catalyzed or inhibited by oxide surfaces such as MnO2, Al(OH)3, TiO2, etc. (heterogeneous process). In 1995, Baldwin et al. [1] investigated the hydrolysis of p-nitrophenyl phosphate (NPP) in the presence of different types of the same metal oxide (TiO2, anatase and rutile) and other (hydr)oxide materials as well such as Al2O3, and FeOOH, Fe2O3, and MnO2. They have reported that all these oxides were able to catalyze the hydrolysis of NPP. However, there are differences in the degree of enhancement of the rate of hydrolysis even among oxides of the same metal. For example, the rate constant for the hydrolysis of NPP in the presence of anatase is almost four times larger than that of rutile [1]. Although metal (hydr)oxides are important in chemical reactions, there are still only a limited number of studies available on the effect of (hydr)oxide materials surfaces on the hydrolysis of OP compounds [1-6]. Metal (hydr)oxides can catalyze the hydrolysis of OP compounds, but in other cases, they can inhibit them as well. Dannenberg and Pehkonen have found that Al(OH)3 acted as inhibitor for the hydrolysis of disulfoton at pH 5.7 and 8.5 [6]. Similarly, FeOOH was found also to inhibit the hydrolysis of thiometon at pH 5.7 and 8.5 [6]. In each case, the hydrolysis rate was compared to that for the substrate in (hydr)oxide-free solution. The authors suggested that the inhibition of hydrolysis by the (hydr)oxide materials is due to "blocking of the nucleophile by metal oxide surface or reduction of the substrate concentration in the water".

More recently, we have studied the hydrolysis of quinalphos at High pHs (11.8 - 13.6) and different temperatures (25o, 35o and 45oC). The rate constant was found to increase with increasing the pH as well as temperature. Our results were also extended to determine the activation parameters (ΔH‡, ΔS‡, and ΔG‡) [7].

The role of metal (hydr)oxides surfaces in catalyzing the hydrolysis of OP compounds has been proposed in some of the chemical literature [2-4,6]. Chelation between surface-bound metals and organic compounds may be necessary for catalysis to occur [2-4]. In this paper, effect of solid materials (MnO2 and TiO2) on the hydrolysis of quinalphos was examined.

MATERIALS AND METHODS

Quinalphos (Q, O,O-diethyl O-quinoxaline-2-yl phosphorothioate, C12H15N2O3PS, 99.8 %) and its hydrolysis product (2-hydroxyquinoxaline, HQ, C8H6N2O, 99 %) were

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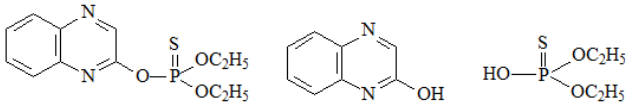
Esbata et al.

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, C4H11O3PS) was prepared as described in ref. 8. The stock solutions of quinalphos, 2-hydroxyquinoxaline, and O,O-diethyl phosphorothioic acid were prepared individually as illustrated in our recent previous publication 10. Standard solutions from each were prepared as needed, by serial dilutions of the stock solutions.

The purities of Q and its hydrolysis products, HQ and PA were verified by electrospray ionization mass spectrometry (ESI-MS) and nuclear magnetic resonance (NMR, 500 MHz). Structure of quinalphos (Q), 2-hydroxyquinoxaline (HQ), and O,O-diethylphosphorothioic acid (PA) is illustrated below.



(**Q**) (**HQ**) (**PA**)

Metal oxides

Titanium dioxide (primarily anatase, TiO2 Type P-25) was purchased from Degussa Corporation (Germany) and used as received.

Source of MnO2

Manganese dioxide (MnO2) was synthesized by slowly adding KMnO4 (Fisher) solution (400 mL; 0.8 mol L-1) that had been heated to 65oC to MnSO4 (Bakers analyzed) solution (300 mL, 1.6 mol L-1) that had been heated to 90oC [9]. The mixture was then kept at 90oC for 20 min. The resulting brown suspension was filtered and washed with ~ 2 L of hot DDW until the pink color (excess KMnO4) was removed. The product was resuspended in cold DDW and filtered again to remove excess electrolytes. This process was repeated until the conductivity of the filtrate was measured as 260 □S cm-1. After that, the MnO2 was placed on a watch glass, dried overnight at 100oC, ground, and kept in a sealed glass bottle [9].

Surface area measurements

In order to explore the reactivity of the oxides surfaces, it was required to know the surface area of each oxide. The surface area (S) of MnO2 and TiO2 was determined using N2 adsorption according to the multipoint BET method [10] using a Micromeritics instrument, Model ASAP-2010. Surface area of MnO2 and TiO2 were determined to be 171 and 47.6 m2 g-1, respectively.

Buffer solutions

The MOPS (3-[N-morpholino] propanesulfonic acid) (C7H15NO4S, SIGMA) buffer solution was prepared in DDW with a concentration of 1.00 x 10-2 mol L-1 and the pH was adjusted to exactly 7.00 by addition of NaOH (1.0 mol L-1) using a Chekmite pH-15 pH meter (Fisher Scientific).

A 1.00 x 10-2 mol L-1 solution of (4-[cyclohexylamino]-1-butanesulfonic acid) (CABS, C10H21NO3S, SIGMA) was prepared. NaOH (1.0 mol L-1) was added to adjust the pH to 10.0.

Unless otherwise noted, hydrolysis experiments were conducted in duplicate in 28 x 95 mm glass vials. An amount of a dried (TiO2 or MnO2) was added to the vial before introduction of the stock solution containing quinalphos. Control experiments were carried out under the same conditions of pH, temperature, and concentration of the substrate in order to follow hydrolysis in the absence of any metal oxides while heterogeneous experiments were carried out with the addition of 1.00 g L-1 of each oxide material (0.025 g in 25 mL). In every case, the concentration of quinalphos was 3.38 x 10-5 mol L-1. Solution pH was adjusted by adding very small amounts of acid (HCl, 1.0 mol L-1) or base (NaOH, 1.0 mol L-1). In order to minimize the possibility of contamination, analysis of quinalphos and product was carried out on one set of samples. A separate set was prepared in the same way and was used to monitor the pH over the extensive time period of the experiments. A Chekmite pH-15 pH meter (Fisher Scientific) was used for all pH measurements. Samples were continuously shaken using a shaker bath (Precision Scientific Company, Model 25) set at 100 oscillations / min, at 25oC. Vials containing TiO2 were wrapped with aluminum foil in order to prevent photochemical oxidation [2,11,12].

Both quinalphos and HQ product standards were always freshly prepared immediately before measurement of the unknowns by using the same concentration of quinalphos as the initial concentration in the hydrolysis experiments and a similar known concentration of the product. At each measurement time, the mean peak area was obtained from at least two injections.

Reaction of 2-hydroxyquinoxaline with oxide materials

In order to confirm whether the product adsorbs on the oxides surfaces, a separate set of experiments was performed in duplicate in glass vials (28 x 95 mm) with the addition of 1.0 g L-1 of each metal oxide in 3.36 x 10-5 mol L-1 of 2-hydroxyquinoxaline solution. The experiments were performed under the same conditions (temperature, pH, and shaking) as described in the previous section. The concentration of 2-hydroxyquinoxaline was determined at different intervals using the LC technique. Adsorption was determined by comparing the peak area of 2-hydroxyquinoxaline in supernatant solutions (after removing the oxides via centrifugation) with those in metal oxide free solutions (standard).

HPLC investigation of experimental conditions for determining Q and HQ

A Varian high-performance liquid chromatography (HPLC) was used in this study. It consisted of a Varian Star 9002 solvent delivery system and a Varian 9050 variable wavelength UV-Visible detector. Separation was performed with an Altech reverse-phase column, Platinum C–18 100 A, 5 □m particle

size, with 150 mm length and 4.6 mm diameter. An Altech guard column, 10 ?m, C–18 cartridge was used to protect the analytical column. At different time intervals, vials were withdrawn from the shaker bath and ~ 0.4 mL was taken for LC analysis using a gas tight syringe. Usually, where samples had been equilibrated in the presence of solid oxide materials, pre-injection centrifugation for 10 minutes at room temperature was done in glass centrifuge tubes using an ADAMS Physician Compact centrifuge (Becton Dickinson and Company, U. S. A). A Hamilton microliter gas tight syringe (10 ?L – 100 ?L) was used to deliver the clear sample into the LC injector port. For experiments where no solid was present, a similar aliquot of solution was periodically injected into the LC without prior centrifugation. A Rheodyne model 7125 syringe loading 20 ?L sample injector was used to load samples onto the column. For quantitation, peak areas were measured using a wavelength of 240 nm. It was necessary to first develop a proper procedure and conditions that allow both quinalphos and its hydrolysis product (2-hydroxyquinoxaline) to be followed during the hydrolysis experiments. From the UV/vis data (Figures 1 and 2), it was found that 240 nm is an appropriate wavelength that could be used to observe the concentration of both compounds. A mixture of acetonitrile and water in ratio 70:30 by volume was found to be the optimum mobile phase that gave baseline separation in minimum total retention time. The mobile phase was used with flow rate of 1.0 mL min-1. Acetonitrile (HPLC grade with purity of 99 %) was obtained from Aldrich. Using this mobile phase, the retention times (tR) for quinalphos and its hydrolysis product, 2-hydroxyquinoxaline were 6.5 and 2.5 min respectively.

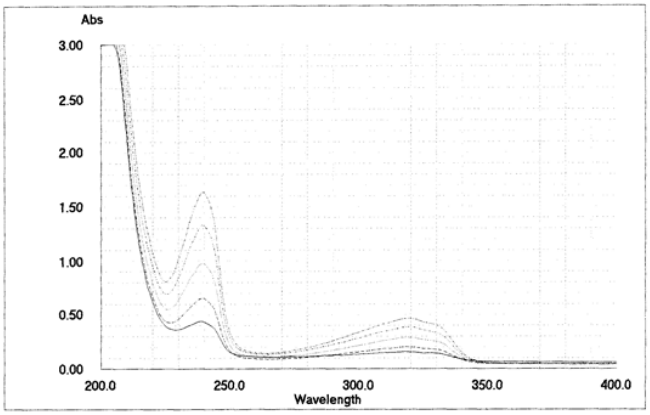


Figure 1 UV/Vis spectra at different concentrations (between 1.35 and 6.76 x 10-5 mol L-1) of quinalphos

Quinalphos (Q) and the hydroxyquinoxaline (HQ) hydrolysis product can be measured by HPLC with UV detection. On the other hand, neither O,O-diethyl phosphorothioic acid (PA), the SN2 (P) hydrolysis product, nor ethyl alcohol, the SN2 (C) hydrolysis product, can be detected by UV-vis absorption measurements at a convenient wavelength.

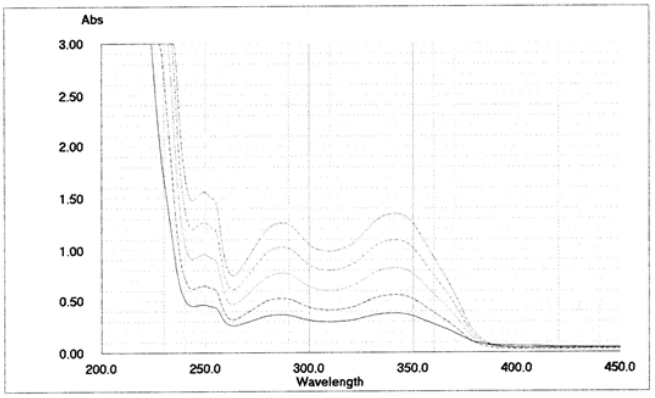
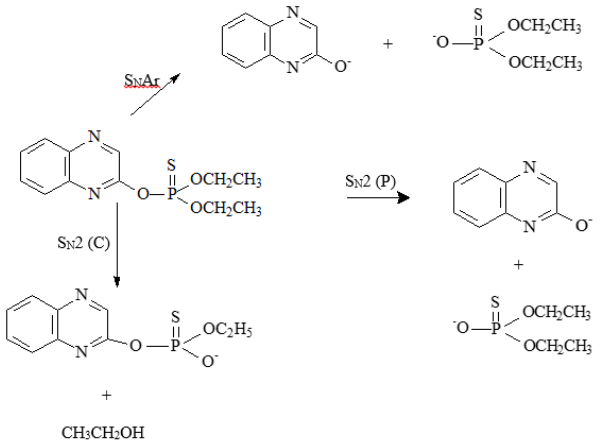


Figure 2 UV/Vis spectra at different concentrations (between 4.40 and 24.0 x 10-5 mol L-1) of 2-hydroxyquinoxaline.

Scheme 1 shows that there are three possible pathways for the hydrolysis of quinalphos, SN2 (P), SN2 (C), and SNAr. If the concentration of hydroxyquinoxaline product is equal to the concentration of parent compound lost, then the hydrolysis occurs via either the SN2 (P) or SNAr pathway, but not by the SN2 (C) pathway. If the concentration of the hydroxyquinoxaline product is less than that of parent compound lost, however, then the hydrolysis may also involve an SN2 (C) reaction. Where mass balance is not achieved in the presence of solid material, loss of the parent compound and / or product by adsorption is another possibility.



Scheme 1 Possible pathways for the hydrolysis of quinalphos

RESULTS AND DISCUSSION

Hydrolysis of Quinalphos

Hydrolysis experiments (control and in the presence of solid materials) were carried out in aqueous solutions with initial pH adjusted to 4.0, 7.0, and 10.0 and temperature 25oC. Under these conditions, the disappearance of Q as well as the appearance of the product (HQ) followed first order kinetics as evidenced by straight-line ln plots. Homogeneous (control) experiments were carried out to provide baseline information to evaluate the catalysis by solid oxides. These experiments

were carried out in unbuffered and buffered solutions as shown below.

Hydrolysis in unbuffered aqueous solutions

Hydrolysis of quinalphos in the absence of solid oxides catalysts was performed at 25oC in unbuffered aqueous solutions having pH 4.0, 7.0 and 10.0 for ~ 50 days. Rate constants (kobs) for both disappearance of Q and appearance of HQ are reported in Table 1. It can be seen from this table that the hydrolysis was found to be very slow throughout the pH range with half lives (disappearance of Q) 119, 84, and 46 days at pH 4.0, 7.0, and 10.0, respectively.

Hydrolysis in buffered aqueous solutions

From the pH measurements, it was found that for the experiments at pH 4.0, the pH had decreased by no more than 0.15 pH unit over the hydrolysis period, whereas with experiments at pH 10.0 and 7.0, the pH decreased from 10.0 to 7.9 ± 0.05, and from 7.0 to 5.3 ± 0.03. The decrease in pH is due to the consumption of -OH and / or the release of acidic species during hydrolysis. Due to the change in pH, it was also necessary to perform these experiments (at pH 7.0 and 10.0) in buffer solutions.

By using MOPS and CABS buffer solutions for the experiments respectively at pH 7.0 and at pH 10.0, the pH was maintained within ± 0.05 pH unit over the hydrolysis period. Results of these experiments are included in Table 1. These data show that the largest kobs was determined at pH 10.0, while the smallest kobs was found at pH 4.0. It can also be seen from the same table that kobs values for the appearance of HQ product are somewhat smaller than those for the loss of Q, except at pH 10.0 in buffer solution. This may be due to the formation of another product, as will be discussed below.

Table 1 Hydrolysis rate constants of quinalphos at 25oC in aqueous unbuffered and buffered solutions.

	pH	Buffer	Disappearance of Q k_{obs} x 10^8 (s^{-1})	Appearance of HQ **k_{obs} x 10^8 (s^{-1})**
Control (unbuffered)	4.0 7.0 10.0	- - -	6.75 ± 0.11 10.3 ± 0.3 6.83 ± 0.39	**5.06 ± 0.36** 4.31 ± 0.28 3.72 ± 0.33
Control (buffered)	7.0 10.0	MOPS CABS	9.50 ± 0.17 17.6 ± 0.0	**3.44 ± 0.08** 18.3 ± 0.0

The error in kobs values were expressed as the average deviation of two independent measurements.

Hydrolysis in the presence of solid oxides

Selection of solids

Affinity of the oxides (MnO2 and TiO2) for a number of chemicals including organic compounds makes them important in surface chemical reactions. As these oxides will potentially interact with OP compounds such as quinalphos, investigation of their effects on the hydrolysis of this kind of compounds can be important. Thus, MnO2 and TiO2 were selected in this study to examine how these oxides affect the hydrolysis of quinalphos.

Measurements of adsorption onto the solids

In order to make a clear comparison between the amount of quinalphos (Q) that had disappeared and the product (HQ) produced, it is necessary to know whether a portion of the reactant and/or product adsorbs onto the oxide materials. Measuring the sum of the concentration of Q and HQ in solution during the hydrolysis experiments was used for this purpose. In most cases, during hydrolysis the sum of the concentrations of Q and HQ was somewhat smaller than the initial concentration of the starting material, indicating that either Q or HQ, or both, were adsorbed on the oxides, or that an undetected product was also formed by reaction.

In order to determine the amount of HQ that adsorbs onto each oxide material, separate experiments were carried out in which the concentration of a 33.6 ±M of HQ in the presence of 1.0 g L-1 MnO2 or TiO2 was followed for about 2 weeks at pHs 4.0, 7.0, and 10.0 and 25oC. The amount of HQ adsorbed was determined by comparing the remaining amount of HQ in supernatant solutions with those in a standard, assuming that the difference represents the adsorbed amount. Table 2 show that the adsorption occurred on the surface of MnO2 is more than that on TiO2. It can be seen from this table also that adsorption of HQ onto the oxides at pH 7.0 and 10.0 in buffered solutions is very similar to its adsorption on the same oxides in unbuffered solution. The amount of HQ adsorbed was also normalized to each oxide surface area. The surface area of MnO2 and TiO2 was found to be 171 and 47.6 m2 g-1, respectively.

Table 2 Adsorption of 2-hydroxyquinoxaline onto MnO2 and TiO2 surfaces at 25oC.

Mineral (hydr)oxide	pH	HQ adsorbed (%) in unbuffer soln.	mol of HQ / m^2 of surface area	HQ adsorbed (%) in buffer soln.	mol of HQ / m^2 of surface area
MnO_2	4.0 7.0 10.0	25 23 21	4.91×10^{-8} 4.52×10^{-8} 4.13×10^{-8}	- 22 20	- 4.32×10^{-8} 3.93×10^{-8}
TiO_2	4.0 7.0 10.0	4 4 4	2.82×10^{-8} 2.82×10^{-8} 2.82×10^{-8}	- 3 3	 2.13×10^{-8} 2.13×10^{-8}

Table 2 shows that the maximum adsorption of HQ product occurred onto the surface of MnO2 (± 20 %). MnO2 has larger surface area than TiO2, and this is one factor that determines adsorptive capacity. As shown by the adsorption per unit area, however, there appears also to be an intrinsic component contributing to the increased retention. On TiO2,

however, adsorption of HQ was < 5 %. From these experiments, it can be assumed that the same ratio of HQ produced during the hydrolysis of quinalphos in the presence of these oxides might be adsorbed. Using this assumption, the total amount of HQ produced can be calculated.

The pH dependence for the adsorption of HQ onto the oxide surfaces was investigated at three pH values (4.0, 7.0, and 10.0). Figure 3 indicates that adsorption of HQ onto TiO2 is almost independent of pH, whereas a small difference in the case of MnO2, indicating a decrease with increasing pH.

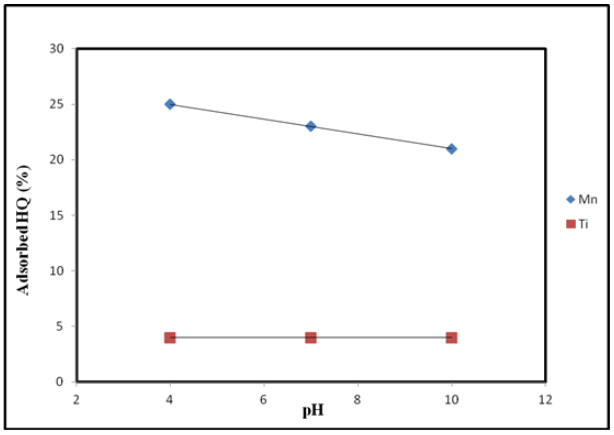


Figure 3 Effect of pH on the adsorption of 2-hydroxyquinoxaline onto MnO2 and TiO2

DISCUSSION

Electrostatic attraction and surface complexation are important processes in adsorption of organic compounds onto mineral surfaces [5,13,14]. In the case of HQ, it is unlikely that electrostatic attraction would contribute significantly to the adsorption process in the presence of the oxides. That is because at pH 4.0 and 7.0, HQ is neutral and TiO2 carry positive charge, whereas, MnO2 is negatively charged. At pH 10.0, both of the oxides and HQ are deprotonated and negatively charged, yet adsorption still occurs under these conditions.

The electron-donating heteroatoms, nitrogen, might play a role in the adsorption process of HQ onto the oxides surfaces. The role of N can be recognized from other studies. In one study, the ratio of adsorbed quinoline onto the surface of SiO2 was greater than that of adsorbed aminonaphthalene onto the same oxide. The authors suggested that this is due to N in quinoline [15]. Other researchers reported adsorption of 3,5,6-trichloro-2-pyridinol (hydrolysis product of the OP compound chlorpyriphos-methyl) onto the surface of FeOOH, Al2O3, TiO2 [4]. In another study, picolinic acid (hydrolysis product of phenyl picolinate) was found to adsorb onto the surface of FeOOH, TiO2, Fe2O3, Al2O3 and SiO2, whereas the phenol (the other hydrolysis product of phenyl picolinate) did not adsorb [2]. According to the published data, adsorption of HQ onto these oxides may be due to the interaction between a metal within the metal oxide surface and nitrogen.

It was not possible to independently measure the adsorptive behaviour of quinalphos because of the possibility that loss by hydrolysis was occurring at the same time. If it is assumed to behave in a similar manner to HQ, then essentially all of the loss by adsorption would have occurred within the first 40 h of the experiments. During this period, the extent of hydrolysis would be very small and therefore, for calculations of hydrolysis rate constants, data for the first 2 days was not used, and calculations were based on results from 50 h to 50 days. At all pHs in unbuffered and buffered solutions, adsorption of the parent compound was estimated to be between 1 and 5 %. The fact that there is some adsorption of the substrate onto different oxides prior to formation of the hydrolysis product was reported by different authors. In one study, Baldwin et al. studied the hydrolysis of p-nitrophenyl phosphate (NPP) in the presence of oxide surfaces. They have reported adsorption of NPP onto the surface of TiO2 [1] prior to appearance of the product. In another study, it was also reported that, during the hydrolysis of phenyl picolinate (PHP) in the presence of metal oxides, before the product could be observed, adsorption of PHP occurred onto the surface of FeOOH and TiO2 [2]. The authors suggested that the adsorption occurred through bidentate chelation between a surface-bound metal and the substrate (PHP) [2]. In another study, it was suggested that lack of adsorption is likely to be one of the reasons for the absence of catalytic activity by Al(OH)3 and Fe2O3 on phorate hydrolysis [16]. Stone and Torrents also suggested that surface catalysis occurs when the reactant adsorbs onto the surface [17].

Rate data based on loss of Quinalphos. In the presence of solid materials, MnO2 or TiO2, some limited catalysis of the hydrolysis of Q was observed. The first-order rate data are given in Tables 3 and 4. It should be noted, however, that neither the way of mixing nor the amount of the oxides were changed during the hydrolysis experiments. Other groups have shown that the change in the hydrolysis rate constant varies linearly with the amount of solid present [1,2]. Tables 3 and 4 show the degradation results for Q at pH 4.0, 7.0 and 10.0 and temperature 25oC. Though TiO2 had only limited impact on the hydrolysis of Q, MnO2 exhibited a somewhat greater catalytic effect in both unbuffered and buffered solutions. As an example, the half-life of quinalphos disappearance in the presence of MnO2 was 46 ⍰ 1, 50 ⍰ 1, and 33 ⍰ 0 days at pH 4.0, 7.0, and 10.0, respectively, compared with 119 ⍰ 2, 84 ⍰ 1, and 46 ⍰ 1 days in the absence of the solid materials. The data in Table 4 indicate also that at pH 7.0, TiO2 catalyzed the hydrolysis of quinalphos, but to a much smaller extent. For example, the half-life (loss of quinalphos) for the control (no solid material present) was 84 ⍰ 1 d compared to 70 ⍰ 2 d in the presence of TiO2. At pH 10.0, the rate constant in the presence of TiO2 (Table 4) is similar to that without solids present (control) and, therefore, this oxide appear to have very little effect on the hydrolysis of quinalphos at pH 10.0.

Table 3 Hydrolysis rate constants of quinalphos (33.8 ⍰M)

reflecting the effect of MnO2 and TiO2 surfaces at 25oC in unbuffered solutions.

Mineral (hydr)oxide	pH	Disappearance of Q k_{obs} x 10^8 (s^{-1})	Appearance of HQ k_{obs} x 10^8 (s^{-1})
Control (unbuffered)	4.0	6.75 ± 0.11	**5.06 ± 0.36**
	7.0	10.3 ± 0.3	4.31 ± 0.28
	10.0	6.83 ± 0.39	**3.72 ± 0.33**
MnO_2	4.0	17.6 ± 0.4	**17.9 ± 0.5**
	7.0	19.5 ± 0.9	12.8 ± 0.5
	10.0	15.0 ± 0.6	15.7 ± 0.6
TiO_2	4.0	7.92 ± 0.06	**5.58 ± 0.14**
	7.0	12.1 ± 0.6	4.69 ± 0.33
	10.0	10.3 ± 0.7	3.47 ± 0.50

The error in kobs values were expressed as the average deviation of two independent measurements.

Table 4 Hydrolysis rate constants of quinalphos (33.8 ?M) reflecting the effect of MnO2 and TiO2 surfaces at 25oC in buffered solutions.

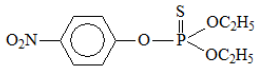
Mineral (hydr)oxide	pH	Disappearance of Q k_{obs} x 10^8 (s^{-1})	Appearance of HQ k_{obs} x 10^8 (s^{-1})
Control (buffered)	7.0	9.50 ± 0.17	**3.44 ± 0.08**
	10.0	17.6 ± 0.0	18.3 ± 0.0
MnO_2	7.0	16.1 ± 0.3	6.78 ± 0.25
	10.0	24.6 ± 0.1	24.0 ± 0.2
TiO_2	7.0	11.4 ± 0.3	5.03 ± 0.06
	10.0	19.8 ± 0.2	19.3 ± 0.1

The error in kobs values were expressed as the average deviation of two independent measurements.

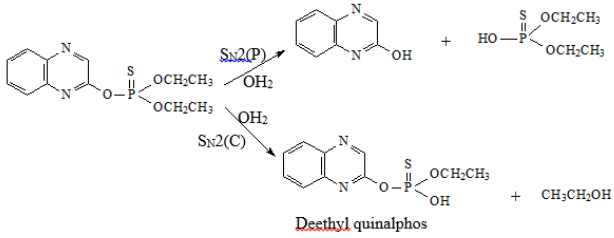
Rate data based on accumulation of 2-hydroxyquinoxaline

Kinetic data based on appearance of the HQ product are included in Tables 3 and 4. From both tables it can be seen that, in the presence of MnO2 at pH 4.0 and 10.0, the amount of Q lost is approximately equal to the HQ produced. However, with the same oxide at pH 7.0, kobs for HQ is smaller than that for Q. Tables 3 and 4 show also that in the presence of TiO2, the rate constants for the accumulation of HQ are smaller than those for the loss of Q, except for the hydrolysis at pH 10.0 in buffer solution. The difference can be explained by the formation of another product as will be discussed bellow. Discussion of the hydrolysis of quinalphos in the absence an presence of oxides.

As stated above, in aqueous unbuffered solutions the pH drifted to lower values during the hydrolysis of quinalphos (Q) in the absence and presence of oxides at pH 7.0 and 10.0; however, the use of MOPS (pH 7.0) and CABS (pH 10.0) buffer solutions maintained the pH close to its initial value. Because changing pH makes interpretation difficult, the discussion here will relate to the results at pH 4.0 (unbuffered) and at pH 7.0 and 10.0 (buffered), the three situations where pH remained relatively constant. In catalyst-free solution, in the case of disappearance of Q, kobs increased with increasing the pH (Table 3). This is typical for a hydrolysis rate, reflecting increases in the concentration of OH-, which is a better nucleophile than water. Table 3 shows also that at pH 4.0 and 7.0 there was a discrepancy between the amount of quinalphos lost and hydroxyquinoxaline (HQ) produced, in that the rate constants for appearance of HQ product at pH 4.0 and 7.0 are somewhat smaller than those for disappearance of Q. Likewise, in the presence of oxide materials at the same pHs (pH 4.0 and 7.0), Tables 3 and 4. The difference in the hydrolysis rates can be explained by formation of another product. Support for the formation of the second product is that a peak at retention time tR=1.3 min was observed in the chromatograms and it grew with time. This second product may be a deethyl quinalphos that forms via fission of the aliphatic C-O bond in an ethoxy side chain. The observation that a second product forms during hydrolysis at pH 4.0 and 7.0 but not at pH 10.0 is in agreement with Greenhalgh et al. [18] who observed that hydrolysis of fenitrothion at pH ? 7.5 occurs at both the aliphatic carbon (H3C-O bond fission) and at phosphorus (P-O bond fission). On the other hand, at pH ? 9.0, the reaction took place only by the SN2 (P) pathway. In a recent study, Balakrishnan et al. have also reported evidence of an SN2 (C) and SN2 (P) pathways during the reaction of fenitrothion with alkali metal ethoxides in ethanol [19,20]. Similarly, hydrolysis of parathion in sea and distilled water occurred via two pathways, dearylation (nucleophilic attack at the phosphorus) and dealkylation (nucleophilic attack at the aliphatic carbon) [21]. Thus, it is not surprising if the hydrolysis of quinalphos under some circumstances (low pH) follows both SN2 (P) and SN2 aliphatic C pathways (Scheme 3).



Parathion



Scheme 3 Possible pathways for the hydrolysis of quinalphos.

Several attempts were made to confirm this hypothesis: ESI-MS experiments, synthesis of the deethyl compound, and 1H and 31P NMR experiments on the quinalphos solution after the hydrolysis was expected to have occurred. In the ESI-MS experiments, aliquots of LC eluent were collected at a time corresponding to the retention of the unknown compound. It

was expected to observe a peak either in the positive ion mode at m/z 271 or in the negative ion mode at m/z 269. However, a peak at either of these m/z values was not observed. This may be because the sample was highly diluted by the mobile phase in the LC separation process. Synthesis of deethyl quinalphos was also attempted by following the method of Chambers and Matthews [22], as given below:

Potassium bromide (0.502 g) was dissolved in 25 mL ethanol to give a concentration of 0.169 mol L-1. Quinalphos (Crescent Chemicals, 1.200 g) was added to the KBr solution. The solution was then refluxed for 20 h, with stirring and argon was passed through the solution in order to ensure that any ethyl bromide was removed. To remove the ethanol, rotary evaporation (under reduced pressure) was used. The quinalphos residual was then dissolved in diethyl ether and any deethyl quinalphos salt was extracted into water. The aqueous phase was acidified with HCl (excess) and any deethyl quinalphos was extracted using diethyl ether. Diethyl ether was then removed by rotary evaporation. 1H and 31P NMR were recorded on the synthesized sample. 1H and 31P spectra were comparable to those of original Q.

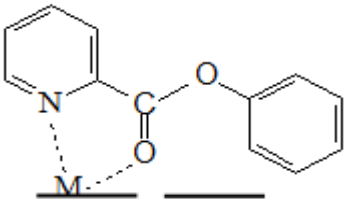
In the hydrolysis experiment, a solution of quinalphos with a concentration of 4.19 x 10-3 mol L-1was prepared in dioxane. 0.3 mL of D2O:DDW (20:80 %) was added to 0.4 mL of the Q solution, and the pH was adjusted to 4.0 with HNO3 (1.0 M). In order for hydrolysis to occur, this solution was left at room temperature for 20 days and then 1H and 31P NMR spectra were obtained. 1H NMR showed peaks comparable to those for quinalphos; 31P NMR (coupled with proton) showed that the phosphorus was coupled with the 4 protons of the two CH2 groups. The spectra were identical with those of the original Q, indicating that no hydrolysis had occurred. The question may be asked as to why no hydrolysis was observed after 20 days, whereas in the kinetic experiments significant hydrolysis took place over the same time period? Most likely, it is due to the high ratio of the cosolvent (dioxane), which is necessary in order to keep the water-insoluble quinalphos in solution. In the kinetic experiments, the dioxane concentration was approximately 0.1 %, whereas in the NMR experiments the dioxane content was 57 %; such a high ratio of cosolvent can be expected to affect the hydrolysis. For example, the concentration of dioxane has been found to affect the hydrolysis rate of another OP compound, phosmet [23]. With 3.8 % dioxane present, the rate constant (kobs) was 7.26 x 10-4 s-1, whereas when dioxane concentration increased to 34.6 %, kobs was found to decrease by approximately 16 fold [23].

In another study, it was also reported that increasing the ratio of cosolvent (methanol) in the case of parathion methyl significantly decreased the hydrolysis rate [3]. As the concentration of methanol increased, the catalytic effect of the (hydr)oxides also decreased. When the ratio of methanol was 0 % (v/v), after six days of hydrolysis the amount of parathion-methyl lost at pH 5.0 was 8 % in (hydr)oxides free solution and 58, 46, and 10 % in the presence of Al2O3, TiO2, and FeOOH, respectively. However, when the ratio of methanol increased as high as 25 %, the amount of parathion-methyl lost at the same pH for the same period of time was negligible (~ 7 % in the absence and presence of each of the (hydr)oxides) [3]. In the present study, the high concentration of dioxane was required in order to dissolve sufficient quinalphos for NMR measurements.

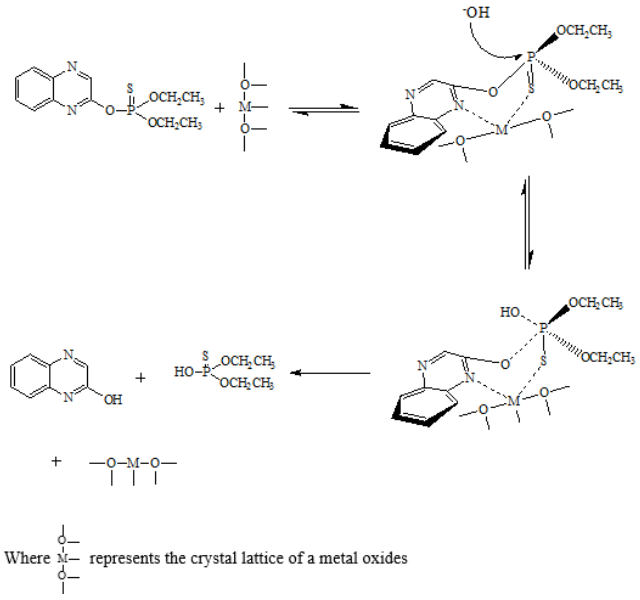
In summary, the rate of production of product HQ was smaller than the rate of loss of Q for hydrolysis at pH 4.0 and 7.0. This can be attributed to a competing SN2 (C) pathway through deethyl quinalphos could not be detected. On the other hand, for hydrolysis at pH 10.0, loss and production rates are the same. This aspect of hydrolysis behaviour has been observed in the case of other OP compounds. From Tables 3 and 4, one can conclude that the presence of MnO2 or TiO2 enhanced the hydrolysis of Q to only a limited degree. Of these oxides, MnO2 catalyzed the hydrolysis of Q to the greatest extent. In a study of the hydrolysis of p-nitrophenyl phosphate, Baldwin et al. [1] also found MnO2 to be the oxide with the greatest catalytic ability among FeOOH, Fe2O3, Al2O3, and TiO2. In that case all rates were, however, increased to a greater extent than occurred here with Q. So, 0.4 g L-1 of MnO2, TiO2, or FeOOH increased the rate constant by 380, 150, and 32 times, respectively relative to catalyst free solution [1]. Other published studies have not examined the effect of MnO2 on the hydrolysis of any of the OP compounds [2-4,6,16].

Similar limited enhancement associated with TiO2 as observed in the present study has also been reported by other groups on structurally similar OP compounds (Chlorpyrifos methyl thionate and diazinon). However, in these studies the experimental conditions are different (the ratio of solid to solution and nature of solvent). Examination of some compounds (Chlorpyrifos methyl thionate, Diazinon, Chlorpyrifos methyl oxon, Phenyl picolinate, Methyl picolinate) leads to a suggestion that a suitably placed N atom plays a role in the catalysis process. On the other hand, when N present in a different position (phenyl isonicotinate), catalysis by any of the (hydr)oxides was not observed. Chlorpyrifos methyl thionate and Ronnel are identical except for the presence of an N atom in the ring of Chlorpyrifos methyl thionate. The hydrolysis of the former was catalyzed by TiO2, FeOOH, and Al2O3, while rate of hydrolysis of the latter was unaffected by either FeOOH or Al2O3. This suggests that the N atom plays a role in the catalytic effect. Similarly, Compounds Chlorpyrifos methyl thionate and Chlorpyrifos methyl oxon are differentiated by having P = S and P = O groups, respectively. The effect of (hydr)oxides on the hydrolysis of Chlorpyrifos methyl thionate was observed to be much smaller than on Chlorpyrifos methyl oxon. Conversely, TiO2, FeOOH, and Al2O3 catalyzed the hydrolysis of Methyl parathion with P = S moiety, while the hydrolysis of Methyl Paraoxon with P = O moiety was enhanced only by TiO2. It is clear that the nature of both the solids and the substrate determined the catalytic effect but no explanation has been provided in the literature regarding the mechanisms of these effects.

pH may influence the catalytic effect through acid – base properties of either the substrate or the oxide material. In terms of the solid, protonation (pH < PZC) or deprotonation (pH > PZC) changes the surface charge, thus influencing the degree to which electrostatic attraction can occur. In the present study, the catalytic effect was usually greatest at low pH; this was especially evident in the case of MnO2. This trend was observed in the case of diazinon [6], but again there were contradictory results found in other cases. Indeed, one study [16] showed inhibition of hydrolysis of phorate in the presence of FeOOH or Al(OH)3 at pH 5.7, but catalysis at high pH. In another study [6], hydrolysis of disulfoton was also inhibited by the presence of FeOOH at pH 5.7, but catalyzed at high pH (pH 8.5). The inhibition was attributed to "blocking of the nucleophile by metal (hydr)oxide surface or reduction of the substrate concentration in the water" [6]. Nevertheless, there has been no clear systematic explanation of pH effects on catalysis by this class of solids. The question may arise, therefore, is what role might the oxides play in catalysis of the hydrolysis of quinalphos? The possible role of metal (hydr)oxides in catalysis of the hydrolysis of OP compounds has been suggested as the chelation between surface-bound metals and organic compounds may be necessary for catalysis to occur [2-4]. This implies that the nature of the metal atoms (Mn or Ti) in the oxides and the electron donating groups (N and S) in quinalphos are important in determining the potential strengths of chemical interaction. Accordingly, the ability of the metal oxide to form a surface complex with quinalphos determines its catalytic ability. By analogy to Compounds Chlorpyrifos methyl thionate, Diazinon, Chlorpyrifos methyl oxon, Phenyl picolinate and Methyl picolinate, quinalphos possesses an N atom suitably placed for chelation, which might play a role in catalysis of the hydrolysis of quinalphos by MnO2 and TiO2. Torrents and Stone [3] concluded that participation of N may be responsible for the high susceptibility of chorpyrifos methyl to catalysis by (hydr)oxides compared to Compounds Methyl parathion and Ronnel. In another study [2], chelation through the N heteroatom and the carbonyl oxygen was suggested for (hydr)oxide-catalyzed the hydrolysis of phenyl picolinate; the chelation was depicted in the following way:



Other researchers have also suggested a bidentate chelation in the case of diazinon [6]. In this case, the surface of the metal (hydr)oxide coordinates N as well as S. Quinalphos is similar to diazinon; it contains also two binding sites (N and S) and by analogy to diazinon, metal oxide surfaces may form complexes with Q facilitating hydrolysis as shown in the following Scheme.



Scheme 3 A proposed representative transition state for the surface-bound metal atoms catalyzed hydrolysis of quinalphos depicting the hypothetical formation of a six-membered ring.

Formation of this type of a six membered ring (chair or boat) favours backside attack by the nucleophile. Thus, again susceptibility of Q to catalysis by these oxides may be due to the formation of surface complex. However, the variation in the enhancement from one oxide to another is probably due to their difference affinities toward N and S. Katagi [24] summarized the role of metal (hydr)oxides in catalysis of the hydrolysis of OP compounds by writing " Although hydrolysis mechanisms on metal oxides surfaces seem very complex, some specific binding possibly via chelation would be essential". In another review article on the hydrolysis of OP compounds, Zhang and Pehkonen [25] said "The mechanism of surface catalyzed hydrolysis of OP compounds remains uncertain at this time, although many mechanisms have been proposed".

The influence of buffer on results obtained in rate measurements is an important issue. Recall that in unbuffered pH 7.0 and 10.0 solutions, pH declined as reaction proceeded. This is due to the consumption of hydroxide ions in the hydrolysis process. With a reduced concentration of this favoured nucleophile, the reaction rate was slower, as was observed in solutions with initial pH = 10.0 (both control and in the presence of each of the oxides). Surprisingly, kobs values in unbuffered solutions (in the absence and presence each of the oxides) with initial pH = 7.0 were larger than those at pH =10.0. There are two factors operating here: (1) the generally reduced rate of uncatalyzed reaction at low pH compared to high pH and (2) the enhanced catalytic effect at low pH compared to high pH. It would appear that, in these unbuffered systems, the second effect is dominant. On the other hand, in buffer solutions kobs in the absence and presence of solids was always greater at pH 10.0 than at pH 7.0.

CONCLUSION

Hydrolysis of quinalphos was investigated in the absence and presence of solid materials (MnO2 or TiO2) at pH 4.0, 7.0, and 10.0 and 25oC. In the absence of metal oxides, hydrolysis of Q was found to be very slow. Presence of either MnO2 or TiO2 enhanced the reaction rate. At pH = 4.00, kobs values for the disappearance of Q were 6.75, 17.6, and 7.92 x 10-8 s-1 in the absence and presence of MnO2 or TiO2, respectively. Catalysis of the hydrolysis of Q by MnO2 and TiO2 may be due to chelation between surface-bound metal atoms in the oxides and the possible binding sites in Q. This kind of chelation enhances the nucleophilic attack and thus accelerates the hydrolysis rate. MnO2 was found to be the most effective catalyst; this could be rationalized as it has higher affinity toward the possible binding sites in the substrate as shown by its ability to adsorb HQ.

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