

THE ROLE OF METAL (HYDR) OXIDES IN CATALYZING THE HYDROLYSIS OF QUINALPHOS

Abdelhamid A. Esbata ^{1*}, Erwin Buncel ², and Gary W. vanLoon ³

¹ Department of Chemistry, Faculty of Pharmacy, Misurata University, Misurata, Libya.

^{2,3} Department of Chemistry, Queen's University, Kingston, Ontario, Canada.

* aesbata@gmail.com

Abstract

Catalysis of the hydrolysis of the organ phosphorus compound, quinalphos (Q) by (hydr) oxides was studied at pH 4.0, 7.0, and 10.0, and at 25°C. FeOOH and Al(OH)₃ were the used solids for this research. Catalysis of quinalphos was followed by determining the disappearance of Q and the appearance of 2-hydroxyquinoxaline (HQ) product in the absence and presence of (hydr) oxides using HPLC with UV detector. Under these conditions, both hydroxides (FeOOH and Al(OH)₃) have catalyzed the hydrolysis of quinalphos. In this study, FeOOH was found to be the best catalyst at the used pHs. It is apparent that at pH 10.0, K_{obs} for disappearance of Q is almost equal to that for the appearance of HQ, which indicates that hydrolysis of Q at pH 10.0 follows S_N2 (P) pathway. On the other hand, at pH 4.0 and 7.0, hydrolysis of Q may have followed two pathways, S_N2 (P) and S_N2 (C), as K_{obs} for producing HQ is smaller than that for loss of Q.

Keywords: Hydrolysis; FeOOH; Al(OH)₃; Quinalphos; Adsorption.

Introduction

(Hydr)oxide materials have the ability to catalyze the hydrolysis of organ phosphorus (OP) compounds (heterogeneous catalysis). Baldwin et al, 1995 obtained good results for the hydrolysis of p-nitro phenyl phosphate by using Al₂O₃, Fe₂O₃, and FeOOH as (hydr)oxides catalysts, while Esbata et al, 2017 used MnO₂ and TiO₂ and found that both (hydr)oxides facilitate the hydrolysis of Q. Moreover, Smolen and Stone, 1998 have reported that FeOOH and Al₂O₃ have catalyzed the hydrolysis of Chlorpyrifos methyl thionate. FeOOH and Al₂O₃ were found to facilitate the hydrolysis of Chlorpyrifos methyl oxon too (Smolen and Stone, 1998). Dannenberg and Pehkonen, 1998 stated that diazinon catalyzed by the same (hydr)oxides (FeOOH and Al₂O₃). In another study, Fe₃O₄ @ MOF-2 also found to enhance the degradation of diazinon (Sajjadi et al 2019).

In other cases, however, metal (hydr)oxides can inhibit the hydrolysis of OP compounds. For instance, Dannenberg and Pehkonen, 1988 have found that Al(OH)₃ acted as inhibitor for the hydrolysis of disulfoton at pH 5.7 and 8.5. Similarly,

FeOOH was found to inhibit the hydrolysis of thiometon at pH 5.7 and 8.5 (Dannenberg and Pehkonen, 1998). In each case, the hydrolysis rate was compared to that for the substrate in (hydr)oxide-free solution. They have 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”.

Recently, we have studied the hydrolysis of quinalphos in the presence of copper (Esbata et al, 2018) and mercury (Esbata et al, 2020) at different pH values and at 25°C. Both metal ions catalyzed the hydrolysis of Q. In another work, we have also investigated the hydrolysis of quinalphos at High pHs (11.8 - 13.6) and different temperatures (25°, 35° and 45°C). The rate constant was found to increase by increasing the pH and temperature.

The mechanism of metal (hydr)oxides surfaces in catalyzing the hydrolysis of OP compounds has been proposed in some literature such as Smolen and Stone, 1998; Dannenberg and Pehkonen, 1998; Torrents and Stone, 1991; and Torrents and Stone, 1994. Chelation between surface-bound metals and organic compounds may be necessary for catalysis to occur (Smolen and Stone, 1998; Torrents and Stone, 1991; and Torrents and Stone, 1994).

In this work, (hydr)oxides were prepared to investigate whether the compounds of our interest adsorb onto these (hydr)oxides or not, and to show how these solids affect the hydrolysis rates of quinalphos.

Materials and Methods

Quinalphos (Q), 99.8 % and its hydrolysis product (2-hydroxyquinoxaline, HQ, 99 %) were obtained from Crescent Chemicals, U.S.A. Both were of the highest purity available so they were used without further purification. A sample of the second product (O, O-diethyl phosphorothioic acid, PA) was prepared as described by Piedad, 2001. The stock solutions of Q, HQ, and PA were prepared as described by Esbata et al, 2020. 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). The structure of quinalphos (Q), 2-hydroxyquinoxaline (HQ), and O, O-diethyl phosphorothioic acid (PA) is illustrated below.

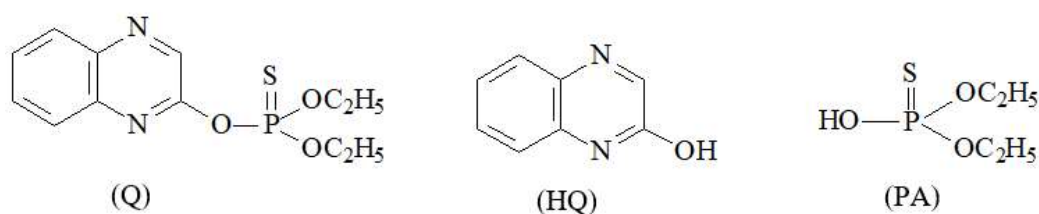


Figure (1): Chemical Structure of Q, HQ, and PA.

Water

Distilled de-ionized water (DDW) was used for the preparation of all aqueous solutions and for the preparation of the HPLC mobile phase.

Acetonitrile

Acetonitrile (HPLC grade with purity of 99 %) obtained from Aldrich was used for preparing the HPLC mobile phase.

Sodium Hydroxide Solution (NaOH)

NaOH solution (1.00 mol L^{-1}) was prepared by dissolving a weighed quantity of NaOH pellets (Aldrich Chemical Company) in DDW and filling the volumetric flask (1.00 L) to the mark. The concentration of the NaOH solution was then determined by its titration against potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$, Aldrich), and using phenolphthalein as an indicator (Harris and Tochtvil, 1981).

Metal (Hydr)Oxides

Goethite

Goethite (FeOOH) was synthesized by using the method of Atkinson i.e. by adding 200 mL of 2.5 mol L^{-1} potassium hydroxide (KOH, Aldrich) to 825 mL of 0.15 mol L^{-1} ferric nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (CALEDON laboratories), the final resulting pH was 11.8. The flocculent precipitate was allowed to age for 24 hours in a 60°C oven. The rust brown precipitate of goethite was dialyzed in cellulose tubing using DDW (Atkinson et al., 1967). The DDW was changed 2-3 times daily for 3 days, while the water was stirred using a Teflon-coated magnetic stir bar. The goethite was then dried, ground, and kept in a sealed glass bottle.

Aluminium (Hydr)Oxide or Hydroxylumina

Amorphous aluminium hydroxide ($\text{Al}(\text{OH})_3$) or hydroxylumina was prepared by dissolving 50.0 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (BDH) in 200 mL of DDW. The solution was

hydrolyzed with NaOH ($\sim 4.00 \text{ mol L}^{-1}$) (Aldrich) until a white precipitate formed, and the precipitate was then allowed to age overnight at room temperature (Sha'ato et al, 2000). The resulting white precipitate of aluminium hydroxide was dialyzed using the same method described above for goethite i.e. dried at 110°C for 24 hours, ground, and kept in a sealed glass bottle.

Surface Area Measurements

Surface area (S) of FeOOH and $\text{Al}(\text{OH})_3$ was determined by using N_2 adsorption according to the multipoint BET method (Brunauer et al, 1938) using a Micrometrics instrument, Model ASAP-2010. Surface areas of FeOOH and $\text{Al}(\text{OH})_3$ were 57.9, and $329 \text{ m}^2 \text{ g}^{-1}$, respectively.

Buffer Solutions

3-[N-Morpholino] Propanesulfonic Acid (MOPS)

The MOPS ($\text{C}_7\text{H}_{15}\text{NO}_4\text{S}$, SIGMA) buffer solution was prepared in DDW with a concentration of $1.00 \times 10^{-2} \text{ mol L}^{-1}$ 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).

4-[Cyclohexylamino]-1-Butanesulfonic Acid (CABS)

A $1.00 \times 10^{-2} \text{ mol L}^{-1}$ solution of CABS ($\text{C}_{10}\text{H}_{21}\text{NO}_3\text{S}$, SIGM) was prepared by using DDW as a solvent. NaOH (1.0 mol L^{-1}) was added to adjust the pH to 10.0.

Hydrolysis experiments were conducted in duplicate in 28 x 95 mm glass vials. An amount of a dried (FeOOH or $\text{Al}(\text{OH})_3$) was added to the vial before introducing 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 (hydr)oxide while heterogeneous experiments were carried out with the addition of 1.00 g L^{-1} of each (hydr)oxides material (0.025 g in 25 mL). In every case, the concentration of quinalphos was $3.38 \times 10^{-5} \text{ mol L}^{-1}$. 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; it 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 25°C .

Both quinalphos and HQ product standards were always freshly prepared immediately before the measurement of the samples 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 (Hydr)Oxides

In order to confirm whether the product adsorbs on the (hydr)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 (hydr)oxide in 3.36 x 10⁻⁵ mol L⁻¹ of 2-hydroxyquinoxaline solution. The experiments were performed at pH 4.0, 7.0, and 10.0 and at 25°C. 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 (hydr)oxide free solutions (standard).

HPLC Technique

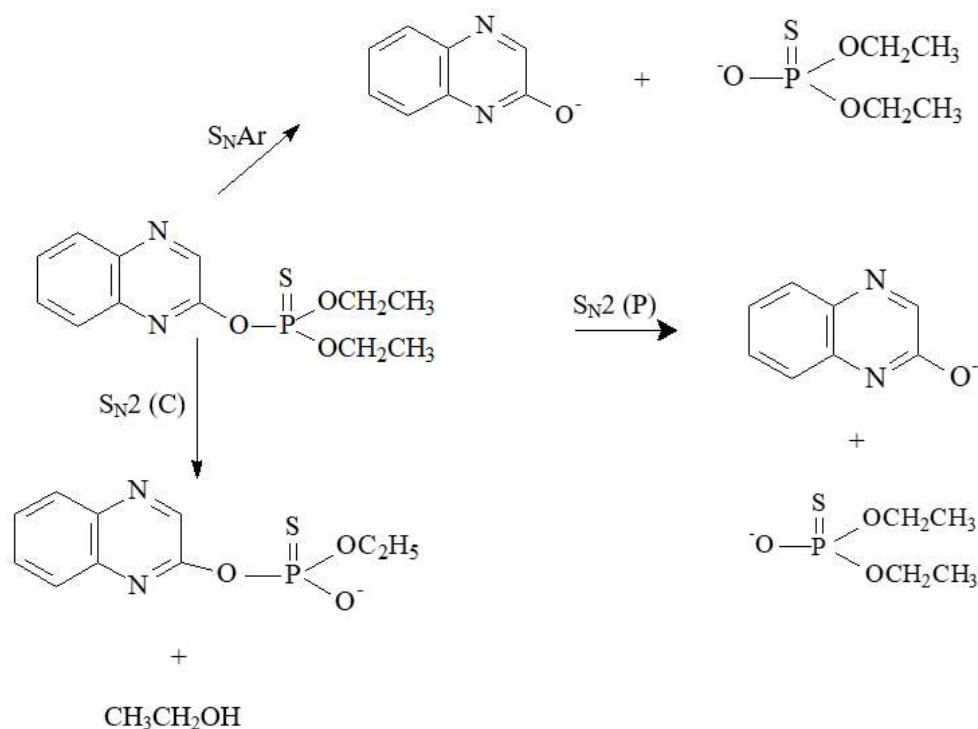
A Varian high-performance liquid chromatography (HPLC) was used in this study. It consisted of a Varian Star 9002 solvent delivery system and a Varian 9050 variable wavelength UV-Visible detector. Separation was performed with an Altech reverse-phase column, Platinum C-18 100 A, 5 µm particle size, with 150 mm length and 4.6 mm diameter. An Altech guard column, 10 µm, 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. Where samples were equilibrated in the presence of solid (hydr)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 µL – 100 µL) was used to deliver the clear sample into the LC injector port. For the 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 µL sample injector was used to load the 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, which allow both quinalphos and its hydrolysis product (2-hydroxyquinoxaline), to be followed during the hydrolysis experiments. From the UV/vis results, it was found that 240 nm is an appropriate wavelength that could be used to observe the concentration of both compounds (Esbata et al, 2017). 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. Using this mobile phase, the retention times (t_R) for quinalphos and its hydrolysis product, 2-hydroxyquinoxaline were 6.5 and 2.5 min respectively.

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 S_N2 (P) hydrolysis product, nor ethyl alcohol, the S_N2 (C) hydrolysis product, can be detected by UV-vis absorption measurements at a convenient wavelength. Scheme 1 shows three possible pathways for the hydrolysis of quinalphos namely S_N2 (P), S_N2 (C), and S_NAr. If the concentration of hydroxyquinoxaline product is equal to the concentration of the parent compound lost, then the hydrolysis occurs *via* either the S_N2 (P) or S_NAr pathway, but not by the S_N2 (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 S_N2 (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

Selection of Solids

Affinity of FeOOH and Al(OH)₃ for organic compounds makes them important in surface chemical reactions. As these (hydr)oxides interact with OP compounds such as quinalphos, investigating their effects on the hydrolysis of such compounds can be important. Thus, FeOOH and Al(OH)₃ were selected to examine how they affect the hydrolysis of quinalphos.

Determination of Adsorption onto the (Hydr)Oxides

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 (hydr)oxides. For this purpose, the sum of the concentration of Q and HQ in solution during the hydrolysis experiments was measured. In most cases, the sum of the concentrations of Q and HQ during hydrolysis was somewhat smaller than the initial concentration of the starting material, which indicates that either Q or HQ, or both, were adsorbed on the (hydr)oxides, or that an undetected product was also formed by the reaction.

In order to determine the amount of HQ that adsorbs onto each (hydr)oxide material, separate experiments were carried out in which the concentration of a 33.6 μM of HQ in the presence of 1.0 g L⁻¹ FeOOH or Al(OH)₃ was traced for about 2 weeks at pHs 4.0, 7.0, and 10.0 and 25°C. 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 1 shows that the adsorption occurred on the surface of FeOOH is more than that on Al(OH)₃. It can be also seen from this table that the adsorption of HQ onto these (hydr)oxides at pH 7.0 and 10.0 in buffered solutions is very similar to its adsorption on the same (hydr)oxide in unbuffered solution. The amount of HQ adsorbed was also normalized to each (hydr)oxide surface area.

Table (1): Adsorption of 2-Hydroxyquinoxaline onto FeOOH and Al(OH)₃ Surfaces at 25°C.

Mineral (hydr)oxide	pH	HQ adsorbed (%) in unbuffered soln.	mol of HQ / m ² of surface area	HQ adsorbed (%) in buffered soln.	mol of HQ / m ² of surface area
FeOOH	4.0	4	2.32×10^{-8}	-	-
	7.0	3	1.74×10^{-8}	3	1.74×10^{-8}
	10.0	3	1.74×10^{-8}	2	1.16×10^{-8}
Al(OH) ₃	4.0	3	3.06×10^{-9}	-	-
	7.0	2	2.04×10^{-9}	2	2.04×10^{-9}
	10.0	2	2.04×10^{-9}	2	2.04×10^{-9}

Table (1) shows that adsorption of HQ onto these (hydr)oxides is almost independent of pH. From these results, it can be assumed that the same ratio of HQ produced during the hydrolysis of quinalphos in the presence of these (hydr)oxides might be adsorbed.

Discussion of the Adsorption

Electrostatic attraction and surface complexation are important processes in the adsorption of organic compounds onto mineral surfaces (Hochella and White, 1990; vanLoon and Duffy, 2010; and Stone, 1989). In the case of HQ, it is unlikely that electrostatic attraction would contribute significantly to the adsorption process in the presence of the (hydr)oxides (Esbata et al, 2017).

The electron-donating heteroatoms, nitrogen, might play a role in the adsorption process of HQ onto the (hydr)oxide surfaces. The role of N can be recognized from other studies. In one study, the ratio of the adsorbed quinoline onto the surface of SiO₂ was greater than that of the adsorbed aminonaphthalene onto the same oxide. The authors suggested that this is due to N in quinoline (Zachara et al, 1990). Other researchers reported adsorption of 3,5,6-trichloro-2-pyridinol (hydrolysis product of the OP compound chlorpyrifos-methyl) onto the surface of FeOOH and Al₂O₃ (Smolen and Stone, 1998). In another study, picolinic acid (hydrolysis product of phenyl picolinate) was also adsorbed onto the surface of FeOOH, Fe₂O₃, and Al₂O₃, whereas the phenol (the other hydrolysis product of phenyl picolinate) did not adsorb (Torrents and Stone, 1991). According to the published data, adsorption of HQ onto these (hydr)oxides may be due to the interaction between a metal within the metal (hydr)oxide surface and nitrogen.

Although the effect of pH on the adsorption of HQ onto these (hydr)oxides was small, in each case the adsorption was slightly larger under acidic conditions (pH 4.0) Table (1). This is in agreement with the results reported by Smolen and Stone who found that the adsorption of 3,5,6-trichloro-2-pyridinol (TCHP) on FeOOH, Al₂O₃, TiO₂ was the greatest under acidic conditions (pH 5.7) (Smolen and Stone, 1998).

It was not possible to measure independently the adsorptive behaviour of quinalphos because of the possibility that loss by hydrolysis was occurring at the same time. If it were 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 the 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 (hydr)oxides

prior to formation of the hydrolysis product was reported by different authors. In one study, it was reported that during the hydrolysis of phenyl picolinate (PHP) in the presence of metal (hydr)oxide, before the product could be observed, adsorption of PHP occurred onto the surface of FeOOH. The authors suggested that the adsorption occurred through the bidentate chelation between a surface-bound metal and the substrate (PHP) (Torrents and Stone, 1991). In another study, lack of adsorption is likely to be one of the reasons for the absence of catalytic activity by $\text{Al}(\text{OH})_3$ and Fe_2O_3 on phorate hydrolysis (Hong and Pehkonen, 1998). Other researchers also suggested that surface catalysis occurs when the reactant adsorbs onto the surface (Huang et al, 1995).

Hydrolysis of Quinalphos

Homogeneous hydrolysis (absence of solid materials) was investigated in aqueous solutions at pHs 4.0, 7.0, and 10.0 and temperature 25°C. Control (Homogeneous) experiments were carried out to provide baseline information to evaluate the catalysis by solid (hydr)oxides. Under these conditions, the disappearance of Q as well as the appearance of HQ product followed first order kinetics as evidenced by straight-line \ln plots. These experiments were carried out in unbuffered and buffered solutions as shown below.

Hydrolysis in Unbuffered and Buffered Aqueous Solutions

Hydrolysis of quinalphos in the absence of (hydr)oxides was performed at 25°C in unbuffered and buffered aqueous solutions having pH 4.0, 7.0 and 10.0 for ~ 50 days. In unbuffered solutions, experiments at pH 4.0, the pH had decreased by ~ 0.15 pH unit over the hydrolysis period. On the other hand, with experiments at pH 7.0 and 10.0, the pH decreased to 5.3 and 7.9, respectively. Due to the change in pH, it was necessary to perform these experiments (at pH 7.0 and 10.0) in buffer solutions. In fact, the decrease in pH was due to the consumption of OH^- and / or the release of acidic species during hydrolysis. Table 2 illustrates the results of the disappearance of Q and appearance of HQ. It is clear from this table that the hydrolysis was found to be very slow in unbuffered and buffered aqueous 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 presented in Table 2. These data show that the largest k_{obs} is at pH 10.0, while the smallest k_{obs} is at pH 4.0. It can also be seen from the same table that k_{obs} 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 (2): Hydrolysis Rate Constants of Quinalphos At 25°C.

	pH	Buffer	Disappearance of Q $k_{\text{obs}} \times 10^8 \text{ (s}^{-1}\text{)}$	Appearance of HQ $k_{\text{obs}} \times 10^8 \text{ (s}^{-1}\text{)}$
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
Control (buffered)	7.0	MOPS	9.50 ± 0.17	3.44 ± 0.08
	10.0	CABS	17.6 ± 0.0	18.3 ± 0.0

The error in k_{obs} values were expressed as the average deviation of two independent measurements.

Hydrolysis in The Presence of (Hydr)Oxides

Rate Data Based on Disappearance of Quinalphos

Hydrolysis of Q data in the absence and presence of solid (hydr)oxides, FeOOH and Al(OH)₃ are given in Tables (3) and (4). It is clear that some catalysis of the hydrolysis of Q was observed. For example, at pH 7.0, FeOOH and Al(OH)₃ Table (4) catalyzed the hydrolysis of quinalphos, the half-life (loss of quinalphos) for the control (no solid material present) is 84 ± 1 d compared to 68 ± 1 and 71 ± 2 d in the presence of FeOOH and Al(OH)₃, respectively.

It should be noted, however, that neither the way of mixing nor the amount of the (hydr)oxide was changed during the hydrolysis experiments. Other groups showed that the change in the hydrolysis rate constant varied linearly with the amount of solid present (Atkinson et al., 1967; Esbata et al., 2018).

Table (3): Hydrolysis Rate Constants of Quinalphos (33.8 µM) Reflecting the Effect of FeOOH and Al(OH)₃ Surfaces at 25°C in Unbuffered Solutions.

Mineral (hydr)oxide	pH	Disappearance of Q $k_{\text{obs}} \times 10^8 \text{ (s}^{-1}\text{)}$	Appearance of HQ $k_{\text{obs}} \times 10^8 \text{ (s}^{-1}\text{)}$
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
FeOOH	4.0	7.69 ± 0.14	6.58 ± 0.25
	7.0	13.4 ± 0.7	5.50 ± 0.06
	10.0	11.9 ± 0.1	3.50 ± 0.08
Al(OH)₃	4.0	7.86 ± 0.17	6.19 ± 0.11
	7.0	13.0 ± 0.8	3.97 ± 0.36
	10.0	10.8 ± 0.8	4.00 ± 0.11
The error in k_{obs} values were expressed as the average deviation of two independent measurements			

Table (4): Hydrolysis Rate Constants of Quinalphos (33.8 μM) Reflecting the Effect of MnO_2 and TiO_2 Surfaces at 25°C in Buffered Solutions.

Mineral (hydr)oxide	pH	Disappearance of Q $k_{\text{obs}} \times 10^8 \text{ (s}^{-1}\text{)}$	Appearance of HQ $k_{\text{obs}} \times 10^8 \text{ (s}^{-1}\text{)}$
Control (buffered)	7.0	9.50 ± 0.17	3.44 ± 0.08
	10.0	17.6 ± 0.0	18.3 ± 0.0
FeOOH	7.0	11.8 ± 0.2	4.53 ± 0.83
	10.0	18.9 ± 0.3	18.6 ± 0.2
Al(OH)₃	7.0	11.2 ± 0.4	3.33 ± 0.06
	10.0	18.2 ± 0.3	17.8 ± 0.2
The error in k_{obs} values were expressed as the average deviation of two independent measurements			

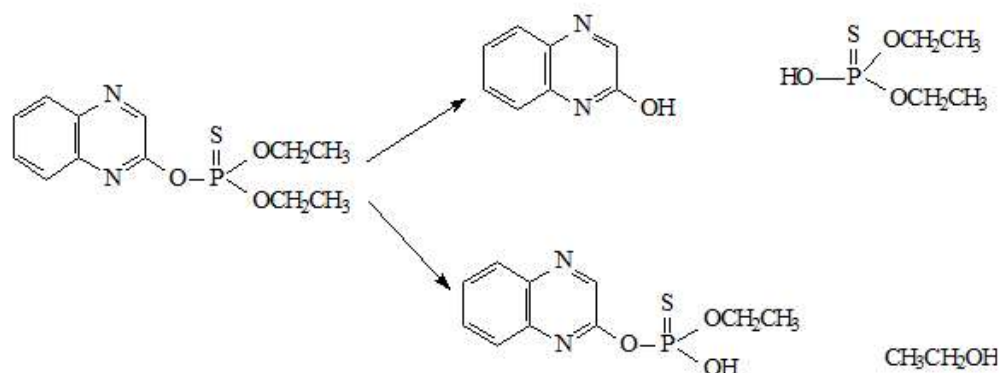
Rate Data Based on Appearance Of 2-Hydroxyquinoxaline

Tables (3) and (4) illustrate the observed rate constants based on the appearance of HQ product. From Table (3), it can be seen that, in the absence and presence of either FeOOH or Al(OH)₃ at pH 7.0 and 10.0, the quantity of HQ produced is smaller than that of Q lost. Similar behaviour was observed in buffered solutions at pH 7.0. However, in buffered solutions at pH 10.0, k_{obs} for Q lost was approximately equal to the HQ produced Table (4). The difference can be attributed to the formation of another product as will be discussed below.

Discussion of the Hydrolysis of Quinalphos

As the pH decreased during the hydrolysis of quinalphos (in unbuffered solutions) in the absence and presence of (hydr)oxides at pH 7.0 and 10.0, it was necessary to use buffer solutions (MOPS and CABS) to maintain 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, Table (3)) and at pH 7.0 and 10.0 (buffered, Table (4)), the three situations where pH remained relatively constant. In the absence of (hydr)oxides (disappearance of Q), k_{obs} increased with increasing the pH (Tables (3) and (4)). This is typical for a hydrolysis rate, reflecting increases in the concentration of OH⁻, which is a better nucleophile than water. The results also show that there was a discrepancy between the amount of quinalphos lost and hydroxyquinoxaline (HQ) produced at pH 4.0 Table (3) and 7.0 Table (4). 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 (hydr)oxides 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 $t_R=1.3$ min was observed in the chromatograms and it grew with time. This second product may be the 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 results published by other researchers who observed that hydrolysis of fenitrothion at $\text{pH} \leq 7.5$ occurs at both the aliphatic carbon ($\text{H}_3\text{C-O}$ bond fission) and at phosphorus (P-O bond fission). On the other hand, at $\text{pH} \geq 9.0$, the reaction took place only by the $\text{S}_{\text{N}}2(\text{P})$ pathway (Greenhalgh et al, 1980). In another study, it was also reported an evidence of an $\text{S}_{\text{N}}2(\text{C})$ and $\text{S}_{\text{N}}2(\text{P})$ pathways during the reaction of fenitrothion with alkali metal ethoxides in ethanol (Balakrishnan et al, 2001). 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) (Weber, 1976). Thus, it is not surprising if the hydrolysis of quinalphos under some circumstances (low pH) follows both $\text{S}_{\text{N}}2(\text{P})$ and $\text{S}_{\text{N}}2$ aliphatic C pathways (Scheme (2)).



Scheme (2): $\text{S}_{\text{N}}2(\text{P})$ and $\text{S}_{\text{N}}2(\text{C})$ 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 ^{31}P NMR experiments on the quinalphos solution after the hydrolysis was expected to have occurred. ESI-MS and ^1H and ^{31}P NMR experiments and their results were reported in our previous publication (Esbata et al, 2017). Synthesis of deethyl quinalphos was performed by following the method of Chambers and Mathews (Chambers and Matthews, 1977).

In summary, the production rate 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 the competing $\text{S}_{\text{N}}2(\text{C})$

pathway through deethyl quinalphos could not be detected. On the other hand, for hydrolysis at pH 10.0, loss and production rates were 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 FeOOH and Al(OH)₃ enhanced the hydrolysis of Q. In another work, we have found that TiO₂ facilitated the hydrolysis of Q, but only to a small extent, whereas, MnO₂ was found to exert a significant catalytic effect (Esbata et al, 2017). In a study of the hydrolysis of p-nitrophenyl phosphate, Baldwin and his coworkers also found MnO₂ to be the oxide with the catalytic ability among FeOOH, Fe₂O₃, Al₂O₃, and TiO₂. Therefore, the 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 (Baldwin et al, 1995). FeOOH and Al(OH)₃ were reported to enhance other OP compounds (Chlorpyrifos methyl thionate and diazinon). However, in those studies the experimental conditions were different (the ratio of solid to solution and nature of solvent).

Examination of some compounds (Chlorpyrifos methyl thionate and Chlorpyrifos methyl oxon (Smolen and Stone, 1998), Diazinon (Dannenberg and Pehkonen, 1998), Phenyl picolinate (Torrents and Stone 1991), Methyl picolinate (Torrents and Stone, 1994) leads to a suggestion that a suitably placed N atom plays a role in the catalysis process. On the other hand, when N was presented in a different position (phenyl isonicotinate), catalysis by any of the (hydr)oxides was not observed (Torrents and Stone, 1994). 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 FeOOH and Al₂O₃, while rate of hydrolysis of the latter was unaffected by FeOOH or Al₂O₃ (Torrents and Stone, 1994). This suggests that the N atom plays a role in the catalytic effect. Similarly, compounds Chlorpyrifos methyl thionate and Chlorpyrifos methyl oxon can be 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 (Smolen and Stone, 1998). Conversely, FeOOH, and Al₂O₃ catalyzed the hydrolysis of Methyl parathion with P = S moiety (Torrents and Stone, 1994), while the hydrolysis of Methyl Paraoxon with P = O moiety was not enhanced by FeOOH or Al₂O₃ (Smolen and Stone, 1998). 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 (hydr)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 usually was the greatest at the high pH. This trend was observed in the case of phorate (Dannenberg and Pehkonen, 1998 and Hong and Pehkonen, 1998).

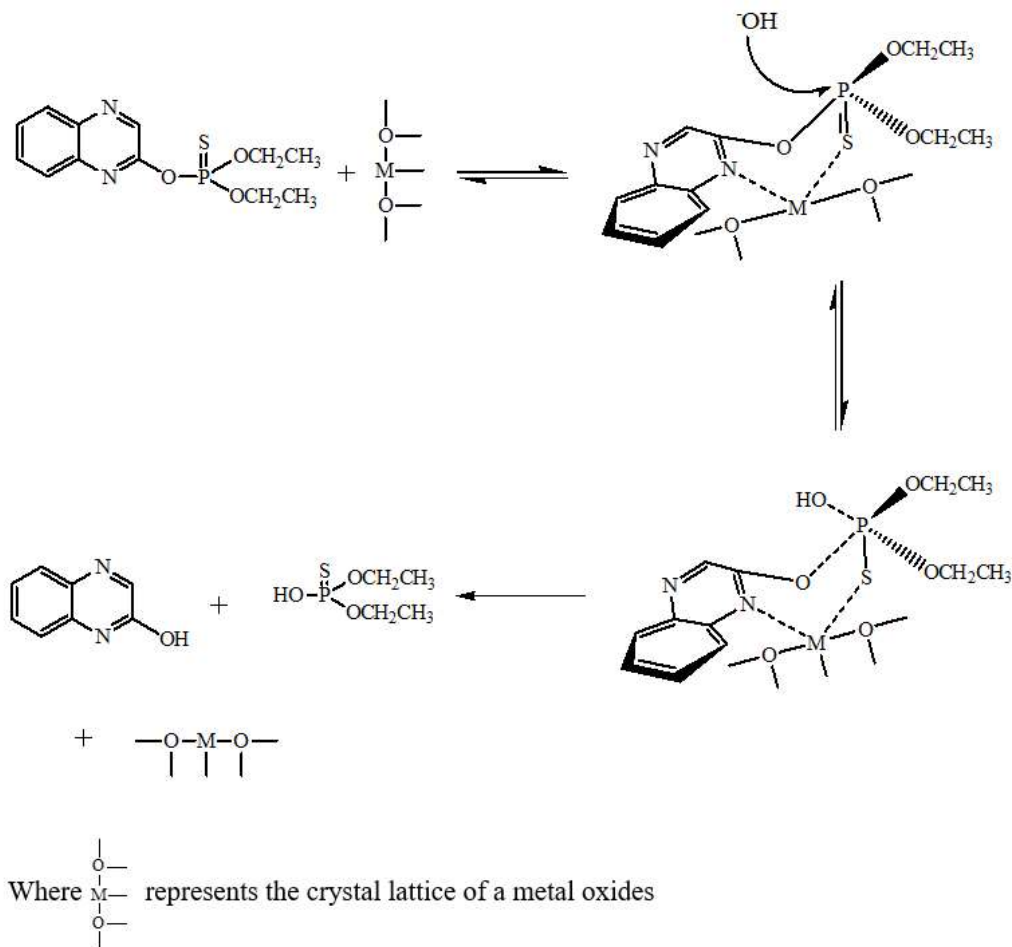
Hydrolysis of disulfoton in the presence of FeOOH also catalyzed at high pH (pH 8.5), but inhibited at pH 5.7 (Dannenberg and Pehkonen, 1998). Inhibition of hydrolysis of phorate in the presence of FeOOH or Al(OH)₃ was also observed at pH 5.7 (Hong and Pehkonen, 1998). The inhibition was attributed to “blocking of the nucleophile by metal (hydr)oxide surface or reduction of the substrate concentration in the water” (Dannenberg and Pehkonen, 1998). Nevertheless, there has been no clear systematic explanation of pH effects on catalysis by this class of solids.

The influence of buffer on the results obtained in rate measurements is an important issue. Recall that in unbuffered pH 7.0 and 10.0 solutions, pH declined as the reaction proceeded. This was 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 (hydr)oxides). Surprisingly, k_{obs} values in unbuffered solutions (in the absence and presence each of the (hydr)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 was dominant. On the other hand, in buffer solutions k_{obs} in the absence and presence of solids was always greater at pH 10.0 than at pH 7.0.

The role of metal (hydr)oxides in catalysis of the hydrolysis of OP compounds has been suggested as the chelation between surface-bound metals and the organic compounds may be necessary for catalysis to occur (Smolen and Stone, 1998; Torrents and Stone, 1991; and Torrents and Stone, 1994). This implies that the nature of the metal atoms (Fe or Al) in the (hydr)oxide and the electron donating groups (N and S) in quinalphos are important in determining the potential strengths of a chemical interaction. Accordingly, the ability of the metal (hydr)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 FeOOH and Al(OH)₃. Participation of N may be responsible for the high susceptibility of chlorpyrifos methyl to catalysis by (hydr)oxides compared to compounds Methyl parathion and Ronnel (Torrents and Stone, 1994). Chelation through the N heteroatom and the carbonyl oxygen was also suggested for (hydr)oxide-catalyzed the hydrolysis of phenyl picolinate (Torrents and Stone, 1991). Other researchers have suggested a bidentate chelation in the case of diazinon (Dannenberg and Pehkonen, 1998). In this case, the surface of the metal (hydr)oxide coordinates N as well as S. Quinalphos is similar to diazinon; it contains two binding sites (N and S) and by analogy to diazinon, metal (hydr)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 (hydr)oxides may be due to the formation of surface complex. However, enhancement variation from one (hydr)oxide to another is probably due to their difference affinities toward N and S. Katagi summarized the role of metal (hydr)oxides in catalysis of the hydrolysis of OP compounds by writing “Although hydrolysis mechanisms on metal (hydr)oxides surfaces seem very complex, some specific binding possibly *via* chelation would be essential” (Katagi, 2002). In another review article on the hydrolysis of OP compounds, Pehkonen and Zhang mentioned that “The mechanism

of surface catalyzed hydrolysis of OP compounds remains uncertain at this time, although many mechanisms have been proposed” (Pehkonen and Zhang, 2002).

Conclusion

Catalysis of the hydrolysis of quinalphos in the absence and presence of metal (hydr)oxides (FeOOH or Al(OH)₃) was studied at pH 4.0, 7.0, and 10.0 and 25°C. In the absence of solid (hydr)oxides, hydrolysis of Q was found to be very slow. Presence of either FeOOH or Al(OH)₃ enhanced the hydrolysis rates. At pH = 7.00 (buffered), k_{obs} values for the disappearance of Q were 9.50, 11.8, and 11.2 x 10⁻⁸ s⁻¹ in the absence and presence of FeOOH or Al(OH)₃, respectively. In fact, catalysis of the hydrolysis of Q by FeOOH and Al(OH)₃ is probably due to chelation between surface-bound metal atoms in the (hydr)oxide and the possible binding sites in Q. This kind of chelation enhances the nucleophilic attack and thus accelerates the hydrolysis rates.

References

- Atkinson R. J., Posner A. M., and Quirk J. P. (1967). "Adsorption of potential determining ions at the ferric oxide aqueous electrolyte interface." *Journal of Physical Chemistry* Vol. 71, Issue 3, pp. 550-558.
- Balakrishnan V. K., Dust J. M., vanLoon G. W., and Buncel E. (2001). "Catalytic pathways in the ethanolysis of fenitrothion, an organ phosphorothioate pesticide. A dichotomy in the behaviour of crown/cryptand cation complexing agents." *Canadian Journal of Chemistry* Vol. 79, Issue 2, pp. 157-173.
- Baldwin D. S., Beattie J. K., Coleman L. M., and Jones D. R., (1995). "Phosphate ester hydrolysis facilitated by mineral phases." *Environmental Science & Technology* Vol. 29, Issue 6, pp. 1706-1709.
- Brunauer S., Emmett P. H., Teller E. J. (1938). "Adsorption of gases in multimolecular layers." *Journal of the American Chemical Society* Vol. 60, Issue 2, pp. 309-319.
- Chambers J. and Matthews W. A. Bull. (1977). "A simple method for the preparation of desmethyl derivatives of some organ phosphorus insecticides." *Environmental Contamination and Toxicology* Vol. 18, Issue 3, pp. 326-330.
- Dannenberg A. and Pehkonen S. O. (1998). "Investigation of the heterogeneously catalyzed hydrolysis of organ phosphorus pesticides." *Journal of Agriculture and Food Chemistry* Vol. 46, Issue 1, pp. 325-334.

- Esbata A. A., Buncel E., and vanLoon G. W. (2017). "MnO₂ and TiO₂ catalyzed the hydrolysis of quinalphos." *Alqalam Journal of Medical and Human Science* Vol. 1, Issue2, pp. 20 – 28.
- Esbata A. A., Buncel E., and vanLoon G. W. (2018) "Hydrolysis of Quinalphos in the presence of copper." *Alqalam Journal* Vol. 7, pp. 51-67.
- Esbata A. A., Buncel E., and vanLoon G. W. (2020). "Mercury catalyzed the hydrolysis of quinalphos." *Alqalam Journal of Medical and Applied Sciences* Vol. 3, Issue 2, pp. 39-46.
- Esbata A. A., Buncel E., and vanLoon G. W. (2015). "Hydrolysis of quinalphos at high pHs and temperatures" *The Journal of Academic Research* Vol. 4, pp. 1-22.
- Greenhalgh R., Dhawan K. L., and Weinberger P. (1980). "Hydrolysis of fenitrothion in model and natural aquatic systems" *Journal of Agriculture and Food Chemistry* Vol. 28, Issue 1, pp. 102-105.
- Harris W. E. and Tochvil B. K. (1981). *An introduction to chemical analysis*, Saunders Golden Sunburst Series.
- Hong F. and Pehkonen S. (1998). "Hydrolysis of phorate using simulated environmental conditions: Rates, mechanisms, and product analysis." *Journal of Agriculture and Food Chemistry* Vol. 46, Issue 3, pp. 1192-1199.
- Huang P. M., Berthelin J., Bollage J. M., McGill W. B., and Page A. L. (1995). "Environmental impact of soil component interactions: Natural and anthropogenic organics" Boca Raton, Lewis Publishers, PP. 275-298.
- Katagi T. (2002). "Abiotic hydrolysis of pesticides in the aquatic environment." *Reviews of Environmental Contamination and Toxicology* Vol. 175, Issue 1, pp. 79-262.
- Pehkonen S. O. and Zhang Q. (2002). "The degradation of organophosphorus pesticides in natural waters: A critical review." *Critical Reviews in Environmental Science and Technology* Vol. 32, Issue 1, pp. 17-72.
- Piedad D. (2001). "Acid and base catalyzed aqueous hydrolysis of the organophosphorus pesticide, diazinon" MSc thesis, Queens University, Kingston, Canada.
- Sajjadi S., Khataee A., Bagheri N., Demirbag E., Karaoglu A. (2019) Degradation of diazinon pesticide using catalyzed persulfate with Fe₃O₄ @ MOF-2 nanocomposite under ultrasound irradiation. *J. Indus. and Eng. Chem.* 77, 280-290.

- Schindler P. W. in Hochella M. F. and White A. F. (1990). "Mineral-Water interface geochemistry." Vol. 23, Mineralogical Society of America.
- Sha'ato R., Buncel E., Gamble D. G., and vanLoon G. W. (2000). "Kinetics and equilibria of metribuzin sorption on model soil components." Canadian Journal of Soil Science, Vol. 80, Issue 2, pp. 301-307.
- Smolen J. M. and Stone A. T. (1998). "Metal (hydr)oxide surface-catalyzed hydrolysis of Chlorpyrifos methyl, Chlorpyrifos methyl oxon, and paraoxon." Soil Science Society of America Journal Vol. 62, Issue 3, pp. 636-646.
- Stone A. T. (1989). "Enhanced rates of monophenylterephthalate hydrolysis in aluminium oxide suspensions." Journal of Colloid and Interface Science Vol. 127, Issue 2, pp. 429-441.
- Torrents A. and Stone A. T. (1991). "Hydrolysis of phenyl picolinate at the mineral water interface" Environmental Science & Technology Vol. 25, Issue 1, pp. 143-149.
- Torrents A. and Stone A. T. (1994). "Oxide surface-catalyzed hydrolysis of carboxylate esters and phosphorothioate esters" Soil Science Society of America Journal Vol. 58, Issue 3, pp. 738-745.
- vanLoon G. W. and Duffy S. J. (2010). "Environmental Chemistry, a global perspective". New York; Oxford University Press Inc. Pp. 273-298.
- Weber K. (1976). "Degradation of parathion in seawater." Water Research Vol. 10, Issue 3, pp. 237-241.
- Zachara J. M., Ainsworth C. C., Cowan C. E., and Schmidt R. L. (1990). "Sorption of aminonaphthalene and quinoline on amorphous silica." Environmental Science & Technology Vol. 24, Issue 1, pp. 118-126.