

The use of yellow phosphorus to destroy toxic organic compounds

Shih-Ger Chang*

Energy and Environment Division, Lawrence Berkeley Laboratory,
University of California, Berkeley, CA 94720

Hu Keyuan, Wang Yizhong

Research Center for Eco-Environmental Sciences, Chinese Academy of
Sciences, Beijing 100085, China

Abstract— A new method for generating reactive species to destroy toxic organic chemicals has been developed. This method reacts yellow phosphorus with O_2 in moist air to produce species such as O , O_3 , PO , and PO_2 , which are capable of reacting with various types of organics. Toxic organic compounds are converted to small molecular weight organic acids, aldehydes, and/or alcohols, while yellow phosphorus is oxidized into phosphoric acid, which may be recovered as a valuable byproduct. This technique has been demonstrated to be effective for destroying many types of toxic organic compounds, including PAH; aromatic chlorides, amines, alcohols, and acids; nitro-aromatics; heterocyclic hydrocarbons; PCB; aliphatic chlorides and sulfides; dyes; and pesticides.

Keywords: toxic organic compounds; yellow phosphorus; chemicals.

1 Introduction

The remediation of hazardous pollutants in water and soil is necessary to avoid the damage to the biological world. Many toxic pollutants possess refractory structures and are difficult to be detoxified by conventional treatment processes. The refractory organics include the derivatives of chemicals such as aromatic amines, biphenyls, dioxines, polycyclic arenes, nitroarenes, chlorinated hydrocarbon and heterocyclic hydrocarbon compounds. Several methods such as ozonation assisted by UV irradiation and plasma-enforced degradation have been developed to destroy these refractory organic compounds; however, they are complicated and expensive to use.

We have recently developed a novel method to generate active species for destroying various types of toxic organic compounds. This method involves the use of the reaction of yellow phosphorus (P_4) with oxygen molecules in moist air to produce

oxygen atoms (O) and ozone (O₃). This method of generating ozone has recently been demonstrated to be very efficient in the abatement of NO from flue gas (Chang, 1990; 1992; Liu, 1991). Ozone is one of the most powerful oxidizing agents which is widely used for destroying refractory organic compounds. In addition to O and O₃, several reactive phosphorus oxide intermediates such as PO, PO₂ are generated during the course of the reaction; these intermediates possess reductive chemical properties and should also contribute to the destruction of some toxic organic compounds. Furthermore, UV (228-272 nm; PO r-system) and near UV/visible (325–337 nm; PO h-system) radiations were observed (Vanzee, 1976; Hamilton, 1986) during the course of the reaction. Therefore, the reaction of yellow phosphorus with moist air provides three concurrent components: oxidative species, reductive species, and UV radiations; each of these is capable of destroying organic compounds and the combination of them may impose synergistic effect. The P₄ is converted to phosphoric acid mists which can be collected for commercial use (Chang, 1992). This technique has been demonstrated in our laboratory to be very efficient for destroying various types of organic toxic waste over a wide concentration range during a short time of treatment. Organic compounds representing different structural types were selected for examination by this technique. The compounds (with corresponding structural types indicated) that have been tested so far include naphthalene (polycyclic aromatic hydrocarbons, PAH); aniline and dimethyl aniline (aromatic amines); phenol (aromatic alcohol); benzoic acid (aromatic acids); nitrobenzene (nitroaromatics); isophorone (cyclic ketone); chlorobenzene (aromatic chloride); Aroclor 1221 and 1242 (PCB); 1,1-dichloro-ethane, chloroform and carbon tetrachloride (aliphatic chlorides); pyridine (aromatic N-heterocyclics); diethylsulfide (dialkyl sulfides); 1-(1-hydroxy-2-naphthylazo)-5-nitro-2-naphthol-4-sodium sulfonate (Eriochrome black T, an azodye); and o,o-dimethyl-s-(N-methyl carbamoyl methyl) phosphorodithioate (dimethioate, an organophosphorus pesticide). This paper demonstrates the destruction feasibility of organic compounds and addresses parameters which affects this destruction. Quantitative results on specific compounds will be presented in a separated paper.

2. Experimental section

Two reactors with different gas-liquid contact arrangements were employed in this study, including: 1. a stirring reactor (SR) where air and aqueous mixtures were enclosed in a 500 ml flask. The aqueous mixtures in the SR were comprised of 100 ml water, P₄, and organics to be treated, and were stirred with a magnetic stirrer during the operation. The enclosed reactor prevented the vaporization loss of organics.

2. an agitating bubbling reactor (ABR, Fig. 1), which is a glass column, 4.5 cm in diameter and 28cm in height, with a sinter glass located near the bottom of the column. The sinter glass served to disperse the air flowing into an aqueous mixture and thus increased gas-liquid contact. Agitation of the aqueous mixtures was performed by a set of circular stainless steel sieve screens installed in parallel, which were at a distance of about 1 inch from each other, on a metallic rod. The metallic rod was attached to an electric motor. As the motor rotated, the rod and the sieve screens oscillated up and down, with an amplitude of about 1 inch and a frequency of 200–300 cpm. P_4 melts at 43°C . It is immiscible with water and forms globules upon stirring. It has a specific gravity of 1.8 and tends to settle. Agitation reduced the size of P_4 globules and improved the mixing of P_4 with air and water. The aqueous mixture could be circulated via a centrifugal pump from the bottom to either the top or the middle inlet of the reactor. The top inlet was equipped with two spray nozzles, while the middle one was equipped with none. Circulation of aqueous mixtures prevented the P_4 globules from accumulating at the bottom of the reactor.

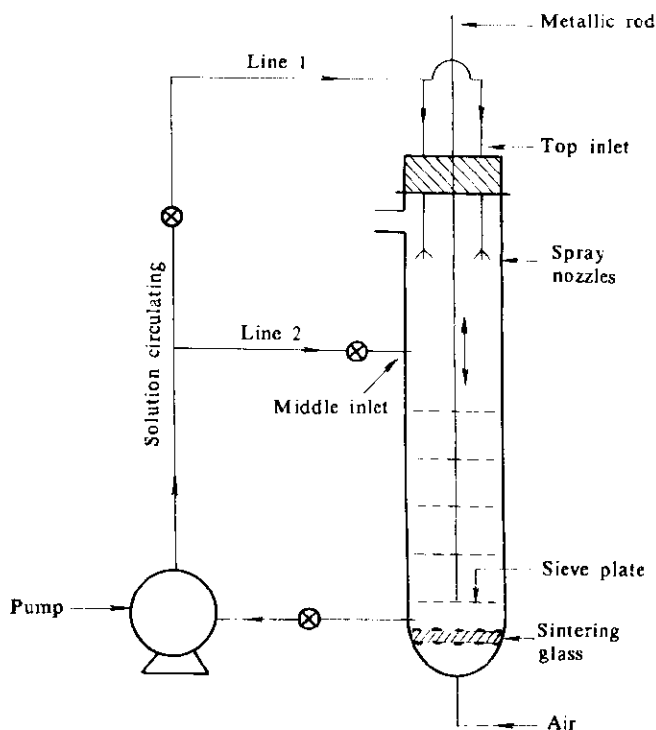


Fig. 1 An agitating bubbling reactor was used for the study of the effect of the relative amount of organics to P_4 , air flow rates, and gas-liquid contacts on the decomposition rate of organics and the effectiveness of P_4 utilization

The experimental procedure can be described as follows: An aliquot of aqueous solution containing organics to be treated was transferred into the reactor and was adjusted to the desired temperature (about 50–55°C). A known amount of P_4 was added to the solution in the reactor (SR and ABR). Treatment was initiated by either stirring the aqueous mixtures (SR) or by flowing air into the system (ABR). The appearance of white fumes is indicative of the formation of phosphoric acid mists.

Of those organics chosen for study, some were tested to determine whether they could be decomposed by this method. The SR reactor was used for this type of survey study. The initial concentration of organics and the initial amount of P_4 were: naphthalene 10 ppm, P_4 0.5 g; aniline 425 ppm, P_4 1 g; phenol 936 ppm, P_4 0.5 g; nitrobenzene 640 ppm, P_4 0.5 g; chlorobenzene 276 ppm, P_4 0.5 g; Aroclor-1221 22 ppm, P_4 0.5 g; Eriochrome black T 50 ppm, P_4 0.5 g. On the other hand, several organics, including dimethyl aniline, phenol, benzoic acid, isophorone, and pyridine were studied in a more detailed manner with an ABR set-up. Parameters influencing their destruction were studied. Initial concentration of organics studied ranged between 240 ppm and 960 ppm, while the amount of P_4 ranged from 0.11 g to 1 g. The total volume of aqueous mixtures was 250 ml. Air flow rate varied from 40 to 170 ml/min. The effect of treatment time, air flow rate, the gas-liquid contact efficiency, the concentration of organics and the dosage of P_4 in solutions on the percent removal of organics were investigated. The percent removal measures the extent of the destruction of organics. The stoichiometric ratio (n_p/n) is defined as the molar ratio of the total phosphorus oxyanions formed to organic compounds destroyed; and thus, it represents the P_4 utilization efficiency.

The concentration of organics during the course of the treatment were monitored periodically by analytical techniques, including UV-visible spectroscopy, and gas and ion chromatography.

3 Results and discussions

One set of experiments determined the destruction feasibility of several different structure-type organics by P_4 treatment. Representative organics from each structure type were chosen for examination with an SR reactor. The decrease in intensity of an absorption band with treatment time was observed for naphthalene (Fig. 2), chlorobenzene (Fig. 3), Aroclor 1221 (Fig. 4), and Eriochrome black T (Fig. 5), indicating that the concentration of organics had decreased upon treatment. The changes in UV-absorption spectrum following the P_4 treatment were also observed

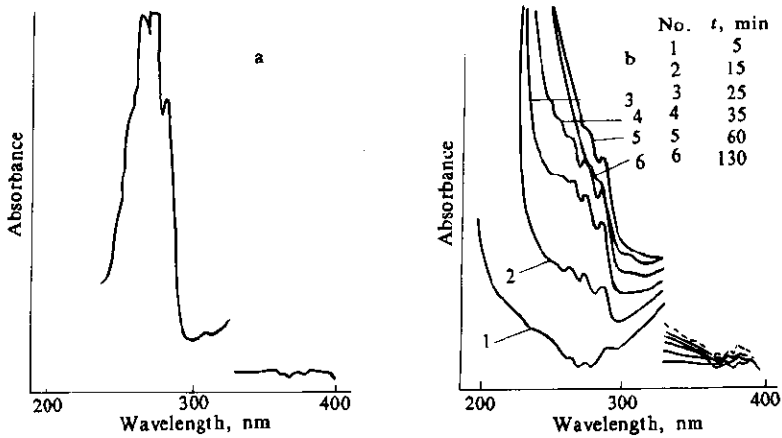


Fig. 2 (a) is an absorption spectrum of naphthalene in water, and (b) is a series of absorption spectra of aqueous solution of naphthalene after the P_4 treatment for 5, 15, 25, 35, 60, and 130 min

for aniline, nitrobenzene, and dimethoate. The oxidation prodation of P_4 , phosphorus oxyanions, do not absorb in the spectrum region shown.

Fig. 2 shows a substantial reduction of naphthalene absorption intensity at 265–285 nm after 5 min of treatment. This could be attributed to the vaporization of naphthalene. A continuous treatment resulted in an increase in absorption intensity of four new absorption bands at 252, 262, 272, and 284 nm, which was probably due to the decomposition products of naphthalene. The decomposition of naphthalene could take place in the gas phase, where yellow phosphorus vapor could initiate a series of chain reaction. Subsequently, the decomposition products can dissolve in water. Yellow phosphorus has a partial vapor pressure of about 320 ppm at 50°C under thermodynamic equilibrium conditions. Fig. 3 shows an initial rapid reduction in absorption intensity at 208 nm, indicating that almost all of the chlorobenzene disappeared from the liquid phase 5 min after the treatment was initiated. The appearance of a new absorption band at 217 nm and the subsequent increase of its intensity, along with the treatment time after 5 min, is probably due to the formation of decomposition products of chlorobenzene. Fig. 4 shows a large reduction of a characteristic absorption band of Aroclor 1221 at 244 nm after 0.5 h treatment,

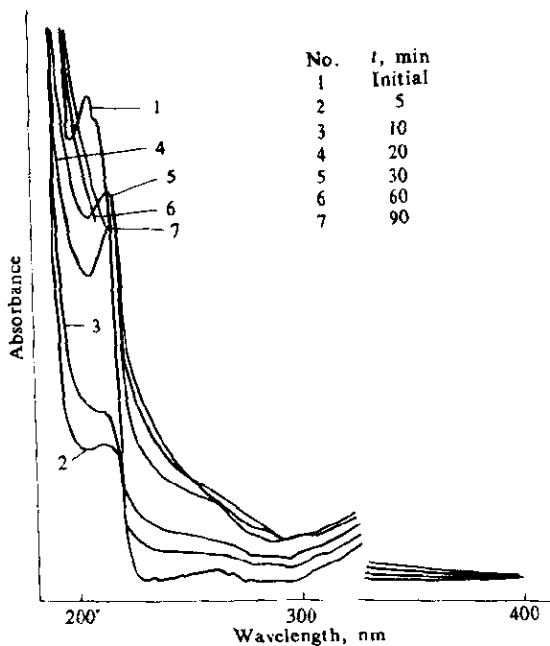


Fig. 3 Absorption spectra of aqueous solutions of chlorobenzene, and its decomposition products subject to the P_4 treatment

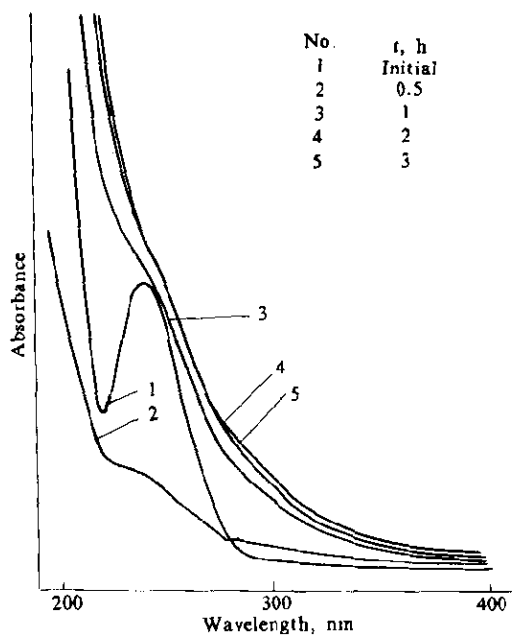


Fig. 4 Absorption spectra of Aroclor 1221 and its decomposition products after the P_4 treatment

indicating an almost complete destruction of the compound. Further treatment resulted in an increase of a structureless continuous absorption band, pointing to the formation of decomposition products. That the non-volatile species contaminated in water can also be decomposed by the P_4 treatment is shown in Fig. 5, where an aqueous solution of the Eriochrome black T was decolorized after the P_4 treatment for 50 minutes. In addition, we have demonstrated that the dimethoate pesticide was decomposed by the P_4 treatment. It appears that the treatment of organic compounds in aqueous solutions with P_4 , the destruction process may take place both in the gas phase and at the interface between liquid phosphorus globulus and gas phases.

A second set of experiments dealt with a parametric study of the efficiency and stoichiometric ratio of organic destruction. The parameters investigated included air flow rate and the concentration of organics and P_4 used. The experiments were carried out in an ABR set-up. Organics chosen for this study were dimethyl aniline, phenol,

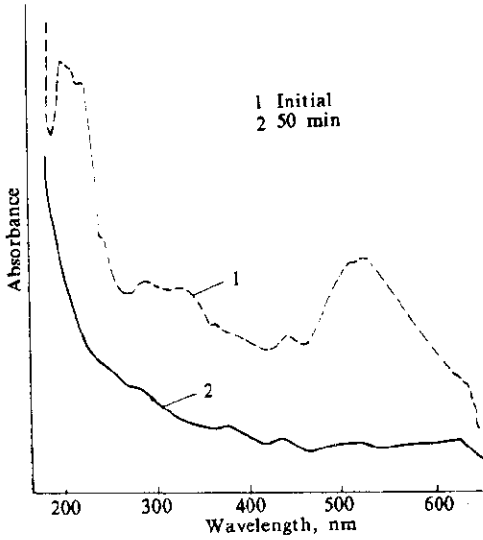


Fig. 5 Absorption spectra of an aqueous solution of the Eriochrome black T dye and its solution after the P₄ treatment

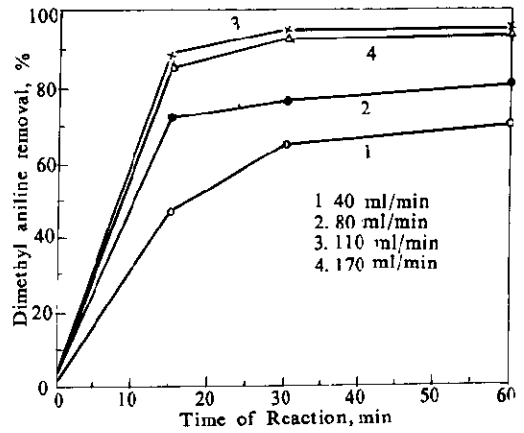


Fig. 6 The effect of air flow rate on the decomposition rates of dimethyl aniline in an agitating bubbling reactor, with a circulation and without spraying

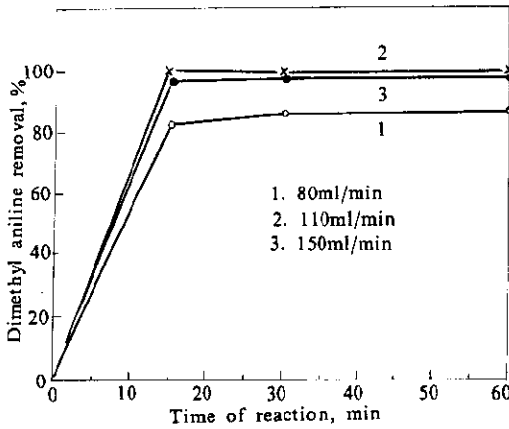


Fig. 7 The effect of air flow rate on the decomposition rates of dimethyl aniline in an agitating bubbling reactor, with a circulation and spraying

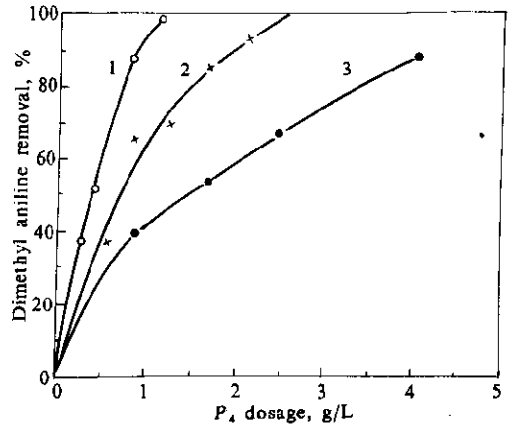


Fig. 8 The effect of the initial P₄ dosages (1.240 mg/L; 2.480 mg/L; 3. 960 mg/L) on the decomposition of dimethyl aniline after 15 min of treatment

benzoic acid, nitrobenzene, isophorone, and pyridine. The concentration of organics and phosphorus oxyanions during the course of the P_4 treatment were determined by ion chromatography. Blank experiments were performed to ensure that the loss of organics due to vaporization was insignificant.

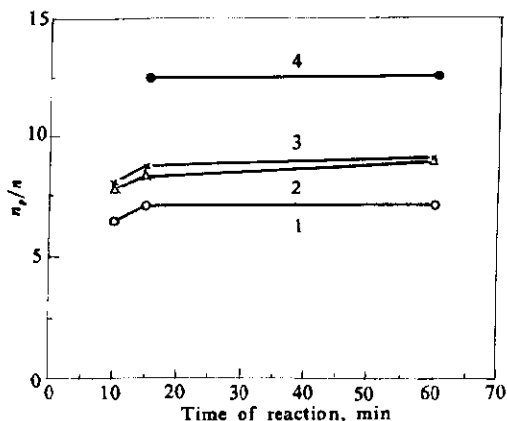


Fig. 9 The effect of the P_4 dosages (1.240mg/L ; 2.400 mg/L; 3.820 mg/L, 4. 1140 mg/L) on the stoichiometric ratio of P_4 dimethyl aniline

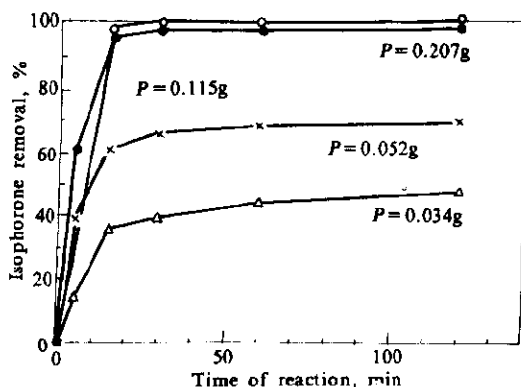


Fig. 10 The effect of the P_4 dosages on the rate of the decomposition of isophorone

Experiments of dimethyl aniline were performed at an initial concentration between 240 and 960 ppm of dimethyl aniline and between 0.3 and 4 g/L of P_4 , and temperature 50–55°C. Air flow rate varied at 40, 80, 110, and 150 ml/min. Results from two different routes of solution circulation were shown: Fig. 6 was a run with solution circulated from the bottom to the middle inlet of the reactor without spraying, while Fig. 7 was a run with a circulation of solution to the top inlet which was equipped with spray nozzles. The removal efficiency was better with spraying; this shows that effective gas liquid contact improved the efficiency. More than 90% of the dimethyl aniline was destroyed in less than 30 min when the air flow rate was 110 ml/min or larger. The results indicated that the removal efficiency increased with increasing air flow rate at a given time of treatment. The increase of air flow rate increased the reaction rate of O_2 with P_4 , thus increasing the concentration of reactive radicals, available for interaction with organics. The increase of removal efficiency showed a slow down and then leveled off with prolonged treatment. This behavior was also observed with the other organics that were examined. The decrease in organic and

P_4 concentrations along with the time of treatment might be the cause of this behavior. Also, decomposed organics might react further and consume reactive radicals which would result in a slow down of the rate of removal of the parent organics. The concentration ratio of parent organics to decomposed products decreased with the increase of treatment time. The effect of concentration of dimethyl aniline and P_4 dosage on the removal efficiency at a 15 min treatment time was shown in Fig. 8. The percent removal was greater with an increase of P_4 dosage, but was less with an increase of dimethyl aniline concentration. At a given organic concentration, the P_4 was more effectively utilized with a smaller initial P_4 dosage as shown in Fig. 9. Destruction products identified, by ion chromatography, in the order of decreasing abundance, were acetic, formic oxalic, and malonic acids.

The destruction of phenol, benzoic acid, and nitrobenzene subject to the P_4 treatment showed a similar behavior as dimethyl aniline did. The percent removal of these organic compounds showed an increase and approached a limit value with the increase of the treatment time. The decomposition products of benzoic acid and phenol that were identified included formic, malonic, and oxalic acids, while the decomposition products of nitrobenzene were nitrate ion in addition to the aforementioned three small molecular weight organic acids.

Isophorone is a cancer suspect reagent. The experiment with isophorone was carried out with a circulation of solution at 50–55°C, and with an air flow rate of 40 ml/min. The initial concentration of isophorone was 224 ppm. The dosage of P_4 initially added to the aqueous mixture varied at 0.034, 0.052, 0.115, and 0.207 g. The concentration of isophorone during the course of the experiments was monitored by gas chromatography. Isophorone was extracted from an aqueous sample with chloroform before the analysis. Fig. 10 and 11 show the effects of P_4 dosages on the removal efficiency and stoichiometric ratio, respectively. The greater the P_4 dosage, the larger the removal efficiency and the smaller the effectiveness of P_4 utilization were observed. Almost all of the isophorone was destroyed in less than 20 min when the initial P_4 was 0.11 g or more. More than 95% removal efficiency with a stoichiometric ratio of less than 5 was achieved when 0.115g P_4 was used. Formic acid and a trace amount of oxalic acid were detected as the destruction products of isophorone.

The relative destruction capability of organic compounds subject to the P_4 treatment was compared. Fig. 12 shows the P_4 dosage dependencies on the removal efficiencies for six organic compounds: 1. isophorone (224 ppm), 2. dimethyl aniline (240 ppm), 3. phenol (297 ppm), 4. nitrobenzene (296 ppm), 5. benzoic acid (240 ppm), and 6. pyridine (242 ppm). Except for phenol and isophorone, the treatment for all the other compounds was carried out under the solution circulated by spraying. The time of treatment was about 30 min. Apparently, the removal efficiency is directly related to the structural stability of the compounds being treated by the P_4 -oxygen reaction. So for the more stable organic compounds, higher P_4 dosage are required to achieve

a similar removal efficiencies; apparently the P_4 was being utilized less effectively by the stabler organic compounds. Of the organics we tested, isophorone is the easiest and pyridine is the hardest to destroy. The relative capabilities of the P_4 technique to destroy organics occurred in the following orders: isophorone > dimethyl aniline > phenol ~ nitrobenzene > benzoic acid > pyridine.

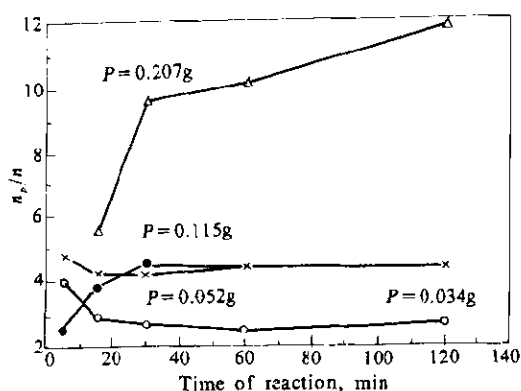


Fig. 11 The effect of the P_4 dosages on the ratio of P_4 isophorone

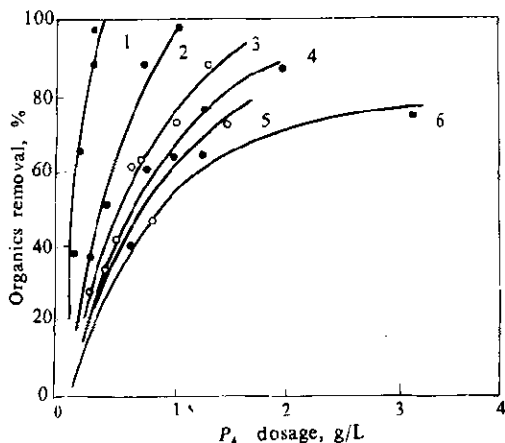


Fig. 12 The comparison of the destruction capability of organic compounds by the P_4 treatment for 30 min.

In addition to the organics mentioned above, several other chemicals were examined in a qualitative manner. When chloroform, carbon tetrachloride, and 1, 1-dichloroethane were treated, chloride ion and small molecular weight organic acids were detected by ion chromatography; formic acid was observed in the case of carbon tetrachloride, while formic, as well as trace amounts of oxalic acids, was detected after chloroform was treated. This demonstrated that saturated aliphatic chloride could be destroyed by this technique. These type of organics cannot be destroyed by ozone treatment alone. Another run dealt with an insoluble toxic waste. Arochlor 1242 is a liquid PCB and is not miscible with water. When aqueous mixture of Arochlor 1242 was treated with this technique, chloride ion was detected, indicating that Arochlor had been decomposed. Also observed was the oxidation of dimethyl sulfide to produce organic acids and sulfate ion.

The destruction mechanism of toxic chemicals by P_4 treatment may be speculated. The reaction of P_4 with O_2 is believed to proceed via a branched-chain mechanism.

Investigators have identified several elementary reactions (Aleksandrov, 1981; Soroka, 1977, Semenov, 1975; Davis, 1968; Husain, 1977) involved in the chain, and have determined rate constants for some of the reactions. However, a complete list of elementary reactions is not yet available. It has been reported that a large amount of atomic O was detected in the reaction zone during the reaction of P_4 with O_2 . Subsequent reaction of O with O_2 produces O_3 . The final oxidation product of P_4 is P_4O_{10} , which is hygroscopic and readily picks up water to form phosphoric acid mists. Many intermediates, such as PO, PO_2 have been identified during the process of P_4O_{10} formation. These intermediates are highly reactive and may participate in the reaction with toxic chemicals. Thus, P_4 treatment of toxic chemicals may proceed not only via the ozone destruction pathway, but also through additional pathways involving reactions of intermediate species with toxic chemicals. The latter pathways might be responsible for the destruction of toxic chemicals such as saturated alkyl chlorides that can not be destroyed by a simple ozone oxidation method. Furthermore, the radiation in the UV and near UV /visible regions were observed resulting from chemilluminance of electronically excited phosphorus oxides. A combination of ozone with UV radiations that was responsible for the dechlorination of saturated alkyl chlorides can not be ruled out.

In conclusion, a new method utilizing the reaction of P_4 with O_2 in moist air to induce the destruction of toxic chemicals has been demonstrated. The effectiveness of P_4 utilization and the efficiency of the organic destruction depend on the concentration of organics to be treated and the amount of P_4 employed. Also, they depend on air flow rate (the concentration of O_2), gas-liquid contact efficiency, and the temperatures. In addition to the aforementioned parameters, another factor affecting the P_4 utilization and organics decomposition efficiency is related to the generation of dissociated organic intermediates. At the start of the treatment of each of the organics, most of the active radicals were exhausted on the destruction of the organics. But as the treatment process progressed, organic intermediates formed. The effect of the intermediates on the treatment process soon became apparent when the P_4 dosage needed to be increased to maintain a constant removal efficiency. More and more P_4 was being exhausted by reacting with the intermediates. Therefore, without exception, the stoichiometric ratio always increases as the destruction of the parent organic progress with treatment time or with increase in the P_4 dosage.

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