PCB DESTRUCTION: A NOVEL DEHALOGENATION REAGENT

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Summary

Alkali metal polyethylene glycolate complexes (APEGs) are being investigated as reagents for the *in-situ* decontamination of soils containing PCBs and other haloorganics in the U.S. Environmental Protection Agency's Industrial Environmental Research Laboratory, Cincinnati, Ohio. APEG reagents can be formulated with either an alkali metal or hydroxide and the corresponding polyglycol or polyglycol monoalkyl ethers. These alkali PEGs were found to be very reactive toward halogenated organics, particularly at elevated temperatures (ca. 60—100°C) and have been applied for decontamination of PCBs in transformer oils. The primary products were an alkali metal halide, i.e., sodium chloride in the case of PCBs and polyglycol ether aromatics. The reaction mechanism is nucleophilic substitution at the halogen—carbon bond. The reactive APEG species is theorized to be a crown ether metal coordinated structure. Previous formulation of these APEGs required reaction of the alkali metals with a desired polyethylene glycol under anhydrous conditions. These formulations were very susceptible to decomposition by water, and dehalogenation rates were likewise vastly reduced. Recent studies have shown that this is not an insurmountable problem when APEGs are formulated with the alkali metal hydroxide.

This work examines the effect of APEG concentration and dilution in water and organic solvent on the dehalogenation of Aroclors 1242 and 1260 with potential application for the *in-situ* destruction of PCBs in soils.

Introduction

The application of alkali polyethylene glycolates (APEGs) for the dehalogenation of toxic halloorganics has aroused considerable interest in use of these reagents as a possible hazardous waste treatment. A major benefit which the APEG reagents possess over both sodium naphthalene and sodium biphenyl reagents is their relative stability with regard to water and atmospheric oxygen. This stability has, along with their reactivity toward organohalogen species, prompted the current research toward potential *in-situ* application of APEGs for distruction of PCBs, PBBs, chlorodioxins and other potentially harmful environmental contaminants in the haloorganic class.

The APEG reaction with PCBs proceeds rapidly (from 10 minutes to several hours) under mild conditions (60—120°C) in nonpolar medium such as transformer oils or hydrophobic solvents such as toluene or hexane [1—4]. Formulations of APEG employing polyethylene glycols molecular weight 400 to 600 form biphasal systems with polar solvents and require agitation for intimate reagent—pollutant contact. In a static system it becomes apparent that reagent at the interphase would become depleted, products would build up and the transport process of diffusion of fresh reagent to the interphase along with product displacement would limit reaction rates. When dealing with haloorganic pollutants which are closely associated and bound to soil constituents we are dealing with such a static system. Viscous reagents such as APEG-400 or 600, though functioning quite well in biphasal agitated reactions, are quite slow·to penetrate and decontaminate soils which contain PCBs. These reagents are useful, however, when dealing with soil extracts where the extraction solvent is hydrophobic and this solvent is desired to be recycled. In this case, the system of decontamination is a two-step process resulting in greater expenditure of labor, materials and energy than one could envision for an *in-situ* approach.

In our investigations of APEG—PCB reactions using a nonpolar solvent for PCB dissolution we have formulated a reagent which is completely miscible with the hydrophobic and hydrophilic solvent. This reagent is based on polyethylene glycol monomethyl ether (av. mol. wt. 350 daltons) and formulated with potassium hydroxide in either the pellet form or as a 60% solution. It is miscible with water as well as hydrocarbons such as toluene, hexane and other nonreactive solvents, and its viscosity is considerably lower than the APEG 400 and 600 reagents. The characteristics of the reagent, henceforth named APEGM, would seem to indicate its being a useful candidate for *in-situ* application. The combination of these desirable features of the APEGM reagent are further enhanced by the discovery that PCBs are solvated by neat PEGM or APEGM systems. Thus the reagent itself becomes the solvent for both the pollutant as well as the reactive dehalogenation species. The reagent proper can be expressed as follows

$$AOH + PEGM \rightleftharpoons APEGM + H_2O$$
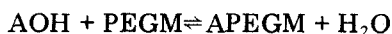
where A represents an alkali metal, for example potassium, and PEGM is the previously described polyethylene glycol monomethyl ether. A further equilibrium reaction in all likelihood occurs in soils which contain PCB as contaminants, such as

$$S \cdot PCB + APEGM \rightleftharpoons S + [PCB \cdot APEGM] \rightleftharpoons S + ACl + B-(PEGM)_n$$

where S·PCB represents soil-bound PCB, [PCB·APEGM] represents PCB solvated by the APEGM reagent, ACl and B-(PEGM)$_n$ both represent products of inorganic alkali chloride and a PEGM substituted biphenyl mixture respectively. Product identification of the APEG and APEGM reaction

products with both chlorobiphenyls and chlorobenzenes under varying conditions has been accomplished by Brunelle and Singleton [1] and others [2—4]. The general structure of low-temperature reaction products of these reactions are shown below, where R is either H or CH_3. Substitution of Cl takes place on both rings, though it is shown for clarity only on one ring of the PCB. At elevated temperatures ($>100°C$), the initial substitution is followed by a slower elimination or substitution step which produces the corresponding biphenylol and an allene glycol of general structure, $H_2C=CH—O—(CH_2CH_2O)_nR$ [1].

$$Cl_n \quad Cl_m \qquad \xrightarrow{\text{APEGR}} \qquad Cl_n \quad Cl_{m-1} \quad \text{OPEGR} \quad + \quad ACl$$
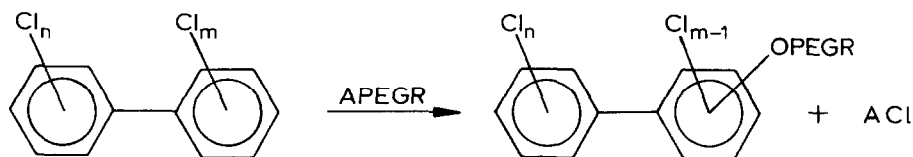
One very important consideration which must be given to a proposed *in-situ* treatment method is determination of the toxicity of the products. The neutralized products of the low-temperature reaction of APEGM and PCB have been described and have been submitted along with controls for toxicity screening both by other groups [1] and by EPA [5]. The low temperature ($20—60°C$ reaction) product mixtures were selected as these would more likely reflect products of an *in-situ* reaction where ground temperatures are not artificially increased past $100°C$. Neither Aroclor 1260 reaction product nor control reagent resulted in an oral toxic effect (max dose 5000 mg/kg; rat), or dermal toxicity (mouse) by absorption, but were found to be mild eye irritants in rabbits [1]. In an ongoing study conducted by ERA Duluth Laboratories [5] no bioaccumulation of the neutralized PCB 1260 glycol substituted reaction product or reagent occurred in fathead minnows as compared to bioaccumulation of the neat Aroclor 1260 in these organisms. In light of these facts we have undertaken preliminary investigations on the reactivity of differing APEGM reagent formulations with respect to dehalogenation of the Aroclors 1242 and 1260.

History

The application of polyethylene glycol based reagents employing an alkali metal or its salt for the purpose of dehalogenation of both halo-aliphatic and aromatic compouds is a relatively new technology. One can trace conceptualization of this technology to the work of Starks [6] who introduced the term "phase-transfer catalysis" in his description of the process of heterogeneous reactions involving two distinct phases of solution, namely aqueous and organic, which are initiated and sustained by use of a small amount of suitable catalyst. The catalyst, as its name implies, permits

transfer of the substance to be reacted upon from one phase to the other. Primarily, investigations centered on exchange of anions such as CN⁻ or OH⁻ from an aqueous phase to substitute a halogen (Cl, Br) on an aliphatic compound residing in the organic phase. The catalysts were primarily of the tetraalkyl ammonium of phosphonium structure. Further applications and improvements of these systems with respect to dehalogenation substitution reactions have been described by Makosza [7], Lehmkuhl et al. [8], and Regen [9]. Both Makosza and Regen concentrated on catalytic routes involving functionality of the previously mentioned tetraalkyl ammonium species; however, Regen has carried the process further by formulating a triphase catalytic system employing a solid-phase catalyst at the organic—aqueous interface. Lehmkuhl et al., were apparently one of the first to employ open-chain polyethylene glycol dialkyl ethers complexed with alkali metal salts as phase transfer agents, and to draw the analogy between these complexed substances and the macrocyclic crown ethers which had been employed in nucleophilic substitution reactions. Work by this group was primarily concerned with substitution reactions on the aliphatic halogen of benzyl bromide. Further applications of the use of both polyethylene glycols and their monoalkyl ethers by Gibson [10] and Kimura and Regen [11] revealed the glycol—alkali moiety to not only behave as its own phase transfer agent or catalyst but to actually be incorporated in the substitution reaction. Gibson employed the use of alkali—polyethylene glycols in phase-transfer catalyzed Williamson ether synthesis, whereas Kimura and Regen revealed the extraordinary effect of these reagents in two-phase dehydrode-halogenation reactions, employing alkylbromo compounds as reactants.

Comparison of the alkali salt polyethylene glycol complexes with modi-fied crown ether catalysts has been studied by Scott et al. [12] based on earlier work of Lehmkuhl et al. [8] and Gokel and Garcia [13]. The results of the Scott group indicated the onium salts and polyethylene glycols were cost-effective catalysts of choice when compared with a series of crown ethers based on 18-crown-6 due to the high price of the macrocyclic crown ethers.

Though we have focused on phase-transfer catalyst employing an alkali metal on its salts for use in dehalogenation reactions, there was reported in the literature by Liggett [14] the application of sodium biphenyl and sodium naphthalene reagents for dehalogenation of both alkyl and aryl haloorganics as early as 1954. Drawing on this earlier work the groups of Oku et al. [15] and Smith and Bubbar [16] applied this information for dehalogenation of PCBs. Both groups' results were very successful in com-plete dehalogenation of Aroclors; however, the method is extremely sen-sitive to oxygen and water and is energy intensive when compared to phase-transfer catalysts employing the polyethylene glycols.

In an excellent article by Brunelle and Singleton [1] dealing with de-chlorination of PCB by use of polyethylene glycol (PEG) KOH it was re-vealed that the PEGs and polyethylene glycol monoalkyl ethers (PEGMs)

act not only as phase-transfer catalysts but also are functional nucleophiles under alkaline conditions. Further it should be stressed that the reactions employing PEG or PEGM formulations are tolerant of oxygen, water and other contaminants, have been found to be of low toxicity, are economically attractive and thus may have application for *in-situ* decontamination of soils, sediments and sludges which have become contaminated by both aryl and alkyl haloorganics. The work of these groups has also spawned a recent series of patents which deal with the application of these phase-transfer agents to detoxification of chlorodioxins [2—4, 17].

Experimental design

Materials
Polyethylene glycol monomethyl ether of average molecular weight 350 daltons (PEG-350M) was obtained from Aldrich Chemical Company, Milwaukee, WI 53201. Potassium hydroxide pellets 89% and toluene, both of reagent quality, were obtained from Fisher Scientific, Cincinnati, OH 45245. The proprietary solvent* (PS) was obtained from either Aldrich Chemical Company, as 99% pure, or from Fisher Scientific, as certified reagent. Water, when used, was house distilled water with no furhter treatment. The Aroclor 1260 used in this study was received from Alltech Associates, Deerfield, IL 60015, Lot Number PE 016.

The reactions proper were carried out in 30 ml glass, round-bottom, Kimax screw-top culture tubes, sealed by means of teflon-faced silicon rubber septa held in place with open ended, plastic screw caps. The septa and caps were obtained from Pierce Chemical Company. For extraction and storage of samples 3.5 ml glass vials also incorporating teflon-faced silicon rubber septa held in place with plastic screw caps were used. These were also obtained from Pierce Chemical Company.

Instrumentation
For gas chromatographic (GC) analysis a Varian 3700 gas chromatograph with the Varian electron capture detector was employed. Six foot long glass columns, 2.0 mm i.d. × 1/4 in o.d., were packed with 3% OV-17 on Gas Chrom Q, 100—120 mesh, for the analysis. Varian heated on-column injectors were used set at 300°C. Nitrogen at a flow set to 30 ml/min was the carrier gas. Detector temperature was set at 330°C. Oven conditions were as follows: initial at 100°C during injection, hold at 100°C for 4 min, program at 10°C/min to 290°C, hold until no more peaks elute (generally 10 to 15 min after final temperature was reached).

These conditions were found suitable for reasonably resolved Aroclor

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*The proprietary solvent used in this work was dimethyl sulfoxide (DMSO). The Galson Research Corporation, E. Syracuse, NY 13057, has recently patented incorporation of DMSO as a catalyst in the reagent formulations.

1242 and 1260 peaks in a minimal time, thus allowing several runs per day. The system enabled quantification of residual Aroclor after the desired reaction time.

Preparation of reagent

The dehalogenating reagent was prepared as follows: to 0.1 mole of PEG-350M was added 0.1 mole of KOH in pellet form. The solution was gently stirred while heating in an open beaker at 60—80°C, until the KOH pellets were fully dissolved (10 to 15 min). In experiments which incorporated the proprietary solvent (PS), this solvent was added after the KPEG-350M had cooled to ambient temperature (20—22°C). The same procedure applied where water was used as a reagent diluent.

Experimental

Initial Aroclor 1260 concentrations on which the KPEG-350M—PS reagent was tested were 1 mg/ml or 1000 ppm. In a typical experiment 1.2 ml of a 10 mg/ml Aroclor 1260 solution in HPLC-quality hexane was pipetted into a 30 ml round-bottom screw-cap Kimax culture tube. The hexane was evaporated by a gentle stream of nitrogen and 12 ml of the reagent to be used was added to the culture tube. The tube was then sealed with a teflon-faced silicon septa held in place with a plastic screw cap. Immediately after sealing, the tube was shaken to dissolve of the Aroclor and the time was noted ($t = 0$). Sample aliquots of 1 ml were removed at $t = 0$, 4 h, 24 h, and as required for monitoring the reduction of the Aroclor 1260 peaks.

The 1 ml sample aliquots were treated as follows. A 1 ml sample was removed and placed into a 3.5 ml glass vial; to this concentrated HCl was added dropwise to lower reaction pH to 5—6 as measured with narrow-range pH paper. The vial was closed with a teflon-faced silicon septum and screw cap, mixed by shaking and cooled under cold water. When the contents were at approximately 20°C, 1 ml of toluene was added, and the vial was sealed and shaken for about 1 min to effect extraction of any unreacted Aroclor 1260 into the toluene phase. Phase separation takes place in less than 5 min and the upper toluene phase is subjected to analysis by packed column GC—ECD with no further cleanup. An Aroclor 1260 control made to the same concentration as the experimental runs of 1 mg/ml in toluene was used for quantification of the runs. A solution of Aroclor 1260 and 1242 at 1 mg/ml in neat PEG-350M were extracted with toluene in the manner described to give an indication of extraction efficiency. The system demonstrated an efficiency of 99% when compared to the Aroclor 1260 and 1242 standards, respectively.

A second series of reagent/Aroclor 1260 and 1242 experiments used an Aroclor concentration of 0.1 mg/ml or 100 ppm. In these cases the Aroclor concentration was 1.2 mg/ml of hexane, which was deposited into the

culture tubes as previously described to give a final concentration of 1.2 mg Aroclor (100 ppm) per 12 ml of reagent under investigation. Sampling, extraction, and analytical procedures were identical to those previously described.

Results

An example of the effect of the KPEG-350M—PS reagent on Aroclor 1260 is qualitatively presented in Fig. 1. In this figure two of the gross effects of the reagent are demonstrated: (1) an increase in reactivity with an increase of temperature, and (2) the more rapid decrease of the later eluting higher chlorinated Aroclor peaks compared to the early eluting peaks. Chromatogram B of Fig. 1, representing the 4-hour reaction on Aroclor 1260 at 60°C, reveals a greater reduction of both number and type of Aroclor peaks when compared to the 20°C reaction (Fig. 1C), which had a 24-hour reaction time. It becomes apparent that there is a temperature effect on the rate of dehalogenation which varies with each of the Aroclor peaks. Though this effect is not unexpected, it does complicate dehalogena-

TABLE 1

Reaction of Aroclor 1260 vs. KPEG-350M—PS at 20°C and 60°C. Initial Aroclor concentration of 1000 ppm. Reagent to proprietary salient ratio of 1:1, v/v

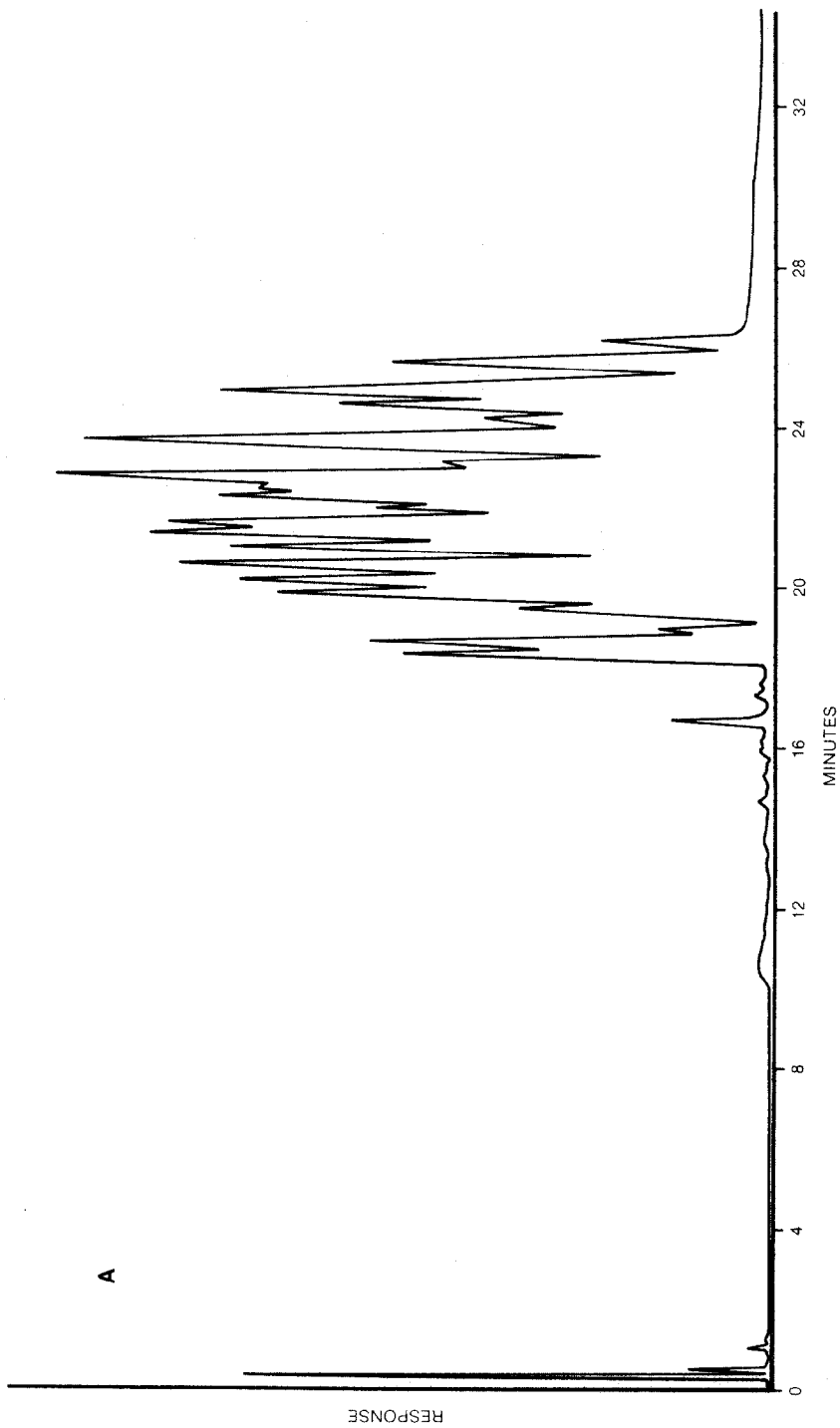| Peak No.	Percent increase (+) or decrease (−)[a]			
	Case 1 (20°C)		Case 2 (60°C)	
	$T = 4$ h	$T = 24$ h	$T = 4$ h	$T = 24$ h
1	+30	+12	+15	−58
2	− 2	−34	−99	−96
3	−20	−77	−99	−99
4	−19	−38	−91	−99
5	−34	−99	−99	−99
6	−49	−98	−94	−97
7	−37	−95	−98	−99
8	−58	−98	−99	−99
9	−98	−98	−97	−99
10	−79	−94	−88	−85
11	−98	−99	−99	−97
12	−96	−97	−94	−95
13	−95	−99	−95	−99
14	−92	−98	−96	−99
15	−94	−99	−98	−99
16	−92	−96	−95	−97
17	−85	−84	−77	−84

[a]Vs. 1260 1000 ppm control ± 5%.

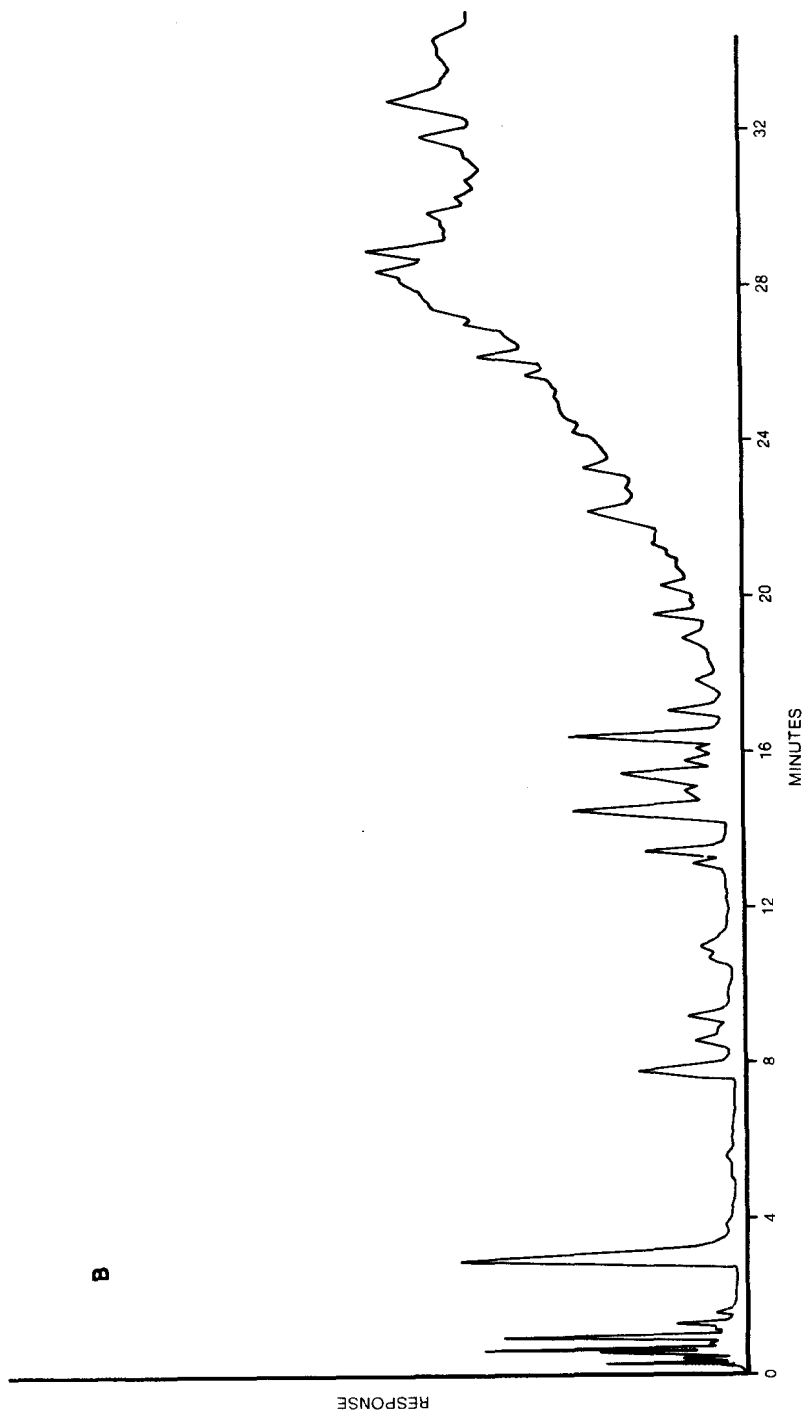Fig. 1A. Gas chromatogram of Aroclor 1260 standard at 100 ppm.

Fig. 1B. Gas chromatogram of Aroclor 1260 (1000 ppm) after treatment with KPEG-350M—PS reagent (1:1, v/v of KPEG-350M—PS) for 4 hours at 60°C.
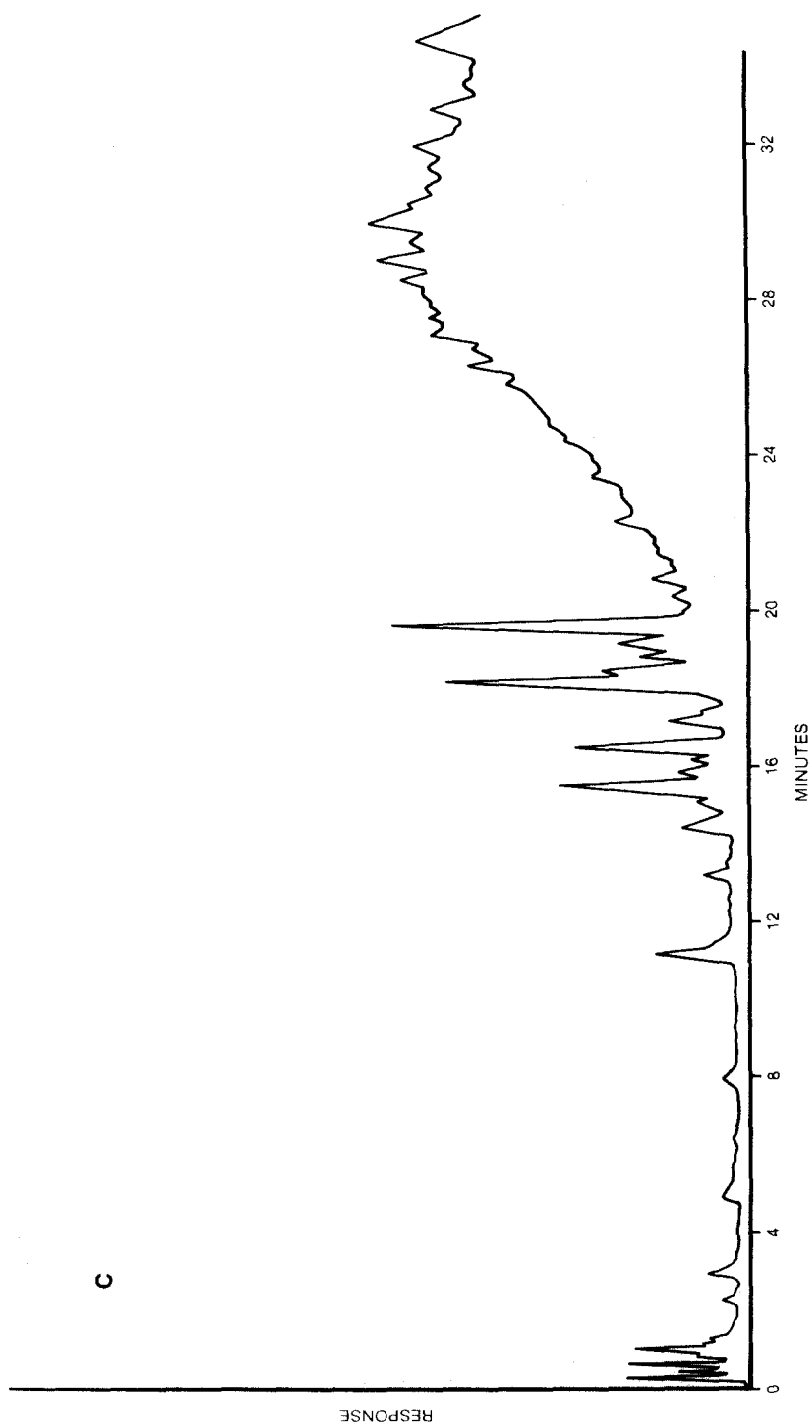
Fig. 1C. Gas chromatogram of Aroclor 1260 (1000 ppm) after treatment as in Fig. 1B except for 24 hours at 20°C.
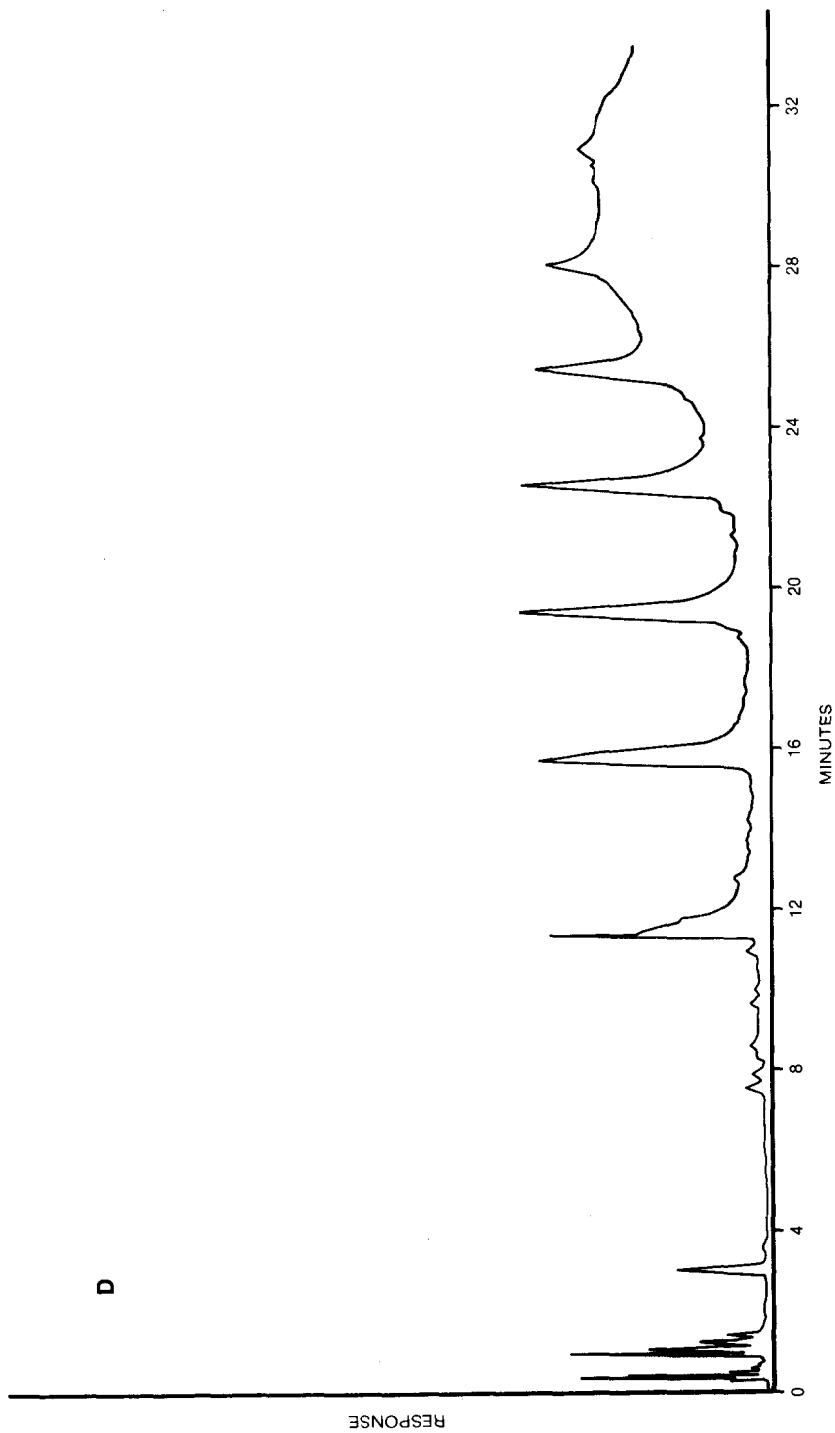
Fig. 1D. Gas chromatogram of the background caused by KPEG-350M—PS (1:1, v/v) without Aroclor present.

tion rate measurements when an attempt is made to apply these rates on PCB mixtures such as the Aroclors. A general statement can, however, be made regarding the dehalogenation rate/temperature effect: the more highly chlorinated PCBs are reduced up to an order of magnitude faster at 60°C than at 20°C, when employing this particular reagent on Aroclor 1260. A more quantitative approach to this problem is presented by the results in Table 1. When comparing the 20°C, 4-hour reaction to the 60°C, 4-hour reaction, peaks 9 to 17 show almost identical reductions whereas peaks 1 to 8 are much more slowly dehalogenated at 20°C. Even after 24 hours at 20°C, peaks 1 to 4 are not reduced as much as after 4 hours at 60°C. This reveals the general trend of the reagent to rapidly dechlorinate the more highly halogenated PCBs.

The KPEG-350M—PS reagent is essentially an anhydrous mixture, containing only the water formed by the initial reaction of the KOH with PEG-350M, as per the scheme

$$KOH + HO(CH_2CH_2O)_nCH_3 \rightleftharpoons KO(CH_2CH_2O)_nCH_3 + H_2O$$
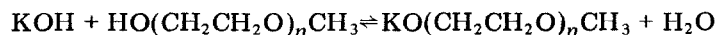
In Tables 2 and 3, where equal volumes of H_2O were mixed with KPEG-350M, significantly slower dehalogenation rates are observed. In the case of

TABLE 2

Reaction of Aroclor 1260 vs. KPEG-350M—H_2O at 20°C. Initial Aroclor 1260 concentration of 100 ppm. Reagent to H_2O ratio of 1:1, v/v

Peak no.	Percent increase (+) or decrease (−)		
	$T = 4$ h	$T = 24$ h	$T = 48$ h
1	+100	+74	+83
2	−5	−16	−12
3	−11	−26	−24
4	−14	−29	−28
5	−11	−27	−29
6	−12	−29	−28
7	−13	−29	−31
8	−11	−28	−34
9	−27	−33	−41
10	−16	−33	−38
11	−11	−25	−43
12	−13	−30	−46
13	−22	−46	−94
14	−19	−37	−68
15	−9	−32	−52
16	−15	−33	−95
17	−14	−86	−100

[a]Vs. 100 ppm 1260 control ± 5%.

Aroclor 1260 (Table 2) in the presence of the aqueous diluted reagent, the 48-hour results at 20°C compare favorably to the 4-hour results in Table 1 (20°C). Also the general statement holds, of higher halogenated PCBs reacting more quickly than do the lesser halogen containing peaks. These slower dehalogenation rates are not surprising when employing an aqueous diluted reagent as the H_2O would upset the equilibrium of reagent formation, favoring more KOH in solution. What is interesting is the fact that the reagent when diluted by 50% with H_2O works at all. In both Tables 2 and 3 a trend appears where there is continual dechlorination of the later eluting peaks and a general leveling off of the early eluters. In Table 2 peaks 1—5 are most resistant whereas in Table 3 peaks 1—19, or the majority of this Aroclor, appears resistant to further attack. Indeed, only peaks 20—24 in Table 3 show the trend of continual dehalogenation with time.

TABLE 3

Reaction of Aroclor 1242 vs. KPEG-350—H_2O at 20°C. Initial Aroclor 1242 concentration of 100 ppm. Reagent to H_2O ratio of 1:1, v/v

Peak no.	Percent increase (+) or decrease (−)[a]		
	T = 4 h	T = 24 h	T = 48 h
1	+24	+11	+11
2	+20	+9	+9
3	+6	+4	+2
4	−2	−6	−2
5	−2	−4	−2
6	−6	−6	−6
7	−2	−4	−4
8	−6	−7	−5
9	−5	−5	−5
10	−12	−14	−11
11	−10	−11	−10
12	−12	−13	−9
13	−7	−10	−6
14	−7	−10	−7
15	−23	−26	−22
16	−16	−22	−16
17	−40	−50	−47
18	−14	−20	−15
19	−45	−53	−48
20	−52	−79	−90
21	−55	−68	−91
22	−57	−73	−95
23	−69	−94	−100
24	−93	−100	−100

[a]Vs 100 ppm 1242 control ±5%.

In view of these findings it was decided to formulate the reagent, incorporating the proprietary solvent at various ratios (v/v) for comparison to both the neat and aqueous diluted reagent, and to measure the effect on both Aroclors 1242 and 1260 at 20°C. The results of this experiment are presented in Tables 4 and 5.

In Table 4 when one compares the various reagent:PS ratios a trend appears with increasing reagent content. This trend, most noticeably in peaks 2, 4 and 5, shows increasing dehalogenation with increase in reagent content until pure reagent is used. Pure or neat reagent, it would appear, does not speed up or benefit the dechlorination of Aroclor 1260. The most effective mixture is apparently the 2:1 (reagents:PS, v/v) solution.

The results of Aroclor 1242 treated with identical reagent:PS mixtures under the same conditions gave similar results. There was, however, a more dramatic effect of reduction and hence dehalogenation of early eluting PCB peaks with the neat reagent system as compared with the various diluted reagent systems. This trend reverses itself when comparing the neat reagent's effect on the later eluting peaks. In this case the diluted reagents (1:1, 1:2, 2:1) had a greater effect on those later eluters than pure reagent as in the study with Aroclor 1260 (Table 4). In all cases where either neat

TABLE 4

Reaction of Aroclor 1260 vs. KPEG-350M—PS at 20°C. Initial Aroclor concentration 100 ppm. Reagent to PS ratios as indicated (v/v). All samples taken at $T = 4$ h

| Peak no. | Percent increase (+) or decrease (−)[a] | | | |
	Ratio 1:2	Ratio 1:1	Ratio 2:1	Reagent only
1	+40	0	+45	+20
2	−80	−70	−72	−95
3	−95	−94	−95	−85
4	−55	−60	−98	−80
5	−95	−96	−99	−85
6	−95	−98	−99	−87
7	−92	−98	−99	−80
8	−95	−98	−99	−80
9	−98	−98	−99	−85
10	−88	−85	−99	−90
11	−88	−95	−99	−80
12	−95	−95	−100	−80
13	−100	−100	−100	−96
14	−95	−95	−95	−93
15	−90	−92	−100	−85
16	−90	−93	−100	−85
17	−100	−100	−100	−52

[a]Vs. 100 ppm 1260 control ±5%.

TABLE 5

Reaction of Aroclor 1242 vs. KPEG-305M—PS at 20°C. Initial Aroclor concentration 100 ppm. Reagent to PS ratios as indicated (v/v). All samples taken at $T = 4$

| Peak no. | Percent increase (+) or decrease (−)[a] | | | |
	Ratio 1:2	Ratio 1:1	Ratio 2:1	Reagent only
1	0	0	+8	0
2	+9	−5	−13	−5
3	+10	+2	+3	−10
4	−25	−18	−20	−15
5	−3	−10	−11	−45
6	−8	−18	−20	−30
7	+1	−20	−30	−40
8	−2	−30	−45	−45
9	−2	−50	−55	−42
10	−8	−30	−48	−65
11	−7	−40	−50	−65
12	−25	−65	−60	−75
13	−7	−70	−75	−75
14	−25	−80	−80	−80
15	−70	−75	−80	−65
16	−95	−80	−88	−67
17	−98	−90	−90	−70
18	−98	−78	−78	−60
19	−98	−95	−98	−65
20	−96	−78	−80	−55
21	−78	−80	−50	−60
22	−80	−62	−80	−55
23	−80	−75	−70	−55
24	−35	+10	+10	−30

[a]Vs. 100 ppm 1242 control ± 5%.

reagent or reagent—PS systems were used they exhibited a faster dehalo-genation of Aroclors 1242 or 1260 than in the reagent—H_2O diluted systems.

Conclusion

It has been suggested to the Industrial Environmental Research Labora-tories of USEPA in Cincinnati by varous sources that NaPEG[TM] or similar reagents could be applied toward *in-situ* or field use for decontamination of soils which contain halogenated aromatics such as PCBs and chlorodioxins. This brief study indicates promise for *in-situ* application of the KPEG-350M reagent formulations. It has been demonstrated that even dilution with H_2O to 50% by volume of the reagent can still yield an active de-chlorination system. Though this aqueous reagent is by no means as effective

as the neat reagent or reagent—PS mixtures, it does nonetheless work. This demonstrates a tolerance toward H_2O hitherto unheard of when dealing with these types of dehalogenation systems. A further promising effect is of the proprietary solvent reagent formulations which appear more reactive than neat reagent toward most Aroclor 1242 or 1260 peaks. Whether the effect of PS is catalytic in nature has not been determined; however, this may well be the case. The effect of increasing reactivity with increasing temperature was also demonstrated. This effect is important for even though one may not normally think of soil heating for *in-situ* decontamination this presents a viable input to the overall *in-situ* application scheme. In relatively recent times technology applied to oil recovery which incorporates radio frequency (RF) heating of the found has proven successful. Indeed, RF ground heating can raise the surrounding strata to temperatures in excess of 400°C; thus, it should be possible to conveniently heat soil to several feet deep over a selected area to 60°C with minimal energy. Thus a combination of reagent selection, PS and RF heating, it would appear are likely candidates for an *in-situ* dehalogenation/decontamination approach for heavily contaminated toxic soils.

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