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## International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

### Evaluation of a Novel Dechlorination Reaction as an Analytically Useful Derivatization Reaction Part 1. Stoichiometry, Mechanism and Yield Optimization

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**To cite this Article** Paleologou, M. , Purdy, W. C. , Misra, S. K. and Korczak, S. Z.(1993) 'Evaluation of a Novel Dechlorination Reaction as an Analytically Useful Derivatization Reaction Part 1. Stoichiometry, Mechanism and Yield Optimization', *International Journal of Environmental Analytical Chemistry*, 50: 4, 215 – 242

**To link to this Article:** DOI: 10.1080/03067319308027600

URL: <http://dx.doi.org/10.1080/03067319308027600>

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# EVALUATION OF A NOVEL DECHLORINATION REACTION AS AN ANALYTICALLY USEFUL DERIVATIZATION REACTION PART 1. STOICHIOMETRY, MECHANISM AND YIELD OPTIMIZATION

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*(Received, 14 April 1992; in final form, 5 October 1992)*

A novel reaction for the dechlorination of polychlorinated biphenyls (PCBs) as well as most other chlorinated aromatic and aliphatic compounds is evaluated and discussed in terms of its potential for analytical purposes. The active dechlorinating agent is prepared through the reaction of molten sodium or potassium with polyethylene glycols (MW >200), in the absence of oxygen, to form the corresponding alkali metal glycolate, a powerful nucleophilic agent. Special emphasis is given to the mechanistic aspects of the reaction and their importance in terms of achieving high and reproducible yields with analytical quantities of substrate, in short periods of time. The contribution of the techniques: ESR, NMR, IR, UV, MS, GC-ECD, LC-EC, CIDNP-NMR, conductimetry and chloride analysis (amperometric) in elucidating the reaction mechanism and providing valuable kinetic data is illustrated. This reaction can potentially be applied to the determination of PCBs in waste oils.

**KEY WORDS:** Dechlorination, polychlorinated biphenyls, potassium glycolate, reaction mechanism, ESR, CIDNP-NMR.

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## INTRODUCTION

The most popular technique for the quantitation of aryl halides and in particular, PCBs, in environmental samples has been Gas Chromatography with Electron-Capture Detection (GC-ECD). Because, however, of the disproportionality of response of the ECD detector<sup>1</sup> and many real-world complexities such as sampling, contamination in the laboratory, extraction, clean-up, organochlorine interferences, non-metabolic and metabolic alterations, original composition and separation, the choice of a suitable reference standard (nearest commercially available PCB formulation) is often a difficult one, and consequently the reported single value for total PCB content may be both inaccurate and misleading. By utilizing a peak-by-peak area comparison approach<sup>2</sup> rather than the total pattern concept, the reliability of results obtained by GC-ECD can be significantly improved; even in this case, however, some overlapping or coincident peaks still occur.

In an effort to minimize separation and interference problems while enhancing sensitivity and speed of analysis, some researchers turned their attention to the development of alternate approaches to analysis involving measurement of a single species rather than a mixture. These approaches can be classified into two major categories of derivatization reactions: perchlorination and dechlorination reactions. Perchlorination has been promoted by a number of investigators<sup>3-5</sup> mostly because of the enhanced sensitivity that is obtained when all PCB isomers are converted to decachlorobiphenyl (DCB). Despite the many advantages of perchlorination, however, some errors may still occur as a result of the conversion of sample constituents other than PCBs, into either DCB or other species with similar retention characteristics to those of DCB. A number of analytical derivatization procedures based on dechlorination have been developed over the last thirty years. These include: dechlorination over a heated catalyst, in a stream of hydrogen gas (hydrodechlorination), to obtain the respective parent hydrocarbons<sup>6,7</sup>; carbon-skeleton GC<sup>8,9</sup> for the quantitative conversion of PCBs into biphenyl on a partly deactivated palladium catalyst; and catalytic on-column dechlorination<sup>10,11</sup>. It must be stressed here, however, that these dechlorination procedures did not gain widespread acceptance because the preparation of a suitable catalyst does not appear to be a very simple task. In 1979, a dechlorination procedure was reported<sup>12</sup> which combined dechlorination with LiAlH<sub>4</sub> with column liquid chromatography using UV detection. De Kok *et al.*<sup>13</sup> further improved this procedure and applied it to the analysis of a wide range of environmental samples. These investigators maintain that their modified and simplified version of the original procedure<sup>12</sup> is as easy to perform as perchlorination and therefore, it is suitable for routine application in the analytical laboratory.

The purpose of this work has been to develop a simple dechlorination procedure for aryl chlorides that satisfied most criteria for an analytically useful derivatization reaction and compared well with other previously reported approaches. In order to develop such a procedure, the literature was searched for relatively new approaches for breaking the carbon-chlorine bond in aryl halides, outside the realm of mainstream analytical and/or organic chemistry. It was found for example that, in the last twenty years, a number of novel approaches have been developed for the dechlorination of PCBs as part of an all-out effort to come up with hazardous waste disposal techniques for a number of chemicals. Examples of such dechlorination approaches include: incineration at high temperatures

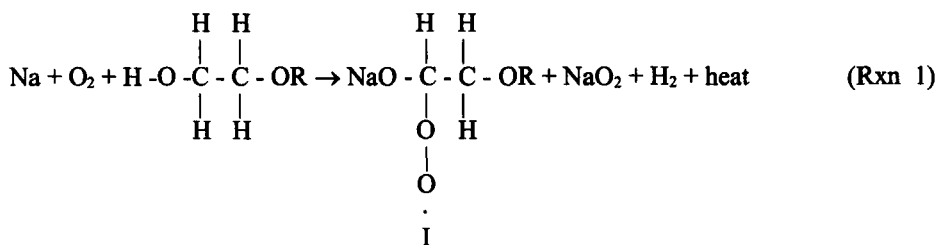
in the absence<sup>14</sup> or presence<sup>15</sup> of molten salt catalysts, thermal oxidation in fluidized beds<sup>16</sup>, electron treatment<sup>17</sup>, UV irradiation in the presence of hydrogen<sup>18</sup>, chlorinolysis<sup>19</sup>, ozonation<sup>20</sup>, and treatment with an aqueous solution of hypophosphite in the presence of a palladium catalyst<sup>21</sup>. Chemical decomposition of highly chlorinated aromatic compounds such as PCBs and DDT has been also achieved using very strong reducing agents<sup>22</sup> such as  $\text{BH}_4$  and alkali metals dissolved in very dry liquid ammonia or other media. Sodium naphthalenide was used<sup>23</sup>, for example, to convert PCBs to a chlorine-free organic material product. A number of other dechlorination methods based on alkali metal reagents has also been suggested. The alkali metals lithium, sodium or potassium, in elementary metallic form have been effective in dechlorinating PCB molecules<sup>24-26</sup>. Most of these reactions, however, present too many problems before and after the reaction to qualify as analytically useful reactions. Drawbacks include: limited breadth of reactivity, expensive reagents, complex apparatus, energy intensiveness, absence of analytically useful reaction products, extremely inert atmospheres, extensive temperature controls, etc.

In the early eighties Pytlewski *et al.*<sup>27,28</sup> reported a dechlorination reaction that, in principle, appeared to satisfy most widely accepted criteria of an analytically useful derivatization reaction. These are: simplicity, high speed, reproducibility, high yield, low cost, safety and no matrix interferences<sup>29</sup>. The present work attempts to evaluate the Pytlewski reaction, further described below, as an analytically useful derivatization reaction. For this purpose, three model compounds were chosen: chlorobenzene, 1,2,3,4-tetrachlorobenzene and hexachlorobenzene. Using these model compounds, the Pytlewski reaction was studied using a number of techniques. These are: Electron Spin Resonance Spectroscopy (ESR), Nuclear Magnetic Resonance Spectroscopy (NMR), Infra-red Spectroscopy (IR), Mass Spectrometry (MS), Gas Chromatography with Electron Capture Detection (GC-ECD), Cyclic Voltammetry (CV), Liquid Chromatography with Electrochemical Detection (LC-EC), Chemically-induced Dynamic Nuclear Polarization – Nuclear Magnetic Resonance Spectroscopy (CIDNP-NMR), Conductimetry and Chloride analysis. First, this paper examines the effect of various parameters on dechlorination reaction yield and subsequently it addresses a number of fundamental questions relating to the mechanism of the reaction under examination. As will be shown in this paper, a number of major and minor discrepancies were found relating to the results reported by Pytlewski *et al.*<sup>27,28</sup>. Based on the findings of this study, an analytical procedure was developed for the determination of PCBs in waste oils; this work is described in a subsequent paper in this issue.

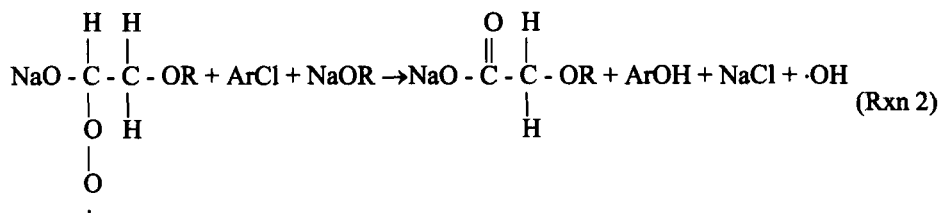
### *The Pytlewski dechlorination reaction*

The Pytlewski reaction was developed for the purpose of providing an inexpensive method for disposing of waste PCB mixtures and other chlorinated environmental contaminants. As part of the reaction mechanism a number of steps were suggested by Pytlewski *et al.*<sup>27,28</sup> which can be summarized in two main steps.

## Step 1: Preparation of active reagent



## Step 2: Dechlorination reaction



In step 1 Pytlewski *et al.*<sup>28</sup> suggested that “rapid oxygen uptake is occurring at PEG ether linkages through insertion between sodium-carbon bonds”. It is further suggested that “a variety of free radicals are generated of which one combines with oxygen to produce species I, designated as the sodium glycolate superoxide radical” which is presumed to be the active dechlorinating agent in step 2.

## EXPERIMENTAL

*Reaction system and procedure*

All reactions were carried out in variations of a reaction system which consisted of a three-neck round bottom flask one neck of which was equipped with a reflux condenser; the other two openings were closed with glass stoppers or rubber septa. The reaction vessel was immersed in an oil bath and the temperature was controlled through a Sybron/Thermolyne thermostat. The solutions were stirred with a magnetic stirring bar, at a constant rate, at all times. The reactions were carried out under nitrogen or air while maintaining open conditions at all times in order to avoid any pressure build-up. The gases were dried by passing through a column of anhydrous calcium sulphate particles (Drierite). The gas flow to the reaction vessel and pressure therein (atmospheric) were controlled by means of a pressure gauge on the gas cylinder and through a T-junction, placed after the drying tube, with one line going to the reaction vessel and the other to a gas bubbler. The reacting solution was composed of PEG (typical MWs: 200–600), previously dried over activated molecular sieves type 3A (8–12 mesh), and metallic sodium or potassium. The molecular sieves were activated by

placing them in an oven, equipped with a vacuum line and held at 300°C, overnight. The active reagent was prepared by reacting PEG and metallic sodium or potassium at a temperature slightly higher than their melting points (98°C and 63.5°C, respectively). Kinetic and other samples were collected at regular time intervals by withdrawing aliquots through the septa using a BLOC syringe. For all kinetic studies the reaction temperature was held at 110°C. Before each experiment all glassware were cleaned using a procedure developed by Bevenue *et al.*<sup>30</sup>.

### *Analysis of reaction products*

IR spectra were recorded using a Varian spectrophotometer. Reaction samples were run neat by placing one or two small drops of the sample between two highly polished pieces of cell material (KBr). Mass spectrometric data were obtained using a Dupont Instruments Model 21-492B mass spectrometer. UV spectra were recorded using a Cary Model 210 spectrophotometer. Kinetic samples of the reaction of PEG with sodium (or potassium) and oxygen for UV analysis were diluted by 231x with PEG in order to reduce their absorbance to conveniently measurable levels. Conductance measurements were made using a Beckman Instruments conductivity bridge. Testing for the superoxide free radical was performed using a procedure described elsewhere<sup>31</sup>. ESR spectra were recorded on a Varian V4502 X-band spectrometer in the Dept. of Physics, Concordia University. The magnetic field was measured using a Bruker Gaussmeter Model B-NM20. Measurements were made with reference to 2,2-diphenyl-1-picrylhydrazine ( $g = 2.0036$ ), used as a standard for calibrating the instrument. The sample vials were stoppered using Serum septa. Samples for ESR analysis were withdrawn from the reaction mixture using a 0.5 mL syringe capable of penetrating through the reaction vessel septa and the sample vial septa. 10  $\mu$ l of reaction product was delivered to the sample cavity of the ESR spectrometer using a 20- $\mu$ l Eppendorf pipette. The precision demonstrated by this instrument was  $\pm 1\%$  for samples of the same concentration analyzed on the same day. NMR and CIDNP-NMR proton spectra were recorded on an XL-200 NMR instrument at room temperature. Samples for analysis using this technique were prepared by dissolving the products of the reaction between PEG and sodium (or potassium) and oxygen, in deuterated benzene.

The disappearance of chlorinated organic compounds during the dechlorination reaction was followed using GC-ECD. A Varian Model 3700 Gas Chromatograph equipped with an ECD was employed under the following conditions: column: 6 ft  $\times$  0.25 inch, 3% OV101 (glass) on Chromosorb W (H/P) 80/100 mesh; carrier gas: nitrogen; flow rate: 60 ml/min; injection temperature: 270°C; ECD temperature: 300°C; column temperature: 185°C; injection volume: 2  $\mu$ l, sensitivity:  $10^{-2}$  range. In this kinetic study, aliquots were collected at various time intervals during the reaction (1 ml) and these were diluted in PEG 400 (10 ml). 1 ml of these solutions was diluted in 4 ml of water (overall dilution factor = 110). The latter solutions were extracted with 10 ml of cyclohexane and diluted, as needed, for analysis in the dynamic range of the GC-ECD method.

The analysis for phenolic compounds in the dechlorination reaction products was performed using a liquid chromatographic method employing a  $\beta$ -cyclodextrin bonded-phase column connected to a UV and/or a thin-layer amperometric detector<sup>32</sup>. The HPLC

system consisted of a Waters Model 590 pump, a Rheodyne Model 7125 injector with a 100- $\mu$ l loop, and a Model Spectroflow 773 variable wavelength UV-VIS detector equipped with a 8- $\mu$ l cell. The UV detector was set at 280 nm at which wavelength most phenols present a maximum in absorbance. The voltage between the reference and working electrodes of the electrochemical detector was set at 1.0 V. The mobile phase was composed of methanol, water mixtures buffered with triethylamine acetate and it was degassed by bubbling nitrogen into it before use. The chromatograms were recorded using a Microhm Model SE 120 strip-chart recorder. The column temperature was controlled through a Heto Model water bath. The flow rate was 1.0 ml/min and the column back-pressure at this flow rate varied from 2000–3000 psig. All standard compounds and reaction samples were dissolved in solutions of the same composition as the mobile phase. Typically 5–20  $\mu$ l of solutions of these standard reference compounds was injected. A Waters C<sub>18</sub>, 250  $\times$  4.6 mm (Zorbax) column was employed whenever the separation of reaction products (reaction between PEGs, sodium and oxygen) was required. In the latter case, a mobile phase composed of a 95:5, buffer:PEG mixture was used. The buffer solution was prepared as 0.2 M in sodium perchlorate and  $5.0 \times 10^{-3}$  M trisodium citrate adjusted to pH 5.0 with glacial acetic acid. The system described above was also employed for the quantitation of an electroactive species (hydrogen peroxide) produced after the reaction products were allowed to react with water or acid.

Reaction yields were evaluated by measuring the amount of chloride produced using an argentometric amperometric titration<sup>33</sup>. The apparatus consisted of a rotating platinum electrode connected to a saturated calomel electrode through a current measuring device. The PAR model 173 was used for applying a potential between the two electrodes and the PAR model 179 for converting cell current to a voltage which was put out to a strip-chart recorder. The electrode was rotated at a speed of about 200 rpm. Using this chloride analysis procedure the reproducibility of the dechlorination reaction yields was found to range from 0.5–2% depending on the substrate and/or the conditions used. As will be shown later on in this paper, the dechlorination reaction yields for a given compound were not significantly affected by changes in such experimental variables as sodium concentration, molecular weight of PEG, substrate concentration, temperature and the duration of the dechlorination reaction.

PEGs, metallic sodium and potassium, triethylamine and NBT chloride monohydrate were obtained from Aldrich. A bovine erythrocyte superoxide dismutase enzyme preparation was obtained from Sigma. HPLC-grade methanol and sodium perchlorate were purchased from Fisher. Trisodium citrate was obtained from Mallinckrodt. Water was deionized by passing distilled water through a Barnstead water purification system. All chlorinated and non-chlorinated standards were purchased from Chem Service.

## RESULTS AND DISCUSSION

*Reaction yields and stoichiometry*

Analytically useful derivatization reactions are usually specialized, synthetic, organic chemical reactions. The main difference between these and other chemical reactions is that they are done on a microscale. As mentioned earlier, from an analytical point of view it is important to achieve high and reproducible yields in a derivatization reaction in order to enhance sensitivity and improve precision. In order to enhance reaction yields, the effect of various parameters on reaction yield was examined. These are: sodium concentration, molecular weight of PEG, substrate concentration, temperature, duration of free radical preparation reaction, duration of dechlorination reaction, nature of the substrate, moisture content of PEG and continuous addition of sodium and/or PEG. Unless otherwise specified all reactions referred to in this section were carried out under oxygen (exposed to air) with 1,2,3,4-tetrachlorobenzene as the substrate.

*Effect of sodium concentration* The effect of sodium concentration on reaction yield was examined for the concentration range of 20 to 60 g/l. The latter concentration of sodium is the maximum that can be attained in PEG 400 and corresponds to the stoichiometric amount of sodium that can react with PEG in the following reaction during the solubilization process:



As shown in Table 1, the concentration of sodium does not seem to affect reaction yields as long as it is in a stoichiometric excess compared to the reaction substrate. A dechlorination reaction yield of about 42% was obtained for all concentrations of sodium in the reaction medium with 1,2,3,4-tetrachlorobenzene as the substrate.

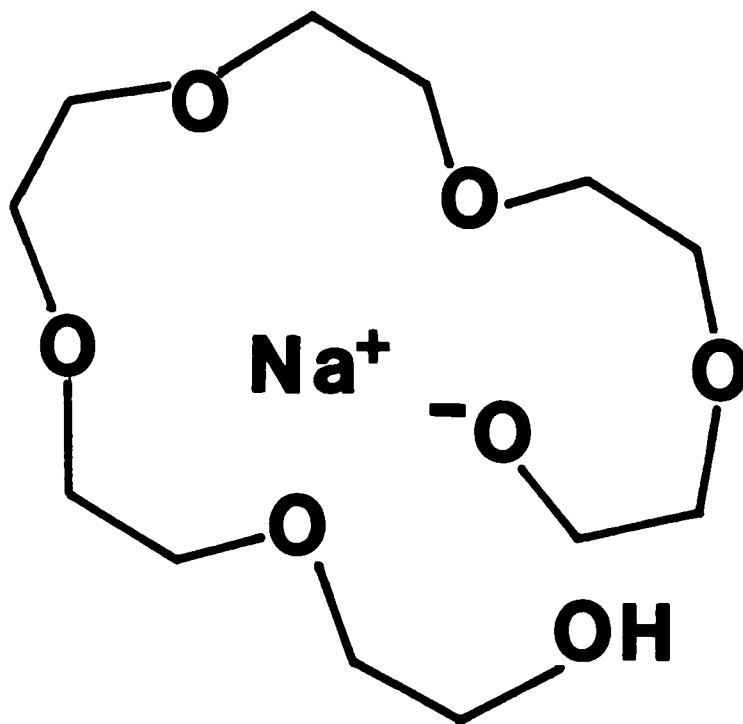
**Table 1** Effect of sodium concentration on dechlorination reaction yield.

<i>Sodium Concentration</i> (g/l)	<i>Reaction Yield</i> (%)
20	42.1
40	43.8
60	42.9
> 60	42.5

Reaction conditions were as follows: Substrate: 1,2,3,4-tetrachlorobenzene, Substrate concentration: 140 µg/ml, MW of PEG: 400 g/mole, Temperature: 120°C, Duration of free radical preparation reaction: 36 min, Duration of dechlorination reaction: 65 min.

*Effect of molecular weight of PEG* PEGs constitute the reaction solvent and, furthermore, are intimately involved in the preparation of the active dechlorinating agent. In the molecular





**Figure 1** Sodium glycolate crown-ether type of structure with internal ion pairing.

weight range of 200–600 no significant effect on the reaction yield was observed. With molecular weights, however, less than 200, a decrease in reaction yields was observed. This observation first suggested that a sodium-PEG complex (crown-ether type) may be involved as an active reagent in the reaction (see Figure 1) Such complexes have been shown to exist by a number of investigators<sup>34–36</sup>. Polyglycol dimethyl ethers or glymes, for example, of the general formula  $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_3$ , have been shown to form solvent separated ion pairs with a number of alkali metal salts (contact ion pairs). Their ability to complex with alkali metal ions was found to depend on the number of available co-ordination sites. For sodium-diglyme complexes it was shown that the complexation constants reach a maximum when the number of oxygens in the diglyme is 5. This was interpreted to suggest that a maximum of five oxygen atoms (this corresponds to a MW of 200 for PEG) co-ordinate with one sodium ion. As the chain length increases beyond glyme-5, the complexation constant is expected to further increase for purely statistical reasons<sup>35</sup>. In fact, it is even higher than what can be predicted using statistical arguments and it accelerates for glymes of longer chain lengths. It appears that there may be certain preferred conformations in the longer glymes which are favourable for cation complexation.

*Effect of the substrate concentration* It was found that no significant change in reaction yield occurs in the concentration range between 135–4360  $\mu\text{g/ml}$  substrate while yields

decline for higher concentrations. These data suggested that for substrate concentrations less than 4360  $\mu\text{g/ml}$  the active reagent is in sufficient excess to carry the reaction to the 42% reaction yield level. Assuming that the reaction is:



then 4360  $\mu\text{g/ml}$  of substrate is close to the stoichiometric limit of the reaction. When the concentration of substrate is further increased the reaction yield drops thus suggesting the possibility that Rxn 4 occurs as written. These data first suggested that NaOR may be the active dechlorinating agent.

*Effect of temperature* In the temperature range of 120–230°C no significant effect of temperature on reaction yields was observed. It should be mentioned, however, that below 98°C (melting point of sodium) the reaction was very slow.

*Effect of duration of free radical preparation reaction* One would expect that the longer the duration of the free radical preparation reaction (see Rxn 1) as perceived by Pytlewski *et al.*<sup>27,28</sup>, more active reagent and hence higher reaction yields would have been obtained. This was not the case, however. In fact, to a small extent, the opposite effect was observed that is a decrease in reaction yield. This evidence suggested for the first time that species I, (see Rxn 1) if it indeed exists, may not actually be the active dechlorinating reagent as suggested by Pytlewski *et al.*<sup>27,28</sup>.

*Effect of the duration of the dechlorination reaction* The time allowed for the reaction between 1,2,3,4-tetrachlorobenzene and the active reagent ("sodium glycolate superoxide radical") had no significant effect on the reaction yield (see Rxn 2 as perceived by Pytlewski *et al.*<sup>27</sup>). This was considered as additional evidence that species I (see Rxn 1) may not be the active reagent, since one would expect ascending yields with increasing reaction times.

*Effect of the nature of the substrate* The effect of the nature of the substrate on reaction yield is seen in Table 2. Chlorobenzenes (mono-, tri-, tetra-, hexa-) give yields that are around the 45% level with a small decline observed as the number of chlorines on the ring is reduced. Pentachlorophenol is dechlorinated, as well, at about the 45% level suggesting that the -OH group presumably does not have any apparent effect on the dechlorination reaction in terms of deactivating the ring or in some other way. Hexachlorocyclohexane (lindane) is dechlorinated with a yield of 65.4%, demonstrating the applicability of the reaction to aliphatic compounds and furthermore suggesting that aliphatic compounds may be easier dechlorinated.

*Effect of the moisture content of PEG* An analysis for water in PEG 400 using the Karl Fischer reagent revealed the presence of 0.172% water. In order to remove all moisture from the reaction system, PEG was dried with molecular sieves 3A and the reaction was performed under air from a tank that was dried by passing through a column of anhydrous calcium sulphate particles (Drierite).

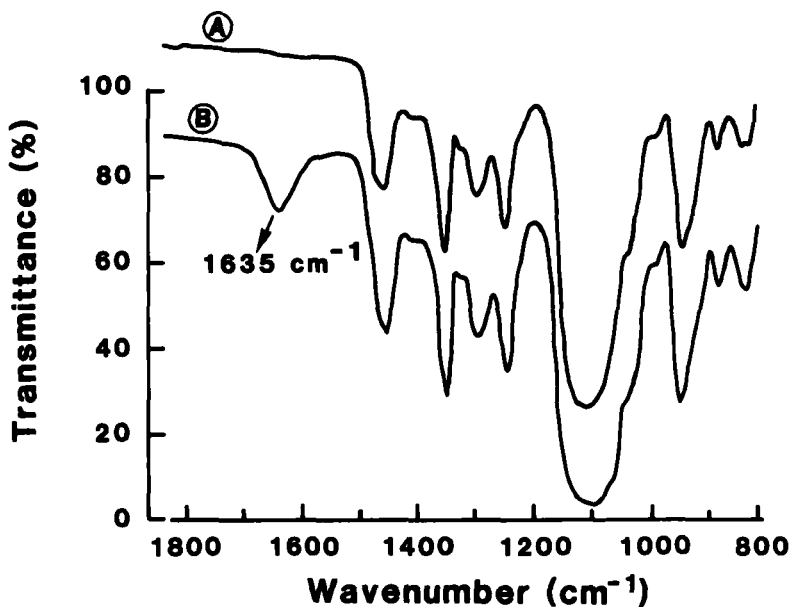
The above measures improved reaction yields from the 40% level to the 60% level even

**Table 2** Effect of the nature of the substrate on dechlorination reaction yields.

<i>Chlorinated Compound</i>	<i>Concentration (<math>\mu\text{g/ml}</math>)</i>	<i>Dechlorination Yield (%)</i>
chlorobenzene	115	35.5
1,2-dichlorobenzene	150	40.3
1,4-dichlorobenzene	138	42.3
1,3,5-trichlorobenzene	132	43.1
1,2,4-trichlorobenzene	95	42.8
1,2,3,4-tetrachlorobenzene	250	44.0
1,2,4,5-tetrachlorobenzene	243	44.3
hexachlorobenzene	303	46.6
Aroclor 1260	438	50.2
pentachlorophenol	109	44.7
hexachlorocyclohexane	234	65.4

Reaction conditions were as follows: MW of PEG: 200 g/mole, Sodium concentration: 60 g/l, Temperature: 120°C, Duration of free radical preparation reaction: 30–42 min, Duration of dechlorination reaction: 60–70 min.

though the reproducibility of the reaction suffered somewhat. The significant improvement in reaction yields due to the elimination of water warranted a more thorough investigation for establishing the role of water in the reaction. Figure 2 shows the IR spectrum of PEG 400 as well as that of the reagent produced after the reaction of PEG with sodium in the presence of atmospheric oxygen. A full description of the features of this spectrum in terms of the identification of the various absorption bands is given elsewhere<sup>37</sup>. The only difference



**Figure 2** IR spectra of PEG 400 (curve A) and products of the reaction of PEG with sodium and oxygen (curve B). An absorption band at  $1635\text{ cm}^{-1}$  (due to  $\text{H}_2\text{O}$ ) is the only difference between A and B.

in the spectra of these two reagents is the absorption peak at  $1635\text{ cm}^{-1}$  which is due to water as can be easily confirmed from the literature or the spectrum obtained after the addition of water to PEG. It appears that water is produced through the decomposition of hydrogen peroxide which, as will be shown later on in this paper, is one of the products of the reaction between PEG, sodium and oxygen. The decomposition reaction is<sup>38</sup>:



The band observed at  $1635\text{ cm}^{-1}$  is not due to any O-O skeletal vibration, that might have arisen from any peroxides or hydroperoxides that may have formed, since this absorption is expected to occur at  $877\text{ cm}^{-1}$ <sup>39</sup>. It should also be mentioned that both peroxide and superoxide show no characteristic sharp bands this being consistent with the theory that both of these ions are homopolar, and thus their vibrations are infra-red inactive<sup>40</sup>. At this point it was thought that it may be possible to eliminate water, as it is produced, by adding excess sodium at the beginning of the reaction since sodium rapidly reacts with water to give sodium hydroxide and hydrogen in the reaction:



As shown in Table 1, however, excess sodium does not improve reaction yields.

*Effect of the continuous addition of sodium on reaction yield* After the above attempt failed to increase reaction yields beyond the 60% level, the question was raised whether the active reagent is being destroyed during the reaction or whether an inhibitor forms before the reaction reaches completion. It was, therefore, decided to keep on adding sodium or sodium and PEG to the reaction mixture gradually, while the reaction was taking place, thus assuring the continued presence of the presumed active reagent. As shown in Table 3 the reaction yields under these conditions surpassed the 80% level. The reaction appeared most successful when both sodium and PEG were added at the same time (see entry 3, Table 3).

**Table 3** Effect of the gradual addition of sodium or sodium/PEG on dechlorination reaction yield.

<i>Mode of Addition of Sodium</i>	<i>Reaction Yield (%)</i>
1. sodium added in three portions	81.5
2. same as 1	83.2
3. sodium and PEG added gradually	85.1

Reaction conditions were as follows: Substrate: 1,2,3,4-tetrachlorobenzene, Substrate concentration: 1200–1500  $\mu\text{g/ml}$ , MW of PEG: 400 g/mole, Sodium concentration: 40 g/l, Temperature:  $180^\circ\text{C}$ , Duration of dechlorination reaction: 180 min.

### *Mechanistic studies*

In order to gain a better understanding of the reactions discussed above, with a view to achieving high and reproducible dechlorination yields, an attempt was made to elucidate the reaction mechanism involved. The mechanistic studies were done with potassium and not sodium since the reaction is faster with the former and also because only  $\text{KO}_2$  (potassium superoxide), which was used for confirmation purposes, was found to be commercially available.

#### *Is a free radical produced during the reaction?*

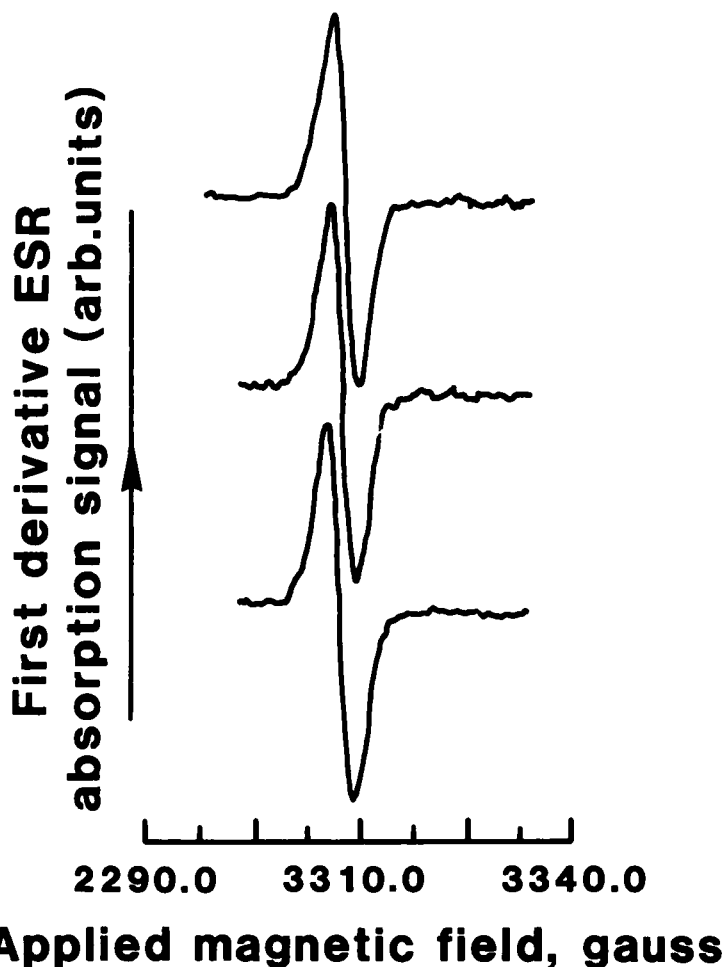
In addressing this question ESR was used for the following reasons:

1. to establish whether any free radicals are involved and/or participate in the reaction as suggested by Pytlewski *et al.*<sup>27</sup>,
2. to determine the structure of the molecule at the free radical site by examining the hyperfine splitting of the absorption band(s),
3. to study the kinetics of the reaction producing the "active" free radical,
4. to study the kinetics of the reaction of the "active" free radical with various chlorinated substrates,
5. to examine the stability of the free radical under various conditions.

Figure 3 shows three ESR spectra of the reaction products demonstrating that a free radical is produced by the reaction of potassium and PEG in the presence of air (oxygen). The ESR signal for this free radical, centred at about 3307.3 G, corresponds to a g-value of 2.0064, which is a measure of the effective magnetic moment of the unpaired electron. Since no hyperfine structure, which indicates the strength of the magnetic interaction between the unpaired electron and each magnetic nucleus in its vicinity, is observed in this spectrum, the possibility of having a carbon-based free radical or the hydroxyl ( $\cdot\text{OH}$ ) or perhydroxyl ( $\text{HO}_2\cdot$ ) free radicals was ruled out (a carbon-based free radical was implied by Pytlewski *et al.*<sup>27</sup> in the reactions leading to the formation of the "sodium glycolate superoxide free radical"). It was not a peroxide-type radical of the type  $\text{R-OO}\cdot$  or a superoxide complex or adduct free radical since the tertiary peroxide-type radicals possess g-values at about 2.014<sup>41</sup>. Moreover, tertiary peroxide-type radicals, in solution, exhibit rather broad linewidths, due to a large spin-rotation interaction<sup>41</sup> unlike the spectrum of Figure 3 which demonstrates a rather narrow signal. Further, the primary and secondary peroxides do not exhibit ESR signals in solution<sup>41</sup>. The only possibility left is that of a PEG-potassium superoxide complex. That, this is indeed the case, is discussed below.

#### *Optimization of the production of free radical*

In order to optimize the production of this supposedly "active" reagent, a kinetic experiment was performed using ESR to monitor the generation of the spin-active species. In this experiment, samples were taken from the reaction at various time intervals, cooled in ice to quench the reaction, and then subjected to ESR analysis. As shown in Figure 4, no ESR signal is obtained in the first 20 minutes probably because the main reaction happening is:

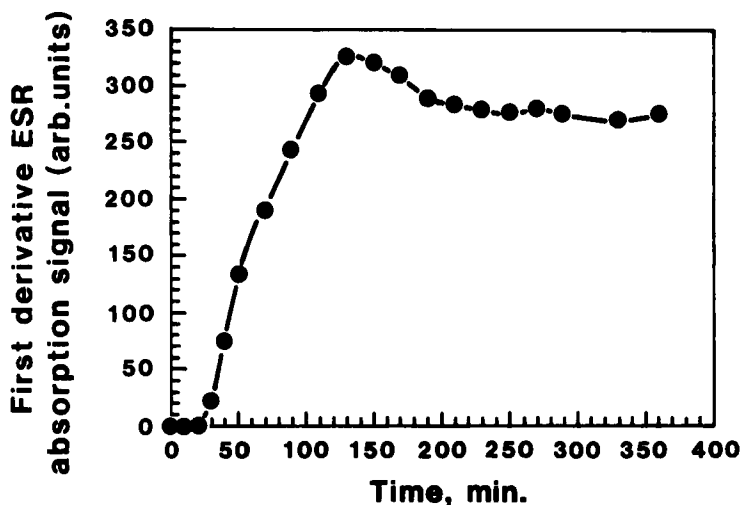


**Figure 3** X-band (9.42 GHz) ESR spectra of products of reaction of PEG with potassium and oxygen. An absorption signal is observed centred at 3307.3 G corresponding to a g-value of 2.0064. The spectra were obtained on a Varian V4502 X-band spectrometer. Conditions:  $\Delta H = \mu\text{m}$  1250 G; Sweep Time = 2.5 min; Modulation Amplitude =  $8 \times 100$ ; sample volume =  $10 \mu\text{l}$ ; temperature = ambient (295°K).

120°C

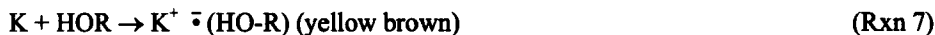


Rxn 3 is likely to be taking place since a gas was seen evolving, heat was produced, potassium was progressively consumed, and the conductance of the solution increased for as long as potassium was seen floating on the reaction mixture. In addition, the colour of the solution became yellow-brown during this period. The colour of the solution may be due to another reaction occurring simultaneously:

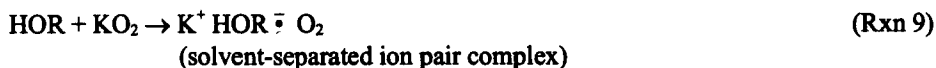


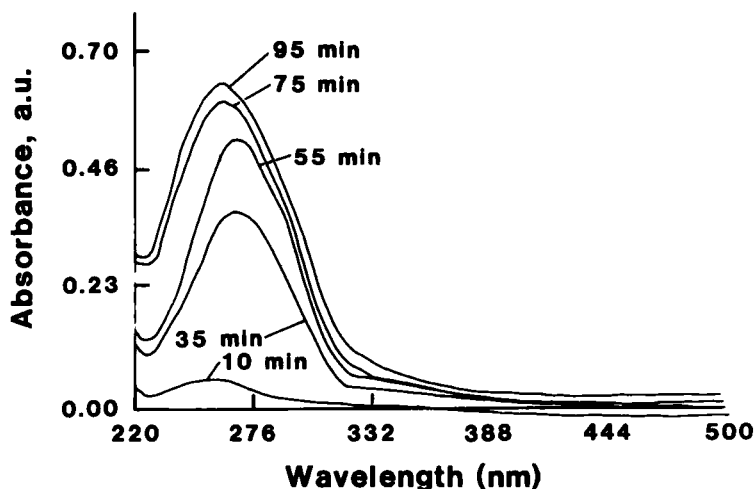
**Figure 4** Kinetic study of the reaction of PEG 400 (75 ml) with metallic potassium (3.0 g) and oxygen (air, gauge pressure: 15 psig) using ESR; reaction temperature: 110°C; conditions for ESR measurements are as those described in the caption of Figure 3. The ordinate represents the peak-to-peak height of the first-derivative ESR spectrum.

120°C



Rxn 7 appears to occur even in the absence of oxygen, which suggests that the colour is not due to a reduced form of oxygen or any oxidation product of PEG. A reaction similar to Rxn 7 was postulated by Matsulevich and Sokolov<sup>42</sup> as the first stage in the oxidation of alkali metals to superoxide in organic solvents (diglymes) catalyzed by aromatic compounds. These investigators also suggested that the existence of an induction period in such reactions can be explained by the topochemical character of the reaction for the formation of radical anions. The reaction starts at the most active centres (corners, faces) of the metal surface, gradually spreading to the whole. With the increase in the “working” surface, the formation of the radical anions of the aromatic compound is accelerated. When this process occurs over the whole surface of the metal, the rate of the oxidation of the latter becomes maximal. The rate-determining step in this oxidation is the formation of radical anions, which goes on the metal surface. After the first twenty minutes (duration of induction period), however, an increasing ESR signal is observed most probably due to the reaction of potassium glycolate radical anion (see Rxn 7) with oxygen to produce an ESR-active species; this appears to be a crown-ether-type of complex between PEG and potassium superoxide as illustrated in reactions Rxns 8 and 9:





**Figure 5** Successive UV spectra of products of the reaction between PEG 400 with potassium and oxygen (air) during the first 105 minutes of the reaction; the measurements were made using a Cary Model 210 spectrophotometer; reaction temperature: 110°C. A slight shift in the absorption maximum is observed with increasing concentration of the absorbing species.

The IR as well as the NMR spectra of the reaction products are identical (except for the presence of water) with the corresponding IR and NMR spectra for PEG, suggesting that this molecule has not been chemically altered in any significant way, as would be expected from Rxns 8 and 9.

The increase in ESR signal continued for the first 120 minutes, that is for about as long as potassium was seen floating on the reaction mixture, and thereafter a slight decrease was observed. Similar behaviour was observed when the same kinetic samples were used for UV analysis at 250 nm. Figure 5 shows a number of successive UV spectra for samples obtained during the reaction. The absorption maximum is about 260 nm; similar maxima were also observed by other investigators<sup>43</sup> for transient  $O_2^{\cdot-}$  in aqueous solutions ( $\lambda_{max} = 240$  nm) and in dimethyl sulphoxide in the presence of the complexing agent 18-crown-6 at ambient temperature ( $\lambda_{max} = 260$  nm)<sup>44</sup>. The absorptivity of superoxide at the wavelength of maximum absorption has been reported to be  $2580 \pm 500 \text{ M}^{-1}\text{cm}^{-1}$ <sup>44</sup> depending on the conditions under which the spectrum was taken. The absorption maximum of  $HO_2^{\cdot-}$  on the other hand, obtained from the pulse radiolysis of oxygen-saturated sodium formate solutions (pH = 2), occurs at about 230 nm and the corresponding absorptivity at this wavelength was about  $1250 \text{ M}^{-1}\text{cm}^{-1}$ <sup>43</sup>. The  $pK_a$  of the  $HO_2^{\cdot-}$  free radical has been reported to be  $4.9 \pm 0.1$ <sup>43</sup> which means that for pH values greater than 5.9 this radical would be almost completely in its dissociated form ( $O_2^{\cdot-}$ ). It appears that the superoxide free radical is quite long-lived at high pH. It has been reported<sup>43</sup> that at pH = 13 a concentration of  $O_2^{\cdot-}$  as high as  $10^{-4}$  M has been generated in water by giving several pulses of radiation to the sample. In PEGs and/or potassium glycolates the lifetime of this species is, therefore, expected to be quite long.

A slight shift in the absorption maximum of the UV spectrum was observed with increasing concentration of the absorbing species (see Figure 5). This shift may be taken as a suggestive evidence for the formation of an inclusion-type complex between potas-



sium superoxide and PEG (see Rxn 9). Similar behaviour was observed by other investigators<sup>34-36</sup> who studied the complexation of lithium, sodium and potassium carbanion pairs (flourenyl) with polyglycol dimethyl ethers (glymes) by means of optical and NMR spectroscopies. These investigators observed, for example, that the contact ion pair  $F^{\cdot-}$ ,  $M^+$  and the glyme-separated ion pair  $F^{\cdot-}$ ,  $G$ ,  $M^+$  have distinctly different absorption maxima.

A number of reactions can be postulated for the slight decline in ESR and UV signals observed when potassium is no longer visible in the reaction mixture. These are:



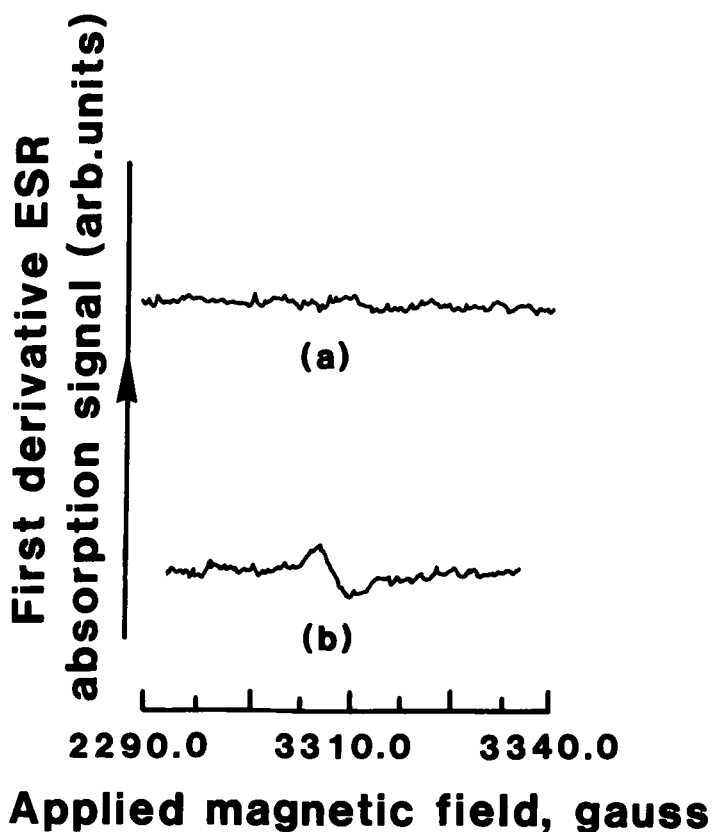
The decline in ESR and UV signals is significantly more pronounced when sodium instead of potassium is used. This difference in behaviour between these two alkali metals may be due to potassium binding being much stronger as compared to sodium binding.

Hydrogen peroxide, itself, is a weak acid,  $pK_a = 11.65^{45}$ . Morgan *et al.*<sup>46</sup> measured molar absorptivities for  $H_2O_2$  and  $HO_2^{\cdot-}$  at a number of wavelengths between 200 and 300 nm from absorbance vs concentration plots. They found that at 250 nm the absorptivity for hydrogen peroxide is  $22.7 \pm 0.5 M^{-1} cm^{-1}$  whereas for the hydroperoxyl anion the absorptivity is  $277.7 \pm 8.3 M^{-1} cm^{-1}$  at this same wavelength. Given the high alkalinity of the reaction mixture it is expected that any peroxide that is produced in the reaction would be in the hydroperoxyl form. Since the absorptivity of this species is lower than that of the superoxide radical, the UV absorbance is reduced after the metallic potassium is consumed. Moreover, the ESR signal is also reduced, since the hydroperoxyl anion is not ESR active. Rxn 8 portrays the reduction of  $O_2$  to the superoxide free radical anion by the sodium glycolate radical anion produced in Rxn 7. Other investigators<sup>42,47</sup> have also shown that oxygen can indeed be reduced to superoxide in a variety of ways. In principle, any substance with a reduction potential more negative than  $-0.5 V$  (n.h.e.) (Gibbs-Stockholm convention) should be capable of reducing molecular oxygen to  $O_2^{\cdot-}$ .

### *Is superoxide the free radical produced by the reaction?*

In order to further substantiate whether the superoxide free radical is indeed produced by the reaction of PEG, potassium and oxygen the reaction mixture was tested for superoxide by employing a commonly used assay for superoxide which involves the reduction of nitrotetrazolium blue (NBT) to its diformazan, which can be monitored by visible spectroscopy<sup>31</sup>. For this purpose the visible spectra of the following solutions were taken:

1. A solution in DMSO of  $KO_2$  in the presence of NBT.
2. A solution in DMSO of reaction products in the presence of NBT.
3. A solution in DMSO of the diformazan of NBT.



**Figure 6** ESR spectra of (a) a solution of pure  $\text{KO}_2$  in PEG 400 in the absence of oxygen, (b) the same mixture as in (a) after having been heated to  $70^\circ\text{C}$  in the absence of oxygen. An absorption signal was observed centred at  $3307.3\text{ G}$ , corresponding to a  $g$ -value of  $2.0064$ .

An examination of these spectra revealed that the spectrum for the reaction products matches the other two spectra suggesting the presence of  $\text{O}_2^-$  or other reducing free radicals. That the radical in question is  $\text{O}_2^-$  and not another reducing free radical was confirmed through the use of the superoxide specific enzyme superoxide dismutase<sup>31</sup>; in its presence, NBT was not reduced to its corresponding diformazan.

That superoxide is indeed produced by the reaction of PEGs, potassium and oxygen was also verified by reacting pure potassium superoxide with PEG in the absence of oxygen. As seen in Figure 6a, a solution of  $\text{KO}_2$  in PEG at room temperature gave no ESR signal. This is to be expected since both the hydroxy and superoxide radicals do not produce ESR signals in the liquid phase because of their orbital degeneracy<sup>48</sup>. However, on heating the reaction mixture, an ESR signal was obtained (see Figure 6b) with exactly the same  $g$ -value as that for the free radical obtained by the reaction of PEG with sodium or potassium in the presence of oxygen. This signal suggests the possible reaction:



A crown ether-type complex is postulated as the reaction product in Rxn 9 which stabilizes the superoxide free radical and makes it ESR-active.

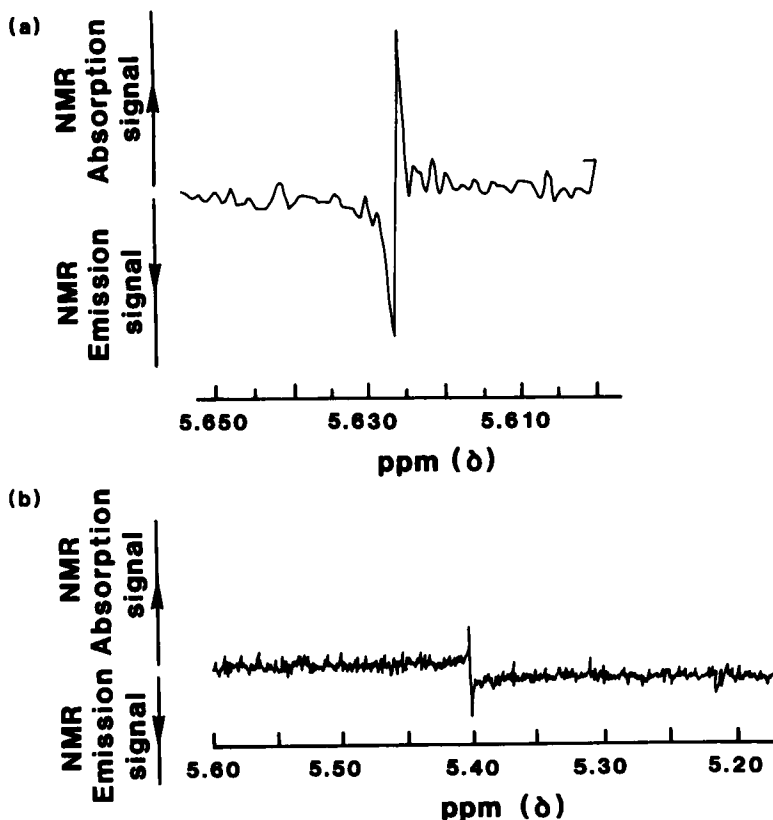
Further to the elucidation of the mechanism of the reaction in question, the kinetics of the reaction between PEG and  $\text{KO}_2$  was studied using ESR. This was done by taking samples at various time intervals during the reaction and subjecting them to ESR analysis. The reaction was carried out under argon at  $70^\circ\text{C}$ . A linear increase in ESR signal with time was observed. Considering that a given quantity of  $\text{KO}_2$  is expected to give rise to a proportional ESR signal, it was thought that it may be possible to construct a calibration curve by heating various solutions of  $\text{KO}_2$  of different concentrations. The problem with quantitating superoxide using this approach, however, was that the signal-to-noise ratio for the ESR signals was quite low for a given quantity of  $\text{KO}_2$  added. In the experiment cited above, the  $\text{KO}_2$  concentration was as high as 1.25 M. Given the low detection limits of ESR spectroscopy, it was thought that a relatively large amount of superoxide is being transformed into a species that is not electron-spin active. A possibility that was investigated was the abstraction by the superoxide of a proton from either water or PEG (terminal OH groups) to form the species  $\text{HO}_2^-$  (see Rxns 10 and 12). This hypothesis was tested by adding water (12% by volume) to a sample of reaction products and then watching the change in ESR signal. By comparing the ESR signals obtained in these two cases, it was observed that there is a reduction in signal in going from a sample with no water to a sample that is 12% in water. This reduction in signal may be due to the reaction:



Further evidence that this reaction may actually be occurring was obtained by using the technique CIDNP-NMR<sup>49</sup>. CIDNP-NMR can be employed for the detection of hydrogen atoms that are adjacent to a free electron. This technique is based on the theory that the nuclear spin states of free radicals may become populated by relaxations due to magnetic electron-nuclear interactions when the electron-spin states of the radicals are equally populated. In such a case the corresponding NMR transitions show emission (negative signal) or enhanced absorption. Figure 7a shows the NMR spectrum of the reaction products after PEG is reacted with potassium in the presence of oxygen. As seen in this figure, a negative peak appears at the chemical shift value of 5.625 ppm. The negative peak observed is assumed to be  $\text{HO}_2^-$  since the spectrum of a solution of pure  $\text{KO}_2$  in 18-crown-6, in the presence of a proton donor (water), presents a negative peak with about the same shift (see Figure 7b).

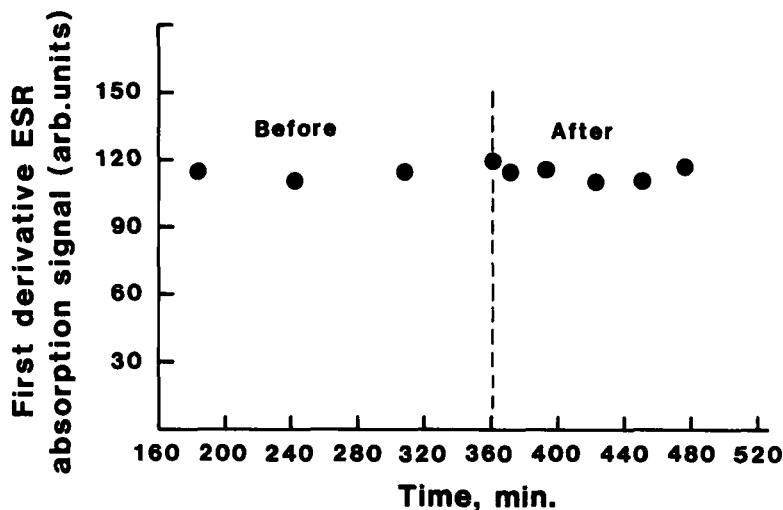
As discussed previously in this paper, the reaction of PEG with potassium and oxygen produces a potassium glycolate superoxide complex. When the potassium superoxide is allowed to react with water or acid, even at low temperatures (ice-cold water), this is reduced to hydrogen peroxide in the following reactions<sup>50</sup>:





**Figure 7** Proton NMR spectra of (a) the products of reaction between PEG 400 and metallic potassium in the presence of oxygen. The sample was dissolved in deuterated benzene. A negative peak (emission band) appears at 5.625 ppm, (b) a solution of  $\text{KO}_2$  in the presence of 18-crown-6 and a proton donor (water) in deuterated benzene.

Hydrogen peroxide is an electroactive species, with an anodic half-wave potential ( $E_{1/2}$ ) of about 0.7 V depending on the working electrode and the medium, and therefore can be easily detected using LC-EC. Using the LC-EC system and conditions described in the experimental section, it was indeed verified that hydrogen peroxide is produced after the sodium glycolate superoxide radical is allowed to react with acid or water (e.g. liquid chromatographic mobile phase). In order to follow the production of the sodium glycolate superoxide free radical, samples were taken at various time intervals during the reaction of PEG 400 with sodium and oxygen, buffer (pH = 5.0) was added to them, and the resulting hydrogen peroxide was monitored using LC-EC. This kinetic study revealed that at as low a temperature as 51°C and 25 minutes after the beginning of the reaction, a signal is obtained demonstrating the presence of hydrogen peroxide. As the temperature increased to 55°C, and after 40 minutes of reaction, the signal for hydrogen peroxide increased dramatically and remained high for as long as the temperature remained below 140°C. At this point the signal was significantly reduced probably due to the evaporation (b.p = 150°C) and/or decomposition of hydrogen peroxide<sup>38</sup>.

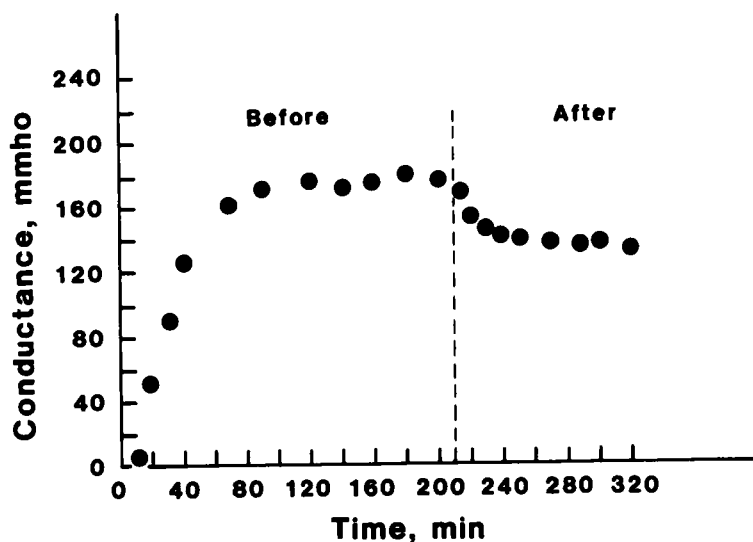


**Figure 8** Intensity of the ESR signal (peak-to-peak height of the first derivative ESR spectrum) before and after the addition of chlorobenzene to a reaction mixture of PEG 400 and metallic potassium exposed to oxygen at 110°C. Even though partial dechlorination took place after the addition of hexachlorobenzene, no reduction in ESR signal was observed, suggesting that the potassium glycolate superoxide complex is not the active dechlorinating agent.

*Is the potassium glycolate superoxide free radical the active dechlorinating agent?*

The central question that the kinetic studies intended to answer was whether the detected free radical was the active reagent in the dechlorination reactions. This question was investigated by studying the ESR signal intensity of the free radical before and after the addition of chlorobenzene to the reaction mixture. As seen in Figure 8, no reduction in ESR signal was observed after the addition of substrate to the reaction mixture. This finding should not be surprising in view of the fact that no case of nucleophilic substitution of unactivated or deactivated aromatic halides by superoxide has ever been previously reported; the nucleophilic reactivity of superoxide has been demonstrated, however, toward other substrates such as the aliphatic and activated aromatic halides<sup>51,52</sup>. In the case of aromatic halides it was shown<sup>52</sup> that, whenever a reaction occurs, the halogen is replaced by a hydroxyl group, leading to the corresponding phenol.

Having established that the potassium glycolate superoxide free radical is not the active dechlorinating agent, it was decided to study whether  $KOR$  and/or  $K^+ \bar{O}^-$  (HOR), two potentially powerful nucleophilic agents under the conditions of this reaction, are the active dechlorinating agents. The above finding also suggested that oxygen, a reagent that was considered essential for the preparation of the active reagent was not actually needed; on the contrary its presence was a liability in terms of contributing to the degradation of the active reagents, potassium glycolate and potassium glycolate free radical, to the non-reactive species, potassium glycolate superoxide radical. In order to substantiate the theory that potassium glycolate and/or potassium glycolate free radical are the active dechlorinating species, potassium was reacted with PEG 400, under nitrogen, for about three hours and well



**Figure 9** Kinetics of dissolution of metallic potassium in PEG 400 in the absence of oxygen at 110°C using conductimetry. After the conductance levelled off, hexachlorobenzene was added to the reaction mixture and the conductance measured again. Samples obtained during the reaction were diluted by a factor of 231 with water. Conductance was measured using a Beckman Instruments Conductivity bridge.

past the point at which potassium was still visible in the reaction mixture. During the reaction, kinetic samples were collected and their conductance measured after dissolving them in water. As shown in Figure 9, an increase in conductance is observed in the beginning of the reaction and for about as long as potassium is seen floating on the reaction mixture, as would be expected by Rxns 3 and 7 (production of potassium glycolate molecule and free radical). Potassium glycolate is expected to hydrolyze in water in the following reaction:



Therefore, the measured conductance is essentially that due to potassium hydroxide. Once the conductance of the solution levelled off, hexachlorobenzene was introduced to the reaction mixture and kinetic samples were collected at various time intervals. Figure 9 shows very clearly a gradual reduction in the conductance of the potassium glycolate solution after the addition of hexachlorobenzene, suggesting that this reagent might be the active dechlorinating agent; this was further confirmed by chloride analysis and a reaction yield of 70.3% after three hours of reaction. In order to achieve reaction yields higher than 70% it was found necessary to add fresh potassium and PEG 400 to the reaction mixture every few minutes during the reaction. This may be explained in terms of the findings of Matsulevich and Sokolov<sup>42</sup> who found that the rate of oxidation of alkali metals in diglymes in the presence of a catalyst is directly proportional to the magnitude of the surface area of the metal and the initial concentration of the catalyst (in this case the catalyst is PEG 400). It is also possible that a crust of potassium hydride forms on the surface of the metal thus inhibiting further

reaction. Such a reaction is known to occur when hydrogen is passed over molten alkali metals at high temperatures<sup>50</sup>.

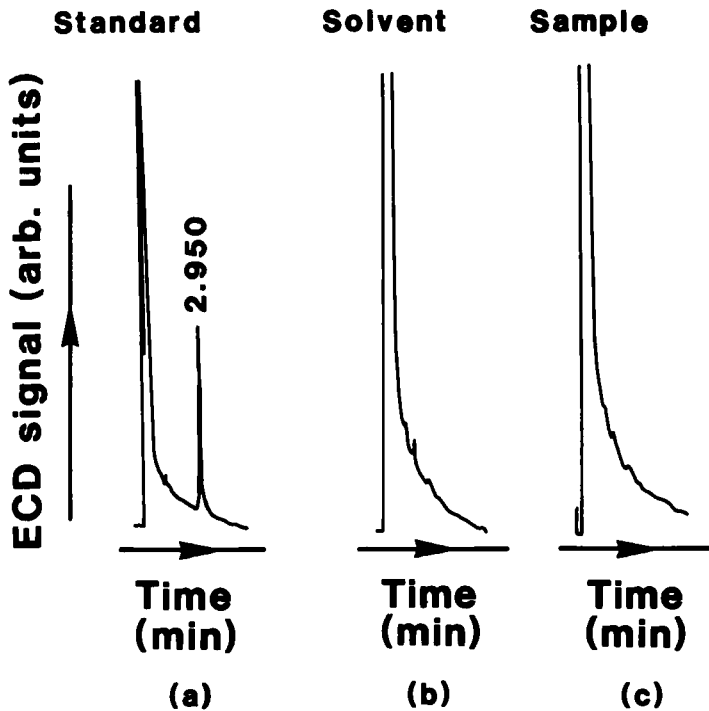
### *Is a benzyne (elimination-addition) mechanism possible?*

Given the high nucleophilicity of the glycolate ions, one possible mechanism that had to be considered was the benzyne (or elimination-addition) mechanism. It is well-established in the literature of organic chemistry that in the absence of electron-withdrawing groups to activate the ring, substitution can be made to take place by use of very strong bases. When this is done, however, substitution does not take place by the bimolecular mechanism, but by an entirely different mechanism, the benzyne (or elimination-addition) mechanism<sup>53</sup>. The elimination stage involves the abstraction by the nucleophile of a hydrogen ion adjacent to the halogen substituent of the benzene ring. Thus, it was assumed that if the dechlorination reaction under examination worked with a chlorinated substrate without any hydrogen substituents, the benzyne mechanism could be excluded as a possibility. The substrate used to test this hypothesis was hexachlorobenzene. As seen in Table 2, hexachlorobenzene can be easily dechlorinated by the glycolate ion thus disproving the possibility of an elimination-addition mechanism.

It should be noted here that the dechlorination reaction yields reported in Table 2 for a number of activated (chlorinated) monoaromatic compounds appear to be generally in line with a bimolecular nucleophilic substitution mechanism.<sup>53-56</sup> Chlorine substituents are known to activate the ring to nucleophilic substitution by stabilizing the carbanion intermediate, postulated in this mechanistic scheme, through the withdrawal of electrons from it. In accordance with this mechanism, chlorobenzene presents the lowest dechlorination yield because the ring is completely deactivated while 1,2- and 1,4- dichlorobenzenes present higher yields since ortho and para chlorine substituents are known to activate the ring. The yields are even higher in the case of 1,2,4-, 1,2,3,4-, 1,2,4,5 since each one of these compounds has two ortho and/or para chlorine substituents, whereas hexachlorobenzene presents the highest reaction yield of all chlorinated aromatic compounds probably because it possesses three ortho and para substituents. Meta substituents are known not to have any effect on reactivity. The fact, therefore, that 1,3,5 trichlorobenzene is dechlorinated at all and/or presents a yield that is higher than that of chlorobenzene is likely to be due to stereochemical and/or other reasons. Moreover, the fact that hexachlorocyclohexane presents the highest dechlorination reaction yield is also in line with the bimolecular nucleophilic reaction mechanism since alkyl halides are characterized by higher reactivities toward nucleophilic reagents like  $OR^-$  as compared to aryl halides.

### *Other products of the dechlorination reaction*

So far we have described the dechlorination reaction on the basis of the chloride yields obtained. In order to further substantiate the suggested mechanism, phenols, the other "supposed"<sup>27</sup> product of the reaction, were sought. In the light of the suggested mechanism, no phenol would be expected to be produced from the reaction of chlorinated organics with



**Figure 10** GCECD of reaction products. (a) standard (b) solvent (c) sample. Conditions: column: 6 ft  $\times$  0.25 inch, 3 % OV101 (glass) on Chromosorb W (H/P) 80/150 mesh; carrier gas: nitrogen; flow rate: 60 ml/min; injection temperature: 270°C; ECD temperature: 300°C; column temperature: 185°C; injection volume: 2  $\mu$ l; sensitivity:  $10^{-2}$  range.

potassium glycolate; ethers are obtained instead. The ferric chloride test for phenols was first applied to the reaction products and was found to be negative. Since, however, the ferric chloride test does not always give a positive test in the presence of certain phenols, it was decided to employ an additional test for confirmation purposes. Indeed, by using LC-EC no phenol was ever detected in any of the reactions attempted with the various substrates (see experimental section). In addition, no phenolic compounds were detected when samples were examined using mass spectrometry in the chemical ionization mode.

Another source of information concerning the proposed mechanism was provided by GC-ECD. This method was used to trace the fate of the chlorinated compounds themselves, during the reaction. The initial intention had been to do a kinetic study of the reaction based on the disappearance of the chlorinated compound. Figure 10a shows the gas chromatogram for hexachlorobenzene for a previously optimized set of conditions (see experimental section). The peak obtained represents a 2- $\mu$ l injection of a standard 10 ng/ml hexachlorobenzene solution in hexane ( $t_R = 2.95$  min). Figure 10b shows the chromatogram obtained when 2 $\mu$ l of solvent (cyclohexane) were injected into the GC (no signal is observed) while Figure 10c presents the chromatogram for a cyclohexane extract of a sample taken after three minutes of reaction time; no signal appears in this chromatogram either, indicating the complete absence of any hexachlorobenzene as quickly as three minutes after the



beginning of the reaction. In order to verify that the absence of a signal is not due to a low extraction efficiency, a sample of hexachlorobenzene was carried through the same dilution and extraction steps (see experimental section) as a reaction sample. The extraction efficiency, however, was found to be close to 100%. Attempts at detecting hexachlorobenzene at higher detector sensitivities as well as spiking of the reaction samples were not successful at demonstrating the presence of any amounts of this substrate. This evidence suggested that at least one glycolate molecule attacks the hexachlorobenzene virtually instantaneously, converting it into the non-hexane extractable PEG phenolic ether (even if some ether is extracted it wouldn't be volatile enough to be detected when using GC-ECD). The nucleophilic substitution reaction appears to continue at a slower rate as a result of ring deactivation and steric factors.

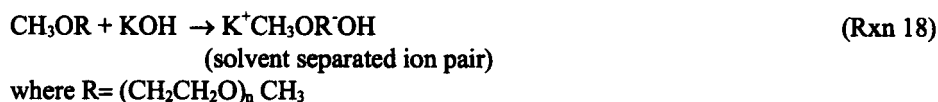
#### *Other analogous dechlorination reactions*

By considering the evidence presented so far on the mechanism of the dechlorination reaction under examination, it was thought that it may not actually be necessary to use alkali metal for the preparation of the active reagent, alkali metal hydroxide should suffice. In other words, assuming that potassium hydroxide is used instead of potassium, the following reaction is expected to take place:



As seen above, Rxn 17 produces the dechlorinating reagent, potassium glycolate as is the case with Rxn 3. When this reagent was reacted with hexachlorobenzene, a reaction yield of 23.5% was obtained. The relatively low yields may be due to the production of water in Rxn 17 which, as was previously shown, has a negative effect on reaction yield.

In addition, it was thought that it may be possible to dechlorinate chlorinated aromatic compounds by using PEG dimethyl ether as the solvent and KOH as the nucleophilic agent. It was assumed that, in this case, the reagent preparation reaction would be:



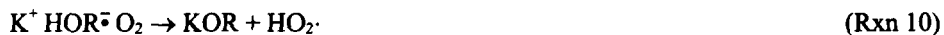
This reaction was also successful, with a yield of 18.4%. The following dechlorinating reaction is assumed to have taken place:



The relatively low yield may be due to the low solubility of potassium hydroxide in tetraethylene glycol dimethyl ether and the relatively small molecular weight of the latter. The fact that Rxn 19 does produce a dechlorinating agent is significant from a mechanistic point of view. It demonstrates the significance of a crown-ether type of structure (see Figure 1) in terms of orienting and positioning the substrate to be dechlorinated. This reaction is

also significant in terms of substituting chlorine substituents with hydroxyl groups; this would allow the direct detection of the dechlorinated species using LCEC.

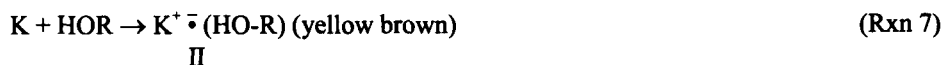
Another reaction that was thought possible was the reaction of potassium superoxide with PEG (Rxn 9 and 10), followed by the dechlorination of chlorobenzene using the products of Rxn 10:



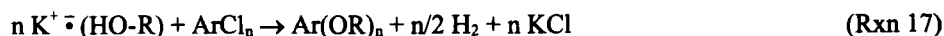
Indeed, when this reaction was attempted, a dechlorination reaction yield of 36% was obtained. Since superoxide is not known to react with unactivated chlorinated aromatics, the nucleophilic reagent is likely to be potassium glycolate formed as shown in Rxns 9 and 10 and participating in dechlorination as suggested in Rxn 4.

#### CONCLUSIONS: REACTION MECHANISM AND YIELD OPTIMIZATION

In light of all the evidence presented to this point relating to the dechlorination reaction initially developed by Pytlewski *et al.*<sup>27,28</sup>, a number of inferences can be made relating to the mechanism of this reaction. In the absence of oxygen, the following reactions appear to take place when PEGs are reacted with alkali metals at temperatures over the melting point of these metals:



The evidence suggests that both reagents I and II are involved in the dechlorination of activated or non-activated aromatic compounds (e.g. chlorobenzene) through nucleophilic substitution reactions as shown below:



The success of this reaction, as compared to other nucleophilic substitution reactions may be ascribed to the following:

1. Both the active reagent and the chlorinated substrate are in the same phase.
2. The concentration of the active reagent is very high since the solvent itself is the active reagent for the reaction.

3. The very structure of the alkali metal glycolate itself (see Figure 1) may be enhancing reactivity due to stereochemical considerations. Such a structure is likely to be able to align aromatic compounds parallel to the plane of the crown-ether complex and thereby better position them for nucleophilic attack. Theoretical considerations<sup>54</sup> indicate that a reagent entering into aromatic substitution should approach from a direction lateral to the plane of the ring.
4. The structure shown in Figure 1 is not only likely to be stabilized by crown-ether oxygens but also by internal ion-pairing. It has been shown in the literature that in such cases the effect of the metal ion could play an important role in such phenomena as binding of the substrate and altering the nature of the anion. A structure such as the one proposed above may also explain why the molecular weight of the PEG used for this reaction should not be very low since not enough oxygens would be available to complex with the alkali metal ion.
5. The displaced group (Cl) has much greater anionic stability than the entering group (OR)<sup>53,54</sup>.

The initial objective of this work has been to evaluate the Pytlewski dechlorination reaction as an analytically useful derivatization reaction. As was shown in this paper, a number of major and minor discrepancies exist with respect to the results initially reported by Pytlewski *et al.*<sup>27,28</sup>. After examining this reaction in terms of its reactants and products, stoichiometry, mechanism and reaction yields, experimental conditions were determined under which it can indeed qualify as an analytically useful derivatization reaction. The dechlorination reaction under examination was found to work best under the following conditions:

1. in the absence of oxygen,
2. when potassium is used instead of sodium,
3. for molecular weights of PEG that are higher than 200 in the case of sodium and 250 in the case of potassium,
4. at temperatures above the melting point of the alkali metals, preferably over 100°C,
5. at a stoichiometric excess of alkali metal over PEG,
6. when fresh alkali metal and PEG are added to the reaction mixture over the course of the reaction,
7. in the absence of water,
8. when a large stoichiometric excess of reagents as compared to substrate is present.

The developed reaction scheme, does indeed meet most criteria for an analytically useful derivatization reaction since, under the optimized conditions reported above, it can achieve high and reproducible yields, with analytical quantities of substrate and in short periods of time. In addition, this reaction is simple, safe and does not involve the use of any toxic and/or expensive reagents. Since, however, this approach, like any other TOX technique, is neither specific to PCBs over any other category of halogenated compounds nor congener-specific, its applicability can only be of a limited scope. The application of this derivatization approach to the development of a screening technique for the determination of PCBs in waste oils is the subject of the subsequent paper in this issue. Such a screening technique would be useful in field testing for the purpose of reducing the number of samples requiring more sophisticated and time-consuming analysis at a subsequent stage.

### Acknowledgements

The authors are indebted to the Natural Sciences and Engineering Council of Canada for financial support of this work.

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