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Dechlorination of diphenyl chlorophosphate with tin and sodium 3,6-di-*tert*-butyl-*ortho*-semiquinones

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Abstract

Dechlorination reactions of diphenyl chlorophosphate $(PhO)_2P(O)Cl$ with 3,6-di-*tert*-butyl-*ortho*-semiquinone complexes of triphenyl tin, $SQSn(Ph)_3$ and sodium, SQNa have been investigated by electron spin resonance (ESR) both in solutions at 300 K and in solid phase at 77 K using mechanochemical activation. Paramagnetic 3,6-di-*tert*-butyl-*ortho*-semiquinone ligand (SQ) was used as spin probe to monitor changes in the Sn coordination sphere during the dechlorination reaction of $(PhO)_2P(O)Cl$ and consecutive formation of tin chloride derivatives $SQSnCl(Ph)_2$, $SQSnCl_2Ph$, and $SQSnCl_3$. Their structure was revealed based on the analysis of hyperfine interaction constants due to ^1H nuclei in the 4,5-positions of the aromatic ring of the SQ ligand, hyperfine interaction constants due to ^{35}Cl and ^{37}Cl nuclei of chlorine atoms in the Sn coordination sphere, and hyperfine interaction constants due to ^{117}Sn and ^{119}Sn nuclei of the central metal ion. Interaction of $SQSnCl_3$ with $(PhO)_2P(O)Cl$ leads to the formation of a meta-stable radical–anion complex $[SQSnCl_4]^{\cdot-}$ $P^+(O)(OPh)_2$, which transforms to $SQSnCl_3\cdots P(O)R_3$, a stable adduct of $SQSnCl_3$ with dechlorinated phosphate of a general formula $P(O)R_3$. Analysis of solution dechlorination reaction products suggests the formation of diphenyl-phosphoryl radical $(PhO)_2P^{\cdot}(O)$, which was not observed in solutions. Dechlorination of $(PhO)_2P(O)Cl$ with sodium 3,6-di-*tert*-butyl-*ortho*-semiquinone SQNa can proceed in solid phase in liquid nitrogen at 77 K via mechanochemical activation using a ball mill. ESR analysis of the cryo-mechanochemical reaction showed the formation of the adduct of $(PhO)_2P^{\cdot}(O)$ radical with 3,6-di-*tert*-butyl-*ortho*-quinone.

Keywords: Phosphorus(V) compounds; Tin(IV) complexes; *ortho*-Quinone ligands; Semiquinone radicals; ESR spectroscopy

1. Introduction

Diphenyl chlorophosphate $(PhO)_2P(O)Cl$ is a structural analog of fluorophosphates $(RO)(CH_3)P(O)F$, chemical warfare agents known as sarin ($R = CH(CH_3)_2$) and soman ($R = CH(CH_3)[C(CH_3)_3]$). As a chemical warfare agent simulant, diphenyl chlorophosphate can be used as a model compound in studies of the reactivity of organophosphorus P(V) compounds and developing of methods for their decomposition. One of the ways to decompose chemical warfare agents like sarin and soman is their dehalogenation. The existing methods for decomposition of chemical warfare agents are based on the traditional solution chemistry [1,2], or heterogeneous reactions of liquid agents with nanosize magnesium or calcium oxides [3,4], hydrolysis via low-temperature microemulsions [5], and decomposition of chemical warfare simulants by micellar iodoso- and

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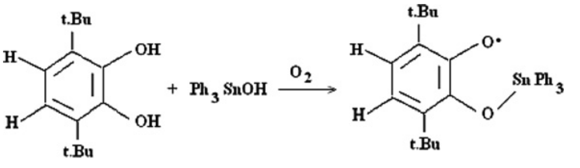
iodoxybenzoate [6]. Nucleophilic or free radical attacks on the P-atom are desirable for deeper decomposition of organophosphorus P(V) compounds [1,7–9]. Mechanochemical decomposition of toxic organic compounds is considered as an emerging technology in the field of waste disposal. Mechanochemical dehalogination of chlorinated organic pollutants has been reported in several studies [10–15], and the results show great potentials for environmentally safer deposition of pollutants.

ortho-Quinones are very attractive molecules for organic, element-organic, and coordination chemistry due to their ability to form chelate complexes and exist in different oxidation forms including *ortho*-semiquinone radical anions. Reactions of *ortho*-quinones with P(V) organic compounds have been reviewed in Ref. [16], showing broad variety of reaction pathways along with different transformations in phosphorus coordination. Organophosphorus radicals, such as phosphoryl radicals, react with *ortho*-quinones by possible addition to any position in the aromatic system or to the oxygen atoms of *ortho*-quinones leading to the formation of P-containing phenoxide or semiquinone radicals [17]. One may expect that similar radical products could be obtained by the reaction of semiquinone radicals with initial P(V) organic compounds. It is of interest to consider the reactivity of quinones with organophosphorus P(V) compounds in terms of the ability of quinones to decompose or transform toxic P(V) compounds to less harmful chemicals.

In this paper we report on thermal dechlorination of $(PhO)_2P(O)Cl$ by tin(IV) 3,6-di-*tert*-butyl-*ortho*-semiquinones in solutions, and on cryo-mechanochemical dechlorination of $(PhO)_2P(O)Cl$ by sodium 3,6-di-*tert*-butyl-*ortho*-semiquinone.

2. Experimental

To obtain tin and sodium 3,6-di-*tert*-butyl-*ortho*-semiquinones, we used 3,6-di-*tert*-butyl-*ortho*-quinone (Q) and 3,6-di-*tert*-butyl-pyrocatechol (QH_2) as initial reagents. Q and QH_2 were synthesized as described in Ref. [18]. Triphenyl-tin 3,6-di-*tert*-butyl-*ortho*-semiquinone ($SQSnPh_3$), i.e. 3,6-di-*tert*-butyl-2-triphenylstannyl-oxyphenoxide radical (I), was obtained by the reaction of QH_2 with triphenyltin hydroxide in toluene according to the method by Stegmann et al. [19]



(1)

(QH_2) (I)

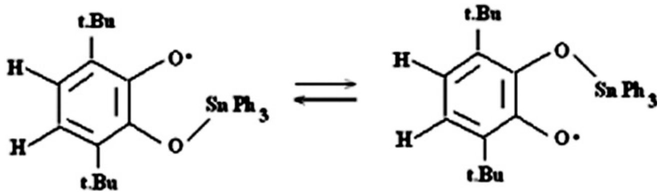
Reaction of radical (I) with diphenyl chlorophosphate $(PhO)_2P(O)Cl$ was investigated by adding different amounts of $(PhO)_2P(O)Cl$ in toluene solution of radical (I). Diphenyl chlorophosphate was purchased from Sigma–Aldrich with 99% purity mark. Deachlorination reaction of $(PhO)_2P(O)Cl$ by $SQSnPh_3$ radical (I) was studied via consecutive changes in the electron spin resonance (ESR) spectra of samples along with the formation of 3,6-di-*tert*-butyl-2-diphenylchlorostannyl-oxyphenoxide, $SQSnCl(Ph)_2$, radical (II), 3,6-di-*tert*-butyl-2-phenyldichlorostannyl-oxyphenoxide, $SQSnCl_2Ph$, radical (III), and 3,6-di-*tert*-butyl-2-trichlorostannyl-oxyphenoxide, $SQSnCl_3$, radical (IV). As it is discussed below, radical (IV) forms an intermediate complex with the $(PhO)_2P(O)Cl$ molecule. To study this complex formation process, the radical (IV) was directly synthesized by the exchange reaction of sodium 3,6-di-*tert*-butyl-*ortho*-semiquinone SQNa with tin tetrachloride $SnCl_4$. Tin tetrachloride was purchased from Sigma–Aldrich with 99% purity mark. Equimolar amounts of Q and $SnCl_4$ were dissolved in 0.1 M solution of NaOH in methanol, so that SQNa was formed and reacted with $SnCl_4$. Then the radical (IV) was extracted to toluene for further ESR investigation and study of its interaction with $(PhO)_2P(O)Cl$.

Concentrations of the radicals in solutions never exceeded 10^{-4} M, to exclude concentration effects on line broadening. Solutions of the radicals were placed in quartz ESR tubes and deoxygenated at 10^{-2} atm. ESR spectra were recorded with a Bruker EMX spectrometer operating at 9.6–9.8 GHz of microwave frequency, modulation frequency 100 kHz, microwave power 2 mW. For EPR spectra in liquid solutions we used 0.05 G modulation amplitude, which is far below the lowest linewidth of 0.2 G observed for individual line components. Hyperfine interaction constants and the line widths were determined using WIN-EPR software from Bruker.

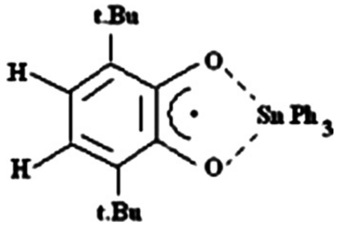
Cryo-mechanochemical activation of the reaction between SQNa and $(PhO)_2P(O)Cl$ in liquid nitrogen at 77 K were performed using a Fritsch *Vibratory Micro Mill Pulverisette 0* with cryogenic camera. SQNa was first obtained by 10 min mechanochemical treatment of solid state mixture of 150 mg of NaOH and 2 mL of frozen 0.1 M solution of Q in toluene. Then 2 mL of frozen 0.1 M solution of $(PhO)_2P(O)Cl$ in toluene was added to solid state reaction mixture at 77 K and exposed to additional 10 min mechanochemical treatment. The mechanochemical reaction products were placed in a quartz dewar for ESR analysis.

3. Results and discussion

3,6-Di-*tert*-butyl-*ortho*-semiquinone (SQ) ligand is a convenient spin probe to study coordination chemistry of elements. In Fig. 1a, we present electron spin resonance (ESR) spectrum of radical (I) in toluene at 300 K. This radical exhibits intramolecular transition of $Sn(Ph)_3$ group between two oxygen atoms,



(2)



(3)

At 300 K the transition is fast in an ESR time scale, i.e. $Sn(Ph)_3$ group is symmetrically located between oxygen atoms, as shown in scheme (3), and the two protons at 4,5-positions of the aromatic ring of the 3,6-di-*tert*-butyl-*ortho*-semiquinone ligand are equivalent ($a_{H,4} = a_{H,5} = 3.9$ G). Satellite lines in the ESR spectra are due to hyperfine interaction of the unpaired electron with ^{117}Sn and ^{119}Sn nuclear isotopes (both isotopes have $I = 1/2$ nuclear spin with slightly different magnetic momentum). In the case of radical (I) the corresponding hyperfine interaction constants are $a_{Sn\text{-}117} = 12.0$ G and $a_{Sn\text{-}119} = 12.75$ G.

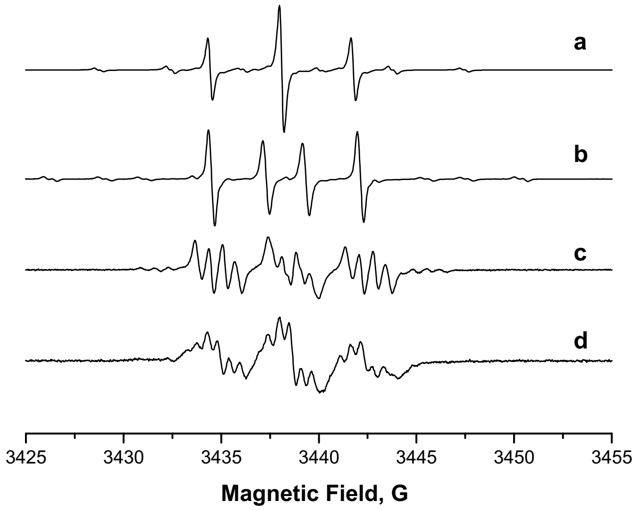
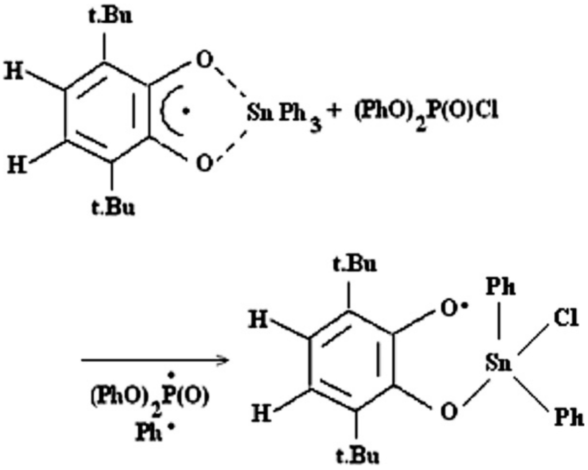


Fig. 1. ESR spectra of 3,6-di-*tert*-butyl-*ortho*-semiquinone complexes of tin recorded at 300 K during the reaction of $SQSn(Ph)_3$ with $(PhO)_2P(O)Cl$: (a) ESR spectrum of the initial $SQSn(Ph)_3$ radical (I) in toluene; (b) ESR spectrum of the $SQSnCl(Ph)_2$ radical (II), a product of the dechlorination reaction (4); (c) ESR spectrum of the $SQSnCl_2Ph$ radical (III), a product of the dechlorination reaction (5); (d) ESR spectrum of the $SQSnCl_3$ radical (IV), a product of the dechlorination reaction (6) when excess amount of $(PhO)_2P(O)Cl$ was used.

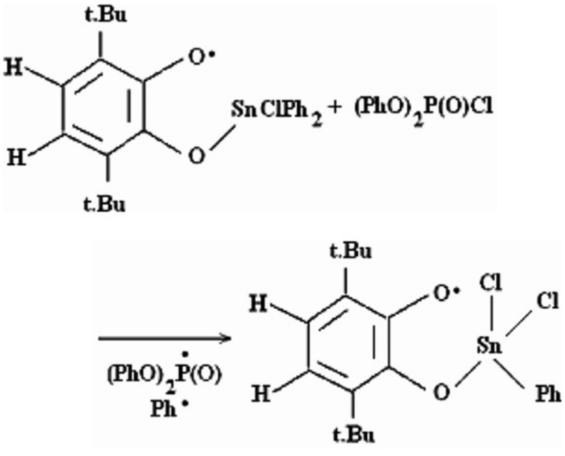
We chose radical (I) as a reagent towards $(PhO)_2P(O)Cl$ and to see the changes in the ESR spectrum during the reaction. The ESR spectrum in Fig. 1a, was obtained for radical (I) in toluene. In Fig. 1b, we present the ESR spectrum observed after adding ~0.1 M of $(PhO)_2P(O)Cl$ to the original toluene solution of radical (I). This ESR spectrum belongs to 3,6-di-*tert*-butyl-2-diphenylchlorostannyl-oxyphenoxide, $SQSnCl(Ph)_2$, radical (II) that, in contrast to radical (I), exhibits significantly lower rate of intramolecular transition of $SnCl(Ph)_2$ group between two oxygen atoms [20]. These leads to the coordination of Sn atom only by one oxygen atom,



(4)

and the two protons at 4- and 5-positions of the aromatic ring of the 3,6-di-*tert*-butyl-*ortho*-semiquinone ligand are non-equivalent ($a_{H,4} = 4.9$ G, $a_{H,5} = 2.9$ G). Hyperfine interaction constants due to central metal ion are $a_{Sn\text{-}117} = 15.9$ G and $a_{Sn\text{-}119} = 16.7$ G. The formation of radical (II) is a result of dechlorination of $(PhO)_2P(O)Cl$ by radical (I) according to scheme (4). The Sn–Cl chemical bond in radical (II) lies in the π-plane of the 3,6-di-*tert*-butyl-*ortho*-semiquinone ligand, so that no hyperfine interaction constant is observed due to chlorine [20].

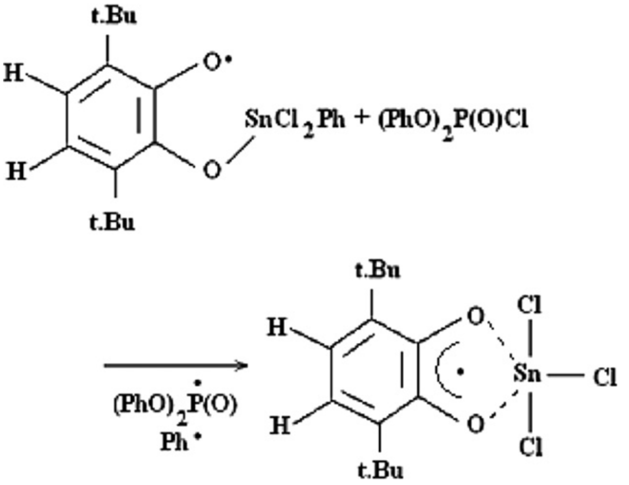
In Fig. 1c, we present the ESR spectrum observed after further increase of the concentration of $(PhO)_2P(O)Cl$ in toluene to ~0.5 M. This ESR spectrum shows the formation of 3,6-di-*tert*-butyl-2-phenyldichlorostannyl-oxyphenoxide, $SQSnCl_2Ph$, radical (III), for which hyperfine interaction due to one of the two chlorine atoms is seen $a_{Cl} = 0.7$ G (nuclear spin $I = 3/2$ for both ^{35}Cl and ^{37}Cl):



(5)

The Cl atom that contributes to the quartet hyperfine structure in the ESR spectrum of radical (III) is located off the π-plane of the 3,6-di-*tert*-butyl-*ortho*-semiquinone ligand. This is in accordance with the hyper-conjugation mechanism of hyperfine interaction in organic π-radicals [21]. Compared to radical (II), the Sn atom in radical (III) experiences more symmetrical oxygen coordination, since hyperfine interaction constants due to two protons in the aromatic ring of the ligand are close to each other ($a_{H,4} = 3.95$, $a_{H,5} = 3.75$ G). However, the structure of the radical (III) is still asymmetric, and smaller difference in proton hyperfine interaction constants $\Delta a = a_{H,4} - a_{H,5} = 0.2$ G is typical for ionic complexes [22], and indicates that the O–Sn chemical bond is more polar in radical (III). This is also supported by significantly lower value of hyperfine interaction constant with tin isotopes, $a_{Sn\text{-}117} \approx a_{Sn\text{-}119} = 6.0$ G. It may seem possible that the ESR spectrum in Fig. 1c represent a dynamic rather than a static spectrum due to migration of the Sn atom between two oxygen atoms of the paramagnetic ligand. However, in contrast to radical (II), the ESR spectrum of radical (III) is temperature independent and indicates the absence of the migration of the Sn atom in this radical.

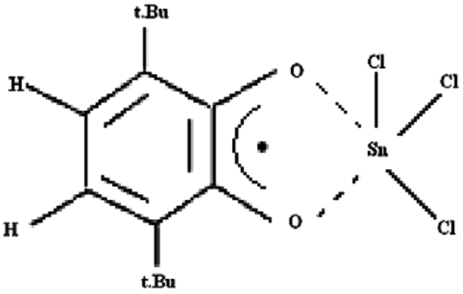
In Fig. 1d, we present the ESR spectrum recorded after we added an excess amount of $(PhO)_2P(O)Cl$ to the solution containing radical (III). In this ESR spectrum a septet structure due to hyperfine interaction with 2 equiv. chlorine atoms is seen, $a_{Cl} = 0.6$ G . This shows the placement of one more chlorine atom in the Sn coordination sphere and the formation of 3,6-di-*tert*-butyl-2-trichlorostannyloxyphenoxide, $SQSnCl_3$, radical (IV),



(6)

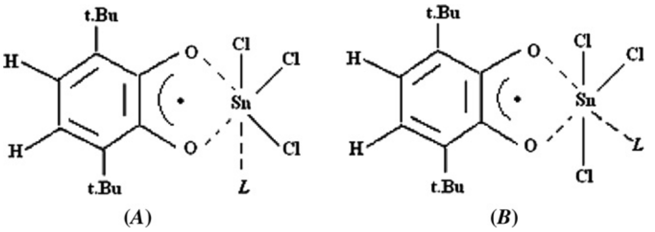
The Sn atom is symmetrically located between two oxygen atoms, since $a_{H,4} = a_{H,5} = 3.70$ G. Smaller value of $a_{Sn\text{-}117} \approx a_{Sn\text{-}119} = 6.0$ G again confirms more polar O–Sn chemical bond.

Radical (IV) has been previously studied in Refs. [20,23]. This radical can be directly obtained by the reaction of 3,6-di-*tert*-butyl-*ortho*-semiquinone radical anion with tin tetrachloride $SnCl_4$. Depending on the solvent and temperature, the ESR spectrum of radical (IV) shows hyperfine interaction due to either one, two or three chlorine atoms. In toluene at room temperature the ESR spectrum of radical (IV) shows hyperfine interaction due to only one chlorine atom suggesting the tetragonal–pyramidal structure,



(7)

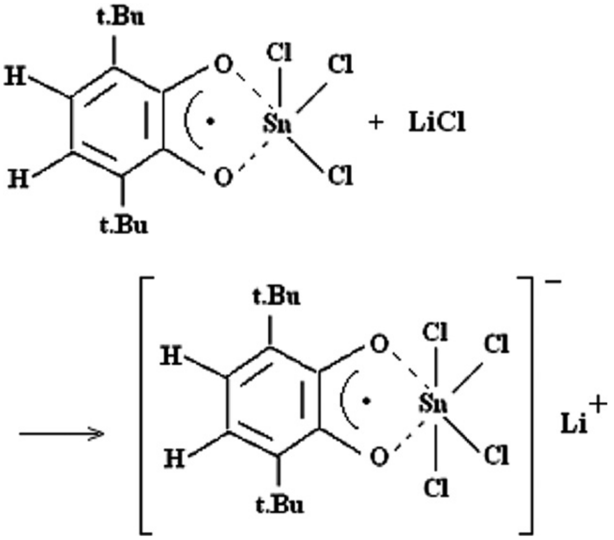
At higher temperatures in toluene the ESR spectrum of this radical shows hyperfine interaction with all three chlorine atoms due to intramolecular rotation of $SnCl_3$ group. In some solvents, where solvent molecules *L* are able to coordinate Sn atom, radical (IV) can have two types of octahedral structures [20],



(8)

Octahedra of the type A were observed in tetrahydrofuran (THF) and liquid phosphates of the general formula $P(O)(OR)_3$, while octahedra of the type *B* were observed in dimethyl formamide, acetonitrile, and tertiary amines [20].

In the presence of LiCl along with crown-ether in toluene, radical (IV) forms octahedral radical–anion complex [20],



(9)

The parameters of the ESR spectrum in Fig. 1d are exactly the same as for the octahedral radical–anion complex above [20], and represents radical (IV) in $(PhO)_2P(O)Cl$ solvent. This is confirmed by ESR spectra shown in Fig. 2. In Fig. 2a, we present the ESR spectrum of radical (IV) in toluene obtained by the direct reaction of 3,6-di-*tert*-butyl-*ortho*-semiquinone radical anion with tin tetrachloride $SnCl_4$. After vaporization of the toluene solvent from the ESR tube in vacuum, we dissolved radical (IV)

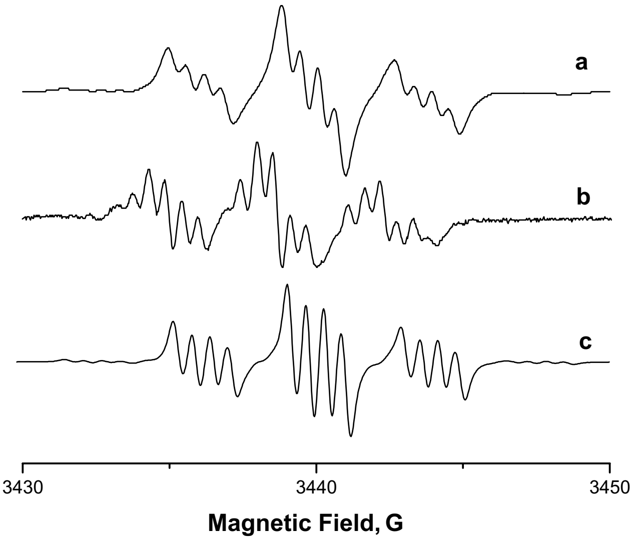
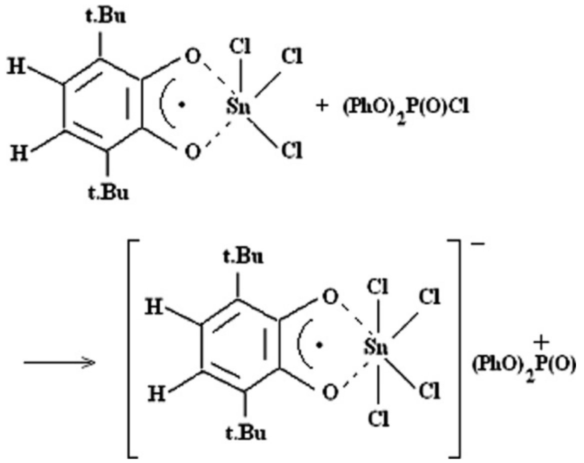


Fig. 2. ESR spectra of the $SQSnCl_3$ radical (IV): (a) in toluene; (b) in $(PhO)_2P(O)Cl$ solvent, initial ESR spectrum of unstable radical–anion complex (V); (c) final ESR spectrum that shows the formation of a stable adduct $SQSnCl_3\cdots P(O)R_3$ with octahedral structure of the type A.

in $(PhO)_2P(O)Cl$ solvent and obtained the ESR spectrum shown in Fig. 2b, which is exactly the same as the ESR spectrum obtained by the sequence of transformations of radical (I) in the presence of $(PhO)_2P(O)Cl$.

It is important to note that intensities of experimental ESR spectra in Figs. 1d and 2b are orders of values lower than the intensities of the ESR spectra for precursor radicals (I)–(III). We found that the ESR spectrum in Fig. 2b disappears within couple of hours and final ESR spectrum of the sample is shown in Fig. 2c. It implies that the low intensity ESR spectra in Figs. 1d and 2b may represent steady-state concentration of an intermediate form of the radical (IV) in $(PhO)_2P(O)Cl$ solvent.

As it was noticed above, the ESR spectrum of radical (IV) in $P(O)(OR)_3$ solvents reveals hyperfine interaction only with one chlorine atom. The fact that in $(PhO)_2P(O)Cl$ solvent we observe hyperfine interaction with two chlorine atoms, indicates that radical (IV) forms a radical–anion complex with $(PhO)_2P(O)Cl$ structurally similar to the complex with LiCl [20],

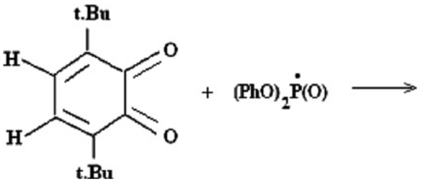


(10)

This complex is unstable, and transformation of the ESR spectrum from Fig. 2b and c shows that the original $(PhO)_2P(O)Cl$ solvent compound transforms to a dechlorinated phosphate $P(O)R_3$, so that radical $SQSnCl_3$ forms a stable adduct $SQSnCl_3\cdots P(O)R_3$ with octahedral structure of the type A. This transformation and the sequence of transformations from radical (I) to radical (IV) suggests the formation of diphenyl-phosphoryl radical $(PhO)_2P^{\bullet}(O)$, which was not observed during the solution dechlorination process. This radical could have reacted with 3,6-di-*tert*-butyl-*ortho*-semiquinone ligand by addition to the aromatic system of the ligand or to its oxygen atom. In solutions, however, we have not observed any additional radical products containing the phosphoryl group. Following the dechlorination reaction, the $(PhO)_2P^{\bullet}(O)$ radical and phenyl radical $Ph^{\bullet}$ may recombine and form phosphonate $P(O)(OPh)_2Ph$ or other similar diamagnetic products.

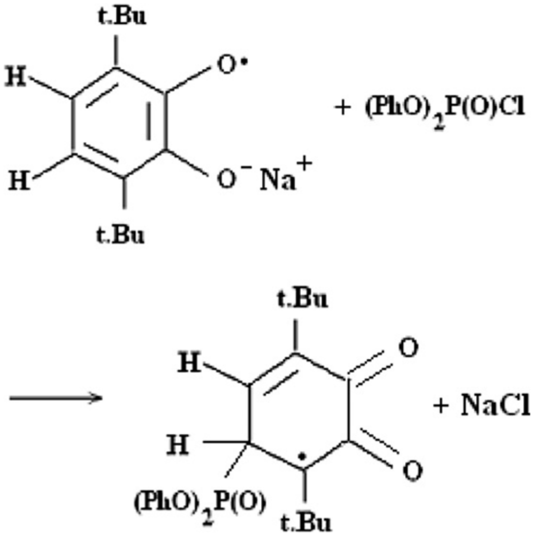
We have also investigated a solution reaction of sodium 3,6-di-*tert*-butyl-*ortho*-semiquinone SQNa with $(PhO)_2P(O)Cl$ in methanol and THF. The ESR analysis of this system showed only rapid and complete disappearance of the ESR spectrum of 3,6-di-*tert*-butyl-*ortho*-semiquinone radical anion, with no observation of new paramagnetic products. Sodium chloride was identified as one of the reaction products. Again, in solution no new stable radical products were observed, although the formation of sodium chloride may indicate the formation of the $(PhO)_2P^{\bullet}(O)$ radical in the initial act of the reaction.

To stabilize the intermediate products of the reaction, we tried to see if the reaction between 3,6-di-*tert*-butyl-*ortho*-semiquinone radical anion and $(PhO)_2P(O)Cl$ can proceed in solid phase with mechanochemical activation at low temperature, 77 K in liquid nitrogen. We first found that sodium 3,6-di-*tert*-butyl-*ortho*-semiquinone radical–anion complex can be obtained by mechanochemical treatment of a solid mixture of 3,6-di-*tert*-butyl-*ortho*-quinone and NaOH, as described in Section 2. After 10 min of mechanochemical treatment of this mixture at 77 K, we observed a singlet ESR spectrum with the *g*-factor value $g = 2.002$ and the linewidth $\Delta = 12$ G. After dissolving the reaction products in THF at room temperature we obtained the ESR spectrum of sodium 3,6-di-*tert*-butyl-*ortho*-semiquinone radical–anion complex SQNa, with $a_{H,4} = a_{H,5} = 3.47$ G and $a_{Na} = 0.57$ G (hyperfine interaction due to ^{23}Na, nuclear spin $I = 3/2$). Therefore, we conclude that sodium 3,6-di-*tert*-butyl-*ortho*-semiquinone radical–anion complex is formed during cryo-mechanochemical reaction between 3,6-di-*tert*-butyl-*ortho*-quinone and NaOH. In the second step of mechanochemical treatment, we added frozen at 77 K solution of $(PhO)_2P(O)Cl$. Then the reaction mixture of sodium 3,6-di-*tert*-butyl-*ortho*-semiquinone radical–anion complex and $(PhO)_2P(O)Cl$ was exposed to mechanochemical treatment at 77 K for 10 min. The ESR spectrum of the reaction products at 77 K is shown in Fig. 3. The single line in the center of the spectrum corresponds to the remaining sodium 3,6-di-*tert*-butyl-*ortho*-semiquinone radical–anion complex, while the doublet ESR spectrum with a splitting of about 50 G corresponds to a new paramagnetic product. Only the presence of phosphorus atom in this paramagnetic product can explain such a large hyperfine interaction constant (^{31}P, nuclear spin $I = 1/2$). The value of $a_P \approx 50$ G is typical for adducts of phosphoryl radicals with 3,6-di-*tert*-butyl-*ortho*-quinone [17], when phosphoryl radicals attack the carbon atom in the 4th position of the aromatic system,



(11)

Hyperfine interaction constants due to protons of the aromatic system in these types of radicals is ⩽10 G [17], and cannot be resolved within larger line broadening of the ESR spectrum in Fig. 3. The formation of such adduct during the mechanochemical process can be represented as



(12)

We found that radical (VI) is unstable at room temperature both in solid phase and in toluene solution, since we were not able to record any ESR spectra after the mechanochemical reaction products were warmed up from 77 K to room temperature. Therefore, instability of the radical adduct (VI) makes it impossible to observe phosphoryl radicals during thermal dechlorination reactions in solutions. It should be noted that radical (VI) cannot be obtained by mechanochemical treatment of the mixture of Q and $(PhO)_2P(O)Cl$, i.e. it is 3,6-di-*tert*-butyl-*ortho*-semiquinone radical anion that decomposes the chlorophosphate molecule.

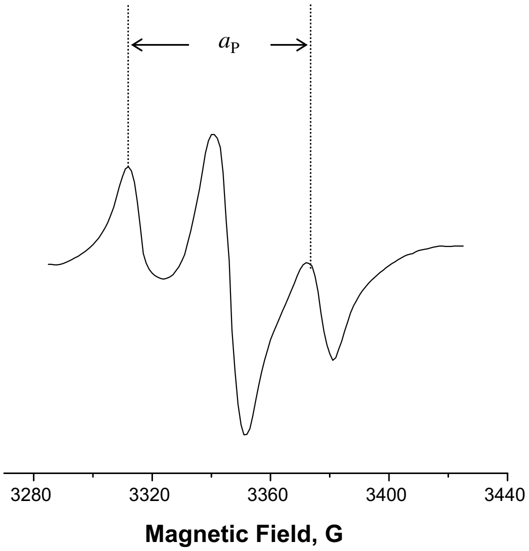


Fig. 3. ESR spectrum of the products of cryo-mechanochemical reaction between SQNa and $(PhO)_2P(O)Cl$ at 77 K. A doublet with the hyperfine splitting $a_P \approx 50$ G is due to the radical (VI). A single ESR line is due to SQNa.

4. Conclusions

Tin and sodium 3,6-di-*tert*-butyl-*ortho*-semiquinones decompose diphenyl chlorophosphate by means of its dechlorination. In our future work we plan to study the kinetics of all solution dechlorination reactions (4)–(6) described above, and report it in a separate paper. Our present data on solution reactions already show that dechlorination of diphenyl chlorophosphate by tin 3,6-di-*tert*-butyl-*ortho*-semiquinone complexes can be achieved by using small initial amounts of tin complex. Observation of an intermediate complex (V), and its transformation to final radical (IV) with the type A octahedral structure with $L = P(O)R_3$ implies catalytic mechanism of dechlorination reaction.

Cryo-mechanochemical dechlorination of diphenyl chlorophosphate by 3,6-di-*tert*-butyl-*ortho*-semiquinone deserves special attention. Deactivation of organophosphorus chemical warfare compounds at low temperatures is a challenging problem [5,24], due to limited solubility of the compounds at cold-weather operations. When toxic liquids such as chlorophosphates are being decomposed below their freezing point, the low-temperature solid state chemical reactions may be less harmful. Therefore, mechanochemical approach to decompose organophosphorus compounds can provide new environmentally friendly decontamination methods.

Acknowledgements

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