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Paramagnetic organolead complexes. EPR investigation of their formation and structures

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Abstract

Various triaryllead hydroxides or chlorides have been shown to react with catechols or *o*-benzoquinones to give paramagnetic complexes, whose structures have been investigated by EPR and ENDOR spectroscopy. The spectra indicate that the formation of these complexes involves either the cleavage of a C–Pb bond or the loss of the inorganic group. The hyperfine splittings for the organometallic radicals were interpreted in terms of a permutation equilibrium between two paramagnetic species. Investigation of the temperature dependence of the EPR-signals has given the kinetic parameters for some typical compounds. In general, complexes consisting of the semiquinone and the triaryllead moiety at room temperature undergo a rapid interconversion on the EPR time scale, but replacement of an aryl by OH or Cl group leads to lower rates and so to the co-existence of two isomeric species at ambient temperature. From the results a cation migration mechanism seems very unlikely and so a permutation isomerisation is proposed.

Semiquinone-triphenyllead complexes can undergo a secondary reaction with photolytically generated alkoxy radicals to give products formed by substitution of one phenyl group by the alkoxy group. These paramagnetic compounds show slow permutation rates.

Introduction

Numerous studies have been reported of organometallic derivatives of semiquinones [1] and semidiones [2]. One reason for the interest in these compounds lies in the use of the carbonyl compounds as spin traps for organometallic radicals. The structures and the conformations of these complexes can be deduced from the EPR and ENDOR spectra and so such investigations have a potential use for analysis of organometallic compounds. A great deal of attention has been paid to organotin compounds [3], but only a little information is available on the corresponding reactions of organolead compounds with diones or catechols [4,5].

In general the radical formation can proceed in two ways. Either (i) the organometallic species reacts with 3-tert-butyl-5-triphenylmethylcatechol, H_2**B**, with elimination of a substituent X and subsequent oxidation by oxygen of the air (Scheme 1, eqs. 1 and 2) or (ii) a single electron transfer between 3,6-di-tert-butyl-*o*-benzoquinone **A** or 3-tert-butyl-5-triphenylmethyl-*o*-benzoquinone **B** and the

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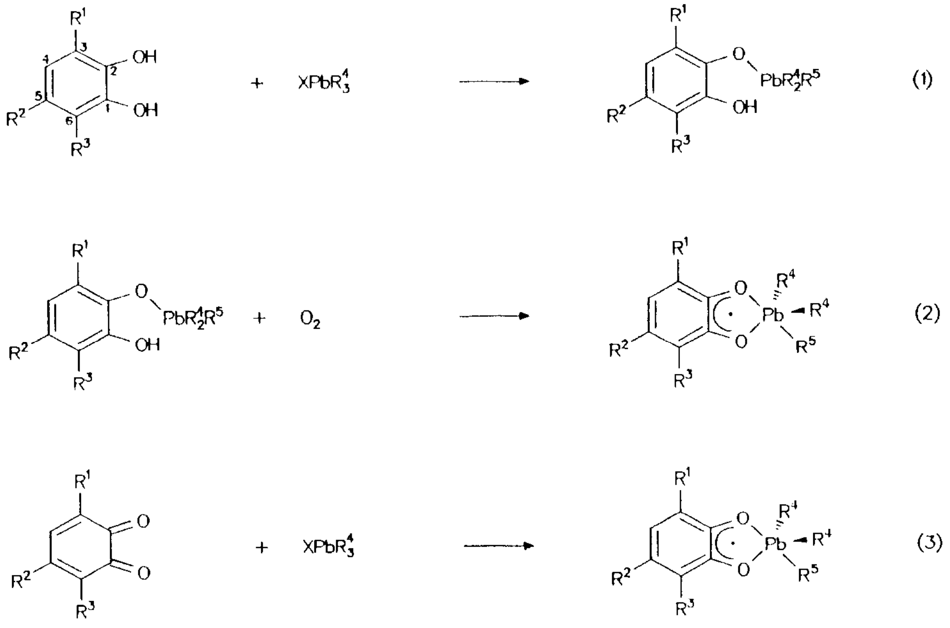


$R^5 = R^4, X$

A
$R^1 = t\text{-}C_4H_9$
$R^2 = H$
$R^3 = t\text{-}C_4H_9$

B
$R^1 = t\text{-}C_4H_9$
$R^2 = C(C_6H_5)_3$
$R^3 = H$

I
$R^4 = C_6H_5$
$X = OH$

II
$R^4 = C_6H_5$
$X = Cl$

III
$R^4 = C_6H_5$
$X = Pb(C_6H_5)_3$

IV
$R^4 = pCH_3\text{-}C_6H_4$
$X = OH$

Scheme 1.

organolead derivative (eq. 3). The radical formation can be accelerated by illumination with UV light. The semiquinolates obtained in both ways persist for, depending on the temperature, at least several hours, and so EPR and ENDOR spectra can be very conveniently obtained.

Results

The EPR and ENDOR data for the organolead radicals generated by either reaction 2 or 3 are summarized in Table 1. These results clearly demonstrate the great variety of the reactions of the quinones **A** or **B** and the corresponding catechol H_2**B** with the lead compounds investigated. In the course of the reactions of **I** or **IV** with **A** or **B** the predominant reaction is loss of the anionic group X, but exposure to daylight leads to a more or less complex mixture of radicals formed by loss of either

Table 1

EPR and ENDOR data for the paramagnetic lead complexes

No.	Radical generation	Plumbyl group [a]	Solvent [b] Temp. [c] (K)	a_{H4} (G)	a_{H5} (G)	a_{H6} (G)	a_{Pb} (G)	g
1	A+I or A+III	$Pb(C_6H_5)_3$	Tol	3.52	3.52	–	2.89	2.0038
2	A+I or A+III	$Pb(C_6H_5)_3$	Pyr	3.43	3.43	–	1.36	2.0042
3	A+I	$Pb(C_6H_5)_3$	EtOH	3.49	3.49	–	2.61	2.0035
4	A+I	$Pb(C_6H_5)_3$	MTHF	3.51	3.51	–	2.57	2.0039
			171	2.20	4.70	–	–	–
5	A+III	$Pb(C_6H_5)_2C_5H_9O$	MTHF	3.10	3.92	–	6.10	2.0032
6	A+III	$Pb(C_6H_5)_2C_4H_7O$	THF	3.12	3.87	–	6.36	2.0032
7	A+III	$Pb(C_6H_5)_2C_4H_7O_2$	Diox	3.12	3.87	–	6.48	2.0033
8	A+III	$Pb(C_6H_5)_2C_2H_4OH$	EtOH	3.20	3.80	–	4.70	2.0032
9	A+I	$Pb(C_5H_5)_2OH$	Tol	2.71	4.25	–	3.2	2.0031
10	A+II	$Pb(C_6H_5)_2Cl$	Tol	−2.90	−4.31	–	4.80	2.0028
			403	3.57	3.57	–	3.72	–
11	A+II	$Pb(C_6H_5)_2Cl$	MTHF	2.97	4.12	–	4.59	2.0030
			413	3.56	3.56	–	3.80	–
12	A+IV	$Pb(p\text{-}CH_3C_6H_4)_3$	Tol	3.50	3.50	–	2.58	2.0038
13	A+IV	$Pb(p\text{-}CH_3C_6H_4)_2OH$	Tol	2.74	4.26	–	3.0	2.0031
14	A+Pb(Ac)$_2$	PbAc	Pyr	3.45	3.45	–	55.9	1.9998
15	A+Pb(NO$_3$)$_2$	$PbNO_3$	Pyr	3.50	3.50	–	32.4	1.9982
16	B+I or B+III	$Pb(C_6H_5)_3$	Tol	−2.86	–	+0.24	1.56	2.0037
17	B+I or B+III	$Pb(C_6H_5)_3$	Pyr	2.65	–	–	2.15	2.0040
18	B+I	$Pb(C_6H_5)_2OH$	Tol	2.78	–	0.40	4.70	2.0033
19	B+I	$Pb(C_6H_5)_2OH$	Tol	4.24	–	0.50	5.30	2.0032
20	B+II	$Pb(C_6H_5)_2Cl$	Tol	−2.84	–	+0.48	3.26	2.0030
			393	3.50	–	–	2.50	–
21	B+II	$Pb(C_6H_5)_2Cl$	Tol	−4.22	–	+0.39	3.18	2.0028
			393	3.50	–	–	2.50	–
22	B+IV	$Pb(p\text{-}CH_3C_6H_4)_3$	Tol	2.88	–	–	1.30	2.0038
23	B+IV	$Pb(p\text{-}CH_2C_6H_4)_2OH$	Tol	2.78	–	0.40	4.20	2.0034
24	B+IV	$Pb(p\text{-}CH_3C_6H_4)_2OH$	Tol	4.22	–	0.50	4.80	2.0032
25	B+Pb(NO$_3$)$_3$	$PbNO_3$	Pyr	3.10	–	–	39.3	1.9970
26	B+Pb(Ac)$_2$	PbAc	Tol	3.43	–	–	77.1	1.9998
27	B+Pb(Ac)$_2$	PbAc	Pyr	3.10	–	–	67.2	1.9995

[a] Ac = $OCOCH_3$. [b] Tol = toluene, MTFH = 2-methyltetrahydrofuran, Diox = dioxane, THF = tetrahydrofuran, Pyr = pyridine. [c] Temperature 293 K unless otherwise indicated.

an aryl or an anionic moiety. Illumination with UV light favors the cleavage of the Pb–C bond, and so the concentration of the radical desired can be controlled. In the reaction of **II** with **A** or **B** an aryl group is generally displaced, whereas in the case of **III** the group X is lost.

Discussion

Table 1 reveals the presence of two types of radicals as indicated by their *g*-values and metal couplings. Complexes with small *g*-factors (ca. 2.0000) and large

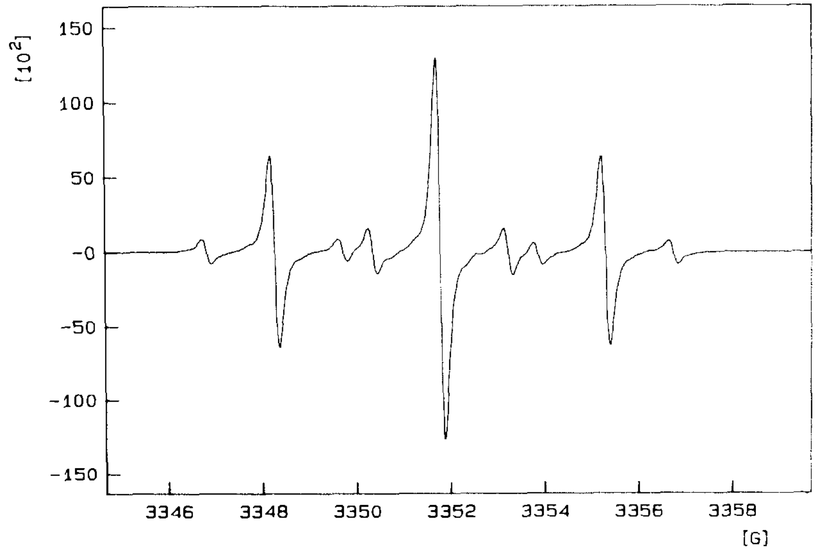


Fig. 1. EPR spectrum of the reaction product formed from **A**+**I** in toluene at room temperature.

lead couplings (50–80 G) are attributed to $\mathrm{Pb^{II}}$ species (compounds **14**, **15**, **25**–**27**, Table 1). These radicals were obtained either by reaction of various phenyllead acetates with the quinones or by addition of the corresponding $\mathrm{Pb^{II}}$ salts to **A** or **B**. The proton couplings show no significant dependence on the salt used (compare **14** with **15** and **25** with **27**) but the metal coupling is very sensitive to variation in the anion. Obviously, at least one anionic group is a component of the complex. Variation of the solvent (compare **26** with **27**) also causes changes in the proton as well as in the lead hyperfine splitting. We thus conclude that there is a significant participation by the solvent and consequent modification of the structure for the radicals investigated.

The paramagnetic complexes of the organolead compounds resonate at lower field than the $\mathrm{Pb^{II}}$ species (see the *g*-values in Table 1). The proton coupling constants observed for **1** (Fig. 1) and **16** in toluene are similar to those for the corresponding organotin semiquinolates [3,6], and so we assume that their structures are closely related to those of the tin complexes. The equivalence of the protons in **1**–**4** at room temperature is thus a result of a rapid exchange between at least two structures. Lowering the temperature causes an increase in the line width of the central line in accord with such interconversion. However, no splitting of the signal into a doublet of doublets was observed in the temperature range available, with toluene, pyridine, or ethanol as solvent.

However, in the case of 2-methyltetrahydrofuran (MTHF) **4** both the slow interconversion and the rapid exchange between the two species was observed. Quantitative analysis by computer simulation [8] of spectra obtained by systematic variation of the temperature yielded the kinetic parameters $\Delta H^{\#} = +5.65$ kcal/mol, $\Delta S^{\#} = +7.32$ Cl/mol, and $k_{293} = 1403$ MHz. These values are rather similar to those observed for the corresponding tin complexes [3].

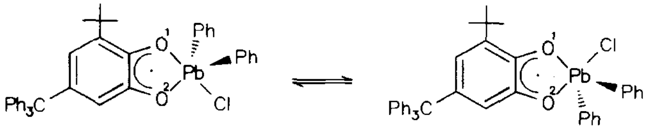
The most striking data obtained by the temperature variation are the proton coupling constants observed for slow interconversion. The values 2.20 G and 4.70 G indicate beyond doubt that the semiquinone acts as a bidentate ligand. In case of the interaction of only one oxygen atom with the metal atom a rapid migration of the plumbyl group at room temperature must be assumed. However, this interpretation requires a phenoxyl-like spin density distribution at low temperatures and thus different signs for the coupling constants at the *para-* and *meta*-positions. For example, 2-methoxy-3,6-di-tert-butylphenoxyl and 2-trimethylsilyloxy-3,6-di-tert-butylphenoxyl show splitting constants of 1.0 G for the *meta-* and 8.40 G for the *para*-positions with respect to the phenoxyl oxygen atom. The temperature dependence of the EPR spectra of **4** is thus due to a permutation isomerisation and cannot be interpreted in terms of migration of the plumbyl group [9,10].

This conclusion is confirmed by the data for reaction product **10**. The EPR spectrum in toluene even at room temperature shows a doublet of doublets, indicating an asymmetric structure for the complex, probably due to a different mode of interaction of the semiquinone oxygens with the metal atom; we assume a bipyramidal structure for the complex with an axial–equatorial bound semiquinone ligand and an axial chlorine atom. Both proton splitting constants are in the semiquinone region and have the same, probably negative, sign. With increase in temperature the two centre lines increase in width, and finally coalesce at approximately 383 K. Variable-temperature EPR spectra of **11** reveal similar behavior; in this case, coalescence was observed at 393 K and the kinetic parameters obtained were $\Delta H^{\#} = 9.06$ kcal/mol, $\Delta S^{\#} = -4.26$ Cl/mol, and $k_{293} = 0.122$ MHz.

Comparison of the data for **4** with those for **11** indicate a significant influence of the chloro-substituent on the permutation isomerisation rate for these complexes. The semiquinolates with Pb–Cl bonds at room temperature reveal a rate constant that is lower by a factor of 10^{-4}. This may be due to the high activation energy for transition states with chloro-substituents in equatorial positions.

The reaction of **B** with **II** in toluene at room temperature gives rise to a more complex EPR spectrum, evidently caused by overlap of different radicals (Fig. 2). ENDOR and TRIPLE experiments allowed the species **20** and **21** with proton coupling constants of -2.84 G and $+0.48$ G or -4.22 G and $+0.39$ G, respectively, to be distinguished. When the temperature was raised to 393 K an EPR spectrum with only one doublet of 3.4 G and lead-hyperfine splitting was observed. The 1.85 : 1 ratio between **21** and **20** in the superimposed spectrum at 293 K was determined by computer simulation. From these results $\Delta G_{293} = 0.36$ kcal/mol was calculated.

These results indicate that the species **20** and **21** are both permutation isomers of the same semiquinolate complex. At low temperature they differ in respect of the positions of the oxygen atoms **1** and **2** in the trigonal bipyramidal structure, as shown in Scheme 2.



Scheme 2.

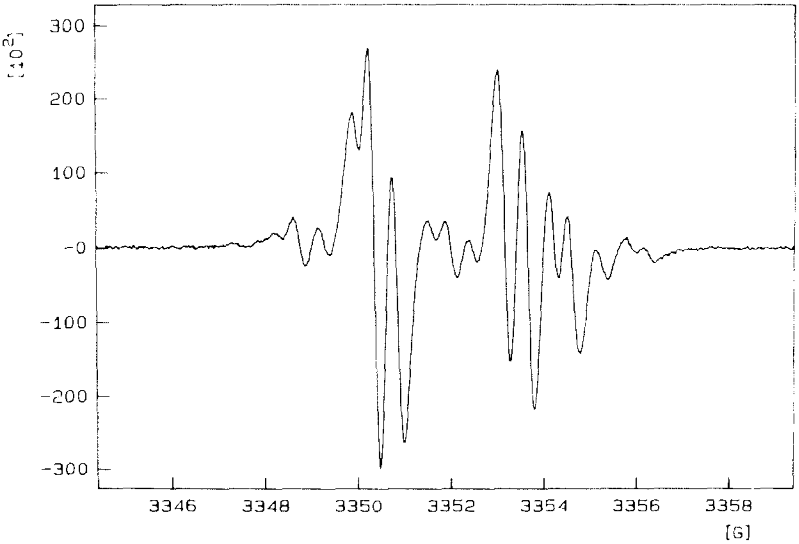


Fig. 2. EPR spectrum of the reaction products formed from **B** + **II** in toluene at room temperature.

If a phenoxyl-like spin density distribution is assumed, the signs at positions 4 and 6 should be negative or positive for both positions, which is not in keeping with the results. Our view, that the semiquinolate anions are bidentate ligands is also consistent with the results obtained with unsymmetrically substituted compounds.

The reaction of **A** with **I** under illumination yields a spectrum arising from superposition of the signals of two stable radicals (Fig. 3). The complex hyperfine

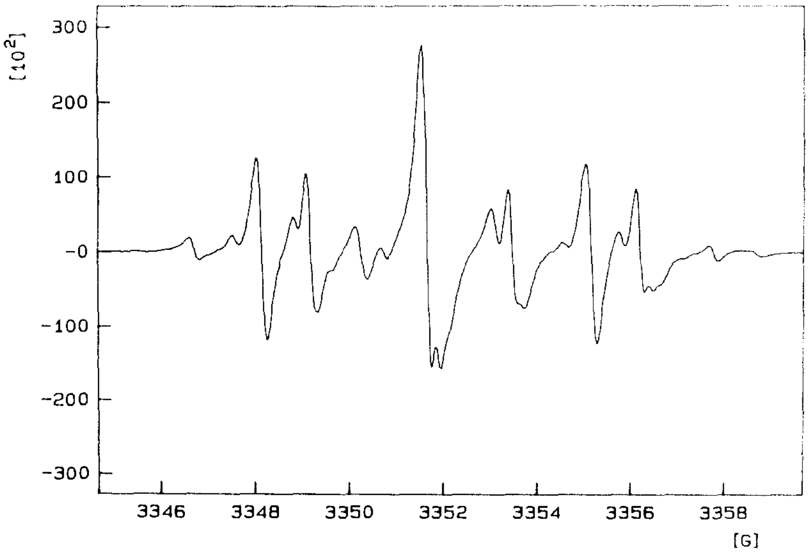


Fig. 3. EPR spectrum of the reaction product formed from **A** + **I** in toluene by illumination with UV light.

structure can be interpreted in terms of a mixture of radicals **1** and **9** in the ratio 1 : 0.75. Radical **1** can also be produced by mixing quinone **A** with hexaphenyldilead **III**; complex **9** cannot be detected under these conditions.

For compound **9** inequivalence of the protons in positions 4 and 5 indicates an asymmetrical structure. Obviously, introduction of electronegative substituents at the central atom generally causes a marked decrease in the interconversion rates of the complexes.

Completely analogous behavior is observed for reaction of **B** with **I** under illumination, which gives complexes **16**, **18** and **19**, whereas the reaction of **B** with **III** under the same conditions gives only species **16**. From these results we conclude that in **1** and **16** the organometallic moiety is the $(C_6H_5)_3Pb^+$ cation, which combines with semiquinones to give the corresponding complexes, whereas in **9**, **18** and **19** the lead is coordinated to the semiquinone, two phenyl groups, and the OH function. The compounds **18** and **19** are permutation isomers of the diphenyllead-hydroxide-semiquinolate complex.

Similar results are obtained in the reaction of **A** or **B** with tritolylleadhydroxide. The radicals **12** and **22**, generated in the dark, at room temperature show hyperfine structures which indicate a rapid equilibrium between two different pentacoordinated structures, as expected from the results for **1** and **16**.

UV irradiation of the quinones **A** or **B** in presence of tritolylleadhydroxide results in radical mixtures consisting of **12** and **13** or **22** and the two permutation isomers **23** and **24**. The data for complexes of semiquinolates with a compound containing three Pb–C bonds, **12** and **22**, can be interpreted in terms of rapid interconversion whereas those for the hydroxy-substituted complexes **13**, **23** and **24** reveal low permutation rates. These results are in good agreement with those obtained for triphenylleadhydroxide under similar conditions.

The reaction of photolytically generated hydroxyalkyl radicals with quinones has been studied by several authors [7]. In repeating these experiments we observed remarkably different coupling constants, indicating a more semiquinone-like spin density distribution rather than a phenoxyl-like behavior. Analoguous radical addition was observed upon illumination of **A** and **III** in ethanol and ethereal solution (THF, MTHF or dioxane), but the species formed show significant lead splitting. We thus conclude that in presence of organolead compounds the alkoxyalkyl radicals generated react predominantly with the organometallic species, and considerable concentrations of the radicals **5**, **6**, **7** and **8** are built up.

The proton coupling constants observed are inequivalent, indicating a slow interconversion at room temperature. However, the difference between the splittings in position 4 and 5 are small compared to those for OH- or Cl-substituted complexes **9**, **10**, **11**, and **13**. For this reason, we assume that in these complexes there is coordination between the lead atom and the two catechol oxygens, two phenyl groups and the hydroxyalkyl group or the ether moiety with formation of a Pb–C bond.

In the case of complex **5** variable temperature EPR data were obtained. Coalescence of the two center lines was observed at 383 K and kinetic parameters are $\Delta H^{\#} = 7.36$ kcal/mol, $\Delta S^{\#} = -9.06$ Cl/mol, and $k_{293} = 0.207$ MHz.

Reactions of the quinone **B** or catechol H_2**B** with the organolead compounds **I**–**IV** in general yield similar results to those obtained for **A**. In particular our interpretation of the temperature dependence of the proton coupling constants is confirmed. Only structures with the semiquinone as a bidentate ligand on the lead atom can satisfactorily account for the low temperature spectra of **18** and **19**, **20** and **21**, **23** and **24** each of which shows a large and a small splitting.

Aroxyl structures require either one pair of large and one pair of small splittings due to the oxygen atom which has the electronic aroxyl configuration, in contrast to our results. Therefore, the interpretation of the temperature dependence of the semiquinone organolead complex in terms of a cation migration can be ruled out, and a permutation isomerisation seems to provide a much better explanation.

Experimental

Preparation of the aryllead compounds

Hexaphenyldilead and triphenyllead chloride were purchased (Alfa Products, Johnson Matthey) and used without further purification. Triphenyllead hydroxide was prepared by hydrolysis of triphenyllead chloride [11]. Tritolyllead hydroxide was made from tetratolyllead [12]; the tetratolyllead was made, by the procedure described for synthesis of tetraphenyllead [13], from 4-methylphenylmagnesium bromide and lead chloride.

Preparation of quinones and catechols

3,6-Di-tert-butyl-*o*-benzoquinone was prepared from catechol and isobutylene with titanium catecholate as catalyst [14]. 3-tert-Butyl-5-triphenylmethyl-*o*-benzoquinone and 3-tert-butyl-5-triphenylmethylcatechol were made by published methods [15].

EPR measurements

The solvents used were dried and purified by the standard methods.

The semiquinolate-aryllead complexes were prepared directly in the EPR tube by mixing the lead compound with the quinone in an approximate 1 : 1 ratio and subsequently adding the chosen solvent. The oxygen was removed by bubbling nitrogen through the mixture for 10 minutes.

Complexes with 3-tert-butyl-5-triphenylmethylcatechol as ligand were prepared in the same manner, using a slight excess of the catechol. A few crystals of sodium carbonate were added. After air oxidation for several hours the oxygen was removed as described above.

The EPR spectra were recorded on a Bruker ESP 300 spectrometer. For the ENDOR spectra a Varian E-Line-Century EPR spectrometer equipped with a Bruker ER 810 unit and a Bruker ER 140 data system was used. The usual sweep time for a 20 G range EPR measurement was 42 s. Depending on signal intensity 1–10 scans were made. For ENDOR spectra 100–200 scans were made. The time per scan for a 14 MHz spectrum was 21 s.

The radicals generated were stable for periods varying from some days up to several weeks.

Acknowledgement

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