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A COMPARATIVE ESR STUDY OF THE REACTIONS OF GROUP IVB ORGANOMETALLIC RADICALS WITH 4,4'-DIMETHOXYBENZOPHENONE, 4,4'-DIMETHOXYTHIOBENZOPHENONE, AND 3-ETHYL-2-THIOXO-4-OXAZOLIDIONE

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Summary

Various reactions of Group IVB organometallic radicals with 4,4'-dimethoxybenzophenone, 4,4'-dimethoxythiobenzophenone, and 3-ethyl-2-thioxo-4-oxazolidione were studied by ESR spectroscopy. The greater involvement of sulfur in comparison with oxygen in spin delocalization is clearly reflected in both the hyperfine coupling constants and the *g*-factors. In general, thiocarbonyl compounds appear to be more efficient in forming radical adducts than the corresponding carbonyl compounds but the overall reactions depend strongly upon the structure of the thiocarbonyl compounds.

Introduction

The photochemical and free radical chemistry of carbonyl compounds and their thiocarbonyl analogs usually affords some interesting comparisons. For example, while only a few carbonyl compounds appear to react with carbon-centered radicals to yield the radical adducts, which are observable by ESR [1—3], thioketones are known to be a fairly good trap for alkyl radicals [4—6]. Numerous examples of additions of silicon-, tin-, and phosphorus-centered radicals to carbonyl compounds are available in literature [7], but only di-tert-butylthioketone has been shown to react with silyl, stannyl, and phosphorus radicals [6]. In general, thiocarbonyl compounds have received much less attention in the studies of reactions of organometallic radicals. In this work we examined and compared the reactions of Group IVB organometallic radicals with 4,4'-dimethoxythiobenzophenone, 4,4'-dimethoxybenzophenone, and

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3-ethyl-2-thioxo-4-oxazolidione which contains both the thiocarbonyl and the carbonyl groups.

Apart from the larger *g*-factors found in sulfur-containing radicals, a remarkably larger metal hyperfine splitting seems always to be associated with thioketyl metal ion pairs, as compared to their ketyl analogs [8]. In the present study we took advantage of the ease of thioketyl metal ion pair formation with sodium and potassium cations and applied further ion-exchange reactions between the metal cations and the transient organometallic species to probe the mechanisms of the radical adduct formation. It is concluded that, in general, 4,4'-dimethoxythiobenzophenone reacts with the entire series of Group IVB organometallic radicals with a much better efficiency than does 4,4'-dimethoxybenzophenone in solution.

Experimental

4,4'-Dimethoxythiobenzophenone and 4,4'-dimethoxybenzophenone were purchased from Aldrich and were vacuum distilled before use. 3-Ethyl-2-thioxo-4-oxazolidione (Aldrich) was used as received. Tetrahydrofuran was dried and stored over Na/K alloy. Spectroscopic grade benzene was dried over molecular sieves and distilled before use. Di-tert-butyl peroxide (MCB), 2-methyl-2-nitrosopropane (Aldrich), triphenylmethane (Aldrich), trimethylsilane (PCR), triphenylsilane (PCR), and other organometals from Alfa were used as supplied. t-Butyl β,β-dimethylperbutanoate was prepared by the method of Bartlett and Hiatt [9]. The procedures for preparation of ion-pair samples and the ion-exchange reactions with organometals are similar to the methods previously described [10]. In photochemical experiments, about 1 ml of benzene containing 0.1 ml of di-tert-butyl peroxide and 5 mg of the particular carbonyl or thiocarbonyl compound and the organometal, was degassed and sealed off under a vacuum of 10^{-4} mm Hg. The sample, contained in a pyrex tube, was irradiated in situ in the ESR cavity by a 200 W super pressure mercury lamp.

ESR spectra were recorded either on a Bruker 420 or a Varian E-3 X-band spectrometer using 100 KHz field modulation. Magnetic field and the microwave frequency were monitored by a Bruker NMR oscillator and by a Hewlett Packard 5342A microwave frequency counter, respectively. The temperature was controlled by a Varian variable temperature accessory and monitored by a thermocouple inserted into the Dewar flask. A Nicolet 1180 computer and the NTCESR program were used to simulate the observed ESR spectra for the assignments of hyperfine coupling constants. The time-resolved laser flash/DC detection CIDEP observation system described previously [12] was used to check the electron polarization of the observed paramagnetic species.

Results and discussion

1. ESR and time-resolved CIDEP study of the photoreductions of 4,4'-dimethoxybenzophenone (DMBO) and 4,4'-dimethoxythiobenzophenone (DMBS) in solution

No CW * ESR signal was observed during the continuous photolysis of DMBO in tetrahydrofuran (THF) within the temperature range of 25 and −80°C.

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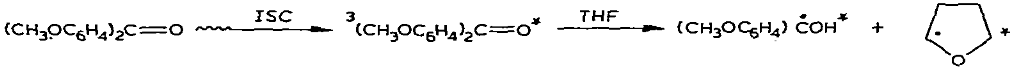
* CW = continuous wave.

However, a polarized signal was detected using the megawatt pulsed nitrogen laser and DC detection system. This was not surprising as the triplet electron polarization of benzophenone is very large and its subsequent transfer to the ketyl radical retains much of the initial polarization resulting in a substantial enhancement of the 'polarized' ESR signal intensity which can be observed by time-resolved DC detection before decay. The transient and polarized ketyl radical can be accounted for by the following mechanism:

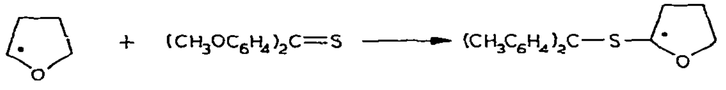


(1)

The more labile THF radical was not observed. Electron polarization is denoted by the asterisk (∗).

On the other hand, when DMBS in THF was photolyzed at —30° C, a strong CW ESR signal was observed but no polarized signal was detected. However, the observed ESR spectrum was not due to the thioketyl radical but rather it was due to a secondary radical formed by the addition of the THF radical to a ground state DMBS molecule (eq. 4) via the following reactions:

(2)

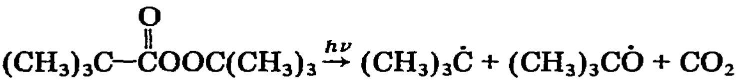


(3)

It is not certain at this time whether the photo-excited state involved in the primary chemical reaction in (eq. 2) is a single or triplet. The fact that no initial polarization was observed in the subsequent radical suggests that either the triplet polarization was very weak or that the photochemical reaction proceeded via a 'long-lived' S_2 excited state instead of a triplet [5]. The intermediate thioketyl radical has not been observed in solution by ESR, but its role in the photoreduction of thioketones has been proposed by other workers [4,5,12]. The experimental results also indicate that DMBS is a better trap for the carbon-centered THF radical than the corresponding DMBO.

2. *Alkyl and organometallic radical addition reactions*

(a) Addition of alkyl radicals to DMBO, DMBS and 3-ethyl-thioxo-4-oxazolidione (ETOD). Continuous photolysis of a benzene solution of DMBS and t-butyl β,β-dimethylperbutanoate gave an ESR spectrum of a persistent radical via the following reactions:



$$(CH_3)_3C{-}\overset{\overset{O}{\|}}{C}OOC(CH_3)_3 \xrightarrow{h\nu} (CH_3)_3\dot{C} + (CH_3)_3C\dot{O} + CO_2 \qquad (4)$$

$$(CH_3)_3\dot{C} + (CH_3OC_6H_4)_2C{=}S \rightarrow (CH_3OC_6H_4)_2\dot{C}{-}S{-}C(CH_3)_3 \qquad (5)$$

(I)

$$(CH_3)_3C\dot{O} + (CH_3OC_6H_4)_2C{=}S \rightarrow (CH_3OC_6H_4)_2\dot{C}{-}S{-}OC(CH_3)_3 \qquad (6)$$

(II)

TABLE 1

ESR PARAMETERS OF RADICAL ADDUCTS, ALKALI ION-PAIRS OF DMBS AND DMBO

Radical adduct [a]	T (°C)	g ± 0.0001	a_H^{ortho}	a_H^{meta}	$a_H^{OCH_3}$	$a_H^{M(CH_3)_3}$	a_M (G)
$(CH_3OC_6H_4)_2CS^{\dot{-}}K^+$	24	2.0065	2.50 ± 0.02	0.99	0.24		0.76
$(CH_3OC_6H_4)_2CS^{\dot{-}}Na^+$	24	2.0064	2.57	0.98	0.26		3.81
$(CH_3OC_6H_4)_2\dot{C}SC(CH_3)_3$	50 [b]	2.0030	2.95	1.10	0.37	0.37	
$(CH_3OC_6H_4)_2\dot{C}OSiPh_3$	79	2.0030	3.19	1.18	0.34		
$(CH_3OC_6H_4)_2\dot{C}SSiPh_3$	78	2.0033	2.94	1.11	0.36		
$(CH_3OC_6H_4)_2\dot{C}SSi(CH_3)_3$	79	2.0034	3.00	1.12	0.34	0.14	
$(CH_3OC_6H_4)_2\dot{C}SGe(C_2H_5)_3$	22		3.0	1.25			
$(CH_3OC_6H_4)_2\dot{C}OSnPh_3$	0	2.0022	3.16	1.14	0.36		
$(CH_3OC_6H_4)_2\dot{C}SSnPh_3$	2	2.0030	2.93	1.09	0.37		
$(CH_3OC_6H_4)_2\dot{C}OSn(CH_3)_3$	2	2.0023	3.21	1.16	0.38		
$(CH_3OC_6H_4)_2\dot{C}SSn(CH_3)_3$	7	2.0033	2.92	1.09	0.37	0.15	
$(CH_3OC_6H_4)_2\dot{C}SPbPh_3$	16	2.0031	2.93	1.07	0.39		
$(CH_3OC_6H_4)_2\dot{C}SPb(CH_3)_3$	16	2.0034	2.91	1.10	0.37	0.10	

[a] All radical adducts were prepared in benzene and radical ion-pairs were prepared in THF solution. [b] The proton coupling constants of this radical reported at room temperature in ref. 5 are slightly different.

An identical ESR spectrum of the persistent radical also was obtained when a benzene solution of DMBS and 2-methyl-2-nitrosopropane was photolyzed with visible light ($\lambda > 680$ nm) [5]. These results suggest that radical I, not II, is the observed persistent radical. This conclusion is consistent with the recent observation [6] that an oxygen-centered radical (such as $R\dot{O}$) does not form any detectable adduct with di-t-butylthioketone. The ESR parameters of the radical I are given in Table 1.

Under similar experimental conditions, it was found that the $(CH_3)_3\dot{C}$ radical did not form a detectable adduct with DMBO and ETOD. The triphenylmethyl radical also did not add to DMBO, DMBS, or ETOD. However, the photolysis of ETOD and t-butyl peracetate in toluene at —60° C produced a weak ESR spectrum which can be attributed to the adduct of methyl radical to the carbonyl group (Table 2).

(b) Organosilyl radical adducts. A relatively stable radical adduct was observed when a degassed benzene solution of DMBS, triphenylsilane, and di-t-butyl peroxide, sealed under vacuum, was heated to about 90° C. The radical adduct was identified as III by comparing the ESR parameters with those of triphenylsilyl adducts of DMBO (IV) produced by similar reactions [7a]:

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{\Delta \text{ or } h\nu} 2(CH_3)_3C\dot{O} \tag{7}$$

$$(CH_3)_3C\dot{O} + R_3SiH \rightarrow R_3\dot{S}i + (CH_3)_3COH \tag{8}$$

$$R_3\dot{S}i + (CH_3OC_6H_4)_2C{=}X \rightarrow (CH_3OC_6H_4)_2\dot{C}\text{-}X\text{-}SiR_3 \tag{9}$$

(III, X = S, R = Ph; IIIa, X = S, R = CH_3; IV, X = O)

The assignment of the thioketone adduct III was further supported by the unequivocal identification of IIIa by the additional resolved hyperfine splittings from the nine methyl protons of the trimethylsilyl moiety. The ESR parameters of III, IIIa, and IV are given in Table 1. It is interesting to note that under identical experimental conditions, DMBO did not yield an observable adduct with trimethylsilyl radicals.

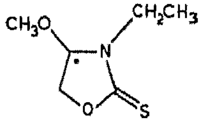
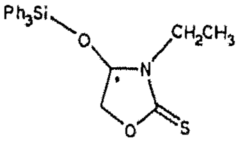
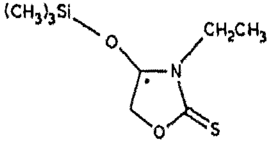
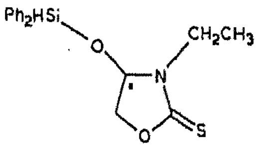
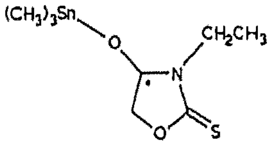
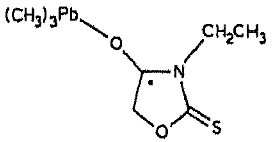
The triphenylsilyl radical was found to react with ETOD to produce a persistent radical which is assigned to an adduct in which the silyl radical has added to the carbonyl oxygen, not the thiocarbonyl sulfur. This assignment was consistent with the observed hyperfine coupling constants of the methylene protons (given in Table 2) and a *g*-factor of 2.0035. Similarly, diphenylsilyl radicals, $Ph_2H\dot{S}i$, also added to the carbonyl oxygen of ETOD and the resulting ESR spectrum exhibited the resolved coupling from the proton of the $Ph_2H\dot{S}i$ moiety. While the trimethylsilyl radical did not appear to react with DMBO, it added readily to the carbonyl oxygen of the ETOD. The ESR parameters of all the silyl radical adducts to ETOD are given in Table 2.

(c) Organogermanyl radical adducts. A weak ESR spectrum was observed when a benzene solution of DMBS, triethylgermane and di-t-butyl peroxide was photolyzed. The tentative assignment of the ESR parameters of the triethylgermanyl radical adduct to DMBS are given in Table 1.

(d) Organostannyl radical adducts. The photolysis of a benzene solution of DMBS, triphenyltin hydride, and di-t-butyl peroxide at 10° C led to the obser-

TABLE 2

ESR PARAMATERS OF METHYL AND GROUP IVB ORGANOMETALLIC RADICAL ADDUCTS OF ETOD IN TOLUENE SOLUTION

Radical Adducts	T (°C)	$g \pm 0.0001$	a_N	$a_H^{CH_2}$	$a_H^{CH_2CH_3}$	a_H^{SiH} (±0.02 G)
	−60	2.0031		10.76		
	0	2.0035	1.04	9.76		
	10	2.0035	0.85	9.61		
	−40	2.0034	0.96	9.96		0.96
	−65	2.0040	0.78	9.85	0.39	
	−65	2.0028		10.65		

vation of an ESR spectrum of the radical adduct V. An identical ESR spectrum was obtained when a trace of triphenyltin chloride was added to a THF solution containing the paramagnetic K^+ DMBS$^{\dot{-}}$ ion pair [8,13]:

$$(CH_3OC_6H_4)_2C{=}S \xrightarrow[\text{THF}]{\text{K}} (CH_3OC_6H_4)_2CS^{\dot{-}}\,K^+ \xrightarrow{Ph_3SnCl} (CH_3OC_6H_4)_2\dot{C}{-}S{-}SnPh_3 + KCl \qquad (10)$$

A similar ion-exchange reaction mechanism has been used previously in this laboratory to prepare a series of Group IVB organometallic radical adducts to furil [14]. Similar methods also have been widely used to synthesize the diamagnetic organotin mercaptides, $R_{4-x}Sn(SR')_x$ [15].

The triphenylstannyl adduct of DMBO also can be observed under similar experimental conditions (Table 1). However, when a benzene solution of ETOD, triphenyltin hydride and di-t-butyl peroxide was photolyzed, the analogous adduct was not observed. Instead, a spectrum consisting of a triplet (11.3 gauss) of doublets (8.7 gauss) was obtained. The same spectrum also could be observed without the presence of the di-t-butyl peroxide. It is not immediately obvious what paramagnetic species were responsible for this spectrum. On the other hand, the organotin radical adduct of ETOD was readily observed when a benzene solution of ETOD, hexamethylditin, and di-t-butyl peroxide was photolyzed. The ESR parameters of the adduct given in Table 2 again suggest that the trimethyltin radical added to the carbonyl oxygen and not the thiocarbonyl sulfur.

When a frozen solution of DMBS and hexamethylditin, prepared at −150°C and in the dark, was allowed to warm up to about 5°C within the ESR cavity, an ESR spectrum of the trimethyltin adduct of DMBS was observed (VI, Table 1), with hyperfine splittings from both the DMBS and the methyl protons of the tin radical moiety being resolved. The mechanism of the formation of adduct VI is rather interesting, since at low temperature (5°C and below) hexamethylditin is not likely to dissociate into two tin radicals (the Sn—Sn bond energy is approximately 53 kcal/mole [16]). Recently, a thermally accessible charge-transfer [CT] process has been proposed [17] to account for the formation of organometallic phenanthraquinone adducts under similar conditions. This process would require that DMBS and hexamethylditin form a low and thermally accessible CT state:

$$(CH_3OC_6H_4)_2C{=}S + (CH_3)_6Sn_2 \overset{\text{CT}}{\rightarrow} ((CH_3OC_6H_4)_2CS^{\dot{-}}\,(CH_3)_6Sn_2^{\dot{+}}) \qquad (11)$$

followed by a rapid dissociation of the CT complex:

$$((CH_3OC_6H_4)_2CS^{\dot{-}}\,(CH_3)_6Sn_2^{\dot{+}}) \rightarrow \underset{\text{(VI)}}{(CH_3OC_6H_4)_2\dot{C}{-}S{-}Sn(CH_3)_3} + (CH_3)_3\dot{S}n \qquad (12)$$

$$(CH_3)_3\dot{S}n + (CH_3OC_6H_4)_2C{=}S \rightarrow \underset{\text{(VI)}}{(CH_3OC_6H_4)_2\dot{C}{-}S{-}Sn(CH_3)_3} \qquad (13)$$

The possibility of forming such a low CT state obviously is strongly dependent upon the two partner molecules. While the first singlet transition of the parent

DMBS molecule lies in the visible region, electron transitions in the DMBO molecular are mainly in the UV. Furthermore, the electron affinity of the two molecules, DMBS and DMBO, is substantially different. Thus, it is not automatic that DMBO and hexamethylditin may also form a low CT state. Indeed, under identical conditions the trimethyltin adduct of DMBO was not produced when a frozen solution of DMBO and hexamethylditin prepared in the dark was warmec up to 5°C. Trimethyltin adducts of both DMBS and DMBO can be prepared by the photolysis of a solution containing the respective ketones, hexamethylditin and di-t-butyl peroxide. Here the common mechanism involves the S_H2 reaction of hexamethylditin with the t-butoxy radicals [18,19] to yield the trimethyltin radical which then adds to either DMBS or DMBO (Table 1).

(e) Organoplumbyl radical adducts. No ESR signal was detected when a frozen benzene solution of DMBS and either hexaphenyldilead or hexamethyldilead was allowed to warm to room temperature in the ESR cavity. A strong signal, however, was obtained immediately after the solution was exposed to light. The ESR parameters of the trimethylplumbyl-DMBS adduct, VII, and the triphenylplumbyl-DMBS adduct VIIa are given in Table 1. Under similar conditions, no organoplumbyl adducts of DMBO were produced, but with ETOD only a very weak spectrum of a broad triplet was observed. The failure to produce the trimethylplumbyl adducts of benzophenone and of acetone has been attributed to the weak Pb—O bond [20].

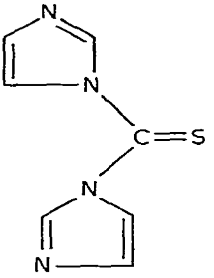
3. The ESR parameters and the structure of radical adducts

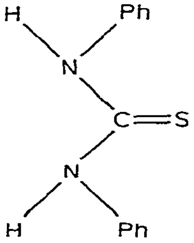
The ESR parameters of the organometallic adducts of DMBS and DMBO, along with those of the sodium and potassium ion pairs of DMBS, are given in Table 1. The parameters of the adducts of ETOD are listed in Table 2. Several trends in the ESR parameters of these radical adducts are worthy of note. There is a dramatic decrease in *g*-factor from a value of 2.0064 for the radical ion-pair to a value of about 2.0034 for the radical adducts of DMBS. This large decrease in the value of *g*-factors is expected, since in the ion-pair the unpaired electron is mainly delocalized onto the sulfur atom, whereas in the radical adducts most of the spin density is located at the thiocarbonyl C atom. This is consistent with the observation that the hyperfine coupling constants of the ring protons in the ion-pairs are smaller than those of the corresponding radical adducts.

Among the radical adducts the proton coupling constants of the ring protons in the thiocarbonyl adducts are smaller than those of the corresponding carbonyl analogs. In turn, the methyl protons of the organometallic moiety were better resolved only in the thiocarbonyl adducts. This indicates that the S atom is probably a better spin transmitter than the oxygen analog. Furthermore, the comparison between the $(CH_3OC_6H_4)_2\dot{C}—S—C(CH_3)_3$ and the $(CH_3OC_6H_4)_2$-$\dot{C}—S—Si(CH_3)_3$ radicals shows that the value of the *g*-factor increases from 2.0030 for the alkyl adduct to 2.0034 for the silyl adduct, while the methyl proton coupling constant decreases from 0.37 gauss to 0.14 gauss, respectively. The comparison between these two analogous radicals suggests that spin delocalization is more efficient in the C—S bond than in the Si—S bond and thus partly accounts for the unusual stability of the alkyl adducts of the thione.

The decrease of *g*-factors from silicon adducts to tin adducts and the fact that the *g*-factor of $(CH_3OC_6H_4)_2\dot{C}OSnR_3$ is smaller than the free electron value probably are due to the involvement of tin *d*-orbitals in the Sn—O and Sn—S bonding [21,22]. If the extent of *d*-orbital involvement in Pb—S bonding is similar to that in Sn—S bond, the larger spin-orbit coupling of the heavier Pb atom should render the *g*-factor of the lead adducts even smaller than that of the tin adducts. Experimentally, this is not the case, as higher *g*-factors are found for the lead-DMBS adducts. It is, however, reasonable to expect that the Pb—S bonding is weaker than the Sn—S bond. The even weaker Pb—O bond would then account for the failure to observe the similar lead adducts with DMBO, as well as with other carbonyl compounds [23].

From the comparative results of radical additions to DMBS and DMBO, it is concluded that the addition of Group IVB organometallic radicals to the thiocarbonyl compound is more efficient than the corresponding carbonyl analog. However, Group IVB organometallic radicals add to the carbonyl instead of the thiocarbonyl group in ETOD. In order to gain some insight into these apparently contradictory observations, the Group IVB organometallic radicals were generated in the presence of other thiocarbonyl compounds, A and B.


(A)


(B)

In both cases, no ESR signal was detected. It appears that although the thiocarbonyl group can react with various organic and organometallic radicals, the addition efficiency is mainly determined by the structure of the molecule as a whole.

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