Journal of Organometallic Chemistry, 156 (1978) 17—23

FORMATION OF FREE RADICALS IN THE REACTION OF ALKYLLITHIUMS WITH TITANIUM TETRACHLORIDE *, **

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(Received February 13th, 1978)

Summary

Alkyl radicals have been detected by electron spin resonance spectroscopy approximately 80 msec after mixing benzene solutions of alkyllithium reagents with titanium(IV) chloride. The methyl, ethyl, isopropyl, n-butyl, sec-butyl, t-butyl and cyclopentyl radicals were observed from the corresponding alkyllithium reagents. The methyl radical easily observed at 40 msec reacts to give a second paramagnetic species with $a^{H}_{CH_2}$ 18 Gauss. It is suggested that this species is derived from $(CH_3Li)_4$ by hydrogen atom abstraction.

Introduction

Alkyllithium reagents react with a variety of π-acceptors by single electron transfer (SET) [2].

$$R{:}^{-}Li^{+} + \pi \rightarrow \pi^{\cdot -} + R^{\cdot} + Li^{+}$$

Thus, stable radical anions have been observed from such diverse π-acceptors as benzophenone, azobenzene, nitrobenzene, or 1,2-bis(4-pyridyl)ethylene. Alkyllithium reagents will also undergo SET with σ-acceptors such as the alkyl halides, and this process is quite a good method for generating alkyl radicals in solution at room temperature in the electron spin resonance (ESR) concentration range (~10^{-7} *M*) [3]***. The reaction must be quite fast because the lifetime of a simple alkyl radical in this concentration range is only a few msec (ethyl radical at

$$n\text{-BuLi} + RI \rightarrow n\text{-Bu}^{\cdot} + (RI)^{\cdot -} \rightarrow R^{\cdot} + I^{-}$$

$$n\text{-Bu}^{\cdot} + RI \rightarrow n\text{-BuI} + R^{\cdot}$$

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[*] Dedicated to Prof. Herbert C. Brown on the occasion of his 66th birthday.

[**] Electron Transfer Processes, Part XV. For Part XIV see ref. 1.

[***] The radicals can also be trapped by nitrosobenzene to form stable spin adducts. Thus, n-butyllithium/TMEDA and t-butyl iodide in benzene containing nitrosobenzene yield t-butylphenylnitroxide.

TABLE 1

HYPERFINE SPLITTING CONSTANTS OBSERVED FOR ALKYL RADICALS, 25—35° C IN C_6H_6

Radical	RLi + $TiCl_4$			n-BuLi + RI [a]		
	α	β	γ	α	β	γ
$CH_3\cdot$ [a]	19.5 ± 0.5 [b]			22.0 [c]		
$CH_3CH_2\cdot$ [d]	21.5	26.3		21.5	26.0	
$(CH_3)_2CH\cdot$	21.0	24.0		21.0	24.0	
$CH_3CH_2CH_2CH_2\cdot$	21.4	27.4	0.5	21.7	27.6	0.5
$(CH_3)(C_2H_5)CH\cdot$	21.0	24.3		21.0	24.3	
$(CH_3)_3C\cdot$		22.2			22.8	
Cyclo-$C_5H_9\cdot$	21.1	34.5	0.5			

[a] Solution also contained ethyl ether. [b] The value of a^H varied for different experiments. [c] n-Butyl radical also observed. [d] g-Value 2.0025. The g-value of ethyl radical is reported to be 2.00260 [4].

—175° C was measured to have a lifetime (τ) of 6.8 msec in ethane solution [4]).

We now report studies by ESR spectroscopy on the formation of the free alkyl radicals by reaction of alkyllithium reagents with titanium(IV) chloride.

Results and discussion

Reaction of 0.05—0.20 *N* solutions of alkyllithium reagents with 0.05 *M* titanium(IV) chloride in benzene in a flow system produced the alkyl free radicals. The maximum ESR signal intensity was observed at ~80 msec after mixing. Alkyl radicals could no longer be detected after 0.5 sec. The radical yield as detected by ESR was comparable to that observed in the alkyllithium—alkyl iodide reaction [3]. Table 1 lists the radicals observed with the experimental hyperfine splitting constants (hfsc).

With the possible exception of the methyl system, which we will discuss later, it seems certain that free radicals are being observed which are not associated or stabilized by the titanium atom. The reaction was quite exothermic, and at the concentrations employed the reaction resulted in an increase in temperature from 25° C at the point of mixing to 35° C when the solution left the apparatus ~0.2 sec later. The effluents contained a dark brown suspension of reduced titanium species. The use of butylmagnesium bromide in ether/benzene solution produced an excellent spectrum of the n-butyl radical contaminated with a broad signal probably of the reduced titanium species. Phenyllithium, phenylmagnesium bromide, or vinyllithium also produced a broad singlet ESR spectrum with no evidence for the free vinyl or phenyl radicals *. In hexane solution the alkyllithium reagents which yielded ESR spectra of high quality in benzene, failed to produce an identifiable spectrum of the alkyl radical. Again broad signals could be observed from reduced titanium species. Addition of 30% of benzene to hexane allowed the radicals to be observed. Apparently the rate of the radi-

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* The phenyl radical can not be seen when n-butyllithium/TMEDA is treated with phenyl iodide, although in the presence of the radical scavenger nitrosobenzene, the diphenylnitroxide radical is observed. However, the diphenylnitroxide could result from the addition of phenyllithium (formed by metal—halogen exchange) to the nitrosobenzene.

cal forming reaction is considerably slower in hexane than in the presence of benzene. For the alkyllithium—alkyl halide SET reaction in benzene the formation of radicals in the ESR concentration range required the presence of ethyl ether or tetramethylethylenediamine to activate the organolithium reagent [5]. These complexing agents were not required in the titanium(IV) chloride reactions, except in the case of methyllithium.

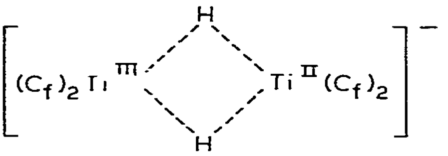
The mechanism of the formations of free radicals does not seem to involve the initial formation of alkyltitanium species followed by homolytic bond sission. Species such as CH_3TiCl_3, $(CH_3)_2TiCl_2$, $(C_6H_5CH_2)_3TiCl$, $(CH_3)_4Ti$ or $(CH_3)_3Ti$ are isolable substances, and although there is evidence that radicals can be produced by homolysis of these substances at room temperature [6], their complete decomposition would have to occur within 1 sec to have produced the alkyl radical concentrations observed in this work. We thus conclude that radical formation occurred by either process 1 or 2 [2].

$$RLi + TiCl_4 \rightarrow R^{\bullet} + [TiCl_4]^{\bullet -} \rightarrow TiCl_3 + Cl^- \qquad (1)$$

$$RLi + TiCl_4 \rightarrow RTiCl_4^- Li^+ \rightleftharpoons R^{\bullet} + [TiCl_4]^{\bullet -} \qquad (2)$$

We know of no evidence inconsistent with the SET reaction 1 *. Polymerization reactions employing titanium(IV) chloride and alkyllithium reagents in aromatic solvents must have a free radical contribution from the initial burst of radicals in the reaction. Of course, the high radical concentration would be rather inefficient for vinyl polymerization, and the period of radical production would be rather short in an aromatic solvent. However, in alkane solution presumably radical production would occur more slowly over a longer period of time. Inclusion of olefins (0.3 *M*, 1-hexene, camphene, norbornene or cyclohexene) in the n-butyllithium/titanium(IV) chloride system in benzene did not have an appreciable effect on the intensity of the free radical signal observed. We were unable to generate sufficient quantities of any adduct radicals to identify them by ESR spectroscopy. We were also unable to identify the benzyl radical when toluene (0.3 *M*) was included in the solvent.

π-$(C_5H_5)_2TiCl$ or π-$(C_6H_5)_2TiCl_2$ react with an excess of alkyllithium reagents or Grignard reagents in ethereal solutions at room temperature to yield $(C_5H_5)_2TiH_2^{\bullet -}$ or $(C_5H_5)_2TiR_2^{\bullet -}$, $g = 1.99$ which can be detected minutes or hours after reaction [7]. Structure I has also been suggested [8]. In the present work we



(I)

have seen no evidence for species of the type $R_4Ti^{\bullet -}$.

Some aspects of the methyllithium reaction deserve further comment. The radical with $a^H = 19.5 \pm 0.5$ (3H) Gauss was observed using a solvent of benzene

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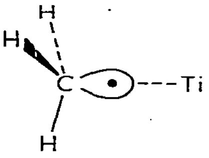
* Process 2 might yield the radical $R^{\bullet}$ with nuclear spin polarization. Careful examination of the spectrum for n-butyl radical fails to reveal any evidence of polarization since the intensities of the ESR transitions are independent of the sign of M_I.

(80%)/ether (20%). Moreover, to detect the radical somewhat faster flow rates (40 msec between mixing and detecting) were required. Higher rates of electron transfer and shorter detection periods may well be required for the methyl radical because of its greater reactivity, particularly in unimolecular radical reactions. The low value of a^H observed is puzzling since the normal value of 22.0 Gauss for the methyl radical was observed in benzene from the alkyllithium—methyl iodide electron transfer reaction [3]. One possibility is that the methyl radical is associated somehow with the reduced titanium species. In water or acetic acid solution there is no evidence that titanium(III) has any effect upon a^H for the methyl radical (a^H 22G, Ti^{III} plus t-butylhydroperoxide [9]; a^H 23.1 G, Ti^{III}, hydrogen peroxide, acetic acid [10]), but in the present work undoubtedly hypovalent titanium species are present. The association could be static, e.g. II, where a slight distortion from sp^2 hybridization for the methyl radical has reduced the value of a^H *. The low value of a^H observed for the



(II)

methyl radical might also be the result of an exchange process. This would explain the variability of a^H (±0.5 Gauss) observed in different experiments and the somewhat broad lines observed for the methyl radical (linewidth ~0.5 Gauss). Methyllithium exists as a tetrameric structure in the solid phase [12], or in ether solutions [13.14] **. One exchange reaction which might explain the present result would be a methyl exchange shown in reaction 3.

$$(CH_3Li)_4 + \overset{*}{C}H_3^{\cdot} \rightleftharpoons (\overset{*}{C}H_3Li)_4 + CH_3^{\cdot} \tag{3}$$

It does not seem possible to formulate a reasonable exchange mechanism going through $^{\cdot}CH_2{:}^-$ formed by the loss of a proton from $CH_3^{\cdot}$ (reactions 4 and 5).

$$CH_3^{\cdot} + \text{methyllithium} \rightarrow {}^{\cdot}CH_2{:}^-Li^+ + CH_4 \tag{4}$$

$$^{\cdot}CH_2{:}^-Li^+ \xrightarrow{?} CH_3^{\cdot} \tag{5}$$

Alternately, a time-averaged situation might be involved, e.g. reaction 6, involving two radical species. The methyl radical might be more prone to undergo this

$$CH_3^{\cdot} + Ti(?) \rightleftharpoons CH_3Ti(?) \tag{6}$$

$$a^H_{CH_3}\ 22\ G \qquad a^H_{CH_3} < 19\ G$$

interaction with the hypovalent titanium species, because of its greater reactivity relative to the other alkyl radicals. Unfortunately, the g-value of the methyl radi-

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* The methyl radical adsorbed in Vycor glass at 25°C has the normal value of a^H 22.8 Gauss [11].

** Evidence for the equilibrium, $R_4Li_4 \rightleftharpoons 2\ R_2Li_2$ exists [13].

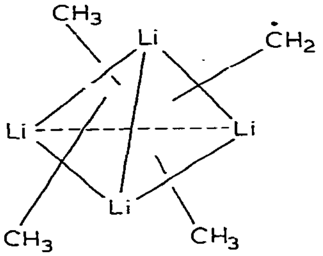
cal observed in this work has not yet been measured, but from instrumental settings it can not be significantly different from 2.002.

At slower flow rates (60 msec between mixing and detection) for the system methyllithium—titanium(IV) chloride in benzene/ether solvent a second paramagnetic species could be detected in addition to the methyl radical. A 1/2/1 triplet with a linewidth of several gauss and $a^{H} \sim 18$ Gauss was observed with a g-value equal to that of the methyl radical. At the normal flow rate of 80 msec between mixing and detection only the species with $a^{H}_{CH_2}$ 18 Gauss was seen. This species was never observed in the reactions of butyllithium with methyl iodide, which yielded a mixture of methyl radicals (a^{H} 22 Gauss) and n-butyl radicals [3] *. Possibly the species with a^{H} 18 Gauss also contains titanium, for example $Cl_3TiCH_2^{\cdot}$. If alkyltitanium compounds have an unusually high reactivity towards methyl radicals (much greater than toluene), reaction 7 might compete with the other reactions of methyl radicals from the initial electron transfer step.

$$CH_3^{\cdot} + CH_3TiCl_3 \rightarrow CH_4 + \underset{(III)}{Cl_3TiCH_2^{\cdot}} \qquad (7)$$

Furthermore, III might contain unresolved chlorine hfs consistent with the broad lines observed. However, the value of $a^{H}_{CH_2}$ of 18 Gauss is considerably lower than the values of $a^{H}_{CH_2}$ observed for $Me_3SiCH_2^{\cdot}$ (21.25), $Me_3GeCH_2^{\cdot}$ (21.50), or $Me_3SnCH_2^{\cdot}$ (21.25) [15]. The presence of β-chlorine atoms in III would probably not cause a significant reduction in the value of $a^{H}_{CH_2}$, since for $Me_2Si(Cl)CH_2^{\cdot}$ the values of $a^{H}_{CH_2}$ 21.0, a^{Cl} 3.5 Gauss have been observed (i.e., hyperconjugation involving silicon or titanium should be inefficient) [16].

It thus appears that the species with a^{H} 18 Gauss is probably derived from the methyllithium. In fact Kochi has shown that at —32° C in ether, t-butoxy radicals abstract a hydrogen atom from methyllithium to yield a species with a^{H} 18.2(2), a^{Li} 1.67(3) Gauss to which he has assigned structure IV [17]. The formation of IV via reactions 8 and 9 seems quite reasonable. However, in the



(IV)

$$(CH_3Li)_4 + TiCl_4 \xrightarrow[Et_2O/C_6H_6]{fast} CH_3^{\cdot} + LiCl + TiCl_3 \qquad (8)$$

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* The reaction of methyllithium and methyl iodide is not a good source of methyl radicals. The present result represents the only example where we have seen the methyl radical in the presence of methyllithium.

$$CH_3^{\bullet} + (CH_3Li)_4 \xrightarrow{\text{slow}} CH_4 + \text{IV} \qquad (9)$$

absence of resolved lithium hfs we can not be certain that the observed species is IV, the methylene radical anion ($^{\bullet}CH_2\!:^-$), or $LiCH_2^{\bullet}$. If the latter two species have the unpaired electron in a *p*-orbital (i.e., are π-radicals) values of a^H close to 18 might occur, and in fact an INDO calculation by Kochi for $LiCH_2^{\bullet}$ has yielded a^H —17 Gauss [17].

Methyl or other simple alkyl radicals have not been extensively studied in the presence of strong bases. Evidence for carbene radical anions has been presented in the liquid [18,19] or gas phase [20], and their formation by disproportionation between a radical and a carbanion (reaction 10) is not unreasonable. However, we find no evidence by ESR spectroscopy for the formation of $:CH_2^{\bullet -}$ or $C_3H_7CH^{\bullet -}$ from the interaction of n-butyllithium with methyl and/or n-butyl radicals. Either reaction 10 occurs too slowly, or the carbene radical anion has too short a lifetime for convenient ESR investigation. The present study of butyllithium plus titanium tetrachloride is a better test for reaction 10 than the previous studies of electron transfer between butyllithium and alkyl iodides, because in the presence of the alkyl iodide the carbene radical anion should rapidly regenerate the alkyl radical via iodine atom abstraction, reaction 11.

$$R_2CH^{\bullet} + R_2\ddot{C}H^- \rightarrow R_2CH_2 + R_2\ddot{C}^{\bullet -} \qquad (10)$$

$$R_2\ddot{C}^{\bullet -} + R_2CHI \rightarrow R_2\dot{C}H + [R_2CI]^- \rightarrow R_2C\!: + I^- \qquad (11)$$

Experimental

Commercially available alkyllithium reagents in benzene were employed. Commercial methyllithium in ether was diluted with benzene.

The flow cell used consisted of flat Pyrex plates (6 × 1 cm) with a 1.5 mm separation. With a 1 mm separation the precipitated titanium species restricted the flow. The $TiCl_3$/benzene and alkyllithium/benzene solutions were mixed under gravity flow (polyethylene tubing) in a cell similar to that described by Dixon and Norman [7]. The reaction mixture flowed upward through the ESR cell in a Varian V-4500 EPR spectrometer. The volume of the cell between the point of mixing and detection was 0.12 ml. The standard flow rate was 85 ml/min, which yields an average residence time in the cavity of 0.08 sec.

Acknowledgment

We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for financial support.

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