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AUTOXIDATION OF SELECTED ALKYLS OF TITANIUM, ZIRCONIUM, MOLYBDENUM AND TUNGSTEN

P.B. BRINDLEY and J.C. HODGSON
School of Chemical Science and Technology, Kingston Polytechnic, Kingston upon Thames (Great Britain)

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Summary

Autoxidation of selected tetraalkyl-titanium and -zirconium and hexaalkyl-dimolybdenum and -tungsten compounds proceeds through a series of very rapid, free radical displacements at the metal centre. Unstable organometallic peroxides were detected, but they reacted rapidly at −74° with the alkyl to form the alkoxy compounds.

Introduction

It has recently been shown that metal alkyls of early transition metals are not inherently unstable [1 - 3] and with isolation of trimethylsilylmethyl [1], benzyl [4] and neopentyl derivatives of Ti, V, Hf [2,4] and Cr, Mo, W [1] it is now possible to study substitution reactions occurring at the metal centre. These metal alkyls were reported to show varying degrees of reactivity towards atmospheric oxygen, thus tetrakis(trimethylsilylmethyl)zirconium(IV) was found to be pyrophoric [2b] while hexakis(tetramethylsilylmethyl)dimolybdenum and -tungsten were stable in air over short periods [1]. It is desirable to establish the scope of such substitutions so that their influence on reactions of potential industrial importance, such as olefin isomerisations [5], oxidations [6], epoxidations [7] and polymerisations [8], can be assessed.

Results and discussions

Our aim was to determine which of these compounds would be most suitable for quantitative measurements and so we measured the oxygen absorbed by tetrakis(trimethylsilylmethyl)-titanium(IV) and -zirconium(IV), hexakis(trimethylsilylmethyl)dimolybdenum(III), tetrabenzylzirconium(IV), hexabenzylditungsten(III) and hexaneopentyldimolybdenum(III) in hydrocarbon solvent at 20° and −74°. The compounds autoxidised with great speed and

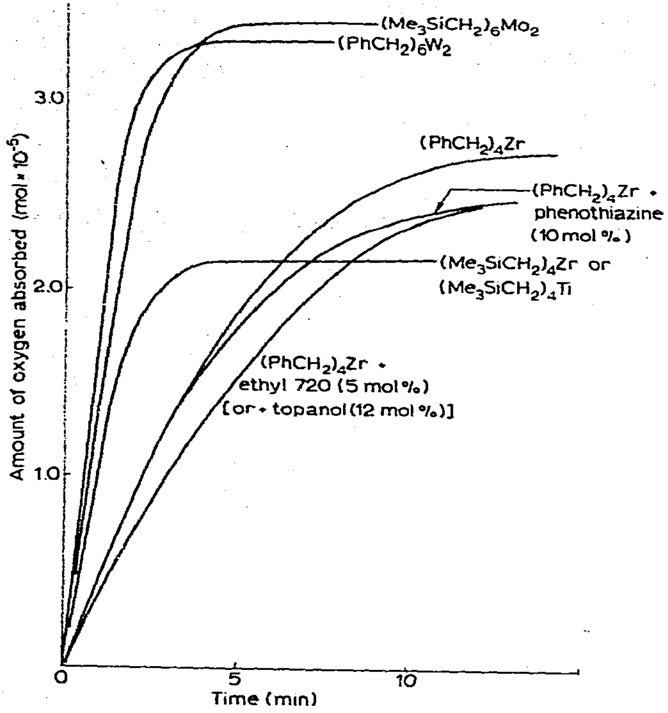

Fig. 1. Autoxidation of organo transition metal compounds in the presence of inhibitors at 20°.

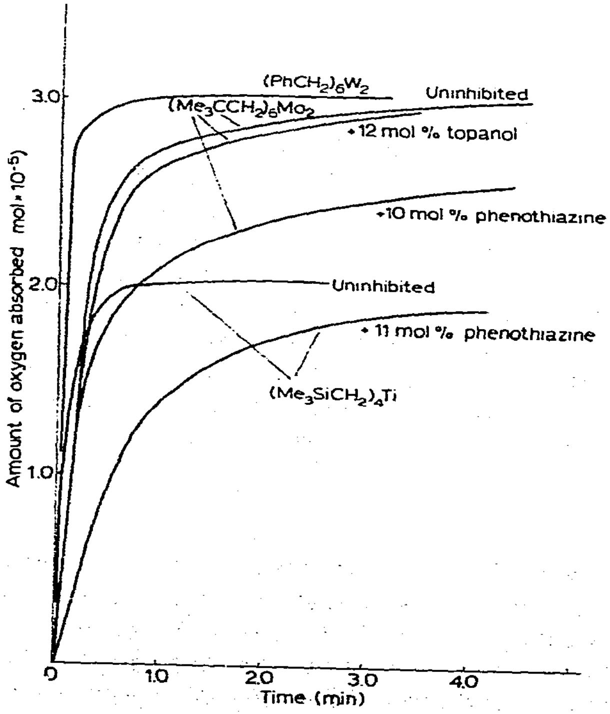

Fig. 2. Autoxidation of organo transition metal compounds at 74°.

at 20° approached diffusion control, with hexaneopentyldimolybdenum(III) being slightly less reactive than the rest (Fig. 1) and comparable to tri-*n*-butyl borane [9]. At −74° there was a small but significant reduction in the overall speed of oxidation, e.g. for $(PhCH_2)_4Zr$ $t_{½}$ = 2 min, but this was sufficient only for qualitative comparisons (Fig. 2).

It seemed likely, in the light of our experience of boron alkyl autoxidations [9], that the Group IVA and VIA metal alkyls would undergo attack by alkylperoxy radicals at the metal centre with elimination of an alkyl group and that a free radical chain reaction was involved. This would be the first example of a bimolecular homolytic substitution (S_H2) by peroxy radicals at an early transition metal centre (eqns. 1 - 3). Davies and Ingold [10] managed to measure the oxidation rates of alkylboranes by reducing the borane concentration through complex formation, the complexed borane not undergoing S_H2 attack. An attempt by us to use this technique was unsuccessful. Although tetrabenzylzirconium formed a complex with excess pyridine [11] autoxidation was still too fast for accurate rate measurements and it would seem that the complex itself underwent substitution by peroxyradicals. A similar effect was found when piperidine was used.

$$R_nM + O_2 \longrightarrow [R_nM \cdot O_2] \rightarrow R^\bullet \text{ initiation} \quad (1)$$

$$R^\bullet + O_2 \xrightarrow{\text{very fast}} RO_2^\bullet \quad (2)$$

$$RO_2^\bullet + R_nM \longrightarrow RO_2MR_{n-1} + R^\bullet \quad (3)$$

The organometallics differed significantly from the tributylboranes at low temperature in that stepwise oxidation of the alkyl groups attached to the metal was not observed and the similarities in activation energies for the S_H2 stage (eqn. 3) must be associated with the low lying, transition metal, vacant *d* orbitals.

With all the compounds studied at 20° the total absorption of oxygen approximated to 0.5 molecules of oxygen for each alkyl group, which suggests metal alkoxides were the stable end products. The ^1H NMR spectrum agreed with this since the high field methylene protons signal of the metal alkyl disappeared on autoxidation and was replaced by a resonance at lower field. Also hydrolysis of the resulting solutions gave the corresponding alcohols in high yield. Lappert et al. [2c] isolated tetraneopentoxyltitanium under similar circumstances from tetraneopentyltitanium.

The detection of the corresponding peroxy transition metal alkyls, which might be expected as reaction intermediates, was complicated by their extremely rapid conversion to alkoxide. Small amounts of peroxide could only be detected for hexaneopentyldimolybdenum, hexabenzylditungsten and tetrabenzylzirconium at 20° (Table 1). At −74° the peroxides derived from the benzyl compounds were much more stable. For tetrabenzylzirconium and hexabenzylditungsten yields of 0.6 and 0.8 mol of peroxide per mol of organometallic were obtained and traces of peroxide were detected in the case of hexakis(trimethylsilylmethyl)dimolybdenum and tetrakis(trimethylsilylmethyl) zirconium. The peroxybenzylzirconium had a half-life of 50 min at 20° but could not be isolated, although hydrolysis of the hydrocarbon solution yielded benzyl hydroperoxide. We conclude that at room temperature the peroxide removing reactions (4) or (5) are comparable in speed to the S_H2 step (3). It is not possible at this stage to decide between intermolecular conversions of peroxide to alkoxide:

$$\text{ROOM} + \text{RM} \longrightarrow 2\text{ROM} \tag{4}$$

or an intramolecular process:

$$\text{ROOMR} \longrightarrow (\text{RO})_2\text{M} \tag{5}$$

However, the greater activation energy of the peroxide removal reactions compared with eqn. (3) allows at −74° separation of the two reactions, autoxidation and peroxide rearrangement.

Galvinoxyl, which had proved effective as an inhibitor for alkyls of boron, cadmium and zinc could not be used to inhibit these autoxidations since there was interaction with the organometallic in a manner similar to that reported by Davies and Roberts for lithium and magnesium alkyls [12]. 2,6-Di-tert-butyl-4-methoxyphenol (Topanol 354) slightly retarded hexaneopentyldimolybdenum at 20° while at −74°, Topanol and 3,3′-di-tert-butyl-4,4′-dihydroxy-5,5′-dimethyldiphenylmethane gave more significant retardation of tetrabenzylzirconium (Fig. 2).

Phenothiazine retarded all the autoxidations, if not at 20° then at −74° (Figs. 1 and 2) with the exception of hexabenzylditungsten and hexakis(trimethylsilylmethyl)dimolybdenum; this reflects the ability of phenothiazine to function as a trap for free radicals and a peroxide decomposer [9]. Unlike hydrocarbon autoxidations, retardation rather than inhibition is observed with common autoxidants and organoboranes when very fast propagation reactions (3) are involved [9,10]. These retardations indicate that a free radical chain reaction of the type shown in eqns. (1) - (3) is operating and it would be surprising if it did not also apply to hexabenzylditungsten and hexakis(trimethylsilylmethyl)dimolybdenum.

Brown and Midland [13] and Grotewold et al. [14] were able to inhibit trialkylborane autoxidations with iodine, the iodine being able to compete with oxygen for the alkyl radicals in reaction (2). When this technique was applied to tetrabenzylzirconium the quantity of absorbed oxygen was reduced, the colour of the iodine was discharged and benzyl iodide was identified in the products. Although Lappert et al. [2b] have reported iodinolysis of tetrakis(trimethylsilylmethyl)titanium and -zirconium, we found no reaction, over the time period of our experiments, when iodine was added to tetrabenzylzirconium in the absence of oxygen.

Hydrolysis of products from tetrabenzylzirconium autoxidation gave, in addition to benzyl alcohol and benzyl hydroperoxide, a considerable amount of benzaldehyde. Although this could have been derived in part from hydrolysis of the peroxide, the yield of benzaldehyde was about twice the amount of organometallic peroxide originally present. This can be explained partly in terms of the known termination reaction:

$$2\,\mathrm{PhCH_2OO^{\cdot}} \rightarrow \mathrm{PhCHO} + \mathrm{O_2} + \mathrm{PhCH_2OH} \qquad (7)$$

The retardation shown by phenothiazine is a reflection of its ability to compete to a limited extent with the transition metal organometallic for peroxy radicals (eqn. 3) and a relative order for this reaction was constructed from a consideration of the degrees of retardation shown by phenothiazine at 20° or −74°, viz.: $[(CH_3)_3SiCH_2]_6Mo_2 \approx (PhCH_2)_6W_2 > (PhCH_2)_4Zr \approx [(CH_3)_3SiCH_2]_4Zr > [(CH_3)_3CCH_2]_6Mo_2 > [(CH_3)_3SiCH_2]_4Ti$.

We conclude that the dominant factor in the examples we have studied is the hindered approach of peroxy radicals to the vacant orbitals at the metal centre.

The autoxidation of tetrabenzylzirconium and the improved stability of the peroxybenzylzirconium cannot be explained in steric terms, and indeed the stability of the benzyl radical might be expected to facilitate the S_H2 reaction [10]; π interactions between the aromatic rings and the metal [15] may be the explanation here.

Experimental

Autoxidations were carried out in a glass cell (ca. 5 ml capacity) fitted with a magnetic stirrer and serum cap. The glass cell was connected to a Bell and Howell pressure transducer (response better than 1 mV for 18 mmHg). The signal was displayed on a potentiometer recorder having a sensitivity of 1 mV and a response better than one second for full-scale deflection. Oxidations were carried out under 1 atm of pure oxygen and the quantity of organometallic was arranged so that ca. 5×10^{-1} mol of oxygen was absorbed. Absence of oxygen diffusion control was checked by varying speed of stirring. Solutions of the organometallic (ca. 0.1 *M* in benzene, toluene or n-heptane) were injected using a gas tight syringe to give a final concentration of ca. 10 m*M*. After absorption had virtually ceased the apparatus was flushed with nitrogen and the contents analysed for peroxide by iodometric titration. n-Heptane was the preferred solvent for the autoxidations but preparative considerations sometimes required the use of the other solvents. It is considered that any solvent effects were small.

All manipulations were carried out under purified nitrogen or argon.

Preparation of organometallics

Tetrakis(trimethylsilylmethyl)-titanium(IV) and -zirconium(IV). These were prepared from the corresponding dialkylmagnesium and the metal tetrahalide according to the method of Lappert et al. [2b]. The ^{1}H NMR spectrum in heptane of $[(CH_3)_3SiCH_2]_4Ti$ showed singlets at τ 9.7 (CH_3) and 7.6 (CH_2) ppm.

Hexakis(trimethylsilylmethyl)dimolybdenum(III). Molybdenum trichloride (5.8 mmol) was added to the dialkylmagnesium compound (8.5 mmol) in n-heptane at −10°. The mixture was filtered under nitrogen and after removal of solvent the brown residue was sublimed at 110°/0.001 mmHg to give yellow crystals (m.p. 96 - 99°)^1. The ^{1}H NMR spectrum in benzene showed singlets at τ 9.6 (CH_3) and 7.8 (CH_2) ppm.

Hexaneopentyldimolybdenum(III). This was prepared from a benzene solution of neopentyllithium (0.38 mol) and molybdenum tetrachloride (0.13 mol) [16]. After filtration and transfer to petroleum ether solvent the brown solution was chromatographed on an alumina column (from which oxygen had been rigorously excluded) using equal volumes of petroleum ether and diethyl ether as eluting solvent. A yellow oil obtained after removal of solvent was shown by its ^{1}H NMR spectrum to be the required compound. [^{1}H NMR spectrum in benzene showed singlets at τ 7.75 (CH_2) and 8.65 (CH_3), and a complex multiplet (attributed to impurity) at 9.2 - 9.4 ppm.

Hexabenzylditungsten was prepared after the method of Wilkinson et al. [1].

Autoxidation of trimethylsilylmethyl compounds

Autoxidations were carried out in n-heptane solvent using the titanium, zirconium and molybdenum alkyls. Peroxides could not be detected in the solution at 20° although traces were detected at −74°. Hydrolysis gave a complex mixture of which trimethylsilylmethanol was the major product; trimethylsilanol was also identified [17]. With complex formation in mind pyridine (5 mmol) was added to a benzene solution of hexakis(trimethylsilylmethyl) dimolybdenum (0.1 mmol). There was no complex formation since there was no change in position of intensity of the ^{1}H NMR methylene resonance at τ 7.8 ppm. A similar absence of complex formation was found in the case of hexaneopentyldimolybdenum.

Autoxidation of tetrabenzylzirconium.

The organometallic (0.08 mmol) in toluene was autoxidised at −74° and peroxide (0.05 mmol) was found in the product. After hydrolysis, peroxide (0.01 mmol) was present; benzyl alcohol (0.1 mmol, 32%) benzaldehyde (0.03 mmol, 10%) and unknown components were determined by GLC on Carbowax at 140°. In a similar experiment the hydrolysed, peroxidic toluene solution was extracted with dilute sodium hydroxide, neutralised with dilute hydrochloric acid and the aqueous solution extracted with ether. A yellow peroxidic oil remained on removal of solvent. Thin layer chromatography on silica gel using benzene—methanol—acetic acid (10/1/1) indicated the presence of an organic peroxide [18]. This was benzyl hydroperoxide; ^{1}H NMR spectrum in carbon tetrachloride showed a broad singlet at τ 2.74 (aromatic), shoulder at 2.78 (OOH), and a singlet at 5.10 ($-CH_2$) ppm [19,20].

Autoxidation in the presence of bases.

To a toluene solution of tetrabenzylzirconium (0.025 mmol) was added pyridine in toluene in order to form the 1/1 complex [12]. There was no noticeable change in the rate or extent of autoxidation when the amount of pyridine added was varied over the range of 5 to 20 mmol.

Autoxidation in the presence of iodine

To a solution of iodine (8×10^{-6} mol) in toluene under oxygen was added tetrabenzylzirconium (2.5×10^{-5} mol) in toluene. The iodine colour was slowly discharged. The rate of oxygen absorption was not noticeably af-

TABLE 1
AUTOXIDATION OF ORGANO TRANSITION METAL COMPOUNDS AT 20°

Compound (mmol) (solvent)	Inhibitor[a] (mol %)	Effect[b]	O_2 uptake (mol × 10^{-5})	Peroxide (mol% per alkyl group)
$[(CH_3)_3SiCH_2]_4Ti$(9.5)	None		2.07	None
(*n*-heptane)	Pheno (11)	R.	2.00	None
	Top (12)		1.90	None
$[(CH_3)_3SiCH_2]_4Zr$(9.5)	None		2.11	None
(*n*-heptane)				
$[(CH_3)_3SiCH_2]_6Mo_2$(7.0)	None		3.00	None
(*n*-heptane)				
$[(CH_3)_3CCH_2]_6Mo$(6.5)	None		3.03	Trace
(benzene)	Pheno (12)	R	2.70	
	Top (12)	S.R.	3.05	
	TAN		2.70	
$(PhCH_2)_4Zr$ (12.0)	None		2.08	ca. 4
(toluene)	Pheno (9)		1.90	ca. 4
	Top (8)		2.00	ca. 4
	E 702 (4)		1.89	ca. 4
$(PhCH_2)_6W_2$ (4.1)	None		3.12	ca. 5
(*n*-heptane)	Pheno (12)		2.71	ca. 5
	E. 702(6)		3.29	ca. 5

[a] Top, Topanol (2,6-di-tert-butyl-4-methoxyphenol). Pheno, phenothiazine. E720, Ethyl 720 (bis(4-hydroxy-3-methyl-5-tert-butylphenyl)methane. E702, Ethyl 702 (bis(4-hydroxy-3,5-di-tert-butylphenyl) methane. TAN, 2,2,6,6,-tetramethyl-4-piperidone nitroxide.

[b] R, retardation, SR, slight retardation.

fected although there was a 15% reduction in the amount of oxygen absorbed. Benzyl iodide was identified by GLC. An identical experiment carried out under an atmosphere of nitrogen (10 min) did not result in any loss of iodine colour and benzyl iodide could not be detected by GLC.

Autoxidation of hexabenzylditungsten

The organometallic in n-heptane was oxidised at 20° and —74° (Tables 1 and 2). Hydrolysis of the products and examination by GLC showed the presence of products identical to those found in the case of tetrabenzylzirconium.

TABLE 2
AUTOXIDATION OF ORGANO TRANSITION METAL COMPOUNDS AT —74°C

Compound (mmol) (solvent)	Inhibitor[a] (mol %)	Effect[b]	O_2 uptake (mol × 10^{-5})	Peroxide (mol %) per alkyl group)
$[(CH_3)_3SiCH_2]_4Ti$(9.5)	None		2.21	None
(*n*-heptane)				
$[(CH_3)_3SiCH_2]_4Zr$(9.5)	None		2.21	Trace
(*n*-heptane)	Pheno (10)		1.85	
$[(CH_3)_3SiCH_2]_6Mo_2$(7.0)	None		3.43	ca. 3
(*n*-heptane)	Pheno (10)		3.36	
	E720 (8)		3.21	
$(PhCH_2)_4Zr$(8.2)	None		2.74	14.5
(toluene)	Pheno (12)	SR	2.58	11.0
	Top (12)	SR	2.67	12.0
	E720 (6)	SR	2.54	14.0
$(PhCH_2)_6W_2$ (2.4)	None		3.34	13.0
(*n*-heptane)	Pheno (12)		2.92	9.0
	Top (10)		3.13	13.0

[a, b] For footnotes see Table 1.

Autoxidation in the presence of inhibitors

Inhibitors dissolved in the appropriate solvent were added immediately before the organometallic solution was injected into the apparatus. In the case of galvinoxyl a magenta colour was immediately formed in the presence or absence of oxygen and there was no retardation of oxidation. Results are summarised in Tables 1 and 2.

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