Journal of Organometallic Chemistry, 141 (1977) 149—156

PHENOXYALUMINIUM COMPOUNDS

V *. HOMOLYTIC CLEAVAGE OF THE ALUMINIUM—OXYGEN BOND OF ORGANOALUMINIUM PHENOXIDES IN THE PRESENCE OF OXYGEN

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(Received June 30th, 1977)

Summary

Oxydation reactions of monomeric alkylaluminium diphenoxides were studied. It was stated that during the oxidation a homolytic cleavage of the aluminium—oxygen bond takes place with the formation of two free radicals stable at room temperature. On the basis of ESR spectra it was found that one of these is the 2,6-di-t-butyl-4-alkylphenoxy radical. The second, more stable radical contains aluminium and the 2,6-di-t-butyl-4-alkylphenoxy group.

Introduction

In the reactions of organoaluminium compounds with oxygen, organoaluminium alkoxides are formed. It has been suggested that the initial step of the oxidation reaction is an insertion of the molecular oxygen into the aluminium—carbon bond with the formation of peroxides [2,3,4], which readily decompose to mono- and dialkyloxides. This reaction proceeds both with trialkylaluminium [2,3,4] and alkylaluminium halides [5,6].

In our previous paper [1] it was stated that monomeric $RAl(DBMP)_2$ ** rapidly reacts with oxygen forming stable free radicals. Further investigations of the oxidation reactions of monomeric alkylaluminium diphenoxides are the subject of the present work.

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* For part IV see ref. 1.

** DBMP = 2,6-di-t-butyl-4-methylphenoxy group.

Results and discussion

A yellow benzene solution of slightly oxidized MeAl(DBMP)$_2$ (the non-oxidised compound is colourless) exhibits a stable multiline signal in its ESR spectrum at room temperature (Fig. 1a). There is no difference between the number of lines in the spectra of oxidized CD_3Al(DBMP)$_2$ (Fig. 1b) and CH_3Al(DBMP)$_2$, but only small differences in the intensities of some lines.

UV irradiation causes homolytic cleavage of the C—Al bond [7] of $(RAlCl_2)_2$. Free radicals were also stated to be present in complexes of alkylaluminium dihalides with a base as e.g. CH_2=CH—C≡N, even without UV irradiation [8]. Formation of free radicals is not, however, observed when RAl(DBMP)$_2$ or its 1 : 1 complex with benzonitrile are irradiated. On the other hand addition of air to a solution of the complex RAl(DBMP)$_2$ · PhCN causes the appearance of ESR signals, although the reaction is slower in comparison with that for pure RAl(DBMP)$_2$.

During oxidation of RAl(DBMP)$_2$ (molar ratio of organoaluminium compounds to oxygen = 1 : 1) gaseous products are evolved. Oxidation of MeAl(DBMP)$_2$ gives methane and isobutylene in a molar ratio of 2 : 1, while for i-BuAl(DBMP)$_2$ only isobutylene and isobutane are evolved. This indicates that saturated hydrocarbons are formed from the alkyl group bonded to aluminium. Neither other hydrocarbons nor hydrogen can be found in the gaseous products. These facts allow us to exclude the formation of a free radical $R^{\cdot}$, which has been suggested as a reagent in propagation steps of the oxidation reaction of organoaluminium compounds [4]. One can expect the saturated hydrocarbon to be formed after heterolytic splitting of the carbon—aluminium bond, because its formation in homolytic splitting should lead to a mixture of hydrocarbons.

Methanol is not observed after hydrolysis. This suggests that the formation of H_3C—O—Al bonds does not take place during the oxidation of MeAl(DBMP)$_2$.

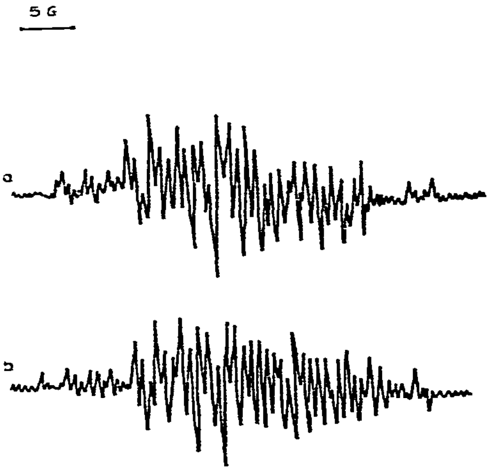


Fig. 1. ESR spectra of free radicals in the system: (a) CH_3Al(DBMP)$_2$—oxygen; (b) CD_3Al(DBMP)$_2$—oxygen.

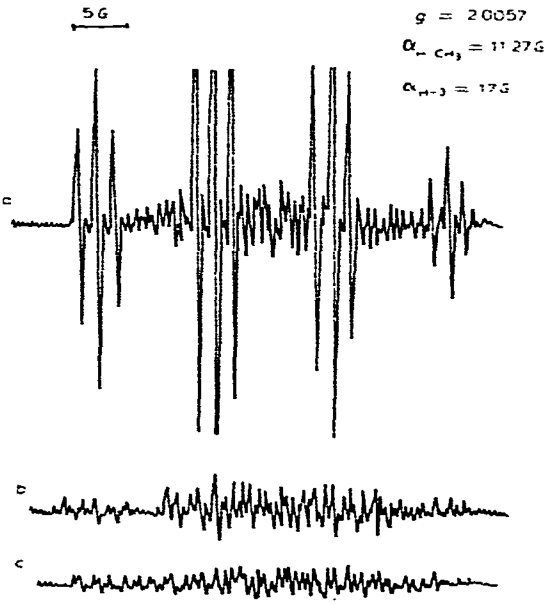
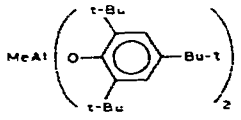


Fig. 2. ESR spectra of free radicals in the system $CH_3Al(DBMP)_2$—oxygen, recorded: (a) 2 minutes; (b) 10 minutes; (c) 30 minutes after oxidation.

To confirm the pathway of the oxidation reaction of $MeAl(DBMP)_2$ detailed ESR studies were carried out. In the ESR spectrum run immediately after the oxidation of $MeAl(DBMP)_2$, a quartet of triplets superimposed on another multiline signal is found (Fig. 2a). The *g* factor equals 2.0057 and the splitting constants of 11.27 *G* and 1.7 *G* are nearly the same as those described for the 2,6-di-t-butyl-4-methylphenoxy radical [9,10]. At room temperature the signal of the phenoxy radical disappears in two minutes, while the second radical is more stable (Fig. 2).

To prove the structure of the more stable radical analogous methylaluminium diphenoxides with t-butyl groups in the *ortho* positions were oxidized. In the ESR spectrum run immediately after oxidation of 

(green solution) a very strong triplet is observed (Fig. 3a). The splitting constant of 1.8 *G* is the same as that for the 2,4,6-tri-t-butyl-phenoxy radical [10,11]. The triplet is superimposed on a multiline weaker signal. After 10 min the signal of the phenoxy radical disappears and the spectrum exhibits 8 lines (Fig. 3b). The reduction of the number of lines of the radical obtained from oxidized $MeAl(TBP)_2$ * (compared to oxidized $MeAl(DBMP)_2$) proves the presence of phenoxyl groups in the more stable radicals.

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* TBP = 2,4,6-tri-t-butyl-phenoxy group.

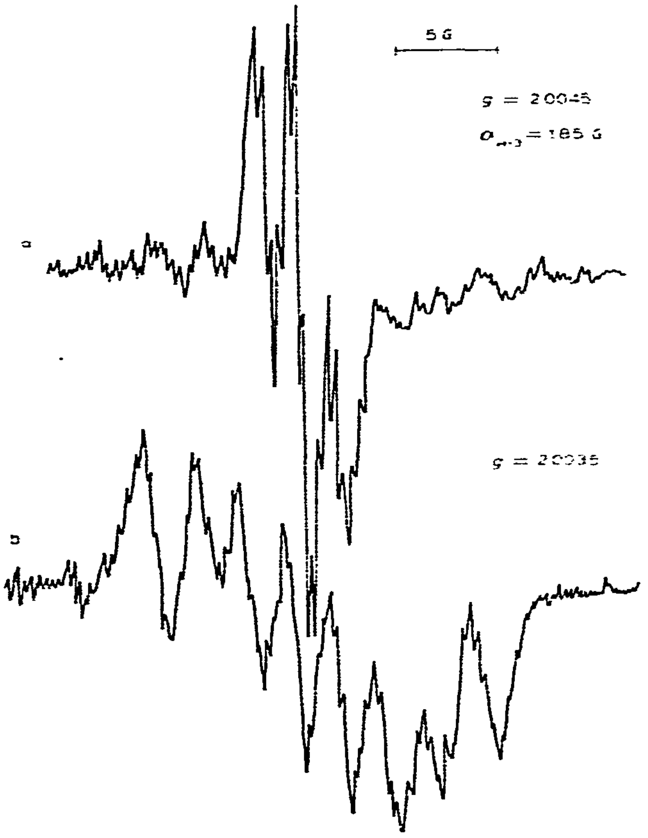
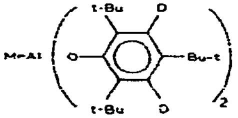


Fig. 3. ESR spectra of free radicals in the system $CH_3Al(TBP)_2$—oxygen, recorded: (a) 3 minutes; (b) 10 minutes after oxidation (different amplitudes).

To eliminate the splitting of the ESR signals caused by *meta* protons of phenoxy groups, *meta* deuterated 2,4,6-tri-t-butyl-3,5-dideuterophenol was synthesized. In the ESR spectrum of oxidized  signals of two free radicals are observed simultaneously (Fig. 4a). After the disappearance of the 2,4,6-tri-t-butyl-3,5-dideuterophenoxy radical singlet six slightly split equidistant lines of nearly equal intensities are observed (Fig. 4c). This is good evidence for the presence of the aluminium atom (nuclear spin number 5/2) in the more stable radical.

To show the presence of an alkyl group bonded to aluminium in the aluminium-bearing radical, phenylaluminium bis(2,4,6-tri-t-butyl-3,5-dideutero) phenoxide was oxidized. Müller [12] while investigating the reaction of triphenylaluminium with the 2,4,6-tri-t-butylphenoxy radical in the molar ratio 1 : 2, stated

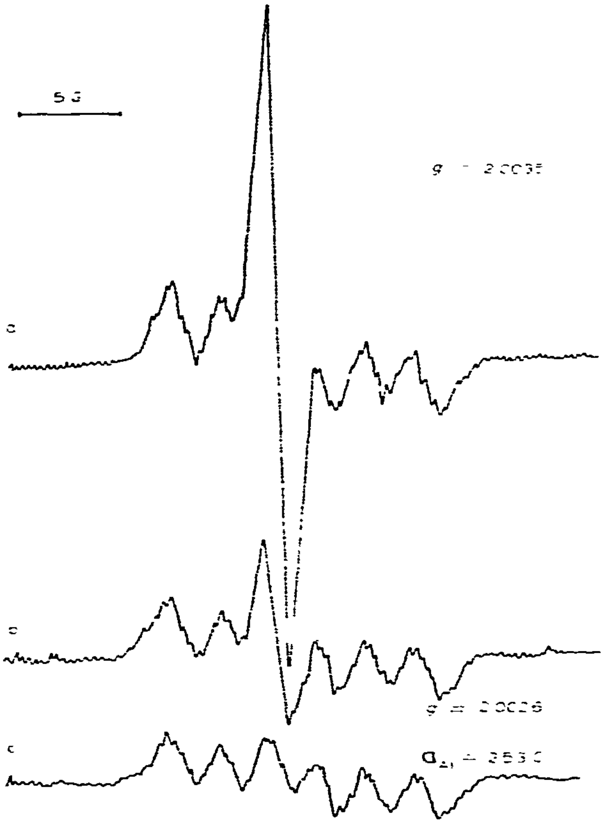
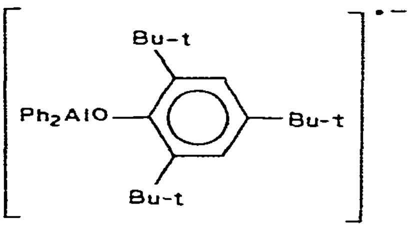


Fig. 4. ESR spectra of free radicals in the system *meta* deuterated $CH_3Al(TBP)_2$—oxygen recorded: (a) 3 minutes; (b) 10 minutes; (c) 15 minutes after oxidation.

the formation of a free radical with proposed structure (I). The ESR signal of the radical (I) was strongly split by *ortho* and *para* protons of the phenyl groups bonded to aluminium.



(I)

In the ESR spectrum of oxidized $PhAl(TBP\text{-}d_2)_2$ * six lines of the aluminium-bearing radical are observed. Each of the lines is slightly split, but an apparent

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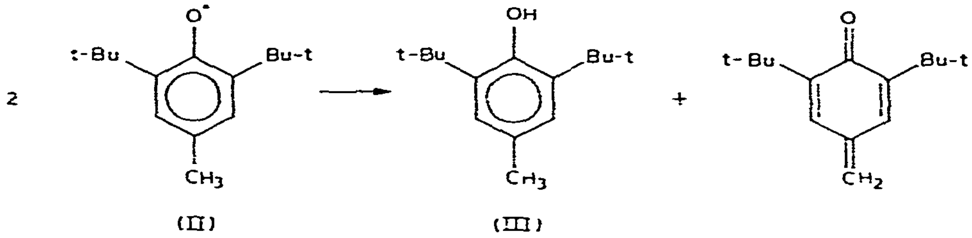
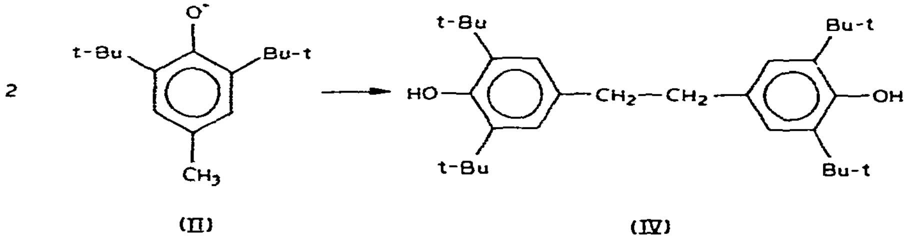
* $TBP\text{-}d_2$ = 2,4,6-tri-t-butyl-3,5-dideuterophenoxy group.

difference in the spectrum compared with that of MeAl(TBP-d_2)$_2$ is not observed. This fact does not exclude the presence of a phenyl group bonded to aluminium. It is probable that during oxidation of RAl(DBMP)$_2$ a new aluminium—oxygen bond is formed. This new strong electronegative substituent is able to decrease the electron density on the alkyl or phenyl group. As a result the splitting caused by the R—Al group protons is not observed.

In the IR spectrum of slightly oxidized MeAl(DBMP)$_2$ a band at 3630 cm^{-1} was observed. The band position corresponds closely to ν(OH) in the *ortho* di-t-butyl substituted phenol. The formation of the phenol can be a result of stabilisation of the 2,6-di-t-butyl-4-methyl-phenoxy radical (II), which was observed in the ESR spectrum. It has been stated that the stabilisation reaction proceeds according to the eqn. 1 [9] or 2 [13].



(1)



(2)

Simultaneously with the appearence of the band at 3630 cm^{-1}, methane is evolved. We found that the RAl(DBMP)$_2$ does not react with the DBMPH *, because of steric hindrance and tried to explain the formation of methane (or isobutane) in the reaction of the phenol III or IV with the Al—R bond of the aluminium-bearing radical. The oxidation of the *para* methyl deuterated MeAl(DBMP)$_2$ leads to the *para* methyl deuterated phenoxy radical II which, while stabilizing, forms phenols III or IV with the deuteroxy group. It was stated however on the basis of mass spectroscopy that the oxidation of *para* methyl deuterated MeAl(DBMP)$_2$ leads to undeuterated CH_4 instead of CH_3D. Thus the result does not confirm the supposition and the mechanism of the formation of the saturated hydrocarbon is still an open question.

On the basis of the above investigations we concluded that the oxidation reaction of monomeric alkylaluminium diphenoxides proceeds according to eqn 3.

We did not manage to identify all substituents of aluminium in the radical V although there is no doubt that the phenoxy group is one of them.

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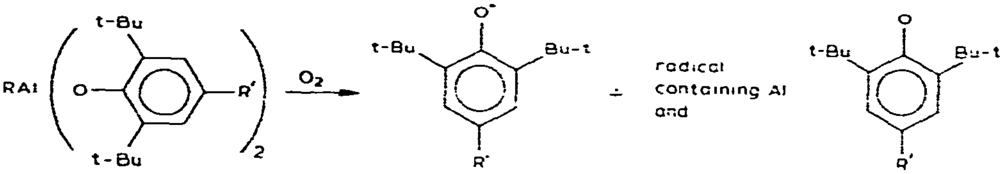
* DBMPH = 2,6-di-t-butyl-4-methylphenol.



(3)

(I)

Experimental

MeAl(DBMP)$_2$ and MeAl(TBP)$_2$ were prepared at room temperature in the reactions of benzene (or cyclopentane) solutions of (Me$_3$Al)$_2$ and the corresponding phenol in molar ratios from 1 : 2 to 1 : 4 respectively. If the molar ratio of the reactants was higher than 1 : 4, free trimethylaluminium was observed in the reaction mixture. After evaporation of the solvent and trimethylaluminium, white solids were obtained. The compounds were crystallized from cyclohexane or n-heptane. PhAl(TBP-d_2) was obtained in the reaction of a benzene solution of Ph$_3$Al with the corresponding phenol in molar ratio 1 : 2.

NMR spectra were recorded on a JEOL 100 MHz spectrometer using 10% solutions in benzene. PMR spectra (upfield to benzene): MeAl(DBMP)$_2$: 4.76 (s, 6H); 5.45 (s, 36H); 7.3 (s, 3H). MeAl(TBP)$_2$: 5.57 (s, 36H); 5.78 (s, 18H); 7.54 (s, 3H) ppm.

Deuterated Me$_3$Al was obtained according to Grosse and Mavity [15] from CD$_3$I (19 g) and aluminium powder (2.4 g). The method was modified by addition of aluminium magnesium alloy (3 g). The product of distillation (3.5% of iodine) was purified by heating with sodium-potassium alloy and redistillation. The product obtained (b.p. 125.5—126°C; 760 mmHg) was iodine-free. Triphenylaluminium was prepared according to Neely [16] in the reaction of Ph$_2$Hg with aluminium powder. 2,4,5-tri-t-butyl-3,5-dideuterophenol was prepared according to Rieker [14] from deuterated benzene-d_6. *p*-Methyl deuterated 2,6-di-t-butyl-4-methylphenol was obtained according to Jerszov [17]. The compound was identified by elemental analysis (C, found: 79.11; calcd.: 80.71%) and mass spectroscopy (M^+ = 223). Mass spectra were recorded on a JEOL IMS 01SG spectrometer.

ESR spectra were recorded on a JEOL ME-3X spectrometer. 2% Benzene or toluene solutions of the compounds were placed under dry nitrogen in quartz tubes closed by Rotaflo stopcocks. Just before each measurement air was introduced to the tube by opening the stopcock for a moment.

TABLE 1

ANALYSIS DATA

Compound	Al (%)	
	Calcd.	Found
MeAl(DBMP)$_2$	5.63	5.4
MeAL(TBP)$_2$	4.79	4.6

Acknowledgement

The authors wish to thank Dr. A. Chodkowska from the Institute of Physical Chemistry PAN Warsaw and Doc Dr. S. Benbenek from the Technical University of Warsaw for helpful discussions on ESR spectra, and the Institute of Low Temperature and Structural Research in Wroclaw for financial support of part of this work.

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