

**Zeitschrift:** Archives des sciences [1948-1980]  
**Herausgeber:** Société de Physique et d'Histoire Naturelle de Genève  
**Band:** 14 (1961)  
**Heft:** 10: Colloque Ampère

**Artikel:** Electron and proton resonance measurements on the systems  
 $\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_2 - (\text{Al}(\text{CH}_3)_2\text{Cl})_2$  and  $\text{Ti}(\text{C}_5\text{H}_5)_2\text{CH}_3\text{Cl} - (\text{Al}(\text{CH}_3)\text{Cl}_2)_2$  at  
room temperature  
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**DOI:** <https://doi.org/10.5169/seals-739612>

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**Electron and Proton Resonance Measurements  
on the Systems  
 $Ti(C_5H_5)_2Cl_2 - (Al(CH_3)_2Cl)_2$  and  
 $Ti(C_5H_5)_2CH_3Cl - (Al(CH_3)Cl_2)_2$  at room Temperature**

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*Summary.*

Nuclear spin resonance measurements at room temperature have shown that in the  $Ti(C_5H_5)_2Cl_2 - (Al(CH_3)_2Cl)_2$  system (I) methyl migrates from the aluminium to the titanium atom, with the result that the system assumes a close resemblance to the system  $Ti(C_5H_5)_2CH_3Cl - (Al(CH_3)Cl_2)_2$  system (II), provided the  $Al/Ti$  ratio in the two systems is unity. This close resemblance is observed also in electron spin resonance measurements; as regards the concentration of unpaired electrons as function of time, the line width, the shape and also the  $g$ -value of the absorption curve the two systems are practically identical.

It has been found that in the range where the concentration of unpaired electrons is below 10 mmol/l, the *esr. spectra* may be considered as being built up of three basic spectra. At concentrations above 10 mmol/l exchange narrowing occurs. For system I it has been shown that there is always one unpaired electron present per trivalent  $Ti$ -atom. The  $g$ -value of the systems investigated suggests that the unpaired electron occurs on a complex in which one  $Cl$ -atom is completely bonded to a  $Ti$ -atom.

## INTRODUCTION

Fairly recently several investigators started to study  $Ti(C_5H_5)_2Cl_2$ -aluminium alkyl systems by means of electron spin resonance [1, 2, 3]. For the results we refer to the relative literature references. We examined i.a. the systems  $Ti(C_5H_5)_2Cl_2 - (Al(CH_3)_2Cl)_2$  (I) and  $Ti(C_5H_5)_2CH_3Cl - (Al(CH_3)Cl_2)_2$  (II) by means of electron spin resonance. We also carried out proton resonance measurements on the systems; as far as we know such measurements have not yet been described in the literature.

## PROTON SPIN RESONANCE

The proton resonance spectrum of  $Ti(C_5H_5)_2CH_3Cl$  dissolved in benzene (concentration 1 M) was recorded at room temperature. The protons of the  $C_5H_5$ -groups yield a resonance line at  $\tau = 4.0$  ppm \*, those of the  $CH_3$ -group at  $\tau = 9.0$  ppm \*; the distance between the resonance lines therefore was 5.0 ppm. The  $CH_3$ -groups of  $(Al(CH_3)_2Cl)_2$  and  $(Al(CH_3)Cl)_2$  dissolved in benzene (concentration 1 M) yield resonance lines located at  $\tau = 10.1$  and  $\tau = 10.2$  ppm respectively \*. This is in good agreement with earlier measurements on solutions of these substances in toluene where the resonance peaks at all concentrations proved to be at  $\tau = 10.1$  and  $\tau = 10.3$  ppm respectively [4] \*\*.

When  $Ti(C_5H_5)_2Cl_2$  and  $(Al(CH_3)_2Cl)_2$  dissolved in benzene were brought together in such amounts that the concentration of both the  $Ti$ - and the  $Al$ -monomer was about 1 M, the proton resonance spectrum did not show the two peaks of the separate components, but three peaks, one of which could be clearly recognized as the  $C_5H_5$ -peak, another one as the  $AlCH_3$ - or  $Al(CH_3)_2$ -peak (our measuring technique at the time of these measurements was not accurate enough to permit a justified distinction to be made between the two), while the third peak, being located at  $\tau = 9.0$  ppm, was considered as being due to a  $CH_3$ -group bonded to  $Ti$ -atom (see above). This migration of the methyl groups from the  $Al$ -atom to the  $Ti$ -atom in the  $Ti(C_5H_5)_2Cl - (Al(CH_3)_2Cl)_2$  system was also confirmed by U.V. measurements carried out in our laboratory [5].

From the area of the surface under the peaks it appears that, at an  $Al/Ti$  ratio = 1, the number of methyl groups bonded to the  $Ti$ - and the  $Al$ -atoms are approximately equal. In consequence the spectrum is virtually identical to that of a  $Ti(C_5H_5)_2CH_3Cl - (AlCH_3Cl)_2$  mixture with an  $Al/Ti$  ratio = 1. The length of time within which the migration is completed, is shorter than the time elapsing between the moment at which the components were brought together and the moment of the proton resonance measurement (appr. 5 minutes) since the proton resonance spectra did not show any variation with time.

\* The location of the lines was measured with reference to benzene. The benzene peak occurs at  $\tau = 2.7$  ppm.

\*\* In lit. 4 the location of the peak is given with reference to cyclopentane. It occurs at  $\tau = 1.6$  ppm.

In view of the distinct separation between the  $Al-CH_3$ - and the  $Ti-CH_3$ -peaks it must be concluded that the frequency of an exchange between these methyl groups must be less than the difference in frequency between the two lines, i.e. less than 40 c/s [6].

We also succeeded in observing migration of methyl groups from  $Al$  to  $Ti$  in mixtures of  $Ti(C_5H_5)_2Cl_2$  with  $(AlCH_3Cl_2)_2$  and  $(Al(CH_3)_3)_2$ . It should be mentioned here that migration of the  $CH_3$ -group in the system  $TiCl_4 + (Al(CH_3)_2Cl)_2$  was already demonstrated in our laboratory some years ago by means of infra-red measurements.

#### ELECTRON SPIN RESONANCE

In view of what has been said above it may be expected that the systems I and II will show an identical behaviour at an  $Al/Ti$  ratio = 1. This assumption is supported by the fact that the concentration of unpaired electrons  $[S]$  as a function of time, the widths of the lines as a function of  $[S]$  and the shapes of the lines were practically identical for the two systems (see figure 1). (It should be pointed out here that the concentrations of the  $Ti$ -components differed slightly, viz. 0.8 M in system I and 0.7 M in system II). The  $g$ -values are also equal, viz.  $g = 1.9759$ .

##### a) *Concentration of unpaired electrons as function of time.*

The number of unpaired electrons at room temperature was determined in the way indicated by one of the authors in a previous article [7]. It has been assumed that we are concerned with unpaired electrons with spin  $\frac{1}{2}$ .

From the curve shown in figure 1a it can be seen that, after an initial retardation, the rate at which the particles are formed is accelerated; this suggests that the particles carrying the unpaired electrons are produced via more or less complicated mechanisms.

The end values of the concentration  $[S]$  of unpaired electrons in both systems approximately equals the concentration of the amount of  $Ti(C_5H_5)Cl_2$  present at the start even if the  $Al/Ti$  ratio differs from unity. In system I we moreover determined the number of trivalent  $Ti$ -atoms as function of time by means of titration. This number proved to be approximately equal to the number of unpaired electrons.

From these facts it seems likely that the unpaired electron is bound to particles containing a trivalent  $Ti$ -atom.

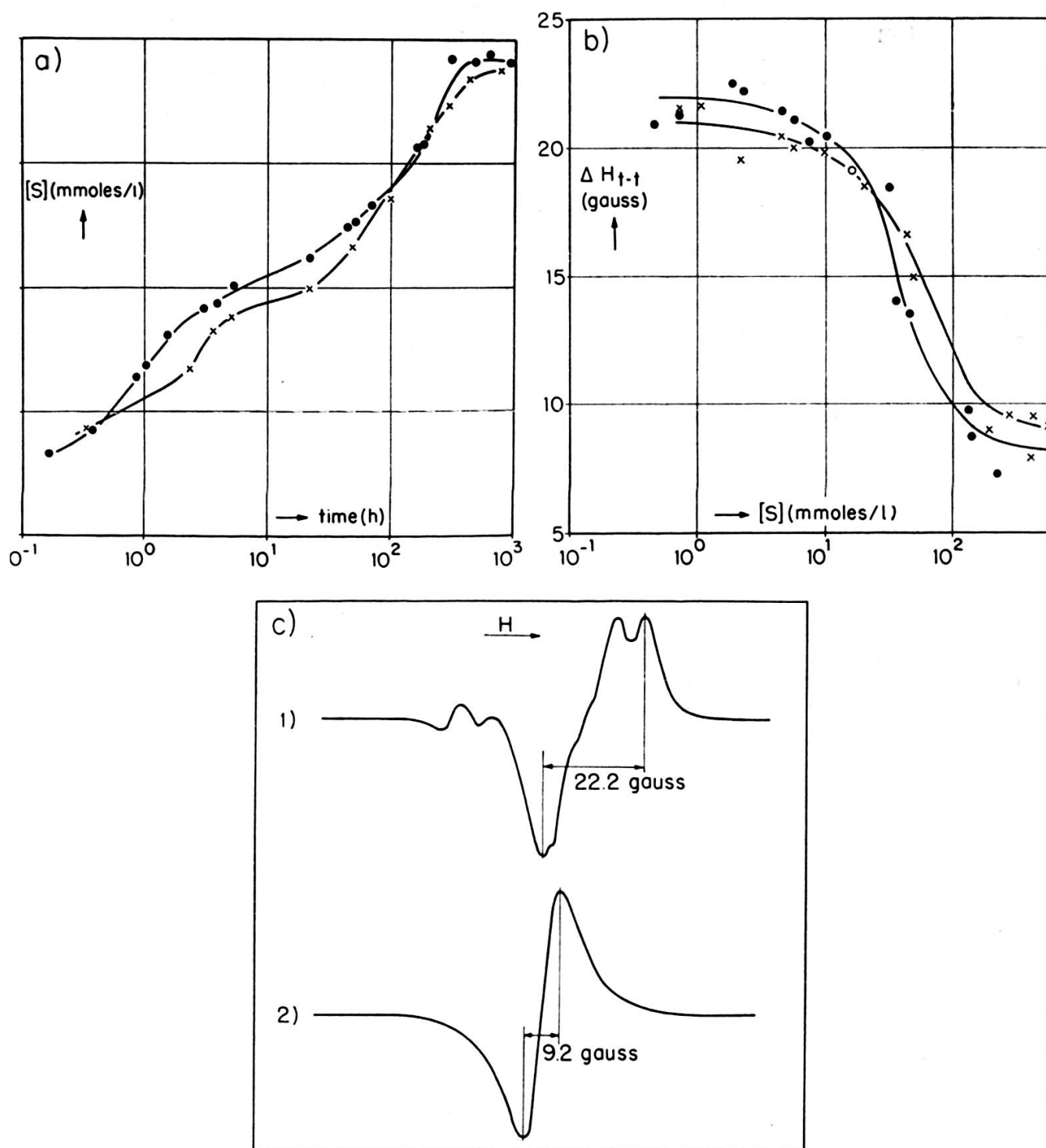


Fig. 1.

- a) Concentration of unpaired electrons  $[S]$  vs. time at room temperature  
 ● system I; × system II.
- b)  $\Delta H_{H}$  (line width between the outer peaks of the derivative of the absorption curve) vs.  $[S]$ .  
 ● system I; × system II.
- c) Two examples of *esr spectra* for the system (I) and (II).  
 1)  $[S] < 10$  mmoles/l.  
 2)  $[S] > 100$  mmoles/l.

b) *Width and shape of the lines as function of [S].*

The systems examined were found to change with time, both as regards the width and the shape of the lines (see figures 1b and 1c). The fact that Maki and Randall [2] did not observe a variation with time in their spectra, except in that of the  $(Al(C_2H_5)Cl_2)_2$  system must probably be ascribed to the much lower concentrations of their solutions. At

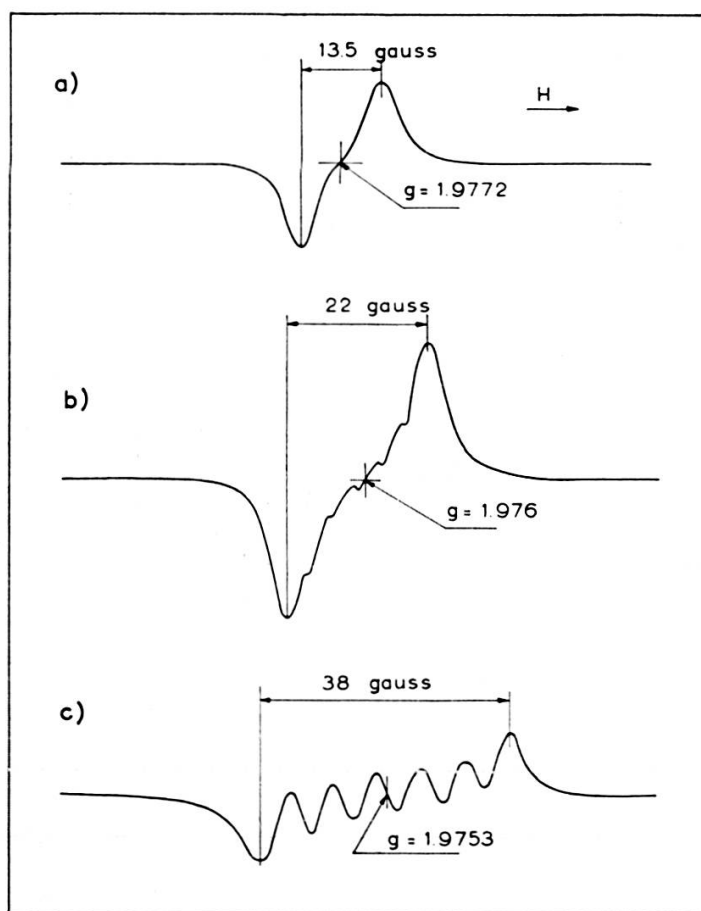


Fig. 2.  
The three basic spectra

$S < \approx 10$  mmol/l the spectra possess a more or less complicated character, at  $S > \approx 100$  mmol/l a single absorption peak is observed while in the intermediate range the two types of spectra merge gradually into one another.

The narrowing of the peaks is due to exchange-narrowing, because upon dilution the narrowed peaks are seen to broaden out again. Analysis

of the spectra has revealed that these may be visualized as being built up of three basic spectra (see figure 2). The basic spectrum (a) is noticed in the  $Ti(C_5H_5)_2Cl_2 - (Al(CH_3)_3)_2$  system when  $S < 10$  mmol/l. As regards shape, line width and  $g$ -value, it shows a fairly close similarity with that determined on this system at very low concentrations by Maki and Randall [2]. We ascribe the shape of the line to an unresolved hyperfine structure produced perhaps by interaction between the unpaired electron with protons of cyclopentadienyl groups and with an  $Al$ -nucleus of a complex.

The basic spectrum (b) makes the principal contribution to the spectra of the systems (I) and (II), as was also observed in other systems measured by us e.g. in  $Ti(C_5H_5)_2Cl_2 - (AlCH_3Cl_2)_2$  [5]. The spectrum is allied to that which Maki and Randall [2] recorded for their  $AlEt_2Cl$  system. We agree with these authors that the six little resolved lines are due to interaction between the unpaired electron and an  $Al$ -nucleus, although this does not mean that we wish to exclude interaction with protons of the cyclopentadienyl groups of the complex particle carrying an unpaired electron as another possible cause.

The basic spectrum (c) was found in the system  $Ti(C_5H_5)_2CH_3Cl - (AlCl_3)_2$  containing a large excess of  $(AlCl_3)_2$ . It shows a close relation with the final stage of the  $AlEtCl_2$  spectrum found by Maki and Randall [2]. Its interpretation is equal to that of the basic spectrum (b), with the difference, however, that the interaction with the  $Al$ -nucleus is stronger.

#### c) $g$ -value.

The  $g$ -values of the systems I and II and of the systems relating to the basic spectra of figure 2 lie in the neighbourhood of 1.97-1.98. In view of the results of other measurements [5] we believe that a  $g$ -value of 1.97 suggests that the unpaired electron occurs on a complex in which either only one  $Cl$ -atom is completely bonded to the  $Ti$ -atom or two  $Cl$ -atoms are bonded to the  $Ti$ -atom in a bridge structure. An increase of the number of completely bonded  $Cl$ -atoms causes a decrease of the  $g$ -value.

The authors wish to thank Mr. C. H. Vrinssen for his assistance in preparing the compounds.

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