

details of the analysis of the absorption spectra of ferrocene and other sandwich complexes as well as a discussion of the relationship of the results to the bonding in these compounds will be published in the near future.

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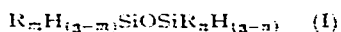
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The catalytic alkaline cleavage of partially substituted methylsiloxanes

Several cleavage reactions of partially substituted organosiloxanes (I) are known¹⁻³. All are characterised by strict stoichiometry between the reactants.



R = lower aliphatic or aromatic hydrocarbon radicals, identical or different

m, n = 1, 2 or 3, identical or different

We have now observed alkali-catalysed cleavage with hydrogen migration between silicon atoms of some siloxanes of type (I) with R = Me. The reaction produces silanes with increased H/Si ratio and siloxanes with increased O/Si ratio. The reactions were carried out under dry argon or nitrogen in dry ether or tetrahydrofuran containing 5% starting material and 1-100 parts per million of sodium. Examples of starting materials and products are listed in Table 1.

All products were identified by infrared spectroscopy⁴, supplemented by gas-liquid chromatography for the gaseous silane mixtures. Nuclear magnetic resonance spectroscopy was used to check the purity of the starting materials. Sodium was determined by flame photometry in the residue after evaporation of 500 ml solvent containing concentrated hydrochloric acid.

Tetrahydrofuran dissolves up to 0.5 parts per million of sodium out of glass, enough to catalyse the cleavage reactions. No reaction was found in quartz apparatus with solvents containing less than 0.01 part per million of sodium.

The same cleavage also occurs in hydrocarbons above 100° in the presence of sodium metal if the solution contains about 50 parts per million water or lower alcohol, but there is no reaction if this quantity is less than 10 parts per million.

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TABLE 1

CATALYTIC SODIUM CLEAVAGE OF METHYL-HYDRO-SILOXANES IN THF

R = CH₃.

Starting materials	Products		Reaction temperature	Approx. time (hours) for 50% conversion
	Silanes	Siloxanes		
HR ₂ SiOSiR ₃	H ₂ R ₂ Si HR ₃ Si	R ₃ SiO(SiR ₂ O) _n SiR ₃ n = 1 or 2	60°	1
(HR ₂ Si) ₂ O	H ₂ R ₂ Si	(R ₂ SiO) ₄	60°	1
(R ₂ SiO) ₂ SiHR	H ₃ RSi	(R ₃ SiO) ₃ SiR	60°	1
(R ₂ HSiO) ₂ SiHR	H ₂ R ₂ Si	[(R ₂ SiO) ₂ RSi] ₂ O (RSiO _{1.5}) _x	-10°	0.1
	HR ₃ Si			
	H ₃ RSi			
(RHSiO) ₄	H ₂ R ₂ Si H ₃ RSi	(RSiO _{1.5}) _x	-10°	0.1

The reaction described here differs from previously reported cleavage reactions in that only catalytic amounts of alkali are used, and thus silanols or silanolates are absent from the products.

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Innere Elektronenanregungen von Tricyclopentadienyli-Komplexen des Ytterbiums

Von den zahlreichen in letzter Zeit beschriebenen Lanthaniden-cyclopentadienyl-Komplexen¹ beanspruchen die Verbindungen des verhältnismässig einfachen Chromophors Yb(III) mit der Elektronenkonfiguration [Xe]4f¹³ besonderes Interesse. Wir berichten hier über die Absorptionsspektren von Lösungen der Verbindungen des Typs Cp₃YbX (Cp = π-C₅H₅; X = basischer Neutralligand) bei Raumtemperatur im Bereich von 9.00 bis 19.00 kK.

Sämtliche Spektren (vgl. Tabelle), einschliesslich dem des Grundkörpers Cp₃Yb, zerfallen offensichtlich stets in vier engere Bandengruppen I-IV. Die Absorptionen der Gruppen I-III ordnen wir auf Grund ihrer Frequenzen², Intensitäten und durchschnittlichen Halbwertsbreiten (Δν_{1/2} ≈ 100 K) f-f-Übergängen innerhalb der Konfiguration 4f¹³ zu. Im hier betrachteten Frequenzbereich sollten die Übergänge von den niedrigsten Stark-Komponenten des Terms ²F_{7/2} nach den drei Kramers-Dubletts liegen, die durch Ligandenfeld(LF)-Aufspaltung aus dem Term ²F_{5/2} entstehen. Zugleich dürften auch einige Schwingungsanregungen auftreten. Die jeweils intensivsten Banden der drei ersten Gruppen (I,2, II,3 und III,1) gehören wahrscheinlich zu den

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