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The Measurement of the Equilibrium Constant for the Formation of a Complex between Olefins and Group IVA Metal Alkyls

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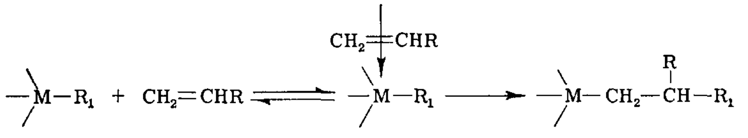
A glc method has been used to measure the equilibrium constant for the formation of a complex between olefins and dienes and zirconium and hafnium tetrakis(trimethylsilylmethyl). The equilibrium constant is very small for all olefins and dienes examined including some polymerization catalyst poisons.

INTRODUCTION

The formation of an olefin–transition metal complex has frequently been proposed as an intermediate in the polymerization of olefins by Ziegler catalysts (*1*) and transition metal alkyls (*2*). The process of initiation and chain growth may be represented by



$$>M-R_1 + CH_2{=}CHR \rightleftharpoons \begin{array}{c} CH_2{=}CHR \\ \downarrow \\ >M-R_1 \end{array} \longrightarrow >M-CH_2-\overset{R}{\overset{|}{C}}H-R_1 \qquad (1)$$

where R and R_1 are alkyl groups and M is a transition metal.

There is no direct experimental evidence for the formation of an olefin complex with the metal in polymerization catalysts, although such complexes are well known for metals at the right of the transition series. These complexes involve the donation of electrons from olefin and back donation of the transition metal *d*-electrons to the olefin (*3*), but for the recently reported complexes of olefins with aluminum alkyls (*4*) no such back donation can occur and the interaction must simply be that associated with Lewis acid–base chemistry. Many polymerization catalysts, e.g., Zr, Ti alkyls have no *d*-electrons and in any such complex the olefin must be behaving as a Lewis base. Complexes of pyridine with zirconium and hafnium benzyls have been reported (*5*). Zirconium and hafnium alkyls are weak homogeneous polymerization catalysts (*2*).

The equilibrium constants for the formation of olefin complexes of silver nitrate (*6–8*), rhodium (*9*) and palladium compounds (*10*) have been determined by glc. This method is particularly suited to air sensitive compounds and consequently has been used in this work.

METHODS

Synthesis of Tetrabenzyl Derivatives of Zirconium and Hafnium and the Tetrakis(trimethylsilylmethyl) Derivatives of Zirconium, Hafnium and Lead

Tetrabenzyl zirconium and tetrabenzyl hafnium were prepared by methods similar to those in the literature (*5*, *11*). Analytical and nmr data are in agreement with those previously published.

Tetrakis(trimethylsilylmethyl) derivatives of zirconium and hafnium were prepared by the method of Collier *et al.* (*12*). Analytical and nmr data are in agreement with those previously reported.

Lead dichloride was dehydrated by refluxing with thionyl chloride and freed from excess thionyl chloride by pumping at 70°C. Tetrakis(trimethylsilylmethyl) lead was prepared by the method of Williams (*13*). The colorless distillate gave colorless crystals, mp 25°C.

Preparation of Column Packings

Squalane (BDH) was extracted with dilute sodium hydroxide solution to remove antioxidant and thoroughly washed with water. A 20% solution of wet squalane in pentane was dried over 5A molecular sieve for 3 days, degassed with nitrogen and the pentane was removed under vacuum.

Diatomite CQ (80–100 μm, 1–1.4 $m^2 g^{-1}$, J. J. Chromatography) was dried at 400°C for 2 hr in a stream of dry nitrogen.

Solutions of known concentration of zirconium and hafnium benzyls in squalane were added to dried diatomite to give 20% squalane on diatomite. Even distribution of the squalane was ensured by addition of dry pentane which was subsequently removed by evacuation.

Tetrakis(trimethylsilylmethyl) compounds are liquids at room temperature and were used undiluted with squalane. Pentane solutions of these compounds were added to dried diatomite such that on removal of the pentane there was 0.158 mmole of metal alkyl/g of packing.

Nature of Metal Alkyl Species on Column Packing

Zirconium and hafnium alkyls react with the surface hydroxyls of silica and alumina and the resulting polymerization catalysts show increased activity over the parents (*2*). In order to ensure that the values measured are those of the metal tetraalkyl it must be shown that reaction with surface hydroxyl does not occur to a significant extent. This was done by rehydrating the diatomite with tritiated water, drying again and exposing to zirconium tetrabenzyl in toluene. Any toluene produced by the reaction with the surface contains a ^3H label which was counted by liquid scintillation counting.

$$\text{Si–O–T} + \text{Zr}(\text{CH}_2\text{–Ph})_4 \rightarrow \text{Si–O–Zr}(\text{CH}_2\text{Ph})_3 + \text{TCH}_2\text{Ph}. \quad (2)$$

One gram of dried diatomite was treated with 36 μl of tritiated water (5 mCi/ml) in 10 ml tetrahydrofuran (THF) for 1 hr. The THF was removed by evacuation and the diatomite was dried. The diatomite was slurried with 10 ml toluene for 30 min and 1 ml of the supernatant liquid was taken for counting. Zirconium benzyl (0.157 mmole) in 1 ml toluene was added to the slurry. After a further 30 min the supernatant liquid was sampled. Counting was performed on an Intertechnique SL30 liquid scintillation spectrometer using 1 ml samples in 10 ml of 0.5% (w/v) butyl PBD in toluene. Counting efficiencies were determined by adding to the sample 50 μl ^3H-hexadecene of known activity. The results show that 2×10^{-4} mmole OH/g of

TABLE 1

Retention Times for Hydrocarbons Relative to Methane

Hydrocarbon	Liquid phase		
	ZrSM	HfSM	PbSM
Methane	1.000	1.000	1.000
Ethane	1.176 ± 0.003	1.179 ± 0.001	1.373 ± 0.004
Propane	1.702 ± 0.004	1.720 ± 0.007	2.467 ± 0.013
Ethylene	1.110 ± 0.001	1.111 ± 0.002	1.214 ± 0.003
Propylene	1.622 ± 0.007	1.625 ± 0.008	
Butadiene	3.196 ± 0.04	3.244 ± 0.014	5.339 ± 0.035
Allene		1.976 ± 0.012	2.813 ± 0.018

diatomite react in this way (i.e., ~0.1% of organometallic added).

Gas–Liquid Chromatography

One microliter samples of alkanes and olefins were alternately injected onto a packed column 4 mm o.d. and ~2 m long using a Pye gas sample valve fitted with a microswitch. Elution was detected by a Perkin-Elmer F11 FID detector and recorded on a Servoscribe recorder. The temperature of the column was controlled by a Gallenkamp viscometer water bath. The helium carrier gas was passed through a pre-column of organometallic to remove reactive impurities. Flow rates were ~10 ml/min.

RESULTS

Preliminary experiments have been performed with ~0.2 *M* solutions of zirconium and hafnium benzyls in squalane. The difference in retention time for ethylene on the sample and squalane blank columns shows that the equilibrium constant for complex formation between ethylene and the metal alkyl is less than 0.3 liter mole^{-1} in both cases.

Subsequent experiments have been performed with a liquid phase consisting of pure zirconium and hafnium tetrakis(trimethylsilylmethyl) (ZrSM and HfSM) and the blank is taken as the equivalent lead alkyl (PbSM). Retention times relative to methane for various hydrocarbons on these columns are given in Table 1.

The partition coefficient k for a solute between the liquid phase and the carrier gas is a function of gas flow rate, pressure drop across the column and dead volume of the column (*14*). By using relative retention times only a dead volume correction need be applied provided equilibrium between gas and liquid is established.

Since the metal alkyls are sensitive to oxygen, water and hydrogen an approximate method for determining the dead volume has been used. Three methods based on the retention data of alkanes have been used. They are:

1. By assuming a linear relationship between the log of the retention volume and the number of carbon atoms in the chain. Such a relationship has been observed for higher alkanes (*14*) but it unlikely to be a very good approximation for C_1 to C_3.
2. By assuming that the ratio of the increments of free energy of solution with increasing number of carbon atoms is equal to the ratio of the corresponding increments in the free energy of vaporization.
3. By assuming that methane retention represents the dead volume. This method

TABLE 2

Dead Volumes from Alkane Retention Data

Column		Dead vol as a proportion of methane retention time for:			Partition coefficient of ethylene relative to PbSM for:	
		ZrSM	HfSM	PbSM	ZrSM	HfSM
Dead volume approximation	1	0.912	0.911	0.807	0.042	0.038
	2	0.845	0.845	0.664	0.035	0.027
	3	1.000	1.000	1.000	0.088	0.080
Calcd range		0.94–0.97	0.93–0.97	0.84–0.93		

has been used previously (*8*, *15*), but in view of the differences in retention among the alkanes it overestimates the dead volume in this case.

The dead volumes calculated by these methods are given in Table 2. Similar values for the shift in ethylene retention are obtained by methods (1) and (2). The results are somewhat different for (3) and this is clearly a poor approximation. A theoretical model (*vide infra*) suggests that method (1) probably gives the best estimate of dead volume. The relative retention times corrected for dead volume by method (1) are given in Table 3.

TABLE 3

Relative Retention Times Corrected for Dead Volume[a]

Hydrocarbon	Retention times relative to ethane for:		
	ZrSM	HfSM	PbSM
Methane	0.334	0.334	0.341
Ethane	1.000	1.000	1.000
Propane	2.991	3.021	2.933
Ethylene	0.749	0.746	0.719
Propylene	2.689	2.664	
Butadiene	8.652	8.730	8.007
Allene		3.471	3.344

[a] True relative values of retention times ±20%. Relative retention times for one hydrocarbon cross series Zr, Hf, Pb to ±1%.

The calculation of the equilibrium constant for complex formation depends on an estimate of the concentration of olefin which has dissolved in the metal alkyl but has not complexed. Lead silylmethyl has been used to estimate this because of the similar chemical structure and molar volume. Olefin complexes of $\mathrm{Pb^{IV}}$ are not known to us. Moreover, there have been two unsuccessful attempts to detect interaction between Group IVB elements and olefins by ir (*16*) and nmr spectroscopy (*16*, *17*) in conditions likely to favor such interaction. Lead silylmethyl is chemically very similar to the zirconium and hafnium compounds, and is similar in shape and size. Calculation (*vide infra*) suggests that the influence of the changes in this series of compounds is much smaller than experimental error. This is discussed in detail below.

The stoichiometric equilibrium constant is calculated using:

$$K = \frac{k_{\mathrm{M}} - k_{\mathrm{Pb}}}{k_{\mathrm{Pb}}} \frac{1}{[\text{metal alkyl}]} \qquad (3)$$

and the results are given in Table 9.

The observed difference between ethylene retention on the zirconium and hafnium silylmethyls and that on lead silylmethyl is small and solution effects may be large enough to account for this difference. The

TABLE 4

Molar Volumes of Organometallic Compounds

	Density (g/cm^3)	MW	Molar vol (cm^3)	Radii (Å)		Electronegativity
				Ionic	Covalent	
ZrSM	0.95	440	464	0.80	1.45	1.4
HfSM	1.10	527	480	0.81	1.44	1.3
PbSM		556	480–508[a]	0.84	1.47	1.8

[a] Range provided by choice of ionic or covalent radius for metal by allowing for electronegativity change. Thus 480 cm^3 is from pure covalent radii and 508 cm^3 arises when allowance is made for change in electronegativity.

magnitudes of these effects are now examined.

The partition coefficient, C_A, of a volatile solution A between the gas phase and the stationary liquid phase, S, is defined in gas chromatography as the ratio of the concentration of A in the liquid phase to the concentration in the gas phase (*18*). For the case where there is no chemical interaction between the solute and solvent, C_A can be defined (*19*, *20*):

$$C_A = \frac{RT}{f_A^0 \nu_S \gamma_A}, \qquad (4)$$

where f_A^0 is the fugacity of the vapor A in equilibrium with the pure liquid A at the column temperature, ν is the molar volume and γ is the activity coefficient.

From classical theories of mixing (*21*) it can be shown that at infinite dilution

$$C_A = \frac{RT}{f_A^0 \nu_A} \times \left[\exp \frac{\nu_A}{\nu_S} - 1 - \nu_A[\delta_A - \delta_S]^2/RT\right], \qquad (5)$$

where δ is the solubility parameter. This equation is used to evaluate the relative C_A's expected from solution effects only. It has been pointed out that the error in the free energy of solution (and hence C_A) arising from an inappropriate model is a second order term and likely to be small (*21*).

The molar volumes of zirconium and hafnium silylmethyls were determined and are given in Table 4. The molar volume of lead silylmethyl has been estimated from these data, the ionic and covalent radii and the electronegativity of the metals. The range quoted represents the limits of reasonable assumption. The worst case $\nu_{PbSM} = 508$ cm^3 is used in the calculation. The molar volumes of the hydrocarbons are calculated from the data of Reid and Sherwood (*22*) and are summarized in Table 5.

The vapor pressures above the critical temperature have been obtained by linear extrapolation of $\log P$ vs $1/T$ data from

TABLE 5

Molar Volume and Solubility Parameters[a] for Hydrocarbons

Hydrocarbon	Solubility parameter δ	V_W	Critical temp, (K)	Molar vol ν_A, cm^{3b}	
				291 K	298 K
CH_4	5.440	5.000	191	51.35	51.90
CH_2H_6	5.880	7.880	305	67.47	68.01
C_3H_8	6.000	10.350	370	83.42	84.00
C_2H_4	5.800	6.880	283	60.44	60.95

[a] Basic data from Ref. (*31*).

[b] Calculated using $\nu_A = V_{W,A}\,(5.7 + 3.0\,T_{r,A})$.

TABLE 6

Fugacities of Hydrocarbons

Hydrocarbon	Temp (K)	Reduced temp (T_r)	Reduced pressure	Activity coefficient	P (ats)	f (ats)
Methane	291	1.524	6.379	0.689	292.2	201.3
	298	1.560	6.919	0.706	316.9	223.7
Ethane	291	0.951	0.731	0.701	35.23	24.70
	298	0.974	0.850	0.681	40.97	27.86
Propane	291	0.786	0.176	0.870	7.39	6.43
	298	0.805	0.213	0.850	8.95	7.61
Ethylene	291	1.028	1.170	0.634	59.09	37.46
	298	1.053	1.338	0.624	67.57	42.16

Ref. (*23*). The activity coefficients have been found by linear interpolation of the data of Curl and Pitzer (*24*) using the expression

$$\log(f/p) = [\log[f/p]]^0 + w[\log[f/p]]^1. \quad (6)$$

The resulting fugacities are summarized in Table 6.

The value of the solubility parameter, δ, is taken from Reid and Sherwood (*22*) for the hydrocarbons. For the organometallics it has been estimated using $\delta_A^2 = E_A^V/v_A$, where E_A^V is the energy of vaporization at the temperature of solution.

The heat of vaporization of a compound at temperature T can be estimated from its boiling point. By using the Hildebrand rule (*21*), known hydrocarbon vapor pressures and the known vapor pressures of the organometallics, values of δ can be estimated (Table 7).

The estimated boiling points of the organometallic are ~370°C, i.e., comparable to C_{22}–C_{23} alkanes (MW ~320). This is surprisingly low for compounds of MW 440–560 but it should be noted that $PbEt_4$ (MW 323) boils at the same temperature as C_{10}–C_{11} alkanes (MW ~150).

TABLE 7

Solubility Parameters for Organometallic Compounds

Compound	MW	Temp (°C) at which VP =		bp (°C)	E (kcal/mole)	δ (cal/cm^3)$^{1/2}$
		10^{-2} mm	10^{-3} mm			
ZrSM	440		50	370[a]	18.4	6.26
HfSM	527		50	370[a]	18.4	6.16
PbSM	556	98		370[a]	18.4	6.05
n-$C_{22}H_{46}$	310	65	49	376		
n-$C_{23}H_{48}$	324	93	78	367		

[a] Estimated from alkane vapor pressure data.

TABLE 8

Calculated Retention Data Assuming No Complex Formation

Organometallic	Temp (K)	Calculated partition coefficients				Calculated relative retention times			
		CH_4	C_2H_6	C_3H_8	C_2H_4	CH_4	C_2H_6	C_3H_8	C_2H_4
ZrSM	291	0.896	5.994	19.42	4.318	0.149	1.000	3.239	0.720
HfSM	291	0.905	6.011	19.41	4.336	0.151	1.000	3.229	0.721
PbSM	291	0.911	5.999	19.29	4.337	0.152	1.000	3.216	0.723
PbSM	298	0.831	5.409	16.60	3.921	0.154	1.000	3.068	0.725

The calculated δ are within the range ($\delta = 6$ to 8) found for alkanes.

The results of the calculations are given in Table 8. Agreement with the observed relative retention data is good giving confidence in the parameterization. The calculated change in relative ethylene retention [$\alpha(C_2^{=})$] at 291 K from Zr to Pb alkyls is an order of magnitude smaller than the experimental changes. The α values are insensitive to the choice of parameters ν_S and δ_S provided that they are approximately correct. A 10% change in ν_S results in a change of only 0.001 in $\alpha(C_2^{=})$, while a change of 3.5% in δ_S, equivalent to 10% error in E_S^V, results in a change of only 0.002 in $\alpha(C_2^{=})$. However, the results become more sensitive to changes in δ_S if our estimate of E_S^V is out by $> \pm 40\%$. A change in E^V of this sort leads to less good overall agreement with the retention data.

The change of temperature from 291 K for Zr and Hf alkyls to 298 K for the lead compound results in small movements in the alkane retention in the direction of the experimentally observed shifts. The calculated change in $\alpha(C_2^{=})$ is small (0.002) and in the opposite sense to the observed shift. However, it should be noted that $\alpha(C_2^{=})$ is extremely sensitive to relative changes in the fugacities of ethane and ethylene which are not easy to estimate.

DISCUSSION

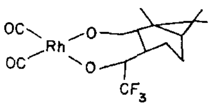
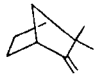
The values of the equilibrium constant for olefin metal alkyl complexes are clearly very small in the region of the periodic table where α-olefin polymerization activity is found. They are at least three orders of magnitude less than those found for silver and rhodium complexes by a comparable method. The heats of solution of monoolefins in $TiCl_4$ (*25*) are compatible with the very weak interactions found here.

There appears to be little difference in the equilibrium constant between zirconium and hafnium alkyls, in contrast with the values for pyridine complexes of zirconium and hafnium benzyls (*5*) where the interaction between hafnium and pyridine is an order of magnitude greater than between zirconium and pyridine.

None of the olefins and dienes interact markedly more strongly than ethylene with zirconium and hafnium alkyls. The strength of complex formation would thus appear to parallel the right hand end of the transition series (Table 9). The rates of polymerization of linear α-olefins are not inconsistent with the variation in K. Surprisingly the known catalyst poisons for olefin polymerizations, such as allene and isobutene, do not form complexes particularly strongly, so that the mechanisms of poisoning cannot be associated with irreversible coordination.

TABLE 9

Comparison of Equilibrium Constants with Literature Values for Olefin Transition Metal Complexes (liters mole^{-1})

Metal complex:	ZrSM	HfSM	$AgNO_3$	$AgNO_3$	Cu(I)	$Rh(CO)_2$ (acac)	$Rh(CO)_2$ $(CF_3CO)_2CH$			Co_3O_4[a]	$PdCl_4^{2-}$[b]
Solvent:	None	None	Ethylene glycol	Ethylene glycol		Squalane	Squalane	Squalane	Squalane		Aqueous solution
Olefin											
Ethylene	0.02	0.02	22.3	13.5		1120	220	10,000	1600	8.4	17.4
Propylene			9.1	5.9		103	37	1100	223	1.0	14.5
Butene-1			7.7	6.8		126	42	1200	264		11.2
c-Butene-2			5.4	3.9		27	14	314	68	2.4	8.7
t-Butene-2			1.4	1.4		9	7	132	46		4.5
i-Butene			3.9			2	2	33	10		
Norbornene			62.0		2×10^4						
											
Cyclohexene			3.6								
Hexene-1			4.3		1×10^2				1		
Butadiene	<0.04	<0.03	4.2	3.6		490		5600			
Hexa-1,5-diene			28.8								
Allene		<0.02	0.8								
Temp (°C)	18	18	40.0	40.0		30	30	30	50		
Ref.	This work	This work	(*7*)	(*8*)	(*26*)	(*9*)	(*9*)	(*9, 10*)	(*9*)	(*27*)	(*29*)

[a] Competitive hydrogenation: values from relative rates and are not absolute.

[b] $K = [PdCl_3 \quad olefin][Cl^-]/[PdCl4^2][olefin]$.

Butadiene does not appear to be more strongly bound than ethylene and thus would appear to be coordinated to the metal in a 1,2 sense. 1,2 Coordination of butadiene has been reported for the complex $PtCl_2(C_4H_8)_2$ (*28*) and is suggested for silver by comparison of the equilibrium constants for coordination of ethylene $K = 22$, butadiene $K = 4$ and hexa-1,5-diene $K = 29$. Hexadiene is thus bound through both olefinic groups. That butadiene is coordinated 1,2 does not preclude 1,4 polymerization.

It is interesting to note that norbornene is held more strongly by silver than any other olefin considered and very much more strongly than the substituted methylene–norbornene included in Table 9. Thus the incorporation of ethylidene norbornene through the cyclic double bond in ethylene–propylene–diene terpolymerization with supported metal alkyls can be explained.

It appears that those metals which polymerize mono-olefins efficiently coordinate mono-olefins weakly. This is consistent with the views of Armstrong *et al.* (*30*) who have performed a CNDO calculation on a soluble "Ziegler" catalyst.

The extension of this work to metal alkyls supported on alumina and other oxides would clearly be of value. This requires that we are able to distinguish between olefin interaction with the supported organometallic and the olefin interaction with Lewis acid sites of the support. The latter may well change as a result of the presence of the metal alkyl and there is infrared evidence that the Lewis acidity of alumina is greater than that of supported hafnium silylmethyl (*31*). Thus the influence of the Lewis acid sites of alumina is likely to be dominant and a prerequisite of a successful experiment would be the blocking of at least the strongest Lewis acid sites.

CONCLUSIONS

The equilibrium constant for olefin–metal alkyl complex formation is very small for all olefins and dienes tested with hafnium and zirconium alkyls.

Polymerization poisons such as allene do not interact markedly more strongly than other olefins.

The equilibrium constant for supported metal alkyls can only be measured if the strongest Lewis acid sites are blocked.

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