KINETIC INVESTIGATION ON ALCOHOLYSIS OF TRIETHYLALUMINIUM BY DIFFERENTIAL THERMAL ANALYSIS

U. HOFFMANN, H. ANDERSON and D. HABERLAND

Department of Chemistry, University of Greifswald, 2200 Greifswald GDR

The alcoholysis of triethylaluminium can be investigated by DTA in the liquid phase. The reaction enthalpy of the alcoholysis with primary alcohols is from -150 to -170 kJ mole^{-1} in tetrahydrofuran/toluene as solvent. The reaction rate in pure hydrocarbons is higher than in the presence of Lewis bases. The reaction mechanism is probably of S_E2 type and the reactivity decreases in the sequence primary, secondary, tertiary alcohol. In the second step of substitution the diethylaluminium alkoxides are less reactive than triethylaluminium because of the stronger association of the alkoxides. For the turnover of two moles of alcohol with one mole of triehylaluminium two DTA peaks appear in accordance with consecutive reactions.

In recent years DTA has been applied to reactions in the liquid phase [1 — 3]. This method is connected with the restricting requirement of the existence of a limited range of temperature in which the reaction starts and finishes. Furthermore, the reaction has to come to a standstill by cooling without the limit of solubility of the reacting components being exceeded.

The essential advantage of DTA in the liquid phase is the determination of the thermodynamic and kinetic parameters of a chemical reaction in only one experiment. Because of the constant stirring, gradients of concentration or temperature practically do not occur. Kinetic evaluation is therefore more easy than in solid-phase reactions. DTA is a suitable method for the investigation of the alcoholysis of triethylaluminium $AlEt_3$ for in a hydrocarbon solvent this reaction is very vigorous.

Evaluation and experimental conditions

For the quantitative evaluation of the DTA curves, both the differential method of Borchardt an Daniels [4] and the integral method of Coats and Redfern [5] have been used. These methods yield identical kinetic data within the margin of error. The thermal analysis was carried out in a special equipment which allowed work under an inert atmosphere [6]. The constant heating rate was 2.5 K min^{-1}. The apparatus parameters were determinded by electrical calibration. The reactions were analyzed in the temperature range between 180 and 370 K.

On treatment with aliphatic or aromatic alcohols triethylaluminium evolves

ethane in an extreme vigorous reaction [7]:

$$(Et_3Al)_2 + 2\ ROH \rightarrow (Et_2AlOR)_2 + 2\ C_2H_6\ .$$
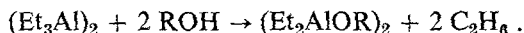
The dimeric diethylaluminiumalkoxides formed in this way are less reactive than triethylaluminium, but most of them react rapidly with further alcohol to give ethylaluminium dialkoxide and subsequently more slowly to give aluminium trialkoxide. The lower reactivity may be ascribed to the strong self-association of the monoalkoxide in ether as solvent, which reduces the Lewis acidity of the aluminium centres.

The reactions were carried out in toluene, tetrahydrofuran and a mixture of both solvents with 58% THF. The concentration of triethylaluminium was about 0.2 mole 1^{-1}.

Results

Alcoholysis of AlEt$_3$ as a one-step reaction. The kinetic evaluation of the reaction with one mole of alcohol by the methods of Borchardt—Daniels and Coats—Redfern in all cases yielded satisfactory straight lines for a second-order reaction the correlation coefficients being $r = 0.85 - 0.95$. Moreover, the reaction rate was a function of the solvent and the nature of the alcohol.

If toluene with its relatively weak donor properties is replaced by tetrahydofuran with a stronger tendency to complex formation, then the reaction rate decreases considerably. Since the coordination site in the molecular compound of AlEt$_3$ + solvent is blocked by the donor, nucleophilic attack by the electron pair of the alcohol is inhibited. This effect is the greater, the higher the portion of THF. In Table 1 the activation parameters for the reaction with isopropanol are given.

Table 1

Dependence of the reaction rate of solvent for the reaction of i-propanol with triethylaluminium

Solvent	E_A, kJ/mole	$\lg k_0$	k_{298} l/mole·min
Toluene	58.2	11.9	46.7
58 vol% THF/toluene	100.1	17.9	1.8
THF	109.9	18.9	0.4

Two solvents (toluene and THF) and a mixture of them were applied. The reaction rate of isopropanol is about one hundred times faster in toluene than in THF.

In addition to the solvent effect, the reaction rate depends on the type of the alcohol. With increasing acidity of the alcohol, corresponding to the autoprotolysis constants [8], the reaction rate likewise increases. In Table 2 thermodynamic

Table 2

Thermodynamic and kinetic DTA-results of the first alcoholysis step of
$AlEt_3$ in toluene/THF

Alcohol	$-\Delta_R H$, kJ/mole	E_A, kJ/mole	$\lg k_0$	k_{298}, l/mole min
Me	154.9 ± 2.1	48.3 ± 1.4	10.19 ± 0.16	53.2
Et	151.3 ± 3.2	61.3 ± 1.5	12.00 ± 0.31	18.4
n-Pr	147.2 ± 1.9	77.4 ± 1.1	13.90 ± 0.17	9.0
i-Pr	143.8 ± 1.9	100.1 ± 0.4	17.90 ± 0.80	2.5
n-Bu	152.9 ± 5.3	71.2 ± 2.5	13.41 ± 0.47	8.6
i-Bu	150.2 ± 2.2	75.7 ± 3.0	14.22 ± 0.60	9.4
s-Bu	130.1 ± 2.6	98.7 ± 1.4	17.33 ± 0.23	1.1
t-Bu	123.8 ± 1.7	103.2 ± 1.2	17.34 ± 0.18	0.18
n-Am	153.6 ± 7.3	76.5 ± 2.1	14.37 ± 0.38	9.1
i-Am	150.2 ± 3.4	78.4 ± 1.8	14.73 ± 0.34	9.7
t-Am	116.0 ± 3.8	110.2 ± 2.2	18.48 ± 0.38	0.14
n-Oct	148.8 ± 2.0	85.7 ± 0.3	15.99 ± 0.15	9.5
Benzyl	150.8 ± 3.3	61.7 ± 1.6	12.48 ± 0.28	46.1
Benzhydrol	121.2 ± 3.7	86.3 ± 1.7	15.60 ± 0.29	3.04
β-Phenyl	151.5 ± 2.0	58.5 ± 1.4	11.69 ± 0.26	27.6
cyc-Hex	136.6 ± 3.6	97.0 ± 3.7	17.00 ± 0.66	2.1

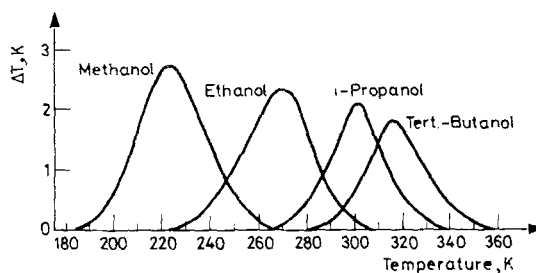Fig. 1. DTA-curves of α-methyl substitued alcohols

and kinetic data obtained by DTA are shown. These reactions were investigated in a mixture of toluene + 58 vol% THF to compare most of the indicated alcohols.

A comparison of the DTA curves shows (see Fig. 1) that with the substitution of the hydrogen atoms in methanol by methyl groups (Et, iso-Pr, tert.-Bu) the reactivity decreases.

Methanolysis and the beginning of the reaction of tert.-butanol with $AlEt_3$ are separated by about 100 K. In the reactions of the isomeric butanols the rate diminishes in the sequence primary secondary tertiary. The linearized graphs are given in Fig. 2.
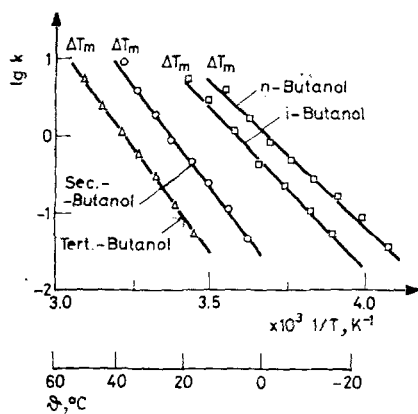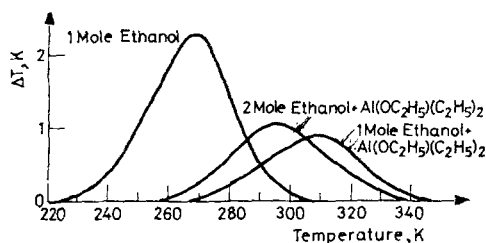
Fig. 2. Linear plot of DTA-curves of isomeric butanoles

Fig. 3. DTA-curves of diethyl-aluminium-ethoxid with ethanol

Alcoholysis of diethylaluminium alkoxide

The second step of the alcoholysis is slower then the first because of the self-association of the alkoxy compound. Likewise, the reaction enthalpy is lowered. Figure 3 shows, for instance, DTA curves of the reaction of diethylaluminium ethoxide with one and two moles of ethanol in toluene/THF. The third step of alcoholysis is very slow and can not be investigated under these conditions.

The enthalpy of the second step is -44 kJ mole^{-1}, while the activation parameters for a second-order reaction are

$$E_A = 95 \text{ kJ mole}^{-1}, \quad \log k_0 = 16.9 \quad \text{and} \quad k_{298} = 1.7 \text{ l (mole min)}^{-1}.$$

Alcoholysis of triethylaluminium as a consecutive reaction

If two moles of alcohol react with triethylaluminium under suitable reaction conditions, two DTA signals are observed. The separation of the two reaction parts becomes more pronounced with decreasing content of tetrahydrofuran in the solution. For a turnover of two moles of isopropanol with AlEt$_3$ in toluene as solvent, we can differentiate two well-separated DTA peaks, which approxi-
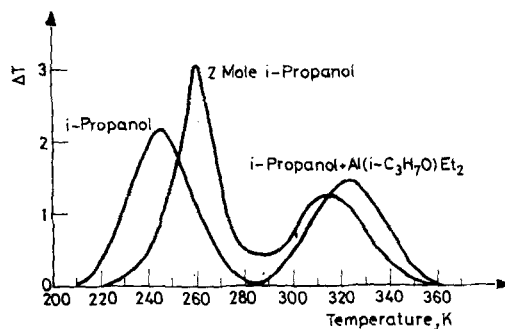
Fig. 4. DTA-curves of the reaction of i-propanol with AlEt$_3$ in toluene

Table 3

Thermodynamic and kinetic parameters of the reaction of i-propanol with AlEt$_3$ in toluene as simple or consecutive reaction

Step		$-\Delta_R H$, kJ/mole	E_A, kJ/mole	k_{295}, l/mole min
simple	1	152.3	58.2	46.7
reaction	2	80.3	85.7	0.26
consecutive	1	154.4	64.4	42.6
reaction	2	80.4	88.4	0.4

mately correspond to the steps of the reaction (see Fig. 4). The relatively small differences in comparison with the one step reactions are caused by the experimental conditions. In Table 3 the enthalpies and kinetic parameters are given for the simple and the consecutive reaction, for which the steps of the consecutive reaction have been evaluated as a simple reaction.

Discussion

The enthalpy for the alcoholysis of triethylaluminium is from -150 to -170 kJ mole^{-1} in a toluene/THF mixture as solvent. The energy balance includes the association heat of the alkoxy compound. In the presence of Lewis bases the reaction rate is lower because the coordination site on the aluminium is blocked by the donor. The reaction between alcohol and AlEt$_3$ is of second order, but of first order with respect to each component. The reaction is the faster, the more acidic the alcohol. The introduction of several methyl groups lowers the proton character of the hydrogen atom as a result of the increasing inductive effects.

Table 4

Relative reaction constants for the reaction of alcohols
with triethylaluminium at 298 K toluene/THF as solvent

ω-substitution		α-substitution		β-substitution	
Me	1	Me	1		
Et	0.35	Et	0.35	Et	0.35
n-Pr	0.17	i-Pr	0.047	n-Pr	0.17
n-Bu	0.16	t-Bu	0.0034	i-Bu	0.18
n-Am	0.17	Phenyl-Me	0.87	β-Phenyl-Et	0.52
n-Oct	0.18	1,1-Diphenyl-Me	0.057		

In Table 4 the relative rate constants are shown for the first alcoholysis step of
AlEt$_3$ when the hydrogen in the ω, α, and β positions is substituted by methyl or
phenyl groups. The rate of reaction with methanol is taken as one. Methanol is
three times more reactive than ethanol and this again ist wice as reactive as *n*-prop-
anol. For the higher linear alcohols the reaction rate exhibits parctically no
change.

In the α-substituted series the reactivity diminishes with further methyl incor-
poration. Increasing inductive effects operate together with steric hindrance.
Substitution in the β-position by a methyl group effects a change in the reaction
rate only between ethanol and propanol. If a carbon atom adjacent to the reaction
centre is unsaturated, then we observe an unusually fast reaction, such as that
with benzyl alcohol.

In the β-position a phenyl group can only attract electrons. In contrast to etha-
nol, it effects weak activation. The inductive phenomena of the alkyl groups may
be described by the Taft equation (see Fig. 5). The positive reaction constant
(= 38.0) shows that the reaction is accelerated by electron drawing.

The reaction mechanism involves S_E electrophilic substitution at the saturated
carbon atom. In toluene as solvent the nucleophilic centre of the alcohol is coor-
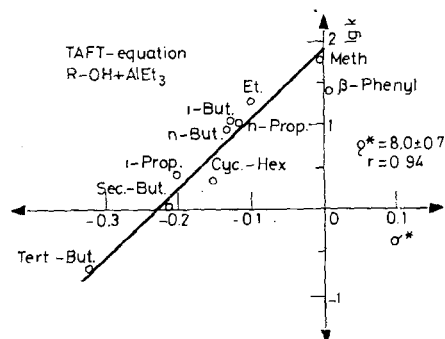

Fig. 5. Taft-equation for the reaction of triethylaluminium with alcohols

dinated in a fast starting step to the aluminium atom, while desolvation takes place.

The following transfer of a proton to the negative ethyl group determines the rate of reaction. The transition state is "four-fold coordinated" and the mechanism according to Abraham—Hill is S_E2_C [9]. The application of stronger basic solvents such as tetrahydrofuran complicates the coordination. Presumably the reaction does not proceed *via* the intermediate complex $Et_3Al-HO-R$, but through an "open transition state" with tetrahydrofuran as stabilizing base. Therefore, an S_E2_0 mechanism is more likely.

The reaction enthalpy $\Delta_R H$ of the alcoholysis of alkoxydiethyl-aluminium is considerably less than that of $AlEt_3$ for the difference of the association heats of $AlEt_3$ and the alkoxy compound is contained in the energy balance of the latter reaction. The association of alkoxydiethylaluminium should be greater, because its association cannot be abolished by strong electron donors.

The reaction is slower than the first step reaction, because of the stable alkoxy association complexes.

For a turnover of two moles of alcohol with $AlEt_3$ we obtain as expected two DTA signals which in toluene correspond to the two simple reactions. In the presence of tetrahydrofuran this was not observed. In this case the consecutive reaction is shifted to lower temperatures, in contrast to the one-step reaction [10].

This may be a result of the higher alcohol concentration. Under these conditions the screening effect of tetrahydrofuran at the aluminium centre is probably diminished.

References

1. E. Koch, Non-isothermal reaction analysis, London— New York— San Francisco, 1977.
2. W. Besch, Diss. Greifswald, 1975.
3. H. Anderson, U. Hoffmann and D. Haberland, Z. Phys. Chem., 261 (1980) 639.
4. H. J. Borchardt and F. Daniels, J. Amer. Chem. Soc., 79 (1957), 41.
5. A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
6. U. Hoffmann, H. Anderson and D. Haberland, J. Thermal Anal., 22 (1981) 245.
7. T. Mole and E. A. Jeffery, Organoaluminium Compounds, Amsterdam— London— New York, 1972.
8. A. P. Kreschkov, N. T. Smolova and T. I. Burmistrova, Zh. Fiz. Khim., 50 (1976) 987.
9. M. H. Abraham and J. A. Hill, J. Organometal. Chem., 7 (1967) 11.
10. U. Hoffmann, Diss. Greifswald, 1980.

ZUSAMMENFASSUNG — Die Reaktion zwischen einer Lösung von Aluminiumtriethyl und einer Reihe von aliphatischen oder aromatischen Alkoholen kann mittels DTA quantitativ verfolgt werden. Die negative Reaktionsenthalpie der Alkoholyse mit primären Alkoholen beträgt 150 bis 170 kJ mol^{-1}, sofern ein Lösungsmittelgemisch aus Tetrahydrofuran/Toluen eingesetzt wird. Die Reaktionsgeschwindigkeit in unpolaren Kohlenwasserstoffen ist grösser als in Gegenwart von Lewis-Basen. Wahrscheinlich ist der Reaktionsmechanismus vom Typ

S_E2, wobei die Reaktivität in der Folge primäre, sekundäre, tertiäre Alkohole fällt. Der zweite Schritt der Alkoholyse, ausgehend vom Diethylaluminiumalkoxid, ist wegen der starken Selbstassoziation weniger reaktiv. Bei Umsatz von 2 Mol Alkohol treten entsprechend der Folgereaktion zwei DTA-Peaks auf.

Резюме — Алкоголиз триэтиламиния может быть исследован с помощью ДТА в жидкой фазе. Величина энтальпии реакции алкоголиза первичными спиртами составляет от —150 до —170 кджмоль$^{-1}$ в растворителе тетрагидрофуран-толуол. Скорость реакции в чистых углеводородах выше, чем в присутствии льюисовских оснований. Возможно, что реакция происходит по механизму S_E2 и реакционная способность уменьшается в ряду первичный, вторичный, третичный спирт. Во второй стадии замещение диэтилалюминий алкоксидов меньше, чем для триэтилалюминия, вследствии более сильной ассоциации алкоксидов. При взаимодействии двух молей спирта с одним молем триэтилалюминия наблюдается два ДТА-пики, в соответствии с последовательностью реакций.