Kinetics of the Intramolecular Four-Center Elimination of Isobutylene from Triisobutylaluminum in the Gas Phase

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Abstract: The gas-phase kinetics and the mechanistics of the unimolecular elimination of isobutylene from triisobutylaluminum have been studied in the presence of excess ethylene or 1-butene for temperatures ranging from 107 to 173°. The 1-alkenes reacted very fast with the diisobutylaluminum hydride formed in the elimination process, thus avoiding complications from back and side reactions. The reaction is apparently homogeneous, when carried out in an all-Teflon reaction vessel. The computed least-squares analysis of the measured rate constants for the unimolecular elimination process yields (with standard errors) $\log k\ (\text{sec}^{-1}) = (11.2 \pm 0.4) - (26.6 \pm 0.7)/\theta$, where θ equals $4.58 \times 10^{-3}T(^\circ\text{K})$. Experiments with β-D-triisobutylaluminum show that the deuterium is transferred to the aluminum atom in the elimination process. It can be concluded that the reaction involves a relatively tight polar four-center transition state. The observed preexponential factor indicates a loss of entropy of ~12 cal/(deg mole) in forming the cyclic transition state. The general applicability of the concept of four-center reaction mechanisms in the chemistry of aluminum alkyls and their derivatives is outlined. The activation energy of the back-reaction, the addition of isobutylene to the diisobutylaluminum hydride, is estimated at 6 ± 3 kcal/mole. The pertinent thermodynamic data have been reviewed.

It is generally accepted that reactions involving aluminum alkyls and their derivatives are largely controlled by molecular mechanisms.[1] Radical reactions only occur at elevated temperatures, concurrent with the molecular reaction paths.[1e]

The preference for molecular reactions (in contrast to most other metal alkyls) originates from the relatively high Al–C and Al–H bond strength involved and from the electron deficiency of the aluminum atom with the valence coordination of three. This leads to the ready formation of electron-deficient or "half" bonds.

The majority of the reactions (both intra- and intermolecular) involving aluminum alkyls and their derivatives can be rationalized with a four-center transition state. In a few exceptional cases six-membered transition states are operative[2,3] as in the addition of butadiene to diisobutylaluminum hydride, where both 1,2 and 1,4 addition have been observed.[2a]

Six-center transition states are possible with a 1,3-diene, allowing for six "half" bonds. With 1,4- or 1,5-dienes, two consecutive four-center additions take place.[1c] With longer chains, the steric effects inhibit the intramolecular addition of the second olefinic bond to the Al–C bond already formed.[4] A general concept of four-center and six-center transition states in chemical reactions has been outlined in view of the predictability of the kinetic parameters of such reactions.[5]

Smith and Wartik[6] studied the gas-phase thermal decomposition of triethylaluminum in a static reaction system and reported for the disappearance of aluminum–ethyl bonds $\log k\ (\text{sec}^{-1}) = 8.2 - 29{,}000/4.58T(^\circ\text{K})$.

Allen, *et al.*,[7] observed the addition of hexene-1 to triethylaluminum in hydrocarbon solutions and reported for the homogeneous process an activation energy of ~20 kcal mole^{-1}.

In this work the elimination of isobutylene from the monomeric triisobutylaluminum has been studied in the gas phase. In order to avoid complications from the back-reaction, an excess of ethylene was added to the system, making use of the fact that the dialkylaluminum hydride formed in the elimination process adds very much faster[2] to *n*-alk-1-enes than to isoalk-1-enes.

Experimental Section

A. **Apparatus and Procedures.** The principal features of the static reaction system used in these studies have been described previously.[8] The pronounced sensitivity of the reaction toward heterogeneous catalysis required the use of reaction vessels with very inert surfaces. Cylindrical stainless steel vessels were coated with a layer of Teflon, using the technique applied in the production of Teflon-coated household goods. A schematic drawing of a vessel is shown in Figure 1. The evacuated, closed-off reaction cell (802 ml) showed no measurable leak rate during the reaction times used. In some experiments, the reaction cell was filled with Teflon wool, which changed the surface-to-volume ratio of the vessel drastically. Greaseless, vacuum-tight stopcocks were specially designed and manufactured. Kept at 120° they connected the vacuum, gas-handling, gas-collection, and inlet systems to the reaction cell. All connecting leads were kept at controlled elevated temperatures to avoid premature precipitation of the reaction mixture.

Triisobutylaluminum was added to the system as a gas and as a liquid. The gas-phase addition was carried out by heating a small degassed aliquot in a special inlet glass tube to about 120° (oil bath). The evaporated sample was expanded into the reaction cell. For

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(1) (a) K. Ziegler in "Organometallic Chemistry," H. H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 194 ff; (b) R. Köster and P. Binger, *Advan. Inorg. Chem.*, 7, 263 (1965); (c) H. Lehmkuhl, *Ann. N. Y. Acad. Sci.*, **125**, 124 (1965); (d) G. E. Coates, M. L. H. Green, and K. Wade, *Organometal. Compd.*, **1**, 295 (1967); (e) Y. A. Tajima and C. J. Marsel, *Progr. Astronautics Aeronautics*, **15**, 403 (1964).

(2) L. I. Zakharkin, L. A. Savina, and L. M. Antipin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 996 (1962); *Chem. Abstr.*, **57**, 2286*d* (1962); (b) E. B. Baker and H. H. Sisler, *J. Am. Chem. Soc.*, **75**, 5193 (1953).

(3) N. S. Ham, E. A. Jeffrey, T. Mole, and J. K. Saunders, *Australian J. Chem.*, 20, 2641 (1967); T. Mole, *ibid.*, **18**, 1183 (1965).

(4) The alkenylaluminum compound formed from 1,6-heptadiene only adds intramolecularly to the extent of ~1%, and 1,7-octadiene forms only bis-hydroalumination products.

(5) (a) S. W. Benson and G. R. Haugen, *J. Am. Chem. Soc.*, **87**, 4036 (1965); *J. Phys. Chem.*, 70, 3336 (1966); (b) H. E. O'Neal and S. W. Benson, *ibid.*, **71**, 2903 (1967).

(6) W. L. Smith and T. Wartik, *J. Inorg. Nucl. Chem.*, **29**, 629 (1967).

(7) P. E. M. Allen, J. P. Allison, J. R. Majer, and J. C. Robb, *J. Chem. Soc.*, 2080 (1963).

(8) (a) K. W. Egger, *J. Am. Chem. Soc.*, **89**, 504 (1967); (b) D. M. Golden, K. W. Egger, and S. W. Benson, *ibid.*, **86**, 5417 (1964).

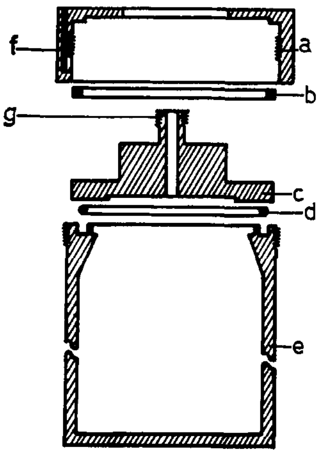

Figure 1. Cut through Teflon-coated reaction vessel. The letters indicate (a) screw-on top; (b) pressure ring, brass; (c) stainless steel cover, Teflon coated; (d) Viton-A O-ring; (e) stainless steel reaction vessel with O-ring groove, Teflon coated; (f) hole for thermocouple; (g) 0.25-in. Swagelok adapter.

the liquid-phase addition the sample was injected with a 100-μl syringe directly into the reaction volume through a silicon rubber septum.

In most experiments, the aluminum alkyl was added first as a gas, and then ethylene or 1-butene was swept into the reaction cell. An experiment was quenched by fractionated condensation of the reaction mixture in the gas collection system. Noncondensable gases were continuously removed through an automatic Toepler pump into a gas buret. The collected hydrocarbon fraction (consisting of alkanes and alkenes) was transferred and measured in the gas buret before sampling for gas–liquid partition chromatography (glpc).

An excess of degassed water was added to the aluminum alkyl fraction, precipitated in the first trap. The gaseous hydrolysis products were dried and transferred through the Toepler pump into the gas buret, where they were measured and sampled for (glpc) analysis. The hydrolysis products included small amounts of alkenes besides the expected alkanes. The pressure change during the reaction was monitored with a Pace pressure transducer with a sensitivity of ±0.05 Torr.

B. Analysis. a. **Gas Chromatography.** The gaseous products, consisting of C_2 and C_4 hydrocarbons, were analyzed using a Model 810 F & M research gas chromatograph, equipped with thermal conductivity detectors. Quantitative separation was obtained with a 30 ft $\times$ 0.25 in. column of 20% BMEA on Chromosorb W, operated at 0° with a helium flow rate of 60 ml/min. The following retention times (after the air peak) relative to isobutane (= 1.00) were observed: ethane 0.130, ethylene 0.165, isobutane 1.000, *n*-pentane 1.639, 1-butene 2.68, isobutylene 2.819, *n*-hexane 5.203. The relative sensitivities of the TC detector for the principal products were determined using five different standard mixtures of hydrocarbons. The following relative response factors (isobutane = 1.000) were measured: ethylene and ethane 1.533 ± 0.015, isobutylene 0.9793 ± 0.008.

b. ***PVT* Measurements.** The gaseous reaction and hydrolysis products were measured volumetrically in a calibrated gas buret.

c. **Mass Spectrometry.** The analyses were carried out on a Atlas CH 4 instrument. The following hydrocarbon fractions were analyzed and identified by mass spectrometry: (a) the hydrolysis and deuterolysis products of triisobutylaluminum and tri-β-D-isobutylaluminum and (b) the products from the olefin elimination from Al(i-Bu)$_3$ and Al(β-D-i-Bu)$_3$.

C. Materials. **Triisobutylaluminum** was obtained from the Schering AG Co. in Bergkamen, Germany. It was purified and degassed by low-temperature vacuum distillation. Handling, distillation, etc., of the trialkylaluminum was always carried out under dried argon gas or under vacuum, and it was stored at 0°.[9]

Tri-β-D-isobutylaluminum was prepared by heating a mixture of AlD_3 and AlD_3 etherate with excess isobutylene in an autoclave at 65° for 8 hr.[9] Subsequent distillation at 10^{-3} Torr yielded in a first fraction (69°) Al(β-D-i-Bu)$_3$ and at 100° Al(β-D-i-Bu)$_3\cdot(C_2H_5)_2O$. The ethylene used was of customary high purity and was provided by the Fawley works of Monsanto in England.

Results

The elimination of isobutylene from monomeric triisobutylaluminum has been studied in the gas phase in the presence of excess ethylene or 1-butene, in the temperature range 107–173°. The principal reaction products are isobutylene, isobutane, and mixed trialkylaluminum compounds, containing ethyl, isobutyl, and small amounts of *n*-butyl groups. The gaseous reaction products have been analyzed directly by gas chromatography. The liquid product fractions, consisting of mixed trialkylaluminum compounds, have been identified with their gaseous hydrolysis products. In contrast to all other reaction products, the amount of isobutane formed was independent of the reaction conditions used. It became evident that isobutane originated from the initial partial heterogeneous pyrolysis when admitting the starting material into the reaction cell.

The product mixtures obtained after quenching experiments immediately after admitting the starting material into the reaction vessel showed about equal amounts of isobutylene and isobutane, and the connecting leads to the reaction vessel were partially covered with aluminum.

The Al(i-Bu)$_3$ did not undergo further heterogeneous pyrolysis in the Teflon-coated reaction cell as evidenced by the following facts. (a) The observed over-all pressure change during the reaction was insignificant. (b) The relative product distributions and the rate constants obtained from experiments carried out in the packed and the nonpacked reaction cell were the same. (c) The mass balance of the Al(i-Bu)$_3$, taking into account the initial decomposition, was satisfactory. (d) No aluminum deposits were found in the reaction cell itself after more than 30 experiments. The problems encountered in admitting the trialkylaluminum undecomposed into the reaction vessel made it unfeasible to follow the rate of the homogeneous elimination of isobutylene by measuring the production of isobutylene. The incorporation of the ethyl group into the trialkylaluminum was used instead for the kinetic analysis of the system.

The over-all mechanism is summarized in Scheme I.

Scheme I

$$\mathrm{Al}(i\text{-Bu})_3 \xrightarrow{\text{a}} \mathrm{HAl}(i\text{-Bu})_2 + (\mathrm{CH_3})_2\mathrm{CHCH_2}$$

$$\mathrm{HAl}(i\text{-Bu})_2 + \mathrm{C_2H_4} \xrightarrow{\text{b}} \mathrm{EtAl}(i\text{-Bu})_2$$

$$\mathrm{EtAl}(i\text{-Bu})_2 \xrightarrow{\text{c}} \mathrm{HAl}(i\text{-Bu})(\mathrm{Et}) + (\mathrm{CH_3})_2\mathrm{CHCH_2}$$

$$\mathrm{EtAl}(i\text{-Bu})_2 + \mathrm{C_2H_4} \xrightarrow{\text{d}} (n\text{-Bu})\mathrm{Al}(i\text{-Bu})_2$$

$$2\mathrm{EtAl}(i\text{-Bu})_2 \overset{\text{e}}{\rightleftharpoons} [(i\text{-Bu})_2\mathrm{AlEt}]_2$$

In the presence of excess 1-olefin, the elimination reaction (a) is the slow, irreversible, and rate-controlling step. The back-reaction (−a) can be disregarded in competition with reaction b, as 1-olefins add much faster to dialkylaluminum hydride than internal olefins.[1b–e] The elimination of ethylene from the mixed trialkylaluminum (−b) does not occur in competition with the much faster elimination of isobutylene[1b–e] (c).

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[9] K. Ziegler, H. G. Gellert, H. Martin, K. Nagel, and J. Schneider, *Ann.*, **589**, 114 (1954).

Table I. Kinetic Data for the Gas-Phase Elimination of Isobutylene from Triisobutylaluminum

		Starting materials				Hydrolysis products				
						Glpc analysis[c]				
		$[Al(i\text{-}Bu)_3]_0$							$[Al(i\text{-}Bu)_3]_f$,[g]	
Temp, °C	Time, min	Torr[a]	mmoles[b]	C_2H_4[d] Torr	$-(\Delta p)_{tot}$,[e] Torr	C_2H_4 + C_2H_6[f]	n-C_4H_8 + n-C_4H_{10}[f]	i-C_4H_8 + i-C_4H_{10}[f]	mmoles	$-\text{Log } k_a$,[g] sec^{-1}
107.0	16	6.6		85.9	...	11.87		88.12		3.870
107.2	126	9.8	0.151	75.5	0.8	52.52	0.60	46.86	0.155	3.998
	61	8.0		64.7	0.0	33.76		66.11		3.947
107.5	180	8.7	0.114	59.1	...	75.98		24.02	0.164	3.879
108.0	45	7.9		67.1	0.3	21.63	4.60	73.76		3.948
	34	6.6		78.7	0.0	20.05	2.51	77.43		3.972
108.3	133	13.3		B 60.2	2.0	8.21	35.79	55.99		4.204
120.0	40	11.8	0.200	B 61.5	0.9		27.08	65.05	0.185	3.839
	40	13.2	0.152	60.5	0.3	29.87	5.32	63.81	0.206	3.702
120.5	20	7.5	0.075	B 91.7	0.2	8.52	22.74	68.75	0.091	3.656
	30	10.2	0.154	88.3	0.4	40.15		59.89	0.189	3.545
	30	13.4	0.262	78.6	0.4	29.98	1.83	68.19	0.216	3.673
	40	6.4	0.085	77.0	0.2	49.12	0.30	50.58	0.110	3.547
	90	16.3	0.240	70.6	0.0	59.94	0.47	38.58	0.245	3.766
132.5	2	6.7		B 102.3	...		9.35	90.64		3.080
	3	5.0		72.0	−0.3	10.44	0.37	89.19		3.197
	3	7.0	0.144	79.9	0.0	23.49	0.35	76.16	0.145	2.857
	6	9.0		192.4	−0.4	31.87	0.49	67.62		2.964
	15	9.2		278.4	...	65.35	0.66	33.99		2.921
140.8	4	11.7		B 73.1	0.2	1.28	30.00	68.70		2.771
144.4	2	9.9		124.1	...	23.73	0.64	75.63		2.633
146.2	2	11.8	0.120	80.1	...	22.42		77.57	0.103	2.674
	2	10.3		B 63.6	...	1.83	18.59	79.58		2.669
	3	12.6		84.4	...	38.82	0.41	60.77		2.558
154.3	2	7.6		96.0	...	42.89	0.41	56.69		2.325
	3	8.8		120.0	0.5	57.76	1.08	41.15		2.291
	4	8.1		B 89.9	0.4	1.84	62.55	35.60		2.363
154.9	4	8.5		97.4	0.5	75.67	0.08	24.23		2.228
	8	6.0		76.2	0.4	93.91	0.88	5.20		2.210
	17	9.2		67.5	1.0	98.77	0.54	0.68		2.310
155.0[h]	3	12.0		111.4	...	59.19	0.80	40.00		2.293
158.7[h]	2	10.6		79.6	...	47.63	...	52.37		2.268
164.3	3	7.6		B 108.4	0.1	3.20	75.20	21.60		2.079
	5	4.8		44.7	0.1	95.97	...	4.03		1.971
168.9	1.25	9.8	0.107	73.5	...	51.52	0.36	48.11	0.106	2.011
	2	10.1	0.113	44.1	...	67.28	0.64	32.06	0.116	2.023
	5	10.8	0.133	74.5	0.2	97.02	0.26	2.70	0.151	1.919
172.6	5	13.7	0.218	66.0	0.2	95.78	0.46	3.46	0.181	1.961

[a] Initial pressure measurements include gaseous products, formed in the partial heterogeneous decomposition of the starting material upon addition to the reaction vessel. [b] Corrected for an average amount of 180 mmoles of initial decomposition products (i-C_4H_{10} and i-C_4H_8). Compare text and footnote *a*. [c] In % of total products. [d] **B** indicates experiments carried out in excess 1-butene. [e] Total pressure change observed during the reaction. [f] The hydrolyses of the trialkylaluminum compounds yield variable small amounts of alkenes beside the alkanes. [g] Based on the amount of hydrolyses products, collected and measured in the gas buret. [h] Experiment carried out in the reaction vessel, packed with Teflon wool.

In order to simplify the kinetic treatment of the system, it appears reasonable to assume that $k_a = k_c$. The validity of this assumption is substantiated by the fact that consistent rate constants are obtained for conversions ranging from 10 to 90%.

While triisobutylaluminum is monomeric down to −70°, the introduction of n-alkyl groups into the compounds enables partial dimerization involving both isobutyl-n-alkyl and n-alkyl-n-alkyl bridges, the latter being more stable. The vapor pressure data of Laubengayer and Gilliam[10] show that in the case of triethylaluminum less than 10% is associated to the n-alkyl-bridged dimer at our highest reaction temperature of 170° and less than 16% at the lowest temperature of 110°. The amount of dimeric materials in the reaction mixture thus never exceeds ~5% of the ethylene incorporated into the aluminum alkyl, in keeping with the insignificant pressure changes observed during the reaction.

The results of the kinetic experiments are summarized in Table I. The elimination of isobutylene follows first-order kinetics under the reaction conditions used. The conversion reached in the system has been followed by measuring the incorporation of ethyl groups into the trialkylaluminum compound, analyzing the hydrolysis products. The first-order rate constant can then be expressed as

$$k_a = \frac{-2.303}{t} \log \left\{ \frac{(i\text{-}C_4H_{10})}{(i\text{-}C_4H_{10}) + C_2H_6} \right\} \qquad (1)$$

Taking into account the small amounts of n-butane formed through reaction d and the fact that variable but small amounts of olefins are formed upon hydrolysis of the aluminum alkyls, one obtains

$$k_a = \frac{-2.303}{t} \times \log \left\{ \frac{(i\text{-}C_4H_{10}) + (i\text{-}C_4H_8)}{(C_4H_{10}) + (C_4H_8) + (C_2H_4) + (C_2H_6)} \right\} \qquad (2)$$

(C_4H_{10}) and (C_4H_8) include both iso- and n-alkyl species.

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[10] A. W. Laubengayer and W. F. Gilliam, *J. Am. Chem. Soc.*, **63**, 477 (1941).

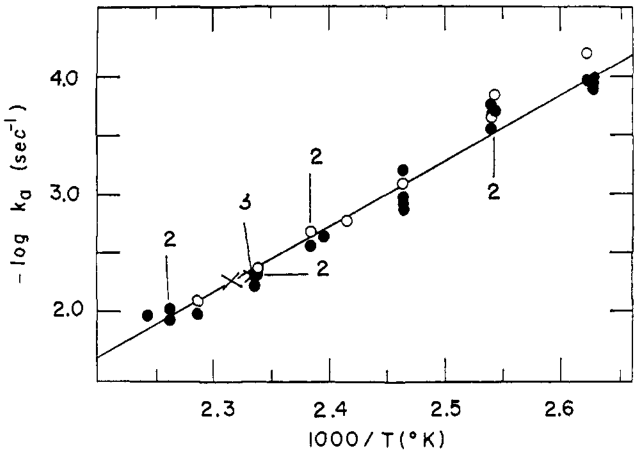

Figure 2. Arrhenius plot of the observed rate constants for the elimination of isobutylene from triisobutylaluminum. Numbers indicate overlapping points. Circles represent data obtained using the nonpacked, crosses those using the packed reaction cell. Open circles have been used for experiments carried out in excess 1-butene, closed circles for those using ethylene as a hydride trap.

From the data listed in Table I it can be seen that consistent rate constants are obtained for conversions ranging from 11 to 99%, for a fivefold change in the pressure of the starting material and a sixfold change in the amount of 1-olefin added. The same rate constants have been observed, whether ethylene or 1-butene was used as 1-olefin and whether the reaction was carried out in the packed (Teflon wool) or unpacked reaction vessel.

Within any given temperature bloc, indicated in Table I, the extreme values of the rate constants differ between 6.6 and 8.4%, which is attributed to the uncertainties introduced by the hydrolysis and analysis procedure. The gas chromatographic analyses and hence the individual rate constants were reproducible to within 0.6%.

Figure 2 shows an Arrhenius plot of the rate constants. The computed least-squares analysis of the data yields (with standard errors): $\log k_9 = (11.22 \pm 0.39) - (26.57 \pm 0.72/\theta)$, where θ equals $4.58 \times 10^{-3}T$(°K). The multiple correlation coefficient of the regression analysis is calculated to 0.974 and would equal 1.000 in case of an ideal fit.

The mass balance with respect to $Al(i\text{-}Bu)_3$ has been roughly checked by applying an average correction to the initial pressure measurement for the amount of gaseous pyrolysis products introduced together with the starting material. These data are listed in columns 4 and 10 of Table I. It can be concluded, that no drastic material losses occur during the reaction. This is further substantiated by the small pressure changes observed during the reaction.

The amount of *n*-butane formed on hydrolysis is a measure of the extent of the addition of ethylene to the trialkylaluminum. It is seen that reaction d is insignificant at low over-all conversions but becomes measurable with increasing reaction time and temperature.

The hydrolysis of the condensed alkylaluminum fraction did not produce any hydrogen, demonstrating the predicted absence of any measurable amounts of dialkylaluminum hydrides in the system.

In order to demonstrate the nature of the anticipated four-center transition state, a few experiments were carried out, using β-D-triisobutylaluminum as starting material.[11] The mass spectrometric results show that the deuterium is indeed transferred from the isobutane to the ethyl group in the trialkylaluminum. The hydrolysis then yields monodeuterioethane and 2-D-isobutane; the deuterolysis yields 1,2-dideuterioethane and 1,2-dideuterioisobutane.

Discussion

The elimination of isobutylene from triisobutylaluminum does indeed involve a cyclic four-center transition state, as proposed in the introductory section. This conclusion is outlined below.

(a) The observed kinetic data satisfy the reaction mechanism summarized in Scheme I.

(b) The observed preexponential factor, when compared with a value of $10^{13.4}$ expected from the transition-state formulation of unimolecular rate constants[12] (taking the entropy contribution $R \ln 3$ from the path degeneracy into account), yields an intrinsic loss of entropy of ~12.3 cal/(deg mole) in forming the transition state. Based on the concept of a loose four-center polar transition-state structure, in which the hindered rotations of the Al–C, C–C, and C–H bonds of the triisobutylaluminum in the ground state are transformed into torsional modes, an entropy loss of about 8 cal/(deg mole) has been estimated.[5,13] The maximum possible entropy loss due to a complete freezing of the internal rotations can be estimated at ≃17 eu. The observed negative entropy of activation of ≃12.3 eu. then implies a reasonably tight structure for a four-center transition state.

(c) Experiments with deuterium-labeled triisobutylaluminum show[11] that the deuterium in the β position of the isobutyl group is transferred to the aluminum atom upon elimination of isobutylene.

A very rough estimate of the energy (E_{pol}) involved in forming the polar one- and three-electron bonds in the four-center transition state can be derived looking at the bond dissociation energies (D) in the ground-state molecule.[5b]

$$E_{pol} \approx {}^1/_2[D(\text{C-H}) + D(\text{Al-C}) - D(\text{C-C}_\pi)] \approx$$
$$(91^{14} + 66^{15} - 60^{5b})/2 \approx 48.5 \text{ kcal/mole}$$

The observed activation energy is only 26.6 kcal/mole which would imply an energy of interaction between the $Al^{+\delta}$ and $H^{-\delta}$ ends of the four-ring of ~22 kcal/mole. This value compares to end interactions of the order of 10–15 kcal[5b] for similar elimination reactions in organic molecules involving a loose four-center transition-state structure. The higher interaction energy between the polar ends in the case of the trialkylaluminum is again consistent with a relatively tight transition-state complex.

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[11] Kinetic studies with β-D-triisobutylaluminum are in progress, and they show the expected kinetic hydrogen deuterium isotope effect.

[12] Assuming a transmission coefficient of unity.

[13] While the C–H bond contributes only about 0.5 eu in rotational entropy, the restriction of the C–C– bond rotor would amount to 3.5 eu and that of the Al–C bond is estimated at 4 eu.[5b]

[14] (a) S. W. Benson, "Methods for Estimation of Thermochemical Data and Rate Parameters," John Wiley & Sons, Inc., New York, N. Y., 1968; (b) J. A. Kerr, *Chem. Rev.*, **66**, 496 (1966).

[15] H. A. Skinner, *Advan. Organometal. Chem.*, **2**, 49 (1964).

Based on the thermodynamic data discussed in the Appendix, the heat of the reaction a (compare Scheme I) has been estimated at $\Delta H \simeq 21$ kcal/mole. When combined with the measured activation energy E_a for the olefin elimination reaction, this yields $E_{-a} \approx 6 \pm 3$ kcal/mole for the addition of isobutylene to the *monomeric* HAl(*i*-Bu)$_2$. The trimeric hydride would require a larger activation energy, which is evidenced by the fact that [(*i*-Bu)$_2$AlH]$_3$ has practically no dipole moment[16] despite the high polarity of the Al–H bond.

The activation energies for the elimination–addition reactions obtained from this study are consistent with kinetic data reported for comparable systems. The elimination of ethylene from triethylaluminum appears to involve about 30 kcal/mole of activation energy[6] compared to 26.6 kcal/mole for the elimination of isobutylene from Al(*i*-Bu)$_3$. In this context it is interesting to note that only very little olefin addition to the Al–C bond has been observed in this study. The relative rates for olefin elimination (R_c) *vs.* olefin addition (R_d) for EtAl(*i*-Bu)$_2$ (compare Scheme I) can be estimated from the data in Table I at $\gtrsim 50$. It is then possible to calculate a lower limit for the activation energy E_d for the addition of ethylene to EtAl (*i*-Bu)$_2$.

$$R_c/R_d \approx 50 \approx \frac{k_c}{k_d(\text{ethylene})} = \frac{10^{11.2}10^{-26.6/\theta}}{10^{7.5}10^{-E_d/\theta}10^{-2.3}} = 10^{6}10^{-26.6+E_d/\theta}$$

For 140° ($\theta = 1.89$) this results in $E_d \gtrsim 18.5$ kcal/mole in good agreement with the comparable value of ~20 kcal/mole reported for the addition of 1-hexene to Al(Et)$_3$.

Appendix

Thermodynamic Data for Trialkylaluminum Compounds and Their Derivatives. Recently Pawlenko[17] reported what appears to be the most reliable values for ΔH_c(l) and ΔH_f(l) of the ethyl-, *n*-propyl-, *n*-butyl-, and isobutylaluminum hydrides and trialkylaluminum compounds.

Skinner[15] reports for the Al(CH$_3$)$_3$ monomer $\Delta H_f°(\text{g}) = -21.0 \pm 2$ kcal/mole and for Al(C$_2$H$_5$)$_3$ $\Delta H_f°(\text{g}) = -19 \pm 5$ kcal/mole. Fic[18] measured a value of -23.9 ± 1.4 kcal/mole for the $\Delta H_f°$(g) of the Al(CH$_3$)$_3$ monomer.

Shaulov, *et al.*,[19] reported data for $\Delta H_c°$(l) and $\Delta H_f°$(l) for Al(C$_2$H$_5$)$_3$, HAl(C$_2$H$_5$)$_2$, Al(*i*-Bu)$_3$, HAl(*i*-Bu)$_2$, etc. They differ by large amounts from the data of Pawlenko.[17]

The following heats of vaporization (in kcal/mole) have been reported: [Al(CH$_3$)$_3$]$_2$, 10.01[20] ± 0.05; Al(C$_2$H$_5$)$_3$, (14.4)[19,21] 17.5 ± 0.5;[15] HAl(C$_2$H$_5$)$_2$, (11.2);[19,21] Al(*i*-Bu)$_3$, 8.9;[21] HAl(*i*-Bu)$_2$, (8.5).[19,21]

Using the liquid-phase data of Pawlenko,[17] one can derive the following $\Delta H_f°$(g) values for monomeric Al(C$_2$H$_5$)$_3$: Al(C$_2$H$_5$)$_3$ = $-56.6 + 17.5$[15] = -39.1 ± 2 kcal/mole. This value is to be compared to the less reliable -19 ± 5 kcal/mole quoted in ref 15. These data are used to derive a value of ~21 kcal/mole for ΔH_a, the heat of the gas-phase reaction

$$\underset{(-75.0)}{\text{Al}(i\text{-Bu})_3} \overset{\text{a}}{\rightleftharpoons} \underset{(-49.8)}{\text{HAl}(i\text{-Bu})_2} + \underset{(-4.04)}{\text{isobutylene}}$$

Values for the $\Delta H_f°$ are indicated in parentheses. These data are arrived at by generating intrinsic "group values", using the concept of additivity of increment properties.[14] The observed values for the heats of formation of Al(CH$_3$)$_3$ and Al(C$_2$H$_5$)$_3$ yield the "group values": *Al*(C$_3$) = 6.3 kcal/mole and *C*-(Al)(C)(H$_2$) = −5.0 kcal/mole.

Assuming that *C*(Al)(H$_3$) equals *C*(C)(H$_3$) = −10.08 kcal/mole,[14] a value of −75.0 kcal is calculated for $\Delta H_f°$(g) of Al(*i*-Bu)$_3$. Compared with Pawlenko's value for the liquid phase (−92.8 kcal), this yields 17.8 kcal/mole for the heat of vaporization of Al(*i*-Bu)$_3$. This is a very reasonable result and compares well with similar data observed for metal alkyl series.[15]

In order to calculate $\Delta H_f°$(g) for the monomeric diisobutylaluminum hydride, a value for the group *Al*(H)(C$_2$) must be generated. A value of +4.3 kcal/mole is estimated based on the data given below (in kcal/mole): *Sn*(C$_4$), 36.2; *Sn*(C$_3$)(H), 34.8; Al(C)$_3$, 6.3, Al(H)(C$_2$), 4.3; *C*(C$_4$), 0.5; *C*(C$_3$)(H), −1.9. This then yields $\Delta H_f°$(g) for HAl(*i*-Bu)$_2$ = −49.8. Pawlenko[17] reports a value of $\Delta H_f°$(l) for [HAl(*i*-Bu)$_2$]$_3$ of 3 × −69.1 kcal/mole. Taking ΔH_v as 8.5 kcal,[19,21] this yields HAl(*i*-Bu)$_2$ = −66.1 kcal/mole, neglecting trimerization. This would result in a heat of trimerization per Al–H bond of ~16.4 kcal, which compares with the reported estimate[16] of 15 kcal/mole.

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(21) Parentheses indicate that it is not clear whether the data refer to the monomeric or oligomeric species.