

BIBLIOGRAPHY

- [1] E. Heilbronner, Israel J. of Chem., in print.
 [2] P. Bischof, J. A. Hashmall, E. Heilbronner & V. Hornung, *Helv.* 52, 1745 (1969).
 [3] R. Hoffmann, E. Heilbronner & R. Gleiter, *J. Amer. chem. Soc.* 92, 706 (1970).
 [4] R. Hoffmann, *Accounts of chem. Research* 4, 1 (1971).
 [5] E. Heilbronner, XXIIIrd International Congress of Pure and Applied Chemistry, Vol. 7, Butterworth, London 1971, p. 9.
 [6] H. D. Martin & D. Forster, *Angew. Chem.* 84, 65 (1972).
 [7] T. Koopmans, *Physica* 1, 104 (1933).
 [8] P. Bischof, J. A. Hashmall, E. Heilbronner & V. Hornung, *Tetrahedron Letters* 1970, 1033; P. Bischof, R. Gleiter, E. Heilbronner, V. Hornung & G. Schröder, *Helv.* 53, 1645 (1970); E. Haselbach, E. Heilbronner & G. Schröder, *Helv.* 54, 153 (1971).
 [9] R. W. Hoffmann, R. Schüttler, W. Schäfer & A. Schweig, *Angew. Chem.*, 84, 533 (1972).
 [10] R. W. Kiser, 'Tables of Ionization Potentials', US Atomic Energy Commission, Washington D.C., 1960; W. J. Wedenejew, L. W. Gurwitsch, W. H. Kondratjew, W. A. Madwedew & E. L. Frankewitsch, 'Energien chemischer Bindungen, Ionisationspotentiale und Elektronenaffinitäten', Deutscher Verlag für Grundstoffindustrie, Leipzig 1971.
 [11] W. Bremser, H. T. Grunder, E. Heilbronner & E. Vogel, *Helv.* 50, 84 (1967).
 [12] D. Chadwick, D. C. Frost & L. Weiler, *J. Amer. chem. Soc.* 93, 4962 (1971).
 [13] D. W. Turner, C. Baker, A. D. Baker & C. R. Brundle, 'Molecular Photoelectron Spectroscopy', Wiley-Interscience, London 1971; D. Chadwick, D. C. Frost & L. Weiler, *J. Amer. chem. Soc.* 93, 4320 (1971).
 [14] H. Tanida, T. Tsuji & T. Irie, *J. Amer. chem. Soc.* 89, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock & J. Haywood-Farmer, *ibid.* 89, 1954 (1967); R. Hoffmann, *Tetrahedron Letters* 1965, 3819.
 [15] P. Bischof, E. Heilbronner, H. Prinzbach & H. D. Martin, *Helv.* 54, 1072 (1971).
 [16] A. D. Walsh, *Nature* 159, 167, 712 (1947); *Trans. Farad. Soc.* 45, 179 (1949).

**148. Reactions of Group 3 Metal Alkyls in the Gas Phase.
 Part 10¹): The Addition of Olefins to the Monomeric Diisobutyl-
 aluminiumhydride**

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(22 IV 72)

Summary. The relative rate constants for adding ethylene (k_1), propylene (k_2) and 2-methylbut-1-ene (k_3) to gaseous diisobutylaluminium hydride produced *in situ* from Al^tBu_3 have been measured in the temperature range 104–169° in the presence of an excess of equimolar olefin mixtures. The following temperature dependences of the relative rate constants have been obtained:

$$\log(k_1/k_2) = 0.6 - 0.8/4.58 \times 10^{-3} T(^{\circ}\text{K})$$

$$\log(k_1/k_3) = 1.2 - 2.2/4.58 \times 10^{-3} T(^{\circ}\text{K})$$

Two compensating factors determine the rate of addition of olefins to Al-H and Al-C bonds: (a) the steric effect, reflected in the differences in the preexponential factors and (b) the polar effects, reflected in differences in the activation energies.

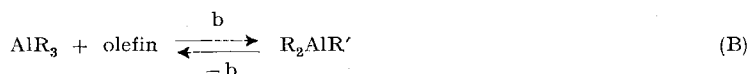
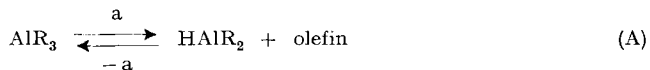
In the addition of olefins to $\text{R}_2\text{Al-H}$ bonds in contrast to $\text{R}_2\text{Al-C}$ bonds, the steric effect (a) does not always overrule the opposing energy effect. At temperatures below 125° e.g., isobutene

¹) Part 9: K. W. Egger, *J. chem. Soc. Faraday* 1, 68, 1017 (1972).

adds slightly faster to Al^iBu_2 than ethylene. These results are in perfect agreement with expectations based on a reaction mechanism involving a tight asymmetric quadrupolar 4-centre transition state similar to that postulated earlier for the addition of olefins to Al-C bonds.

Introduction. – A series of thermochemical kinetic studies involving aluminium trialkyls and olefins in the gas phase have been carried out in this laboratory in the last two years in an attempt to arrive at a reasonable interpretation of the detailed reaction mechanisms.

Olefin oligomerizations, catalyzed by gaseous or liquid AlR_3 species (where R stands for an alkyl group) can be represented with the following general reaction mechanism:

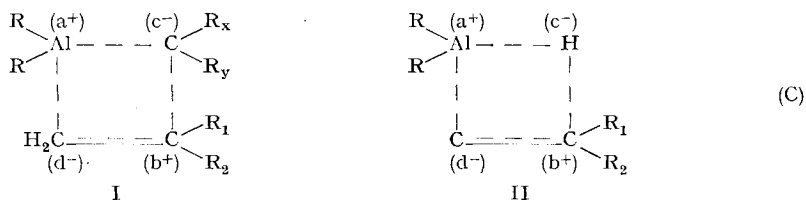


For reaction system A, which is an integral part of the overall oligomerization mechanism, activation parameters for the unimolecular eliminations of olefins from the following trialkylaluminium compounds have been obtained: $(\text{CH}_3)_2\text{Al}^n\text{Bu}$ [1], AlEt_3 [2], Al^iBu_3 [3] and β -deuterio- Al^iBu_3 [4].

For the back reaction, k_{-a} , there are no direct measurements in gas phase available to date. Considerations of the equilibrium positions in systems of the type A lead to the conclusion, that the addition of olefins to Al-H-bonds is very fast indeed, with activation energies ranging between less than 5 to 7.6 kcal mol⁻¹ [1]–[4]. It is then evident, that a direct study of the addition rate under static reaction conditions is not possible.

A study of the competitive rates of addition should however reveal the controlling factors for the backreaction (–a) even though the absolute rate constants are inaccessible.

The kinetics of the addition of olefins to AlR_3 species (k_b) in the gas phase have been studied for the systems $\text{AlEt}_3 + \text{C}_2\text{H}_4$ [5], $\text{AlMe}_3 + \text{C}_2\text{H}_4$ [6] and $\text{AlMe}_3 + \text{C}_3\text{H}_6$ [7]. These data have been discussed [5]–[7] in terms of a relatively tight four-centre asymmetric quadrupolar transition state. Differences in steric hindrance to the addition of the various olefins were found to overrule the extra stabilization resulting from the interaction of the alkyl substituents with the polar centres in the transition state, depicted below as (I).



whereby

$$(a^+ + b^+) = 1$$

$$(c^- + d^-) = 1$$

It was then interesting to check, whether the same principles are applicable for the addition of olefins to Al-H bonds, involving a transition state of the type II.

Experimental Part

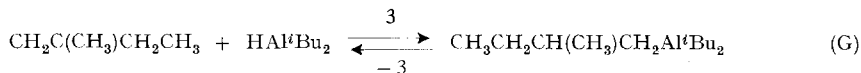
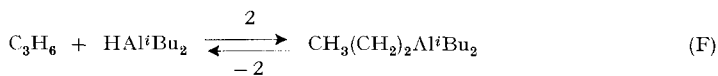
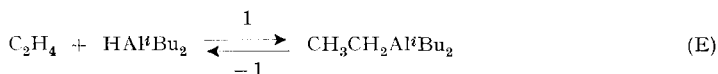
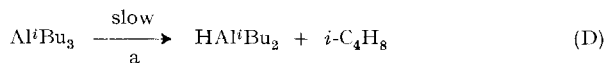
Apparatus and Procedures. – The general procedures and the static reaction system used in these studies have been described earlier [3]. Two stainless-steel reaction vessels of 802 and 1750 ml, respectively, coated with "Teflon" were used. An experiment was started by injecting a liquid aliquot of Al^tBu_3 into an evaporation chamber above the reaction vessel immediately followed by sweeping in an excess of an equimolar mixture of ethylene, propene and 2-methyl-but-1-ene. In a few experiments (marked with an asterisk in Table 1), a prepressure of the olefin mixture was established in the reaction vessel prior to the addition of the aluminium trialkyl. An experiment was stopped, by condensing the reaction products at liquid nitrogen temperature, followed by quantitatively distilling the olefin fraction from the aluminium alkyl residue. Gases, non condensable at liquid nitrogen temperature were continuously transferred and collected, but were always negligibly small.

The retained aluminium trialkyl fraction, containing the alkyl groups $>\text{Al}-\text{CH}_2\text{CH}_3$, $>\text{Al}-\text{CH}_2\text{CH}_2\text{CH}_3$, $>\text{Al}-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and $>\text{Al}-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$, was hydrolyzed with excess water and the gaseous hydrolyses products (ethane, propane, isobutane, 2-methylbutane) were quantitatively transferred and measured in a gas buret and analyzed by gas-liquid partition chromatography (g.l.p.c.).

Materials. – Ethylene was of customary high purity and was provided by the Fawley-works of Monsanto in England. Propene and 2-methylbut-1-ene were obtained from Fluka Chemicals Corp., Buchs, Switzerland, and were found (after redistillation) to be 99.9% and 99.8% pure, respectively. Triisobutylaluminium was obtained from the Schering AG & Co in Bergkamen Germany.

Analyses. – Gas chromatographic analyses were carried out on a *F+M* instrument using thermal conductivity detectors. Quantitative separation of the hydrolyses products and of the olefin mixtures was achieved with a 30 feet $1/4$ inch column of 20% BMEA on Chromosorb W, operated at 0° with a helium flow rate of 60 ml/min. The following relative response factors, reproducible within 0.5%, have been obtained, using a variety of standard samples of the various components: ethane 1.467, ethylene 1.533, propane 1.141, propene 1.225, butanes 0.989, butenes 1.000, 2-methylbutane 0.942, 2-methylbut-1-ene 0.852. In most experiments repetitive analyses were carried out and the observed product ratios usually agreed within a few percent, with an expected trend towards larger uncertainties with smaller overall conversions. A calibrated gas buret served for measuring the gases.

Results. – The relative rates for the competitive addition of ethylene, propylene and 2-methylbut-1-ene to diisobutylaluminium hydride ($= {}^t\text{Bu}_2\text{AlH}$) were studied in the gas phase at temperatures from 375 to 442°K. The ${}^t\text{Bu}_2\text{AlH}$ was produced *in situ* in the reaction vessel from Al^tBu_3 in presence of an excess of the olefin mixture.



k_1 , k_2 and k_3 are fast compared to k_a , and the concentrations of ethylene, propylene and 2-methylbut-1-ene are initially the same and at any time much larger than the amount of isobutene, set free in reaction D.

The results of the kinetic experiments are summarized in Table 1.

It is seen, that the ratio of [olefin]/[AlⁱBu₃] varies from 32 to 4 for each of the three olefins and was about 10 for most experiments. The conversion with respect

Table 1. *The Relative Rate of Addition of Ethylene, Propene and 2-Methylbut-1-ene to Diisobutylaluminium Hydride^{a)}*

Temp. °K	Vessel b)	Time min	Starting Materials ^{c)}		P _{tot} ^{d)} Torr	Hydrolysis Products ^{e)}		Con- version ^{f)} in %	-log k _a		
			[Al ⁱ Bu ₃] ₀ mM/l	[Olefin] ₀ mM/l		C ₂ H ₆ C ₃ H ₈	C ₂ H ₆ C ₅ H ₁₂		obs.	calc. h)	
				Mix- ture ^{g)}							
376.9	2	40	0.0898	a	8.86	211.8	1.38	0.80	–	–	–
377.1	2	70	0.188	a	4.88	121.8	1.32	0.58	6.22	4.82	4.20
377.2	2	81	0.137	a	5.20	127	1.27	0.61	11.12	4.61	4.16
377.2	2	90	0.130	a	6.01	145.7	1.17 ^{k)}	0.43 ^{k)}	9.72	4.72	4.20
377.7	2	20	0.172	a	5.75	142.3	1.46	0.94	4.49	4.24	4.13
381.9	2	120	0.0867	a	2.81	70.5	1.36	0.80	–	–	–
390.3	1	64	0.203	b ⁱ⁾	5.53	145	2.73 ^{k)}	5.63 ^{k)} 1)	44.1	3.82	3.64
394.2	1	31	0.269	c	11.73	295	1.64	0.990 ^{k)}	33.5	3.66	3.50
394.4	1	20	0.189	c	4.91	127	1.57	0.903	20	3.73	3.50
395.3	1	30	0.250	c	7.05	184	1.51	1.03 ^{k)}	22.1	3.86	3.46
397.3	1	60	0.37	c	15.22	366	1.51	1.64 ^{k)}	64.3	3.54	3.38
397.5	1	45	0.45	c	5.99	167	1.45	1.31 ^{k)}	43.7	3.67	3.37
433.8	2	3.2	0.299	C ₂ H ₄	16.90	470.8	–	–	54.4	2.12	2.15
434.9	2	0.83	0.213	a	12.15	340.5	1.46	1.17	22.7	2.29	2.11
435.4	2	0.933	0.336	d	7.13	207.3	1.61	1.16	19.64	2.41	2.10
435.4	2	2.0	0.261	d	6.84	199.4	1.70	1.45 ^{k)}	24.67	2.63	2.10
436.2	2	1.16	0.383	a	10.95	311.4	1.43	1.22	23.24	2.42	2.08
436.4	2	3.45	0.263	e	10.86	309.1	1.63	2.36 ^{k)}	50.63	2.48	2.07
438.9	2*	3.516	0.197	e	7.07	204	1.73	2.90 ^{k)}	34	2.71	2.00
442	2*	7.0	0.270	e	8.28	242	2.12 ^{k)}	7.57 ^{k)}	38.1	2.94	1.86
475	2	2.16	0.768	d	8.73	288.2	9.14 ^{k)}	5.9 ^{k)}	36.6	2.46	0.96
474.1	2*	3.63	0.188	d	8.10	249.9	10.7 ^{k)}	95 ^{k)}	64.5	2.32	0.98

a) Formed *in situ* from AlⁱBu₃ via elimination of isobutene.

b) 1 and 2 refer to "Teflon" coated reaction vessels of 1750 and 802 ml, respectively. In the experiments, marked with an asterisk, a prepressure (~50 Torr) of the olefin mixture was established in the reaction vessel prior to the addition of the aluminium alkyls.

c) Starting concentrations derived from the amount of hydrolysis products (AlⁱBu₃) and initial pressure measurements (olefin).

d) Total initial pressure.

e) Consisting of ethane, propane, isobutane and 2-methylpentane.

f) Apparent conversion based on the relative amounts of hydrolysis products and relating to "total" conversion, i.e. the sum of the alkyl-groups.

g) Five independently prepared equimolar mixtures of ethylene, propylene and 2-methylbut-1-ene have been used. The g.l.p.c. analysis of the mixtures showed ratios deviating by no more than two percent from 1.00.

h) On the basis of earlier work on the system AlⁱBu₃ + C₂H₄, Ref. [3].

i) 2-methylhex-1-ene used instead of 2-methyl-pent-1-ene.

to the total of the aluminium-alkyl groups present, ranges from 1.5 to 21 percent for *each* of the three olefins.

Based on the assumption, that the backreactions – 1, – 2 and – 3 can be neglected, the relative amounts of hydrolysis products would directly relate to the relative rates of addition, $k_1/k_2 = [C_2H_6]/[C_3H_8]$ and $k_1/k_3 = [C_2H_6]/[C_5H_{12}]$. As was to be expected from our earlier work and the data in Table 2 show, this assumption is strictly valid only for relatively mild reaction conditions, i.e. low conversions and temperatures. The rate of the backreactions, i.e. the elimination of olefins from the trialkylaluminium species decreases in the series $R_2Al^iBu > R_2Al^nPr > R_2AlEt$. The corresponding kinetic parameters obtained from independent studies are summarized in Table 2.

Table 2. *Activation Parameters for Olefin Eliminations from Group 3 Metal Alkyls in the Gas Phase:*
 $M(alkyl)_3 \rightarrow HM(alkyl)_2 + olefin$

Compound ^{a)}	$\log A^b$	$\log A^{*b}$	E_a (kcal mol ⁻¹)	Ref.
Al ⁱ Bu ₃	11.2 ± 0.3	11.2 ± 0.3	26.6 ± 0.7	[3]
(Me) ₂ Al ⁿ Bu	10.9 ± 0.2	10.6 ± 0.2	27.8 ± 0.4	[1]
AlEt ₃	10.9 ± 0.1	10.5 ± 0.1	30.1 ± 0.3	[2]
Ga ⁱ Bu ₃	11.6 ± 0.3	11.6 ± 0.3	30.4 ± 0.6	[8]
B ⁱ Bu ₃	11.8 ± 0.5	11.8 ± 0.5	30.4 ± 1.0	[9]

^{a)} Me, Et and Bu stand for methyl-, ethyl- and butyl groups, *n* and *i* for normal and iso structures, respectively.

^{b)} *A* in units of s⁻¹ and *A*^{*} represents path degeneracy corrected preexponential factors.

Based on the data listed in Table II it can be concluded, that aluminium-propyl and aluminium-ethyl groups should be stable at the reaction conditions used. This is indeed the case. The ratio $[C_2H_6]/[C_3H_8]$ observed in the hydrolysis products, i.e. k_1/k_2 is essentially constant at a given temperature. Only with very large conversions and at the highest temperature, consistently larger ratios of k_1/k_2 are obtained, indicating a significant contribution from the backreaction – 2.

Experiments were also carried out at 475 °K, a temperature which is clearly above the limit of the temperature range feasible for kinetic studies of this type on this system. The results of two of these experiments are incorporated in Table 1. The data show, that the backreactions – 2 and – 3 are so fast, that the system is kinetically ill defined, approaching an equilibrium state in which the thermally most stable aluminium-ethyl groups eventually persist to the practical exclusion of isobutyl-, propyl- and 2-methylbutyl groups.

The temperature dependence of the k_1/k_2 ratios is best represented by $\log(k_1/k_2) = 0.6-0.8/\Theta$, where Θ equals 2.303 RT in kcal mol⁻¹. Taking the limiting extremes in the *Arrhenius* plot the data could also be represented by $\log(k_1/k_2) = 0.2-0.0/\Theta$ or $1.0-1.6/\Theta$.

Considering the experimental error limits and the fact that the feasible temperature range was limited to about 60° the uncertainties are of the expected order of magnitude.

In contrast to the ratios k_1/k_2 , the data for k_1/k_3 show a pronounced dependence on the overall conversions reached in the system. At the lowest temperature block of $\sim 377^\circ\text{K}$ the ratio $[\text{C}_2\text{H}_6]/[\text{C}_5\text{H}_{12}] = k_1/k_3$ appears to be constant within experimental error limits and an average value of 0.75 ± 0.15 can be derived. At the 395°K temperature block the values increase consistently with increasing conversion, due to the back-elimination of 2-methylbut-1-ene ($=k_{-3}$) from the corresponding aluminium-isopentyl group. A value of 0.9 can be extrapolated from these data. Despite the very short reaction times used for temperatures of about 438° the values of k_1/k_3 increase steadily with reaction time, i.e. conversion. Nevertheless it is apparent, that at these temperatures k_1/k_3 cannot be very different from 1.10.

Based on these data, the following temperature dependence of k_1/k_3 is derived:

$$\log(k_1/k_3) = 1.2 - 2.2/\Theta$$

with the limiting values

$$\log(k_1/k_3) = 0.7 - 1.2/\Theta \quad \text{and} \quad = 1.9 - 3.7/\Theta.$$

Equations (1) and (2) combined yield for k_2/k_3 :

$$\log(k_2/k_3) = 0.6 - 1.4/\Theta. \quad (3)$$

In the last two columns of Table 1 rate constants (k_a) for the elimination of isobutene from Al^tBu_3 are given. Considering that step (a) is by far the slowest step in the overall reaction system it should be possible to calculate rate constants for k_a from the total conversions observed, provided the backreaction ($-a$) can be neglected. For small conversions this should be the case. Data for k_a resulting from this work are listed in the second to last column in Table 1, and are compared with values calculated on the basis of our earlier study on the system $\text{Al}^t\text{Bu}_3 + \text{ethylene}$ [3].

Discussion. – Activation energies (in kcal mol^{-1}) for adding ethylene (< 5), propene (5.2) and 2-methylbut-1-ene (6.1) to $\text{R}_2\text{Al-H}$ bonds in the gas phase can be estimated [1] on the basis of the equilibrium positions in reactions (E), (F) and (G) (derived from thermochemical data) when combined with the observed rate data for the backreaction. The competitive rate studies reported here substantiate essentially the assumption of only small differences in activation parameters between the olefins. The maximum ratio in relative rates of addition for any pair of the three olefins was observed to be about 1.8.

In view of the overall mechanism proposed for these reactions [1]–[7] it is particularly interesting to note, that in contrast to the addition to $\text{R}_2\text{Al-C}$ bonds, 2-methylbut-1-ene adds faster to HAL^tBu_2 than propene and, below 120° , even faster than ethylene.

This is perfectly in line with expectation based on the concept of a relatively tight, quadrupolar, 4-centre transition state involved in these reactions [7], whereby activation energy and entropy work in a compensating manner.

The analysis of the rate expressions (1), (2) and (3) suggests essentially incremental behaviour of both, activation energy and entropy with increasing alkyl substitution

on the olefin moiety. The A-factor is lowered by each additional alkyl group, bonded to the 2-carbon atom in 1-olefins, by about $10^{0.6}$, which is partly due to the increased steric hindrance in the tight transition state. In compensation of this effect the activation energy is lowered with each alkyl group by about 1 kcal mol⁻¹, resulting from a stabilization of the positively induced charge on the olefinic 2-carbon atom in the transition state (compare equation B).

In the detailed analysis of the data we have so far neglected any effect of path degeneracy onto the relative rates of reaction. Depending on the detailed reaction mechanism involved, a path degeneracy of 2, favoring ethylene compared to propene or 2-methylbut-1-ene should be taken into account. For the postulated tight quadrupolar 4-centre transition state the intrinsically comparable rate data would then yield

$$\log(k_1'/k_2) = 0.3 - 0.8/\theta \quad (5)$$

$$\log(k_1'/k_3) = 0.9 - 2.2/\theta \quad (6)$$

It is reasonable that the entropical difference between the ethylene and propene addition (1.4 cal/grade/mol) is only about half that observed between propene and 2-methylbut-1-ene (2.8 cal/grade/mol). These results are perfectly in line with observations from the addition of olefins to R₂Al-C bonds [5]–[7]. In the case of Al(Me)₃ the relative rate of ethylene versus propene addition was observed [6] [7], to be

$$\log(k_{\text{ethylene}}/k_{\text{propene}}) = 1.4 - 2.15/\theta \quad (4)$$

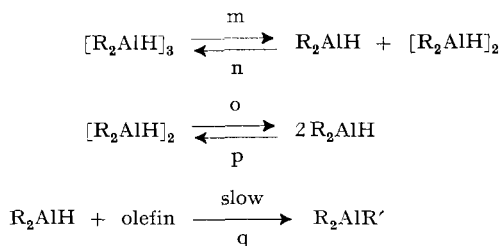
whereby at the reaction temperatures used, the entropy term always overruled the opposing energy effect of alkyl substituents.

As was to be expected, the additional loss of entropy when substituted olefins are added to R₂Al-H bonds is with 2.5 cal/grade/mol per methyl group much smaller than that observed for addition to R₂Al-CH₃ bonds (~7 cal/grade/mol). Even larger differences would have to be expected and are indeed apparent for the addition of olefins to larger R₂Al-alkyl groups.

The results of this work then substantiate the assumption of relatively tight quadrupolar 4-centre transition states operative in additions of olefins to both R₂Al-H and R₂Al-C bonds [7].

There is no apparent reason to assume the formation of [R₂AlH × olefin]-complexes. [AlR₃ × olefin]-complexes are then probably not rate determining intermediates in the addition of olefins to AlR₃ as has been suggested [6] earlier.

In conclusion it is recalled, that in liquid phase R₂AlH exists predominantly in the trimeric form. The rate of addition of olefins to dialkylhydride in liquid phase has been reported to follow kinetics with between 0.37 [10] and 0.5 [11] order dependence in [R₂AlH] and first order dependence in [olefin] [10] [11]. A mechanism involving the rate determining addition of the olefin only to the monomeric form of the hydride has been suggested [10] [11] in perfect agreement with our concept of a quadrupolar 4-centre transition state. Also in line with the gas phase data, activation energies of between 3 and 10 kcal mol⁻¹ for the addition in liquid phase (k_q) can be estimated from the data in references 10–12. The reaction system can essentially be visualized as shown below:



whereby the backreaction ($-q$) can be neglected and k_m , k_n , k_o and $k_p \gg k_q$.

I thank Dr. *A. T. Cocks* for stimulating discussions.

BIBLIOGRAPHY

- [1] *K. W. Egger & A. T. Cocks*, *Trans. Faraday Soc.* **67**, 2629 (1971).
- [2] *A. T. Cocks & K. W. Egger*, *J. chem. Soc. Faraday I*, **68**, 423 (1972).
- [3] *K. W. Egger*, *J. Amer. chem. Soc.* **91**, 2876 (1969).
- [4] *K. W. Egger*, *Int. J. chem. Kinetics* **1**, 459 (1969).
- [5] *K. W. Egger*, *Trans. Faraday Soc.* **67**, 2638 (1971).
- [6] *K. W. Egger & A. T. Cocks*, *J. Amer. chem. Soc.* **94**, 1810 (1972).
- [7] *K. W. Egger*, *J. chem. Soc. Faraday I*, **68**, 1017 (1972).
- [8] *K. W. Egger*, *J. chem. Soc. A*, 3603 (1971).
- [9] *A. T. Cocks & K. W. Egger*, *J. chem. Soc. A*, 3606 (1971).
- [10] *J. J. Eisch & S. G. Rhee*, *J. Organometal. Chem.* **31**, C 49 (1971).
- [11] *J. N. Hay, G. R. Jones & J. C. Robb*, *J. Organometal. Chem.* **15**, 295 (1968).
- [12] *F. Asinger, B. Fell & F. Theissen*, *Chem. Ber.* **100**, 837 (1967).

149. Untersuchungen der Symmetrieverhältnisse in äquatorial koordinierten 2:1-Arylazo-Co^{III}-Komplexen mit Hilfe der Protonenresonanz

von **G. Schetty** und **E. Steiner**

Zentrale Forschung der *CIBA-GEIGY AG*, Basel

Herrn Prof. Dr. *E. Ziegler*, Universität Graz, zum 60. Geburtstag gewidmet

(3. III. 72)

Summary. The magnetic equivalence of ligand protons was examined with aid of NMR spectroscopy for a large number of 1:2 Co^{III}-complexes of tridentated azo dyestuffs forming a representative cross section of the whole class of substances. It was established by this investigation that ligands with a moderately polarised azo group have a particular inclination to form asymmetrical complexes in which the protons of the two ligands are not magnetically equivalent. On the other hand, ligands having a non-polarised or a strongly polarised azo group tend to form symmetrical complexes. In three cases both symmetrical and asymmetrical complexes were isolated. As in previous investigations [1], up to a total of 5 complexes were again observed, which indicates at least two causes governing the symmetry conditions. The phenomena described here could be explained with an alternative coordination of the two azo nitrogen atoms. On the basis of the NMR. results, however, preference is given to an exchange of the azo with the hydrazone form.