Appendix I

The rate of the photosensitized reaction, as obtained from eq 1–8 on the basis of conventional steady-state considerations, is given by

$$\frac{d[Co(CN)_5H_2O^{2-}]}{dt} = \frac{k_5[Co(CN)_6^{3-}]}{k_3 + k_4 + k_5[Co(CN)_6^{3-}] + k_6[Co(CN)_5H_2O^{2-}]} \times \frac{k_8}{k_7 + k_8}\frac{I}{V} = \Phi_R{}^A \frac{I}{V} \times \frac{k_5[Co(CN)_6^{3-}]}{k_3 + k_4 + k_5[Co(CN)_6^{3-}] + k_6[Co(CN)_5H_2O^{2-}]} \quad (11)$$

where I is the rate of light absorption (einsteins/minute), V is the volume (liters) of the irradiated solution, and $\Phi_A{}^R$ is the aquation efficiency of the triplet state of the complex. Since only a negligible per cent decomposition of the reagent complex was achieved in the sensitization experiments, $Co(CN)_6^{3-}$ can be considered as a constant parameter corresponding to the initial concentration value. Thus, the rate expression (eq 11) can be easily integrated to give

$$[Co(CN)_5H_2O^{2-}](k_3 + k_4 + k_5[Co(CN)_6^{3-}] + \frac{1}{2}k_6[Co(CN)_5H_2O^{2-}]) = \Phi_R{}^A \frac{I}{V}k_5[Co(CN)_6^{3-}]t \quad (12)$$

If eq 12 is first divided by $(k_3 + k_4)$ and then substitution with $K_q{}^r$ and $K_q{}^p$ is carried out according to eq 9, all the unknown parameters are eliminated. The resulting expression is

$$[Co(CN)_5H_2O^{2-}](1 + K_q{}^r[Co(CN)_6^{3-}] + \frac{1}{2}K_q{}^p[Co(CN)_5H_2O^{2-}]) = \Phi_R{}^A \frac{I}{V}K_q{}^r[Co(CN)_6^{3-}]t \quad (13)$$

Equation 13 may be rearranged to give

$$R = \frac{V}{I}[Co(CN)_5H_2O^{2-}] \times \frac{1 + K_q{}^r[Co(CN)_6^{3-}] + {}^1/_2K_q{}^p[Co(CN)_5H_2O^{2-}]}{K_q{}^r[Co(CN)_6^{3-}]} = \Phi_R{}^A t \quad (10)$$

Reactions of Group III Metal Alkyls in the Gas Phase. VI. The Addition of Ethylene to Trimethylaluminum

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Abstract: The gas-phase thermal reactions of monomeric trimethylaluminum with excess ethylene have been studied in the temperature range 455 to 549°K. The initial ethylene pressures were varied between 312 and 603 Torr (41.6–80.4 kN m^{-2}) and the ratio of ethylene to trimethylaluminum was in the range 7–50. The primary reaction involved the addition of ethylene to the aluminum–methyl bond followed by the fast elimination of propene and subsequent addition of ethylene to the dimethylaluminum hydride to yield propene and ethyldimethylaluminum ($EtAl(Me)_2$) in equal amounts. A secondary reaction of ethylene with $EtAl(Me)_2$ to yield but-1-ene did not significantly affect the kinetic analysis under the conditions employed. The rate constant k_1 (l. mol^{-1} sec^{-1}) for the addition of ethylene to the aluminum–methyl bond, corrected for path degeneracy, is given by the Arrhenius relationship: $\log k_1 = 7.27 \pm 0.20 - (22.50 \pm 0.45)/\theta$, where $\theta = 2.303RT$, with R in kilocalories per mole and T in degrees Kelvin. The results of this work and earlier data for similar systems cannot be rationalized with a simple four-center one-step process involving a quadrupolar four-center transition state, as has generally been assumed. It is suggested that olefin–aluminum alkyl complexes are formed in these reactions as intermediate products. The relevant thermodynamic data for these systems are reviewed.

In the course of our studies of the reactions of group III metal alkyls in the gas phase, we have shown that the kinetics of the elimination of olefins from triisobutylaluminum, ($Al(i\text{-}Bu)_3$),[2a] β-$DAl(i\text{-}Bu)_3$,[2b] $(CH_3)_2Al(n\text{-}C_4H_9)$,[3] $Ga(i\text{-}Bu)_3$,[4] $B(i\text{-}Bu)_3$,[5] and $Al(C_2H_5)_3$[6] are consistent with a concerted mechanism involving tight quadrupolar four-center transition states.

The effective charge separation, *i.e.*, the polar character of the transition state, is assumed to be much less pronounced than, *e.g.*, for the concerted four-center olefin eliminations from alkyl halides and related compounds,[7] involving loose transition states.

The very fast back-reactions, the addition of olefins to the corresponding monomeric dialkyl hydrides, require activation energies of only 4–6 kcal mol^{-1} for R_2AlH, 8.5 for R_2GaH, and ~12 for R_2BH.

In view of the catalytic potential for polymerizations of olefins, the addition of olefins to aluminum alkyls

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[1] Postdoctoral research associate.

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[3] K. W. Egger and A. T. Cocks, *Trans. Faraday Soc.*, **67**, 2629 (1971).

[4] K. W. Egger, *J. Chem. Soc. A.*, 3603 (1971).

[5] A. T. Cocks and K. W. Egger, *ibid.*, 3606 (1971).

[6] K. W. Egger and A. T. Cocks, *J. C. S. Faraday I*, in press.

[7] G. R. Haugen and S. W. Benson, *J. Amer. Chem. Soc.*, **87**, 4036 (1965); (b) *J. Phys. Chem.*, **70**, 3336 (1966); (c) *Int. J. Chem. Kinet.*, **2**, 235 (1970).

and related compounds in the liquid phase has obtained widespread attention since the early work of Ziegler and coworkers.[8,9]

Early liquid-phase data[10] indicated that $Al(CH_3)_3$ does not measurably add ethylene under experimental conditions that would lead to fast addition and oligomerization with higher aluminium alkyls. It was also reported that $Al(CH_3)_3$ in mixtures with $Al(C_2H_5)_3$ drastically reduced the reactivity of $Al(C_2H_5)_3$.

Recently, Hay and coworkers,[11a] in a reevaluation of their earlier data,[11b-e] using dilatometric methods to follow the addition of 1-octene to $Al(CH_3)_3$ and $Al(C_2H_5)_3$ in decahydronaphthalene solutions, reconciled the observed lower overall rates for $Al(CH_3)_3$, with both a higher heat of dissociation (by $\approx$4.4 kcal mol^{-1}) of the predominant dimeric structure and with a higher activation energy (by about 5 kcal mol^{-1}) of the process.

The observation that only the monomeric form of the aluminum alkyls is involved in the liquid-phase additions of olefins[11] has been substantiated recently by kinetic studies carried out in these laboratories on the dimerization of ethylene in the gas phase, catalyzed by gaseous monomeric $Al(C_2H_5)_3$.[12] It was emphasized that some well-known experimental observations, *e.g.*, the lowering of rates with increased substitution on ethylene or the drastic differences observed between aluminum and gallium alkyls, are inconsistent with the simple, concerted four-center mechanistics involving a quadrupolar type transition state, similar to that proposed for the addition of olefins to R_2AlH.[2-6]

It was suggested that the reaction involves aluminum alkyl–olefin complexes which would be unstable and not detectable by any conventional techniques. The observation of Hata[13] that the infrared absorptions of certain olefinic substituents in aluminum alkenyls are shifted compared to those of the parent molecules appears to substantiate the assumption of coordinate $[AlR_3 \cdot \text{olefin}]$ complexes.

Experimental Section

(A) **Apparatus and Procedures.** The apparatus and procedures used in this study closely resembled those described earlier.[2-6]

Initial experiments showed that in the range 455–549°K, $Al(Me)_3$ alone was thermally stable. In a typical run, gaseous $Al(CH_3)_3$ was expanded from a heated gas pipet into the static "Teflonized" reactor. After recording the pressure of the aluminum alkyl, excess ethylene was swept into the reaction cell and the total initial pressure was measured. The overall pressure loss during the reaction was recorded immediately preceding the quenching of the reaction products at the end of a run over liquid nitrogen. The observed total pressure change $(\Delta p)_{\text{tot}}$ relates to the total change in ethylene pressure as $2(\Delta p)_{\text{tot}} = \Delta(C_2H_4)_{\text{tot}}$.

Noncondensable gases were continuously transferred by an automated Toepler pump into a calibrated gas buret assembly. With the exception of three experiments, they amounted to less than 0.5% of the total pressure in the reaction vessel.

The condensed reaction products were separated into an *aluminum alkyl* fraction (retained at 240–250°K) and a *hydrocarbon fraction.* For several experiments, this latter fraction was subsequently separated at 137°K into a fraction containing most of the propylene and all the but-1-ene, and an ethylene fraction, containing some propylene. These fractions were then analyzed volumetrically and by gas–liquid partition chromatography (glpc), and the results are shown in column 7 of Table I. For most of the experiments the hydrocarbon fraction was not analyzed.

The *aluminum alkyl fraction* was carefully hydrolyzed with degassed water, taking care to avoid local overheating generated by the exothermic process.

Test hydrolyses with $Al(Me)_3$ showed that uncontrolled hydrolysis led to the formation of hydrogen, ethylene, and ethane in addition to methane. A measure of the amount of hydrogen produced was given by the excess pressure of hydrolysis gases at liquid nitrogen temperature above the vapor pressure of methane ($\sim$9 Torr or 1.2 kN m^{-2}).

The gaseous hydrolysis products of the aluminum alkyl fraction were separated at liquid nitrogen temperatures into a methane fraction and retained fraction, containing mainly ethane.

The methane fraction amounted to between 100 and 300 Torr (13.3–40 kN m^{-2}) at room temperature. The observed residual pressure upon condensation over liquid nitrogen usually ranged between 9 and 13 Torr. In 3 out of 29 experiments, the condensation pressures were 15, 18, and 18 Torr, respectively.

Both hydrolysis fractions were collected and measured in the gas buret and by glpc. The ethane fractions obtained from the experiments at $\sim$450 and 480°K contained between 1 and 6% propane and between 1 and 6% *n*-butane, while the experiments carried out at the higher temperatures yielded exclusively ethane as condensable hydrolyses product.

(B) **Gas Chromatography.** The same analytical equipment and procedures were used as previously described.[2-6] The relative response factors for ethane, propane, and butane were found to be 1.533, 1.225, and 1.000, respectively.

(C) **Materials. Trimethylaluminum** ($Al(Me)_3$) was obtained from K & K Laboratories, Plainview, N. Y., and was further purified by distillation at reduced pressures. Test hydrolyses resulted in >99.8% noncondensable gases (CH_4) and less than 0.2% ethane. The *ethylene* used was of customary high purity and was provided by the Fawley works of Monsanto, England.

Results

The addition of ethylene to trimethylaluminum in the gas phase has been studied in the presence of excess ethylene in the temperature range 452–549°K. The primary reaction products are propylene and mixed aluminum alkyls containing methyl and ethyl groups. Secondary reactions lead to the formation of 1-butene, and, particularly in the lower temperature range, very small amounts of 1-pentene are also observed.

Using the abbreviation al for $Al(CH_3)_2$, the detailed reaction scheme in excess ethylene is summarized below.

$$\mathrm{alCH_3 + C_2H_4} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{alC_3H_7} \tag{1}$$

$$\mathrm{alC_3H_7} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{alH + C_3H_6} \tag{2}$$

$$\mathrm{alH + C_2H_4} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{alC_2H_5} \tag{3}$$

$$\overline{\mathrm{alCH_3 + 2C_2H_4 \longrightarrow alC_2H_5 + C_3H_6}}$$

Step 1 is the rate-determining reaction step, as $k_2 \gg k_{-1}$ and $[C_2H_4]k_3 \gg [C_3H_8]k_{-2}$. Under the reaction conditions used, the half-life of alC_2H_5 is of the order of 1 min at 450°K and about 10 sec at 550°K. This implies that at the highest reaction temperatures near equilibrium is established for reaction step 3, whereby the concentration of the dimethylaluminum hydride is very small.

In the presence of excess ethylene, the reaction products alC_2H_5 and alC_3H_7 can act as dimerization catalysts,[12] leading to the secondary overall reaction.

$$\mathrm{alC_2H_5 + 2C_2H_4 \longrightarrow alC_2H_5 + but\text{-}1\text{-}ene} \tag{4}$$

$$\mathrm{alC_3H_7 + 2C_2H_4 \longrightarrow alC_2H_5 + pent\text{-}1\text{-}ene} \tag{5}$$

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[8] K. Ziegler in "Organometallic Chemistry," H. H. Zeiss, Ed., Reinhold, New York, N. Y., 1960, p 194.

[9] H. Lehmkuhl and K. Ziegler in "Methoden der Organische Chemie," E. Müller, Ed., G. Thieme, Stuttgart, 1970.

[10] K. Ziegler, *et al.*, *Justus Liebigs Ann. Chem.*, **629**, 132 (1960).

[11] (a) J. N. Hay, P. G. Hooper, and J. C. Robb, *J. Organometal. Chem.*, **28**, 193 (1971); (b) *ibid.*, **15**, 295 (1968); (c) *Trans. Faraday Soc.*, **65**, 1365 (1969); (d) *ibid.*, **66**, 2045 (1970); (e) *ibid.*, **66**, 2800 (1970).

[12] K. W. Egger, *ibid.*, **67**, 2638 (1971).

[13] G. Hata, *Chem. Commun.*, 7 (1968).

Table I. Kinetic Measurements for the Gas-Phase Addition of Ethylene to Trimethylaluminum

		Starting materials				
Temp, °K	Time, min	$[\mathrm{al(CH_3)}]_0$,[a,b] mol $\mathrm{l.^{-1}} \times 10^3$	$[\mathrm{C_2H_4}]_0$,[a] mol $\mathrm{l.^{-1}} \times 10^3$	Conversion,[c] %	$k \times 10^3$, l. $\mathrm{mol^{-1}\,sec^{-1}}$	$[\mathrm{1\text{-}C_4H_8}]_f$,[d] $M \times 10^3$
548.9	18.16	0.463	14.36	57.7	56.10	0.16
546.5	4	0.521	14.21	18.6	60.68	
	5	0.880	13.34	20.8	57.99	
	7	0.340	14.18	26.6	52.38	0.16
	10	0.350	16.80	15.5	62.63	0.07
546.4	7	1.210	15.02	31.3	61.21	
505.8	50	1.035	14.33	38.9	11.72	0.34
	50	0.813	17.66	45.1	11.57	0.13
505.4	71.75	0.331	12.45	37.4	8.825	0.13
505.3	20	0.284	13.13	13.9	9.531	
	49	0.249	13.69	39.0	12.12	
	69	0.747	16.42	50.1	10.49	0.20
503.5	33	0.231	9.94	18.1	10.21	
479.1	90	0.563	20.03	31.2	3.302	0.22
478.7	40	1.800	19.49	12.6	2.727	
	83	0.445	14.87	18.0	2.688	
	145	0.367	15.91	28.0	2.394	0.13
476.7	30	0.788	16.18	9.0	3.254	
	64	0.348	15.33	15.8	2.936	
455.8	198	0.538	19.57	11.7	1.220	
455.4	156	1.683	15.15	14.1	1.013	
455.2	105	2.314	16.67	9.01	0.9119	
454.9	163	0.808	16.47	10.0	0.6626	
454.6	225	0.523	14.02	19.3	1.141	
453.5	247	0.624	17.26	17.3	0.7462	0.11
453.2	139	0.997	17.79	9.46	0.6737	
452.6	337	0.893	10.07	16.84	0.9336	0.15
452.4	336	0.876	13.13	16.20	0.6747	0.06
452.2	882	0.711	13.77	37.90	0.6979	0.59

[a] al symbolizes $\mathrm{Al(CH_3)_2}$. 0 and f stand for initial and final concentrations, respectively. [b] Based on the results of the hydrolyses of the collected aluminum alkyl reaction products, setting $[\mathrm{al(CH_3)}]_0 = [\mathrm{al(CH_3)}]_f + [\mathrm{al(C_2H_5)}]_f$. [c] Based on the reaction $\mathrm{al(CH_3) + C_2H_4 \rightarrow alC_3H_7}$, which would amount to 100% for the exchange of one of the methyl groups in $\mathrm{Al(Me)_3}$. [d] Butene fraction separated off from the collected hydrocarbons and analyzed volumetrically and by gas chromatography.

At the lowest temperatures, pent-1-ene amounting to only a few per cent of the but-1-ene formed in reaction 4 was observed. This indicates that reaction 5 does not effectively contribute to the overall conversion.

Preliminary experiments in the gas phase as well as literature data based on liquid phase studies[10,11c] showed that, overall, ethylene adds much faster to the ethyl than to the methyl bonds in $\mathrm{(CH_3)_2Al(C_2H_5)}$. Care was therefore taken to keep the overall conversion low, in order to minimize the secondary reaction 4. Under the reaction conditions used, aluminum alkyls are thermodynamically stable only as monomers, and it has been shown[9,11] that alkyl group exchange *via* monomer–dimer equilibria is so fast that equilibrium is established practically instantaneously.

At low conversion, the aluminum alkyl consists practically exclusively of $\mathrm{(CH_3)_2Al(C_2H_5)}$ and only insignificant equilibrium quantities of $\mathrm{(CH_3)Al(C_2H_5)_2}$ or $\mathrm{Al(C_2H_5)_3}$ are present. Neglecting the secondary reactions 4 and 5 and using the stoichiometric relationship $[\mathrm{C_2H_4}]_0 = [\mathrm{C_2H_4}]_f + 2[\mathrm{C_3H_6}]$, setting $[\mathrm{al(C_2H_4)}] = [\mathrm{C_3H_6}]$ and $[\mathrm{al(CH_3)}]_0 = [\mathrm{al(CH_3)}]_f + [\mathrm{C_3H_6}]$, the following rate expression can be derived (0 and f denote initial and final concentrations, respectively).

$$\frac{-\mathrm{d(alCH_3)}}{\mathrm{d}t} = \frac{\mathrm{d(C_3H_6)}}{\mathrm{d}t} = k_1[\mathrm{alCH_3}][\mathrm{C_2H_4}] =$$
$$k_1\{[\mathrm{alCH_3}]_0 - [\mathrm{C_3H_6}]_f\}\{[\mathrm{C_2H_4}]_0 - 2[\mathrm{C_3H_6}]_f\}$$

Integration yields

$$k_1 = \frac{2.303}{t\{[\mathrm{C_2H_4}]_0 - 2[\mathrm{alCH_3}]_0\}} \times \log\left\{\frac{[\mathrm{alCH_3}]_0([\mathrm{C_2H_4}]_0 - 2[\mathrm{C_3H_6}]_f)}{[\mathrm{C_2H_4}]_0([\mathrm{alCH_3}]_0 - [\mathrm{C_3H_6}]_f)}\right\} \quad \mathrm{(I)}$$

$[\mathrm{C_2H_4}]_0$ and $[\mathrm{alCH_3}]_0$ could be deduced from the initial pressure measurements and $[\mathrm{C_3H_6}]_f$ by combining the volumetric and gas chromatographic analyses. However, because of the difficulties connected with the quantitative analyses of relatively small amounts of propylene in a large excess of ethylene, the analysis of the hydrolysis products of the condensed aluminum alkyl fraction was preferred as a more convenient and reliable method for the kinetic analysis of the system.

As $\mathrm{al(CH_3)}$ by itself was found to be thermally stable under the reaction conditions used, $[\mathrm{al(CH_3)}]_0 = [\mathrm{al(CH_3)}_f] + [\mathrm{al(C_2H_5)}]_f$. If $[\mathrm{CH_4}]$ and $[\mathrm{C_2H_6}]$ represent the amounts of methane and ethane in the hydrolysis products (mol $\mathrm{l.^{-1}}$) and V (l.) the volume of the reactor, then k_1 (l. $\mathrm{mol^{-1}\,sec^{-1}}$) is given by

$$k_1 = \frac{2.303V}{\{[\mathrm{C_2H_4}]_0 - 0.6667([\mathrm{CH_4}] + \mathrm{C_2H_6}])\}t} \times \log\left\{\frac{([\mathrm{C_2H_4}]_0 - 2[\mathrm{C_2H_6}])([\mathrm{CH_4}] + [\mathrm{C_2H_6}])}{([\mathrm{CH_4}] - 2[\mathrm{C_2H_6}])([\mathrm{C_2H_4}]_0)}\right\} \quad \mathrm{(II)}$$

The observed overall pressure change could also be used in deriving rate data, but the results would be perturbed by the secondary reactions 4 and 5. Nevertheless, rate constants calculated on the basis of eq I and II agreed within the experimental error limits.

For relatively large conversions, the depletion of C_2H_4 due to the formation of but-1-ene was taken into account by using in eq II instead of the initial pressure measurement for $[C_2H_4]_0$ a mean value $\overline{[C_2H_4]} = [C_2H_4]_0 - [C_4H_8]$. The corrected rate constants never differed by more than a few per cent from those calculated by neglecting the side reaction.

The results of the kinetic experiments are summarized in Table I. The ratio $[C_2H_4]_0$ to $[al(CH_3)]_0$ varies overall from 7.3 to 55 and about fivefold within a given temperature block. The conversion as based on reaction 1, *i.e.*, the replacement of only one methyl group of $Al(CH_3)_3$ by an ethyl group varies overall from 9 to 58%, and about fourfold within a given temperature block. Despite the variations in experimental conditions, consistent data for k_1 were observed with maximum differences of the mean value of 17% at the highest temperature, 58% at the lowest, and 31% at the two middle temperatures. The combined experimental error limits are estimated at ±10%, originating primarily from the uncertainties in the hydrolysis, fractionation, and analysis procedures. It appears that with decreasing temperatures the scatter of the data increases, in parallel with the observation of small amounts of *n*-butane and propane in the hydrolysis products, *i.e.*, *n*-butyl and *n*-propyl groups in the aluminum alkyl products. As has been mentioned previously, these small amounts of side products, when taken into account in calculating the rate constants, did not change the values of k_1 significantly. Nevertheless, additional uncertainties are introduced into k_1 by the small extent of these side reactions.

The overall pressure decrease $(\Delta p)_{tot}$ agreed within the expected error limits with the measured amounts of propene and but-1-ene. Based on the hydrolysis products, the amount of AlR_3 recovered from the reaction mixtures always agreed within ±10% with the amount of $[al(CH_3)]_0$ calculated from the initial pressure measurement.

Mass balances on the hydrocarbon fraction were always within a few per cent. Careful hydrolysis of the aluminum alkyl fractions did not produce any hydrogen, demonstrating again the absence of measurable quantities of dialkylaluminum hydrides in the reaction products. The computed least-squares analysis of the data listed in Table I yields (with standard deviations) the following Arrhenius relationships for k_1 (l. mol^{-1} sec^{-1}): (a) total set of data, $\log k_1 = (7.76 \pm 0.20) - (22.50 \pm 0.45)/\theta$; (b) reduced set, disregarding the lowest temperature block, $\log k_1 = (7.87 \pm 0.24) - (22.73 \pm 0.55)/\theta$; (c) reduced set, taking only the two highest temperatures, $\log k_1 = (7.76 \pm 0.33) - (22.48 \pm 0.77)/\theta$, where $\theta = 2.303RT$, with R in kilocalories per mole and T in degrees Kelvin. An Arrhenius plot of the observed rate constants is shown in Figure 1.

Discussion

Ethylene adds to aluminum-methyl bonds in the gas phase in a relatively simple and clean reaction forming propylene and aluminum-ethyl bonds.

Based on the thermodynamic data derived in the Appendix, the heat of the first reaction step, $\Delta H_{1,-1}$, is calculated to 24.9 kcal mol^{-1}, yielding an activation energy E_{-1} of 47.4 kcal mol^{-1} for the back-reaction.

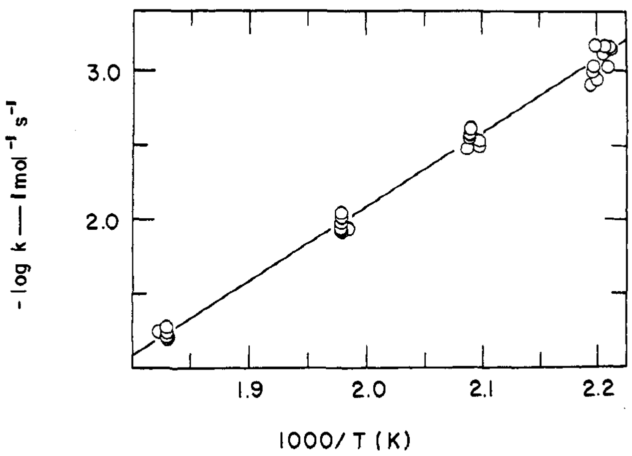


Figure 1. Arrhenius plot of the rate constants for addition of ethylene to trimethylaluminum.

It is then evident that the addition step 1 is essentially irreversible, in competition with reaction 2, with an activation energy E_2 of ~28 kcal mol^{-1}.[5]

The path degeneracy (= 3) corrected rate constant for the addition of ethylene to the Al–Me bond, k_1' (l. mol^{-1} sec^{-1}), is given by the Arrhenius relationship

$$\log k_1' = (7.27 \pm 0.20) - (22.50 \pm 0.45)/\theta$$

This result is to be compared with earlier results for the addition of ethylene to $Al(C_2H_5)_3$,[12] which yield the preferred Arrhenius relationship for the path degeneracy corrected rate constants k' (l. mol^{-1} sec^{-1})

$$\log k' = (6.27 \pm 0.67) - (17.6 \pm 1.4)/\theta$$

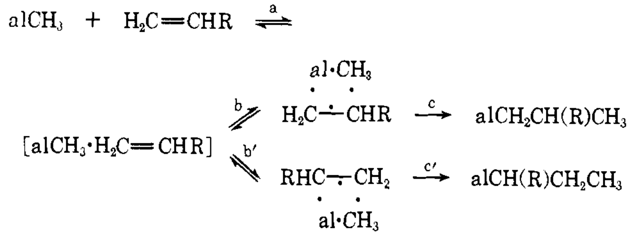
The preexponential factors for the addition of ethylene to Al–ethyl and Al–methyl bonds differ by a factor of 10, which appears to be outside the experimental error limits. The difference of ~5 kcal mol^{-1} in the activation energies would then be responsible for the observed differences in rates, favoring the addition to the aluminum–ethyl bond by a factor of about 50 at 500°K. This finding is in agreement with the conclusion reached recently by Hay, *et al.*,[11c] in a reevaluation of their observed activation parameters based on liquid-phase studies (compare introductory section).

Considering the products formed and the relatively low activation energies observed, there is little doubt that the addition of olefins to the monomeric aluminum alkyls involves a concerted four-center type of process. The observations that gallium and boron alkyls do not react with ethylene in the gas phase at temperatures of ~300° and that α-olefins practically exclusively add the α-carbon atom to the aluminum center suggest some polar control of the reaction.

It has been assumed[12] that the ground-state dipole and relatively easy longitudinal polarizability of the aluminum-carbon bonds contribute substantially to the lowering of the activation energy in the case of the aluminum alkyls. (The polar character of the $Al-CH_3$ bond can be estimated to be similar to that of the $BrCH_3$ bond. The relative net charge of the methyl group using the method of Sanderson[14] is −0.17 compared to +0.17 for CH_3–Br or +0.15 for CH_3–O.) Despite extensive literature data primarily on the liquid-

[14] (a) R. T. Sanderson, *J. Chem. Educ.*, **29**, 539 (1952); (b) *ibid.*, **32**, 140 (1955); (c) *J. Inorg. Nucl. Chem.*, **7**, 157 (1958).

phase addition of olefins to aluminum alkyls and related compounds, the detailed mechanism has not been demonstrated. It has generally been assumed[9-11] that some type of a four-center process is involved similar to that for hydrogen halides + olefin.[7] For the addition of group III dialkylmetal hydrides to olefins such a tight, quadrupolar transition state was shown to be consistent with experiments.[2-6] As has been outlined previously,[12] several experimental observations, *e.g.*, the decrease in rates in the series $C_2H_4 \gg C_3H_6 >$ but-1-ene $\gg$ 2-methyl-propene, etc., are incompatible with a simple four-center polar transition state model. The large differences in the activation parameters for $Al(C_2H_5)_3 + C_2H_4$ and $Al(CH_3)_3 + C_2H_4$ observed in this work further substantiate this conclusion. Any model based on a polar transition state concept would predict the inverse substituent effects from those actually observed, since the substituents would stabilize any induced positive—and to a lesser extent also negative—charges on the adjacent carbon atoms.[7] It is therefore suggested that these addition reactions might involve a coordinately bonded transient olefin complex as an intermediate product.



(In the case of ethylene, routes b and b′ are equivalent.) Depending on the relative magnitude of the rate constants, three possible cases can be distinguished whereby k_c and $k_{c'}$ respectively are essentially irreversible: case a, $k_{-a} > k_b$, kinetically equivalent to the direct rate-determining formation of the quadrupolar four-center transition state which has been shown to be inconsistent with the observed data; case b, $k_b > k_{-a}$, the steady-state treatment results in $k_1 \approx k_a\{1 - [k_{-a}/(k_{-a} + k_b)]\}$ and hence $k_1 \approx k_a$, *i.e.*, the rate of formation of the complex would determine the overall rate; and case c, $k_b \approx k_{-a}$, the observed rate constant k_1 would then equal about $0.5k_a$. The observed product-determining polar concept would then only enter the reaction through the intermediate quadrupolar states, whereby $k_b > k_{b'}$. The observed outstanding reactivity of aluminum alkyls toward olefins when compared with the other group III metal alkyls would then result from differences in the activation energies for complex formation and in the ratio of k_a to k_b. While coordinate olefin complexes have often been assumed as intermediates in a variety of reactions involving metal organic compounds in the liquid phase, thermodynamically stable olefin complexes have only been observed for transition metals,[15,16] especially for Rh, Pt, Ag, Cu, and Hg, whereby the σ,π bonding scheme first forwarded by Dewar[17] for Ag complexes has generally been accepted. On this basis, the bonding in aluminum–olefin complexes is expected to be very weak, as it would involve practically *exclusive* σ bonding, compared, *e.g.*, to silver complexes with a *predominant* σ component or the rhodium complexes with a predominant π component of the coordinate bond.

Based on literature data and reasonable thermodynamic estimates outlined in the Appendix, $K_{a,-a}$ (l. mol^{-1}) can be estimated to be given by $\log K_{a,-a} = (-5.5 \pm 0.5) - (0 \pm 3)/\theta$, resulting in complex concentrations of the order of $10^{-3}\%$ of the free al(CH$_3$) species. Unless special experimental techniques are applied, such low concentrations would escape direct analysis. The concept of AlR$_3$–olefin complexes[15] as intermediate products is substantiated by the observation of a shift in the infrared frequencies of alkenyldiisobutylaluminums compared to the parent olefins,[13] in accord with observations for boron alkyls[18] and for Ag complexes.[19] It could also explain the observed relative reactivities of substituted olefins with a given trialkylaluminum species, as ethylene can approach closer to the metal center without losing as much rotational entropy as substituted ethylenes, forming a stronger complex. It should be pointed out, however, that the observed preexponential factors appear to be low in view of the proposed loose transition state in forming the [AlR$_3$·olefin] complex. In conclusion, it can be said that, while the individual kinetic data on the systems $Al(Et)_3 + C_2H_4$ and $Al(Me)_3 + C_2H_4$ can be rationalized with a mechanism involving the direct formation of a polar four-center transition state, they are, for reasons of overall consistency in these systems, better interpreted in terms of the formation of an intermediate [olefin·AlR$_3$] complex. The system $Al(CH_3)_3$ + propylene presently under study should provide additional evidence.

Appendix

(1) Thermochemical Data of Aluminum Alkyls. The most reliable enthalpy data[2,12,20] are based on heat of combustion measurements by Pawlenko.[21] The error limits in these data must be of the order of ±3 kcal mol^{-1}, which is apparent from the incremental inconsistencies in the series Al(Et)$_3$, Al(*n*-Pr)$_3$, Al(*n*-Bu)$_3$. For $Al(CH_3)_3$, the only available value is that derived from the heat of reaction with CH_3CO_2H.[22] Heats of vaporization have been reported for $[Al(CH_3)_3]_2$[11c,23,24] and $[Al(Et)_3]_2$,[11c,25] based on vapor pressure measurements. Owing to the possibility of partial dissociation upon vaporization,[11c] these data constitute lower limit values. From the ΔH_V data for group III, IV, and V alkyls, it is evident that for a given element ΔH_V/mol wt is approximately a constant, which increases slightly with increasing molecular weight within a group. For aluminum alkyls, a value

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Table II. Thermochemical Data for Aluminum Alkyls

Compound	$-\Delta H_f°(l)$	$\Delta H_V°$ [a]	$\Delta H_D°(l)$	$-\Delta H_f°(g)$ [b] (monomer)
$[Al(CH_3)_3]_2$	72.0	(9.6)[d] 10.0[c] (9.9)[e] (13)[f]	20.4[e] (20.2)[d]	20.8
$[Al(C_2H_5)_3]_2$	111.8 (109.2)[g]	16.0 (14.4)[g] (19)[f]	14 (16.9)[h] (12.5)[f]	40.9
$[Al(C_3H_7)_3]_2$	154.0	21.9	(20.9)[i]	55.8[j]
$[Al(C_4H_9)_3]_2$	178.0	27.8	(9)[i]	70.6[j]
$[Al(i\text{-}C_4H_9)_3]_2$	185.6	27.8	8.0[k] (4.1)[i]	76.8[j]
$HAl(CH_3)_2$				15.9[j]
$(CH_3)_2Al(C_3H_7)$				33.2[j]

[a] Calculated based on a value of 0.07 for ΔH_V/mol wt derived from data for boron, gallium, and indium alkyls. Compare also ref 11c. [b] Refers to the AlR_3 monomer. [c] J. P. McCullough, J. F. Messerly, R. T. Moore, and S. S. Todd, *J. Phys. Chem.*, **67**, 677 (1963). [d] Reference 23. [e] Reference 24. [f] Reference 11c. [g] Reference 25. [h] M. B. Smith, *J. Phys. Chem.*, **71**, 364 (1967). [i] Calculated from the data listed in columns 2, 3, and 4. [j] Based on principle of direct incremental additivity of thermodynamic properties. Increments taken from ref 3 and S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968. [k] M. B. Smith, *J. Organometal. Chem.*, **22**, 273 (1970).

of 0.07 has been derived for ΔH_V/mol wt. The data are summarized in Table II

(2) Estimate of the Equilibrium Constant $K_{a,-a}$ and the Stability of Olefin Complexes. Useful quantitative equilibrium or thermochemical data on metal–olefin complexes are very scarce.

(a) $\Delta H_{a,-a}$. Heats of association for ethylene complexes (kcal mol^{-1}) have been reported for Ag^+ in molar trifluoroacetate[26] (−7.4), in nitrate[19] (−5.8), and in glycol (−3.5).[27] For CuCl(s), a value of −10 has been reported.[28] From measurements of displacement reactions in solution of the type $(C_2H_4)M(R)_x$ + olefin $\rightleftarrows$ (olefin)$M(R)_x + C_2H_4$ with rhodium[29] and silver complexes in closed systems, it can be concluded that the thermodynamic stability of the complexes decrease in the series $C_2H_4 > C_3H_6 >$ 1-butene > *cis*-2-butene > *trans*-2-butene, etc. The differences are much less pronounced for Ag than for Rh complexes, which has been discussed on the basis of steric and electronic effects.[9,29] The formation of aluminum alkyl–olefin complexes is thus estimated to be closely thermoneutral and $\Delta H_{a,-a} \approx 0 \pm 5$, whereby ethylene complexes should be relatively more stable ($-\Delta H_{a,-a}$ more positive) than complexes with substituted ethylene.

(b) $\Delta S_{a,-a}$ (cal °K^{-1} mol^{-1}). To a first approximation, the entropy change for the formation of a loose complex is given by the change in translational entropy. Calculated (in concentration units) on the basis of the Sackur–Tetrode equation[30] for $Al(Me)_3 + C_2H_4$, this yields for 300°K −21.9. $(\Delta \bar{C}_p°)_{a,-a}$ is estimated at −1.5, resulting in $(\Delta S_{a,-a})_{tr}(500°K) \approx -22.6$. Changes in contributions from the vibrational frequencies are small and can be neglected. It then follows for 500°K $(\Delta S_{a,-a})_{tot} \approx -22.6 + (\Delta S_{a,-a})_{rot}$. Differences in $(\Delta S_{a,-a})_{tot}$ among systems involving different olefins then originate primarily from the relatively small differences in rotational entropy $(\Delta S_{a,-a})_{rot}$, which are estimated to amount to less than 3.

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