Reactions of Group 3 Metal Alkyls in the Gas Phase

Part 9.—Addition of Propene to Trimethylaluminium *

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The thermal gas phase reaction of propene with monomeric trimethylaluminium has been studied at temperatures from 455 to 549 K using a static reaction system and Teflon coated reaction vessels. Initial propene pressures ranged from 190 to 370 Torr (25.33 to 49.33 kN m^{-2}) and the ratio of propene to $AlMe_3$ varied from 4.9 to 24.1. Overall conversions between 0.4 and 12.4 % with respect to alkyl groups were observed. In excess propene the overall reaction involves the rate determining addition of propene to the Al—CH_3 bond (k_1) to give Me_2AlBu^i followed by the fast elimination of isobutene and subsequent addition of propene to Me_2AlH, yielding Me_2AlPr^n.
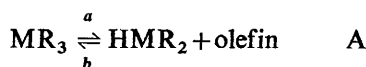
The rate constant k_1, corrected for path degeneracy, is given (with standard errors) by the Arrhenius relationship

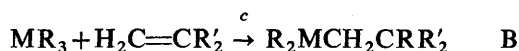$$\log(k_1/\text{l. mol}^{-1}\,\text{s}^{-1}) = 5.60 \pm 0.18 - (20.35 \pm 0.44)/\theta$$

where $\theta = 2.303\,RT/\text{kcal mol}^{-1}$. †

These results when compared with earlier data for the systems $AlEt_3$+ethylene and $AlMe_3$+ethylene appear to support a one-step 4-centre concerted process rather than the concept of olefin-aluminium alkyl complexes as intermediates formed in these reactions, as proposed earlier.

A series of kinetic studies involving Group 3 metal alkyls and olefins in the gas phase have been carried out in this laboratory in an attempt to arrive at a reasonable interpretation of the detailed reaction mechanisms. Two principal reaction systems have been investigated :

$$MR_3 \underset{b}{\overset{a}{\rightleftharpoons}} HMR_2 + \text{olefin} \qquad \text{A}$$

and

$$MR_3 + H_2C{=}CR'_2 \overset{c}{\rightarrow} R_2MCH_2CRR'_2 \qquad \text{B}$$

For system A, which is an integral part of the overall mechanistics involved in B, activation parameters for the unimolecular eliminations of olefins (k_a) from the following metal alkyls have been obtained : $AlEt_3$,[6] $AlBu^i_3$,[1] β-deutero-$AlBu^i_3$,[2] $Me_2AlBu^n_3$,[3] $GaBu^i_3$[4] and BBu^i_3.[5] These data have been shown to be consistent with a one-step 4-centre concerted elimination mechanism, involving tight quadrupolar transition states. Thermodynamic estimates lead to the conclusion, that the very fast backreaction (b), the addition of olefins to the monomeric R_2Al—H bond, requires activation energies ranging from about 5 to 12 kcal mol^{-1}. Recent investigations [7] of the relative rates of addition revealed, that ethylene adds about twice as fast as propylene, but about equally as fast as isopentene. This is consistent with the 4-centre concept if repulsive steric interactions overcome any stabilizing alkyl substituent effect in the transition state.

In contrast, the available literature data for the addition of olefins to $R_2Al—C$ bonds, following reaction scheme B did not appear to fit the simple concept of a polar 4-centre transition state. While the activation parameters obtained for the addition of ethylene to $AlEt_3$ [8] and $AlMe_3$ [9] could be rationalized individually with a rate determining 4-centre process, for reasons of overall consistency, it was considered preferable to assume the formation of an [olefin + AlR_3]-intermediate.[8, 9] To obtain further direct evidence pertaining to the true mechanism involved, we have investigated the addition of propene to $AlMe_3$, which should yield quantitative data on the substituent effect on the olefinic reactant.

EXPERIMENTAL

APPARATUS AND PROCEDURE

The experimental procedures, the static reaction systems and Teflon coated reaction vessels used, have been described previously.[8] $AlMe_3$ has previously been shown to be thermally stable in the gas phase under the reaction conditions used. An experiment was started, by adding $Al(CH_3)_3$ to the reaction vessel immediately followed by the addition of excess propene. Usually only the total pressure change was measured shortly before the experiment was stopped by quenching the reaction products in traps kept at liquid nitrogen temperature. In a few experiments pressure changes were recorded periodically during the run. Non condensable gases, collected in a gas buret, amounted to less than one percent of the total of the reaction products and were not analyzed further. The condensed reaction products were carefully separated into a hydrocarbon fraction containing the excess propene and isobutene (identified by g.l.c.) and into an aluminium alkyl fraction. The hydrocarbon fraction was usually discarded, except in the few experiments in which the overall mass balance was checked. The aluminium alkyl fraction was hydrolyzed with excess water and methane was quantitatively separated from the products at liquid nitrogen temperature. The residual gaseous hydrolysis products, consisting of propane and small amounts of ethane, ethylene, propene and butane were analyzed volumetrically and by g.l.c. Various amounts of propylene, ethane, ethylene and butane were observed besides propane, the major product.

The residual pressure of the methane fraction over liquid nitrogen served as a measure of the purity of methane. It usually ranged from 9.0 to 11 Torr (expected 9.0 Torr). Only in few experiments with unsatisfactory hydrolysis processes, residual pressures up to 25 Torr were observed due to the formation of hydrogen.

It was very important to ensure a slow and controlled course of hydrolysis in order to avoid partial pyrolysis, leading to the formation of hydrogen, ethane, ethylene and butane. The formation of these side products from the hydrolyses of AlR_3 was taken into account in calculating the rate constants, assuming that ethylene and ethane were formed stoichiometrically from two methyl groups and butane from a methyl and a propyl group. Propene is formed by unimolecular thermal olefin elimination [1-7] from $R_2Al—Pr^n$.

GAS CHROMATOGRAPHY

The analytical equipment and procedures used in this study have previously been described.[8, 9] The relative response factors for ethane, propane and butane were 1.533, 1.225 and 1.000 respectively.
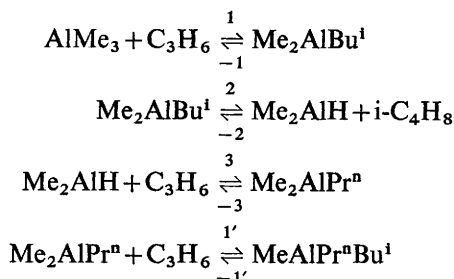
MATERIALS

TRIMETHYLALUMINIUM ($AlMe_3$) was obtained from K + K Laboratories, Plainview, New York and was further purified by distillation at reduced pressures. Test-hydrolyses resulted in > 99.8 % of methane and less than 0.2 % ethane. PROPYLENE was obtained from Fluka Chemicals, Buchs, Switzerland.

RESULTS

The addition of propene to monomeric [9, 10] trimethylaluminium has been studied in the gas phase at temperatures ranging from 478.1 to 587.2 K. The detailed reaction scheme in excess propene is summarized in scheme A. As $k_2 \gg k_{-1}$ and $[C_3H_6]k_3 \gg k_{-2}[i\text{-}C_4H_8]_2$, k_1 is the slow and rate controlling step in the overall reaction mechanism.[8, 9]

reaction scheme A

$$AlMe_3 + C_3H_6 \underset{-1}{\overset{1}{\rightleftharpoons}} Me_2AlBu^i$$

$$Me_2AlBu^i \underset{-2}{\overset{2}{\rightleftharpoons}} Me_2AlH + i\text{-}C_4H_8$$

$$Me_2AlH + C_3H_6 \underset{-3}{\overset{3}{\rightleftharpoons}} Me_2AlPr^n$$

$$Me_2AlPr^n + C_3H_6 \underset{-1'}{\overset{1'}{\rightleftharpoons}} MeAlPr^nBu^i$$

overall: $AlMe_3 + 2C_3H_6 \rightarrow Me_{3-x}AlPr^n_x + xCH_2C(CH_3)_2$.

While reactions 1 and 2 are essentially irreversible, equilibrium is established for reaction step 3 in the order of seconds at the lowest and fractions of seconds at the highest temperature used.[3, 6, 8, 9] The equilibrium concentration of Me_2AlH is immeasurably small.[1-9] As has been demonstrated for similar systems,[8, 9] it can be assumed, that $k_1 = k'_1$ and furthermore it has been well established that alkyl group exchange via monomer-dimer equilibria is so fast that equilibrium is established practically instantaneously.

Considering the relatively low conversions attained in this work, ranging between 0.38 and 12.4 % with respect to the total of Al-alkyl groups present, the only important AlR_3 species are $AlMe_3$ and Me_2AlPr^n.

Secondary reactions such as the addition of propene to Al-propyl bonds were not observed in contrast to the system $AlMe_3$ + ethylene. In order to avoid any kinetically significant contribution from the backreaction k_{-1}, conversions were kept low.* Based on the outlined reaction scheme, using the stoichiometric relationship $[C_3H_6]_0 = [C_3H_6]_f + 2[i\text{-}C_4H_8]$ and setting $[AlMe_3]_0 = [AlMe_3]_f + [i\text{-}C_4H_8]$ and $[Me_2AlPr^n] = [i\text{-}C_4H_8]$ the following rate expression can be derived: (0 and f denote initial and final concentrations respectively)

$$k_1 = \frac{2.303}{([C_3H_6]_0 - 2[AlMe_3]_0)t} \log \left\{ \frac{[AlMe_3]_0([C_3H_6]_0 - 2[i\text{-}C_4H_8]_f)}{[C_3H_6]_0([AlMe_3]_0 - [i\text{-}C_4H_8]_f)} \right\}.$$

As was observed in previous investigations, the combined volumetric-g.l.c. analysis of the hydrolysis products of the condensed aluminium alkyl fraction resulted in more reliable data for $[AlMe_3]_f$ and Me_2AlPr^n than pressure measurements or measurements of isobutene.

$[C_3H_6]_0$ was derived from the initial pressure readings. If $[CH_4]$ and $[C_3H_8]$ represent (in mol l.$^{-1}$) the corrected † amounts of methane and propane in the hydro-

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* Independent experiments [7] have shown, that isobutene at these temperatures adds about as fast as propylene to R_2Al—H bonds.

† Corrected for the amounts of hydrogen, ethane, ethylene and butane in the hydrolysis products. For details see experimental section.

lysis products of the aluminium alkyl fraction then

$$k_1/1.mol^{-1}s^{-1} =$$

$$\frac{2.303 \times 1.75}{\{[C_3H_6]_0 - 0.6667([CH_4]+[C_3H_8])\}t} \log \left\{ \frac{([C_3H_6]_0 - 2[C_3H_8])([CH_4]+[C_3H_8])}{([CH_4]-2[C_3H_8])([C_3H_6]_0)} \right\}$$

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

TABLE 1.—KINETIC DATA FOR THE ADDITION OF PROPYLENE TO TRIMETHYLALUMINIUM IN THE GAS PHASE

| temp./K | time/min | \multicolumn{2}{c}{starting materials/10^{-3} mol l.$^{-1}$} | conversion (g.l.c.) in % ethyl groups in AlR_3 | $10^4 k$/l. mol^{-1} s^{-1} |
		AlMe$_3$	C$_3$H$_6$		
478.1	40	1.469	17.94	0.893	6.32
478.3	30	2.468	13.24	0.401	5.18
479.2	67	1.445	17.72	2.68	11.2
479.6	92	2.813	20.54	2.39	6.48
479.8	120	1.906	21.28	2.63	5.38
479.9	70	2.495	18.38	1.96	7.92
481.2	98	1.823	17.88	2.90	8.74
503.7	80	1.535	14.99	3.52	15.7
504.2	120	1.385	17.52	7.69	21.2
505.0	110	0.874	18.32	7.85	22.5
505.6	5.167	0.597	12.65	0.376	23.1
505.4	80	1.076	19.25	4.90	17.4
506.6	75	1.946	13.25	3.22	17.3
506.6	130	1.577	13.59	5.53	17.5
508.3	172	2.121	10.38	5.70	18.2
531.1	7	0.835	17.56	1.08	44.8
534.4	15	1.338	14.42	2.10	50.5
536.1	30	1.361	16.71	5.24	57.1
536.4	30.5	1.111	16.45	5.99	66.7
536.4	45	1.279	19.76	8.60	59.6
538.9	60	1.226	19.74	12.4	67.4
559.5	20	0.697	16.82	7.73	132
560.6	10	1.282	16.68	5.71	190
560.6	21	1.027	9.625	5.62	140
562.1	9	1.396	13.21	4.11	187
562.9	6	0.993	17.16	2.91	149
581.8	3	1.345	13.09	2.64	353
583.7	5	1.257	15.06	4.52	326
584.6	8	1.023	13.24	5.03	261
584.8	10	0.5965	12.76	7.51	332
585.5	7	2.163	12.41	3.55	220
585.5	4.2	0.8663	14.92	4.19	359
587.2	10.083	0.5538	13.37	5.83	241

The ratio of propene to AlMe$_3$ varies overall from 4.9 to 24.1 and at a given temperature bloc from 4.9 to 21.2. The initial pressure of propene varied from 190 to 365 Torr (9.63×10^{-3} to 21.3×10^{-3} mol). The initial pressure of AlMe$_3$ varied overall by a factor of five. The concentration of AlMe$_3$, based on the initial pressure measurements and on the hydrolysis products agreed for most experiments to within 10 %.

The conversions based on the total pressure loss were on average 0.8 times those

obtained fiom the analysis of the hydrolyses products. Mass balances on the hydro-carbon fraction were always within a few percent.

As can be seen from the data in table 1, consistent rate constants were obtained despite the large variations in the parameters involved in the equation.

The computed least squares analysis of the data in table 1 yields with standard errors the following Arrhenius relationship for k_1:

$$\log (k_1/\text{l. mol}^{-1}\,\text{s}^{-1}) = (6.08 \pm 0.18) - (20.35 \pm 0.44)/\theta$$

where θ equals 2.303 RT/kcal mol^{-1} or

$$\log (k_1/\text{l. mol}^{-1}\,\text{s}^{-1}) = (6.08 \pm 0.18) - (85.14 \pm 1.84)/\theta'$$

where θ' equals 2.303 RT/kJ mol^{-1}.

DISCUSSION

In table 2 the activation parameters obtained in this work are compared with those observed for the similar systems AlMe$_3$+ethylene [1] and AlEt$_3$+ethylene,[2] using the same static reaction systems and experimental procedures.

TABLE 2.—ACTIVATION PARAMETERS FOR THE ADDITION OF OLEFINS TO ALUMINIUM ALKYLS

reaction	$\log(A/$ l. mol^{-1} s^{-1}) [a]	$E_a/$ kcal mol^{-1}	$\Delta G^{\ddagger}_{500}/$ kcal mol^{-1}	$10^3 k/$l. mol^{-1} s^{-1} at 500 K	ref.
AlMe$_3$+C$_2$H$_4$	7.76 $\pm$0.20 (7.0 $\pm$0.2)	22.5 $\pm$0.45	34.5	8.58	(1)
AlMe$_3$+C$_3$H$_6$	6.08 $\pm$0.18 (5.6 $\pm$0.2)	20.35 $\pm$0.44	36.2	1.60	this work
AlEt$_3$+C$_2$H$_4$	6.75 $\pm$0.75 (6.0 $\pm$0.75)	17.6 $\pm$1.4	31.9	114	(2)

[a] intrinsic A-factors, corrected for path degeneracy are given in parentheses.

As can be seen, both, substitution on the α-carbon atom and the olefin moiety apparently reduces activation energy and pre-exponential factor. These data are discussed in view of the two proposed alternate reaction mechanism, involving either a 4-centre polar transition state or the formation of [AlR$_3$ + olefin] complexes.

Based on a simplified electrostatic model, similar to that outlined by Haugen and Benson,[12] for alkyl halides the overall activation energy for a concerted 4-centre addition of an Al—C bond to olefins involving a semi-ion quadrupolar transition state as shown in scheme B

reaction scheme B
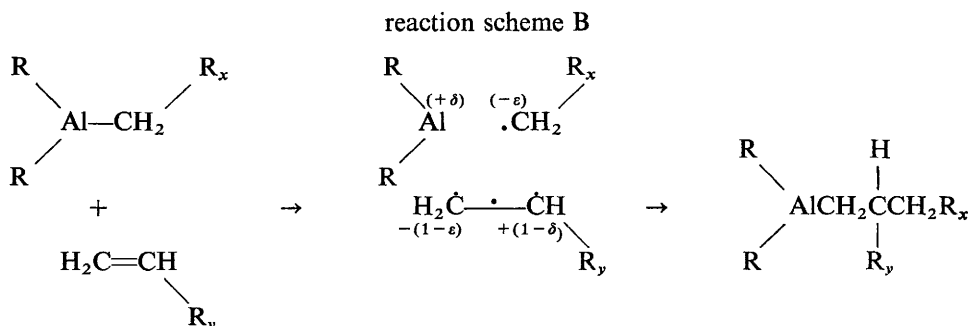
would be largely determined by the energies required to polarize the two bonds, reduced by a combined term of the dipole-dipole interaction and the repulsive energy in the transition state and the ground state polarization energy in the Al—C bond.

The available kinetic data for the " classical " addition of hydrogen halides to olefins show,[12, 13] that alkyl substituents on the olefin stabilize a positively induced charge on an olefinic carbon centre by 5.5 kcal mol^{-1}, a negative charge * by 1.5 kcal mol^{-1} in excellent agreement with the calculated stabilization energies of 5.8 and 1.6 kcal mol^{-1} respectively based on the simplified concept of an idealized charge-dielectric sphere interaction.[12]

For the addition of olefins to Al—C bonds (compare table 2) only 2.2 kcal mol^{-1} of stabilization energy of a methyl group on the adjacent positively induced charge on the olefinic carbon atom can be derived, which would be consistent with a relatively tight transition state structure involving a less pronounced and more unevenly distributed charge separation than was proposed e.g. for alkyl halides.[12] This is in accord with our earlier data on systems of the type R_2AlH+olefin [7] and with the observed low pre-exponential factors shown in table 2. The lower effected polarization of the olefin in the transition state would also reduce the stabilizing effect of substituents attached to the olefin.

The stabilizing effect of an extra polarizable alkyl substituent attached to the negative carbon centre, which attains penta-coordination in the transition state is difficult to assess. While a relatively large difference in polarization is to be expected between the ground and the transition states of the Al—C bond which is being broken, part of the excess electron density on this negatively polarized carbon atom is dissipated in the 4-centre transition state towards the positively induced olefinic carbon centre, reducing the induced positive charge at this position.

If the 4-centre concerted reaction mechanism involving a quadrupolar transition state as shown in scheme B is accepted for the systems $AlEt_3+C_2H_4$ and $AlMe_3+C_2H_4$, then the observed activation parameters listed in table 2 would imply a direct stabilizing effect of alkyl groups bonded to the negatively induced carbon centres of 4.9 kcal mol^{-1}.

This value appears to be too large [12, 13] and it seems preferable to scale the differences in the activation parameters between the two systems down within the experimental error limits, resulting in $\Delta E_a \simeq 3$ kcal mol^{-1}.

The observed lowering of the pre-exponential factors with increased substitution shown in table 2 is also consistent with a concerted 4-centre mechanism.

In order to explain the qualitatively well documented " inverse " olefin substituent effect, i.e. a decrease in the rate of addition with increasing substitution we suggested previously [8, 9] that a reaction mechanism, involving the rate determining formation of [olefin+AlR_3] complexes † might be operative.

Comparing the results of the present work with the earlier data it now appears, that this effect is primarily due to steric repulsions, offsetting the stabilization energies introduced by the substituents. It is then possible to rationalize the data consistently with a one-step concerted polar 4-centre mechanism. Particularly the pre-exponential factors observed in this work and for the addition of C_2H_4 to $AlEt_3$ appear to be too low for a mechanism involving the rate determining complex formation.

* The well documented decrease in stability with increasing substitution [14] of carbanions in liquid phase, which appears to contradict this concept, has been explained by pronounced solution effects, offsetting the stabilizing effects of the alkyl groups.[15]

† Using the concept first outlined by Dewar [16] for Ag-complexes, one would expect for [AlR_3+ olefin] practically exclusive σ-bonding, i.e. overlap of the occupied bonding π-orbital of the olefin with the vacant metal orbital. The absence of a π-bonding component would make these complexes very weakly bound.

It would thus appear that a quadrupolar 4-centre transition state is indeed involved in the addition of olefins to both R_2Al—C and R_2Al—H bonds.

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[1] K. W. Egger, *J. Amer. Chem. Soc.*, 1969, **91**, 2867.
[2] K. W. Egger, *Int. J. Chem. Kinetics*, 1969, **1,** 459.
[3] K. W. Egger and A. T. Cocks, *Trans. Faraday Soc.*, 1971, **67**, 2629.
[4] K. W. Egger, *J. Chem. Soc. A*, 1971, 3603.
[5] A. T. Cocks and K. W. Egger, *J. Chem. Soc. A*, 1971, 3606.
[6] A. T. Cocks and K. W. Egger, *J. C. S. Faraday I*, 1972, **68**, 423.
[7] K. W. Egger, *Helv. Chim. Acta*, submitted for publication.
[8] K. W. Egger, *Trans. Faraday Soc.*, 1971, **67**, 2638.
[9] K. W. Egger and A. T. Cocks, *J. Amer. Chem. Soc.*, 1972, **94,** in press.
[10] J. N. Hay, P. G. Hooper and J. C. Robb, *J. Organometallic Chem.*, 1971, **28,** 193.
[11] H. Lehmkuhl and K. Ziegler in *Methoden der Org. Chemie*, E. Müller ed. (G. Thieme, Stuttgart, 1970).
[12] G. R. Haugen and S. W. Benson, *J. Amer. Chem. Soc.*, 1965, **87,** 4036; *Int. J. Chem. Kinetics*, 1970, **2,** 235; *J. Phys. Chem.*, 1966, **70,** 3336.
[13] K. W. Egger and A. T. Cocks, *The Chemistry of the Carbon-Halogen Bond*, S. Patei ed. (Wiley, New York, in press).
[14] D. J. Cram, *Fundamentals of Carbanion Chemistry* (Academic Press, New York, 1965).
[15] J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, 1970, **92,** 5986.
[16] M. J. S. Dewar, *Bull. Soc. Chim. France*, 1951, **18,** C79.