On the Reactivity of Organometallic Compounds towards Functional Substrates. Part III.[1] The Kinetics of the Reaction between Tri-isobutylaluminium and Benzonitrile

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The first-order rate constants for unimolecular thermal decomposition of Bu_3^iAl–PhCN complex to benzylideneamino(di-isobutyl)aluminium are given at several temperatures. The rate of reduction of PhCN is shown to be independent of the presence of toluene as solvent. For this reaction $E_a = 25{\cdot}0 \pm 1{\cdot}0$ kcal mol^{-1} and $A = 10^{12}$ s^{-1}: all the data obtained are consistent with the hypothesis that the reduction involves a six-centre transition state. In the presence of an excess of Bu_3^iAl di-isobutyl-(α-isobutylbenzylideneamino)aluminium is formed. On the basis of the experimental results, possible mechanisms for the addition are discussed.

It is known that the reaction between benzonitrile and organoaluminium compounds yields both reduction and addition products, the percentage of which is related to the structure of the aluminium-linked alkyl group and to the molar ratio PhCN to R_3Al.[2-4] β-Branched alkylaluminiums, and in particular Bu_3^iAl, react with PhCN to give benzylideneamino(di-isobutyl)aluminium together with small amounts of di-isobutyl-(α-isobutylbenzylideneamino)aluminium.[5]

However, despite the large amount of data on the reactivity of organoaluminium compounds towards nitriles,[2-7] very little is known about the kinetics of this reaction.[8] The present work deals with a kinetic study of the reaction between Bu_3^iAl and PhCN under various experimental conditions.

EXPERIMENTAL

Tri-isobutylaluminium (Texas Alkyl Inc., Houston) and benzonitrile (C. Erba, Milan) were commercial products which were distilled before use and handled under nitrogen. The n.m.r. spectrum, at 60 MHz, of Bu_3^iAl after distillation, b.p. 40° at 0·2 mmHg, showed the absence of the broad peaks, characteristic of the aluminium–hydrogen bond in dialkylaluminium hydrides,[9] in the range τ 6—8.

The products were not isolated from the kinetic experiments because of the small amount of substrates used, and were identified by g.l.c. analyses by the comparison of their retention times with those of pure compounds.[5] G.l.c. analyses were performed on a C. Erba Fractovap model GT two column instrument, with flame ionization detectors. The columns (200 × 0·30 cm) were packed with 10% butanediol succinate (BDS) on 60—80 mesh Chromosorb W, and were used with a nitrogen flow rate of 24 ml min^{-1} at 160°.

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[5] L. Lardicci and G. P. Giacomelli, *J. Organometallic Chem.*, 1971, **33**, 293.

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[7] K. Starowieyski, S. Pasynkiewicz, and M. Boleslawski, *J. Organometallic Chem.*, 1967, **10**, 393.

[8] S. Pasynkiewicz and W. Kuran, *Roczniki Chem.*, 1965, **39**, 979.

[9] E. G. Hoffmann, *Z. analyt. Chem.*, 1959, **170**, 177; J. J. Eisch and S. G. Rhee, *J. Organometallic Chem.*, 1972, **42**, C73.

For the kinetic experiments, reaction vessels equipped with a Teflon stopper with a rubber septum, and a glass stopcock were used. At least two runs were performed for all reaction conditions. In a typical run $Bu_3{}^iAl$ (1·258 g, 6·34 mmol) was transferred to the reaction vessel from sealed glass vials; PhCN (0·654 g, 6·34 mmol) was injected by hypodermic syringe after cooling the reaction cell to −10° by an ice–salt bath. Then the flask was placed in a thermostatted oil bath, the temperature of which was kept constant at 66·5 ± 0·3°. At intervals samples of the mixture (0·4 ml) were withdrawn by a 500 μl hypodermic syringe and quenched in 10% H_2SO_4 solution (1 ml). G.l.c. analyses were performed directly on the ether extracts, and showed benzonitrile : benzaldehyde ratios of 5·93, 3·10, 2·02, 1·35, 0·74, and 0·31 after 1, 2, 3, 4, 6, and 10 h respectively.

RESULTS

Stoicheiometric Reaction between $Bu_3{}^iAl$ *and* PhCN.—The formation of benzylideneamino(di-isobutyl)aluminium from the stoicheiometric reaction between $Bu_3{}^iAl$ and PhCN has been studied in the absence of solvent in the temperature range 40—90°. Upon hydrolysis, benzaldehyde and unchanged benzonitrile were the only products, the amount of isobutyl phenyl ketone being negligible at all temperatures ($\leqslant$0·1%). Under the conditions employed, the reaction exhibited first-order kinetics (Figure 1). The first-order rate constants (Table 1) were calculated by computed least-squares analysis of the data obtained. For all temperatures, the individual rate constants were reproducible to within 3·0%. The error is attributed to uncertainties introduced by hydrolysis and the g.l.c. analysis procedure. The Arrhenius relationship (Table 1) and standard equations[10] were used to calculate the activation parameters. From the data, at 70°, E_a = 25·0 ± 1·0 kcal mol^{-1}, $\Delta H^‡$ = 24·3 ± 1·0 kcal mol^{-1}, $\Delta F^‡$ = 26·8 ± 1·0 kcal mol^{-1}, log (A/s^{-1}) = 11·7 ± 0·6, $\Delta S^‡$ = −7·4 ± 2·9 cal mol^{-1} K^{-1}.

TABLE 1

Rate constants for the stoicheiometric reaction between PhCN and $Bu_3{}^iAl$ in the absence of solvent [a]

Run	Temp. (°C)	$t_{\frac{1}{2}}$/min	10^3k_1/min^{-1}
1	46·5 ± 0·2	3400	0·2 ± 0·01
2	56·5 ± 0·2	1000	0·7 ± 0·04
3	66·5 ± 0·3	290	2·4 ± 0·1
4	76·5 ± 0·2	110	6·3 ± 0·1
5	86·5 ± 0·3	36	19·3 ± 0·3

[a] The computed least-squares analysis gave (with standard errors) the Arrhenius relationship log (k_1/s^{-1}) = (11·7 ± 0·6) − (25·0 ± 1)/θ where θ = 4·58 × $10^{-3}T$.

Reaction between $Bu_3{}^iAl$ *and* PhCN *at Various Molar Ratios*.—The reactions were carried out in toluene in the range 40—80°; for a molar ratio $Bu_3{}^iAl$: PhCN of 2 : 1, isobutyl phenyl ketone was obtained on hydrolysis. The disappearance of PhCN followed, even for this case, first-order kinetics. Figure 2 shows the concentrations of the reactants, and the products after various times. In Table 2 the experimental data obtained under various conditions are collected. The rate constants for the addition were evaluated from the knowledge of the ratio of reduction to addition products[10] (which is practically constant during the reaction),[1] and from the relationships $k_1 : k_2{}'$ = reduction : addition product, $k_{obs} = k_1 + k_2{}'$, and $k_2 = k_2{}'/[Bu_3{}^iAl]$ where $[Bu_3{}^iAl]$ represents the excess of the organoaluminium compound over PhCN.

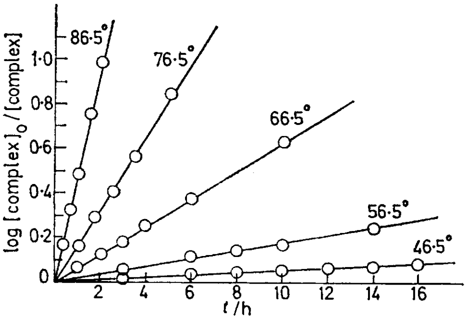

FIGURE 1 Kinetic dependence of the unimolecular decomposition of the PhCN–$AlBu_3{}^i$ complex

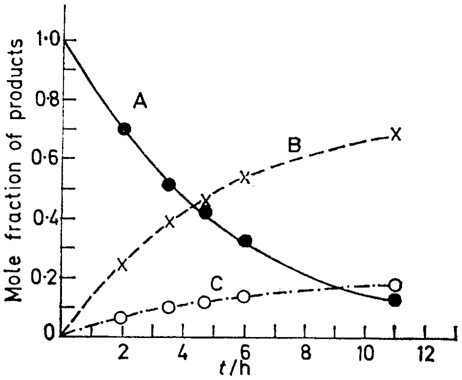

FIGURE 2 Reaction between $Bu_3{}^iAl$ and PhCN (molar ratio 2 : 1) at 66·5°: A, PhCN; B, PhCHO; C, $PhCOBu^i$

TABLE 2

Rate constants for the reaction between PhCN and $Bu_3{}^iAl$ at various molar ratios

Run	Temp. (°C)	$[Bu_3{}^iAl]$/M	[PhCN]/M	10^3k_{obs}/min^{-1}	$k_1 : k_2{}'$ [a]	10^3k_1/min^{-1}	10^4k_2/l mol^{-1} min^{-1}
6 [b]	46·5 ± 0·2	3·54	1·77	0·7 ± 0·05	3·1	0·5 ± 0·05	1·1 ± 0·5
7 [b]	66·5 ± 0·3	3·50	1·75	4·8 ± 0·1	3·6	3·8 ± 0·1	7·6 ± 0·5
8 [c]	66·5 ± 0·3	1·83	1·83	2·4 ± 0·1		2·4 ± 0·1	
9 [c]	66·5 ± 0·3	1·76	0·88	2·7 ± 0·1	7·9	2·4 ± 0·1	3·4 ± 0·5
10 [c]	66·5 ± 0·3	2·65	0·88	3·0 ± 0·1	4·0	2·4 ± 0·1	3·4 ± 0·5
11 [c]	76·5 ± 0·2	0·88	0·88	6·3 ± 0·1		6·3 ± 0·1	

[a] From the average value of the ratio of reduction to addition product. [b] In the absence of solvent. [c] In toluene.

DISCUSSION

The reduction of benzonitrile by $Bu_3{}^iAl$, at a molar ratio of 1 : 1, follows first-order kinetics both in the

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[10] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley, New York, 1961, pp. 98—100.

absence and in the presence of toluene. The rate constants are unaffected by the presence of this solvent, at least in the temperature range investigated. These results support the previously suggested mechanism of equations (1) and (2).[1,5]

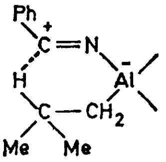
$$\mathrm{Bu_3{}^iAl + PhCN \rightleftharpoons PhC\overset{+}{N}{-}\overset{-}{A}lBu_3{}^i} \qquad (1)$$

$$\mathrm{PhC\overset{+}{N}{-}\overset{-}{A}lBu_3{}^i \xrightarrow{k_1} PhCH{=}NAlBu_2{}^i + Bu^i(-H)} \qquad (2)$$

The formation of the stoicheiometric complex between PhCN and $Bu_3{}^iAl$ should be rapid and governed by a very large equilibrium constant;[1] the rate-determining step is therefore the thermal rearrangement of this complex, to give the benzylideneamino-derivative and the olefin, through the migration of the β-hydrogen atom from the alkyl group of $Bu_3{}^iAl$ to the nitrile carbon atom.

The frequency factor (10^{12}) is reasonable for an elimination involving a cyclic six-centre transition state;[11] moreover the negative entropy of activation (*ca.* −7 cal mol^{-1} K^{-1}) agrees substantially with that estimated from the A factor expected for six-centre unimolecular reactions taking into account the loss of internal rotations when the activated complex is formed.[11,12]

These data are consistent with a six-membered, polar ring (A), which is based on the hypothesis that, in the activated complex, the nitrogen atom has changed its hybridization from sp to sp^2,[4,7] and consequently the distance of the nitrile carbon atom from the β-hydrogen has become much shorter than in the ground state.



(A)

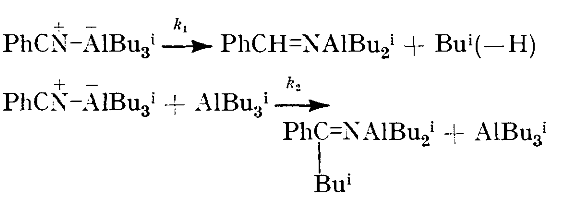
By means of such a hypothesis we can estimate roughly the polarization energy involved in forming the transisition state, which can be derived from the bond dissociation energies in the ground state [equation (3)].[11]

$$E_{\mathrm{pol}} = \tfrac{1}{2}[D(\mathrm{C{-}H}) + D(\mathrm{Al{-}C}) - D(\mathrm{C{-}C})_{\pi}] \simeq \tfrac{1}{2}[91\ (\text{ref. } 11) + 58\ (\text{ref. } 13) - 60\ (\text{ref. } 11)] \simeq 44{\cdot}5\ \mathrm{kcal\ mol^{-1}} \qquad (3)$$

The activation energy is *ca.* 25 kcal mol^{-1} which would imply an energy of interaction between the C^+ and H^- poles of *ca.* 19 kcal mol^{-1} and this agrees well with the theoretical energies of dipolar interactions for similar eliminations if the presence of substituents which are able to stabilize the positive centre of the activated complex are also considered (according to the considerations of ref. 11).

The presence of an excess of $Bu_3{}^iAl$ results in the formation both of reduction and addition products;[5] the amount of the latter is dependent on the $Bu_3{}^iAl$ concentration in the solution, and decreases as the dilution increases.[1] This suggests that di-isobutyl-(α-isobutylbenzylideneamino)aluminium is derived mainly from a reaction between $Bu_3{}^iAl$ and the complex $Bu_3{}^iAl$–PhCN. The kinetic results (Figure 2) are moreover consistent with parallel first-order reactions, in accordance with equations (4) and (5).

$$\mathrm{PhC\overset{+}{N}{-}\overset{-}{A}lBu_3{}^i \xrightarrow{k_1} PhCH{=}NAlBu_2{}^i + Bu^i(-H)} \qquad (4)$$

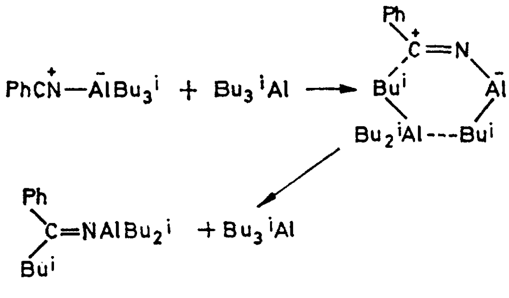


$$\mathrm{PhC\overset{+}{N}{-}\overset{-}{A}lBu_3{}^i + AlBu_3{}^i \xrightarrow{k_2} \underset{\displaystyle |\atop Bu^i}{PhC}{=}NAlBu_2{}^i + AlBu_3{}^i} \qquad (5)$$

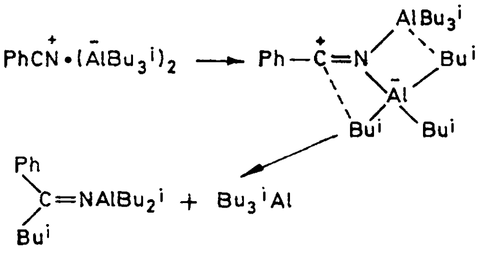
Equation (5) should give first-order kinetics since the $Bu_3{}^iAl$ concentration does not change during the addition. On this basis the overall reaction rate is given by equation (6) where $k_2[\mathrm{Bu_3{}^iAl}] = k_2'$ and $k_1 + k_2' = k_{\mathrm{obs.}}$

$$-\,\mathrm{d[PhCN]}/\mathrm{d}t = k_1[\text{complex}] + k_2[\text{complex}][\mathrm{Bu_3{}^iAl}] = (k_1 + k_2')[\text{complex}] \qquad (6)$$

The results (Table 2) show that the reduction rate, in toluene solution, is unchanged by the presence of uncomplexed $Bu_3{}^iAl$ (runs 8 and 9), and that the addition occurs at a *ca.* 10 times lower rate with respect to the reduction.



(7)



(8)

In the absence of solvent and at a molar ratio $Bu_3{}^iAl$: PhCN of 2 : 1 (run 7) both the rate of reduction and of addition (Table 2) are higher than in toluene solution (runs 9 and 10).

Regarding the increase of the rate of reduction, the intervention of $Bu_2{}^iAlH$ (from thermal decomposition

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[11] H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 1967, **71**, 2903.

[12] K. W. Egger, *J. Amer. Chem. Soc.*, 1969, **91**, 2867.

[13] H. A. Skinner, 'Advances in Organometallic Chemistry,' Academic Press, New York, 1964, vol. 2, p. 49.

of Bu_3^iAl) in the reaction does not explain this result completely, as previously suggested; [1,5] in fact, even at 46·5° [12] (run 6), the rate of reduction is greater than the rate measured at a molar ratio Bu_3^iAl : PhCN of 1·0 (run 1). It is therefore our opinion that in these conditions (Table 2) the PhCN–$AlBu_3^i$ complex may be reduced by a different and competitive mechanism.

In the light of literature suggestions [2-5,14] and bearing the kinetic results in mind, the different rate of the addition in the presence (runs 9 and 10) and in the absence of solvent (run 7) may be connected, in principle, with alternative mechanisms [equations (7) and (8)] related to weak associative phenomena of differing magnitude among the molecules of Bu_3^iAl [15] for the reaction conditions we have adopted.

Unfortunately, the extent of addition decreased rapidly on raising the temperature,[5] and this did not permit us to carry out a more accurate investigation on the activation parameters of the reaction. Therefore we cannot define the actual mechanism of the addition with certainty.

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[14] E. A. Jeffery and T. Mole, *Austral. J. Chem.*, 1970, **23**, 715.

[15] M. B. Smith, *J. Organometallic Chem.*, 1970, **22**, 273.