Kinetics and Mechanism of the Titanium Tetrachloride-catalysed Cyclotrimerisation of Aryl Cyanates

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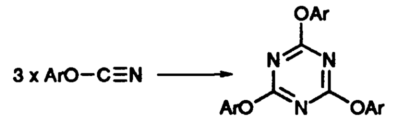
Aryl cyanates are converted cleanly at 25 °C to 1,3,5-triazines by catalytic amounts of titanium tetrachloride in dichloromethane. Based on IR spectroscopic, kinetic and product analysis, a mechanism is proposed involving rate-limiting nucleophilic attack of the cyanate nitrogen on the cyanato carbon of a cyanate–titanium tetrachloride complex. Subsequent steps are fast, with no evidence for dimeric or acyclic trimeric intermediates; it is suggested that these steps involve a series of fast stereoselective reactions of nitrillium ion intermediates.

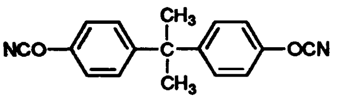
The development of cyanate (–OCN) chemistry followed the discovery by Grigat and Putter in 1964 of a convenient and reliable preparation involving treatment of alkoxide or phenolate with cyanogen halide.[1] Several other methods of preparation are known, but are less widely applicable.[2] Alkyl cyanates readily isomerise to the corresponding isocyanate (–NCO), but aryl cyanates **1** do not rearrange and their chemistry is dominated by attack of nucleophiles on the cyanato carbon.[3] A particularly important reaction is the cyclotrimerisation to yield 1,3,5-triazines (or *s*-triazines) **2** (Scheme 1); the reaction is promoted by heat and a range of catalysts including protic acids, Lewis acids, bases and metal ions.[4]



1 **2**

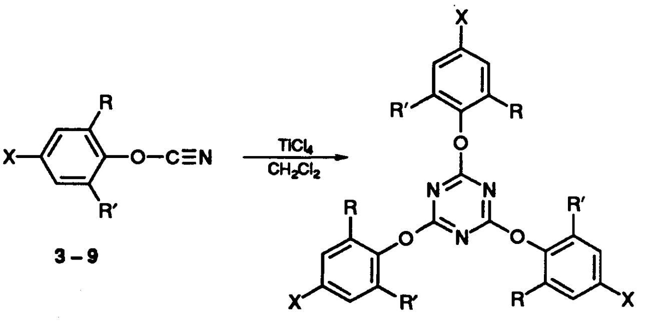
Scheme 1

The cyclotrimerisation of a dicyanate gives rise to a network structure[4,5] and cyanate ester resins formed by homopolymerisation of the dicyanate of bisphenol A **3**, or closely related compounds, are an important class of high-performance polymers.[6] The resins possess high glass transition temperatures (190–290 °C), show low dielectric loss and low moisture absorption, are tough, and show good peel strength; they are seen as potential replacements for epoxy resins and bismaleimides.[6]



3

Despite the importance of cyanate cyclotrimerisation the mechanism of the reaction is uncertain and a matter of some speculation;[4] theories range from cyclotrimerisation of a species where three cyanates are coordinated to a metal ion,[7] to those proposing stepwise reaction of cyanate with a reactive species such as a carbonic ester imide,[8] a pseudo-imidoyl halide,[9,10] a pseudo-amidine,[11] or any of a range of cyanate–Lewis acid complexes.[4,10] Some mechanistic information has come from thermal analyses of neat dicyanate polymerisations or monocyanate cyclotrimerisations,[12] and from IR[9,10] and NMR[13] monitoring directed towards the detection of possible intermediates.



3–9 **10–15**

	R	R'	X
3	H	H	4-NCO–Ph–C[CH$_3$]$_2$–
4, 10	H	H	Ph–C[CH$_3$]$_2$–
5, 11	H	H	Ph–O–
6, 12	H	H	Ph–SO$_2$–
7, 13	CH$_3$	CH$_3$	Ph–CH$_2$–
8, 14	CH$_3$	CH$_3$	Ph–CO–
9, 15	H	CH$_2$CH=CH$_2$	H

Scheme 2

We have based our study of this reaction around a small range of cyanates **3**–**9** (Scheme 2) with structures similar to those (such as **3**) important in polymerisation. Furthermore, we have chosen a catalyst and solvent system, titanium tetrachloride ($TiCl_4$) in dichloromethane (CH_2Cl_2) which is homogeneous and which (*vide infra*) gives triazine cleanly and rapidly at room temperature. Our findings are reported in this paper.

Results

Preparation of Cyanates and Triazines.—Cyanates **4**–**9** were prepared by cyanation of the corresponding phenol;[1] all showed the cyanate doublet at 2271–2291 and 2237–2266 cm^{-1} in the IR spectrum (CH_2Cl_2 and CCl_4 solvent). The triazines **10**–**15** were prepared by $TiCl_4$-catalysed cyclotrimerisation of the cyanates and all showed a strong peak around 1566 cm^{-1}. All compounds gave ^1H NMR spectra consistent with proposed structures. Details of yields, melting points and microanalyses are given in Table 1.

IR Spectroscopic Monitoring.—The reactions of cyanates **3**, **6**–**9** at [$TiCl_4$] = 0.0075 mol dm^{-3}, of **5** at [$TiCl_4$] = 0.0045 mol dm^{-3}, and of **4** at [$TiCl_4$] = 0.0025, 0.0045, 0.015 and 0.030 mol dm^{-3} ([cyanate] = 0.15 mol dm^{-3} except for **3** at

Table 1 Yields, melting points and microanalysis data for cyanates and triazines

Compound (formula)	Yield (%)[a] (solvent)	M.p./°C (lit. M.p.)	Found (required) (%)		
			C	H	N
3	—	81	—	—	—
($C_{17}H_{14}N_2O_2$)		(81–82)[b]	(—)	(—)	(—)
4	90	c, d	—	—	—
($C_{16}H_{15}NO$)			(—)	(—)	(—)
5	71	30	73.9	4.1	6.5
($C_{13}H_9NO_2$)			(73.9)	(4.3)	(6.6)
6	69	102	60.1	3.4	5.3
($C_{13}H_9NO_3S$)			(60.2)	(3.5)	(5.4)
7	45	c	80.8	6.2	5.7
($C_{16}H_{15}NO$)			(81.0)	(6.3)	(5.9)
8	93	66	76.5	5.2	9.1
($C_{16}H_{13}NO_2$)			(76.5)	(5.1)	(8.8)
9	86	c, d	75.3	5.2	5.5
($C_{10}H_9NO$)			(75.5)	(5.7)	(5.6)
10	87	163	—	—	—
($C_{48}H_{45}N_3O_3$)	(ethanol)	(163–164)[e]	(—)	(—)	(—)
11	92	221	73.7	4.15	6.6
($C_{39}H_{27}N_3O_6$)	(chloroform)	(219–221)[f]	(73.9)	(4.3)	(6.6)
12	65	175	59.6	3.4	5.3
($C_{39}H_{27}N_3O_9S_3$)	(dichloromethane–hexane)		(60.2)	(3.5)	(5.4)
13	54	117	80.6	6.3	6.0
($C_{48}H_{45}N_3O_3$)	(hexane)		(81.0)	(6.3)	(5.9)
14	60	172	76.2	5.15	5.5
($C_{48}H_{39}N_3O_6$)	(ethanol)		(76.5)	(5.2)	(5.6)
15	52	106	75.2	5.5	8.8
($C_{30}H_{27}N_3O_3$)	(hexane)		(75.5)	(5.7)	(8.8)

[a] Based on the corresponding phenol for cyanates and cyanate for triazine. [b] Ref. 5. [c] Compound was an oil. [d] Ref. 12. [e] R. F. Cozzens, P. Watterand and A. W. Snow, *J. Polym. Sci.*, 1987, **34**, 601. [f] F. J. Allen, G. Allen, G. Graham, T. Mattila and P. Mauranen, *Acta Chem. Scand.*, 1969, **23**, 1903.

0.075 mol dm^{-3}) in CH_2Cl_2 were followed by scanning FTIR spectroscopy. The spectra showed a smooth conversion of the cyanate to the triazine, but in addition, a small peak at *ca.* 1675 cm^{-1} was observed in all cases. This peak formed instantaneously upon addition of $TiCl_4$, its intensity increased with the amount of $TiCl_4$ added, and it remained almost unchanged throughout the reaction persisting long after t_∞ (< 10 h). Apart from this, spectra at t_∞ were identical to those of artificial triazine–$TiCl_4$–CH_2Cl_2 solutions. On further standing for up to 24 h the only changes were a decrease of the peak at 1675 cm^{-1} and the appearance of small peaks in the 1700–1800 and the 3500 cm^{-1} regions; similar changes were observed following aqueous workup or upon exposure of the reaction to the atmosphere.

For triazine **10** (the product from cyanate **4**) in CH_2Cl_2 additional peaks at 1645, 1400 and 1325 cm^{-1} were seen in the presence of $[TiCl_4] = 0.015$ and 0.030 mol dm^{-3}; these were also present at t_∞ in the analogous cyanate reaction mixtures. These peaks are attributed to a $TiCl_4$–triazine complex; further evidence of an interaction is provided by the change in triazine solutions from colourless to orange–brown upon addition of $TiCl_4$.

Product Analysis.—Reactions of cyanates **5**–**9** (0.15 mol dm^{-3}) with $TiCl_4$ (0.015 mol dm^{-3}) gave, after aqueous workup, crude triazines in > 95% yield; only trace impurities in the crude products were seen by TLC and by ^{1}H NMR, typically less than 3% based on cyanate consumed. The reaction of **4** was investigated in more detail by HPLC (cyanate **4**, its corresponding phenol (**19**, Ar = Ph–C[CH_3]$_2$–Ph–), and the triazine **10** are difficult to distinguish by ^{1}H NMR) at [cyanate] = 0.15 mol dm^{-3} and $[TiCl_4] = 0.0025$, 0.0045, 0.015 and 0.030 mol dm^{-3}. The crude products were obtained in 93–99% yield and seen to contain, in addition to triazine, only the corresponding phenol in yield (based on cyanate) increasing from 2–4% as the $[TiCl_4]$ increased. Furthermore HPLC analysis following workup with aqueous hydrogen carbonate during the first $\tau_{\frac{1}{2}}$ (approx.) of the reaction showed only phenol in addition to cyanate and triazine (the cyanate was stable to workup with aqueous hydrogen carbonate).

The dicyanate **3** gave a resinous product which was not characterised.

Initial Rate of Loss of Cyanate.—The decrease in the cyanate absorbance peak in the 2237–2266 cm^{-1} region did not quite follow first order kinetics, becoming slightly slower after about one $\tau_{\frac{1}{2}}$ and therefore an initial rate method was used to determine the reaction order in cyanate and in catalyst. Monitoring over the first 20% of the reaction, an initial instantaneous (on the scale of our experiments < 30 s) drop in the cyanate peak of a magnitude approximate to the catalyst concentration was seen for all reactions where the molar ratio of catalyst to cyanate was $\geq 3\%$; a rapid red–brown colouration also developed. Examples are shown for two cases in Table 2, although the effect was general. The term $[OCN]_{init}$ is the cyanate concentration prior to addition of the $TiCl_4$, while $\Delta[OCN]$, the initial drop, was calculated from the difference between the absorbance prior to addition of the catalyst and that obtained by interpolaring the subsequent linear dA/dt (*vide infra*) back to $t = 0$; the term $[OCN]_0 = [OCN]_{init} - \Delta[OCN]$. For the benzyldimethylphenyl cyanate **7** ([cyanate] = 0.15 mol dm^{-3}, $[TiCl_4] = 0.0075$ mol dm^{-3}) where the overall reaction is relatively slow, a scan after 20 s showed loss of cyanate corresponding to about 0.009 ± 0.002 mol dm^{-3} with no formation of triazine during this period.

Following this initial drop, for all reactions the decrease in the 2237–2266 cm^{-1} peak (with the corresponding increase in the triazine peaks) followed pseudo-linear behaviour over the next 5–10% of the reaction (generally several minutes) and dA/dt_0 (a pseudo initial rate!) was determined over this part of the

Table 2 Initial drop in cyanate concentration on addition of $TiCl_4$ at 25 °C. All concentrations in mol dm^{-3}

Compound **6**			Compound **5**		
$[OCN]_{init}$	$[TiCl_4]$	$\Delta[OCN]$	$[OCN]_{init}$	$[TiCl_4]$	$\Delta[OCN]$
0.025	0.0045	0.002 ± 0.001	0.15	0.0025	0.002 ± 0.002
0.050	0.0045	0.004 ± 0.001	0.15	0.0075	0.006 ± 0.002
0.075	0.0045	0.004 ± 0.001	0.15	0.0125	0.013 ± 0.003
0.100	0.0045	0.004 ± 0.002	0.15	0.0150	0.020 ± 0.002
0.150	0.0045	0.005 ± 0.002	0.15	0.0225	0.038 ± 0.002

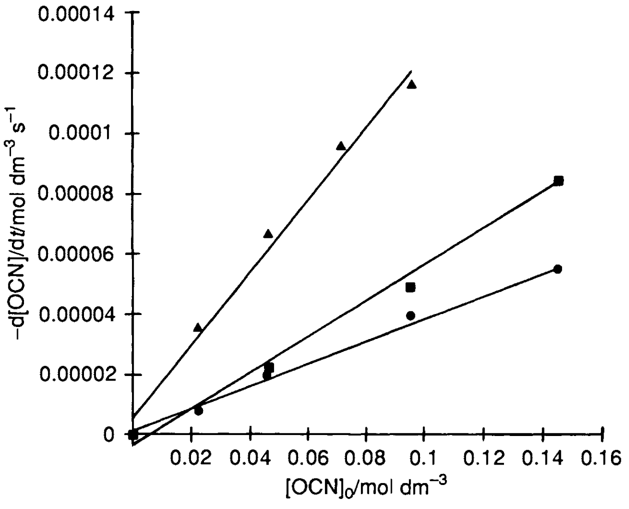


Fig. 1 Variation of the rate of cyanate loss with $[OCN]_0$ for **4** (■), **5** (●) and **6** (▲) at $[TiCl_4]$ = 0.0045 mol dm^{-3} (**5**, **6**) and 0.010 mol dm^{-3} (**4**) in CH_2Cl_2 at 25 °C

reaction. Values of $d[OCN]/dt_0$ were calculated using predetermined extinction coefficients from a mean of at least three determinations of dA/dt_0 with standard deviations ≤ ±6%.

Plots of $d[OCN]/dt_0$ against $[OCN]_0$ for the cyanates **4**–**6** are linear (r > 0.99) (Fig. 1). Having established a linear dependence of $d[OCN]/dt$ on $[OCN]$, the term $(d[OCN]/dt_0)/[OCN]_0$ (to allow for differing amounts of cyanate consumed in the 'initial drop') can be plotted against varying $[TiCl_4]$ and shown also to be linear (r > 0.99) (Fig. 2).

Therefore the rate equation for the reaction subsequent to the rapid initial drop is (1). Values of the second order rate

$$-d[OCN]/dt = k[OCN][TiCl_4] \qquad (1)$$

constant k for cyanates **4**–**6** at 25 °C were obtained from Fig. 2 and are given in Table 3; other values of k in Table 3 are derived using eqn. (1) from measurements at a single concentration of cyanate and catalyst (typically 0.15 mol dm^{-3} and 0.0045 mol dm^{-3}, respectively). Activation parameters derived from plots of ln k against $1/T$ (r > 0.99 in all cases) are also given in the Table.

Product Inhibition.—Prior addition of triazine **10** to reaction solutions of **4** resulted in a decrease in rate as shown in Table 4; a plot of $1/d[OCN]/dt_0$ against $[triazine]_0$ is linear (r > 0.99) with a slope of $5.2 \pm 0.1 \times 10^4$ s mol^{-2} dm^6.

Detection of Complex Peaks.—Others have reported the formation of peaks in the 2300 cm^{-1} region when cyanates are treated with excess Lewis acid.[4,10] Unfortunately, in the present case, the CH_2Cl_2 solvent peak in this region obscured any small complex peaks during the reaction. However, a strong peak at 2320 cm^{-1} was formed upon addition of 1-5 equiv. of $TiCl_4$ to **4** (Table 5); no 'free' cyanate was detectable in these cases and formation of triazine was slow. A repeated scan of the reaction of **4** in CCl_4, a solvent which shows no interfering peaks in the 2300 cm^{-1} region is shown in Fig. 3. In this the peak at 2315 cm^{-1}, attributed to a cyanate–catalyst complex, is formed rapidly on mixing before gradually disappearing at the end of the reaction. It should be noted that the peak at 1675 cm^{-1} (*vide supra*) also formed on mixing, but persisted past t_∞.

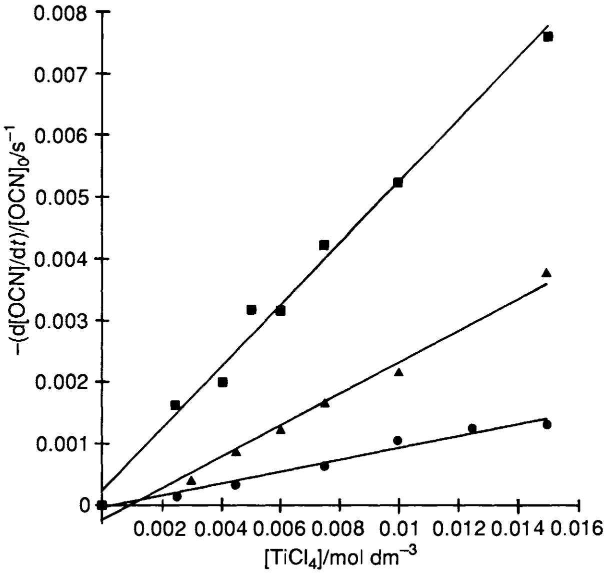


Fig. 2 Variation of the rate of cyanate loss with $[TiCl_4]$ for **4** (■), **5** (●) and **6** (▲) at $[OCN]_0$ = 0.15 mol dm^{-3} in CH_2Cl_2 at 25 °C. The points for **4** have been multiplied by a factor of 7 for clarity.

Effect of Added Water on the Reaction.—Addition of **5** to a $TiCl_4$–CH_2Cl_2 solution (0.01 mol dm^{-3} in $TiCl_4$) to which water had been added (0.01 mol dm^{-3} in water) resulted in an enhancement of the peak at 1675 cm^{-1}, but a large reduction in the rate of loss of cyanate when compared to the 'water-free' case.

Discussion

The results pertaining to the mechanism can be briefly summarised. Conversion of cyanate to triazine occurs cleanly and in almost quantitative yield *via* a reaction that involves an initial interaction of cyanate and $TiCl_4$ followed by a subsequent rate-limiting reaction first order in 'free' cyanate and a species derived from $TiCl_4$. Candidates for the reactive product of the initial interaction are a substance with an IR peak at *ca.* 2320 cm^{-1} or another with a peak at *ca.* 1675 cm^{-1}. Weak triazine–$TiCl_4$ complexation leads to product inhibition.

Martin and Weise have examined IR spectra of aryl cyanates when treated with Lewis acids and have also noted peaks in the 2320 and 1670 cm^{-1} regions.[4,10] The former was ascribed to a simple cyanate–Lewis acid complex, and we propose in our case the complex **16**. Titanium halides can give complexes of the

Table 3 Second order rate constants and activation parameters for the $TiCl_4$-catalysed cyclotrimerisation of cyanates **3–9** in CH_2Cl_2

Cyanate	$k/s^{-1}\ mol^{-1}\ dm^3$ 20 °C	25 °C	30 °C	$\Delta H^\ddagger/kJ\ mol^{-1}$	$\Delta S^\ddagger/J\ mol^{-1}\ K^{-1}$
3	0.058	0.090	0.115	48 ± 7	−104 ± 23
4	0.065	0.081[a]	0.109	36 ± 4	−146 ± 13
5	0.073	0.090	0.110	27.8 ± 0.1	−171.9 ± 0.3
6	0.190	0.261	0.340	40 ± 2	−121 ± 6
7	0.015	0.023	0.041	71 ± 7	−40 ± 23
8	0.158	0.220	0.304	45.8 ± 0.2	−104 ± 1
9	0.028	0.040	0.052	45 ± 3	−122 ± 11

[a] $k = 0.227\ s^{-1}\ mol^{-1}\ dm^3$ in CCl_4.

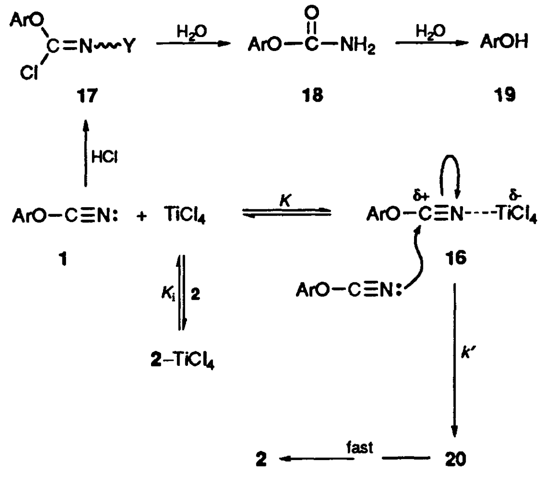
Table 4 Effect of added triazine **10** on rate of reaction of cyanate **4**. $[\mathbf{4}]_{init} = 0.15\ mol\ dm^{-3}$, $[TiCl_4] = 0.005\ mol\ dm^{-3}$

$[\mathbf{10}]/mol\ dm^{-3}$	$-d[OCN]/dt/10^{-5}\ mol\ dm^{-3}\ s^{-1}$
0	6.13
0.05	5.26
0.10	4.64

Table 5 Effect of excess $TiCl_4$ on spectrum of cyanate **4** in CH_2Cl_2 at 25 °C. $[OCN]_{init} = 0.05\ mol\ dm^{-3}$

A_{2238}[a]	$[TiCl_4]/mol\ dm^{-3}$	A_{2320}[b]	A_{1566}[b]
0.42	0.05	0.88	0.07
0.42	0.10	0.77	0.08
0.44	0.15	0.80	0.09
0.42	0.20	0.80	0.10
0.46	0.25	0.66	0.10

[a] Absorbance at 2238 cm^{-1} prior to addition of $TiCl_4$. No absorbance could be detected at 2238 cm^{-1} after the addition. [b] Recorded within 60 s of addition of $TiCl_4$.



Scheme 3

form TiX_4L or TiX_4L_2,[14] and although the peak around 2320 cm^{-1} suggests that **16** may be similar to the complexes between cyanide and $TiCl_4$,[15] it is not obvious which form is prevalent here. Nonetheless, the arguments which follow are not qualitatively changed by substituting the TiX_4L_2 form for the TiX_4L form shown for **16** in the schemes. Peaks around 1675 cm^{-1} are most likely due to compounds related to imidoyl chlorides **17** formed by transfer of chloride to the cyanato carbon. In this work we believe that the 1675 cm^{-1} compound can be excluded as an intermediate in the reaction. Firstly, it is difficult to envisage a mechanism whereby the reactive intermediate persists well after the end of the reaction, as is the case here. Secondly, there is the observation that addition of water (and also therefore HCl) to the reaction enhances the 1675 cm^{-1} peak, but slows the loss of cyanate; while a steady state of intermediate is possible provided reaction of cyanate maintains its concentration, a reduction in the rate of cyanate loss is incompatible with the enhanced 1675 cm^{-1} species being a reactive intermediate. We believe this species to be a by-product **17** (Y = H) formed from rapid, but unproductive, reaction of the cyanate with traces of HCl[16] which must be present in the $TiCl_4$ solutions. Subsequent reaction of **17** with water on standing or during workup would explain the 1700–1800, and 3500 cm^{-1} peaks observed as being due to **18** and the phenol **19**,[13b,17] this latter being the main product contaminant. Interestingly, it has been reported that Lewis acid catalysis of cyanate cyclotrimerisation may be enhanced by the addition of water,[4] clearly this does not occur for $TiCl_4$.

We propose the mechanism in Scheme 3 where **20**, the product of the reaction of cyanate **1** with complex **16**, is in steady state (the reverse reaction **20** to **16** is presumed to be negligibly slow), and **2** is the triazine product. A kinetic analysis yields eqn. (2), for the rate of loss of cyanate (the putative reaction with HCl to yield **17** appears to be complete almost immediately and to account for only a trace amount of the reaction flux, and so can be ignored for kinetic analysis).

$$-d[ArOCN]/dt = \frac{k'K[ArOCN]^2[TiCl_4]}{(K[ArOCN] + K_i[triazine] + 1)} \quad (2)$$

Most important is the K[ArOCN] term which is equal to $[\mathbf{16}]/[TiCl_4]_{free}$ assuming a pre-equilibrium and which reflects the ratio of complexed to free $TiCl_4$; despite the difficulty in detecting **16** during the reaction, the evidence that this term is $\gg 1$ is strong. Firstly, is the observation in Table 5 of strong 2320 cm^{-1} peaks for relatively modest excesses of $TiCl_4$; the fact that their intensity does not increase as $[TiCl_4]$ increases and that no 'free' cyanate is seen shows that essentially all of the cyanate is bound as complex. Consideration of the triazine 1566 cm^{-1} peak shows that $\leqslant 20\%$ of cyanate has cyclotrimerised, and assuming that an equilibrium concentration of 'free' cyanate of > *ca.* 0.01 $mol\ dm^{-3}$ (A_{2238} *ca.* 0.07) would be easily detectable, the lack of observed 'free' cyanate at 2238 cm^{-1} implies a value for $K \gg 100\ mol^{-1}\ dm^3$. The slight decrease in the absorbance at 2320 cm^{-1} as $[TiCl_4]$ is increased may be due to preferential and irreversible reaction of cyanate with HCl since the 1675 cm^{-1} peak is seen to increase. Secondly, the amount of initial cyanate loss from Table 2 suggests that all of the $TiCl_4$ is complexed; any additional cyanate loss may reflect a dicyanate complex or the reaction to the 1675 cm^{-1} compound **17**. Thirdly, a mechanism involving a strong complex requires that [**16**] be

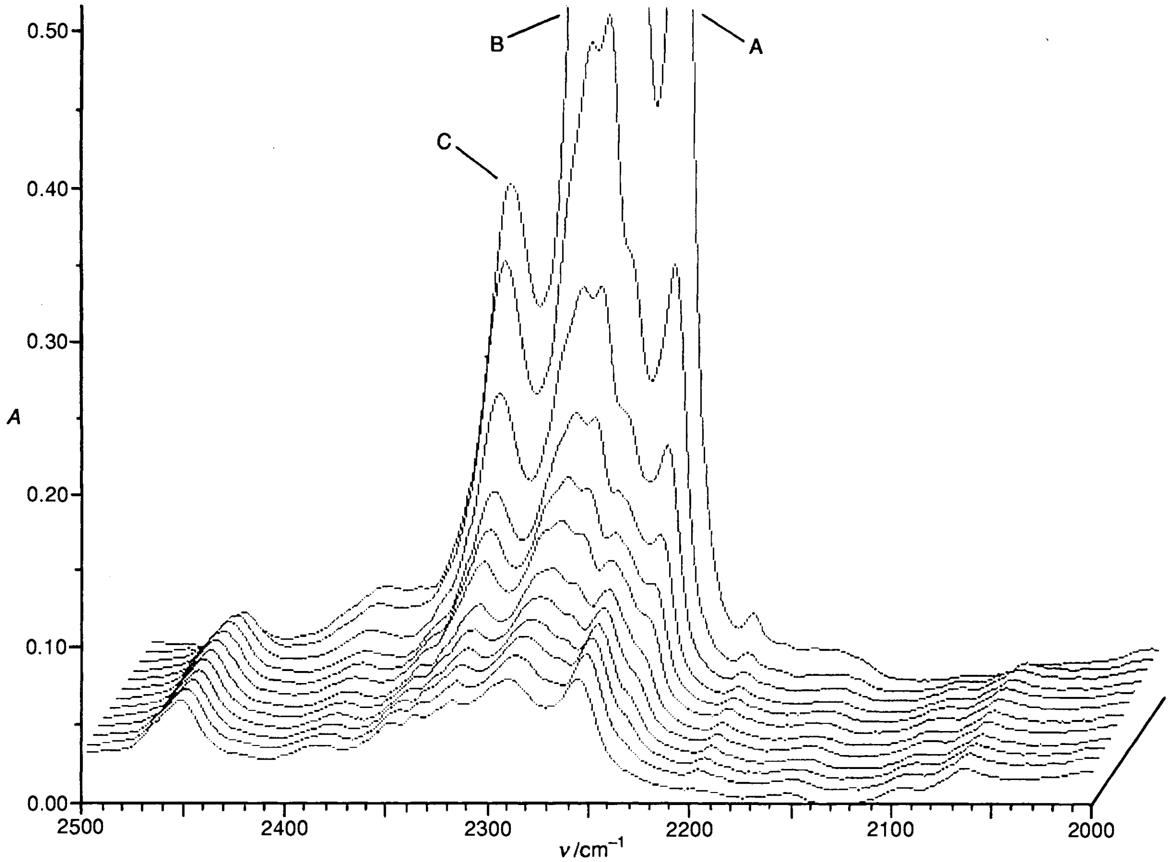


Fig. 3 IR repscan every 3 min of the reaction of **4** in CCl_4 at 25 °C showing the decrease in the cyanate doublet at 2238 (A) and 2270 (B) cm^{-1} and the change in the $TiCl_4$-induced peak at 2315 (C) cm^{-1}. The absorbance at t = 0 for the off-scale 2270 cm^{-1} peak is 0.901. $[OCN]_{init}$ = 0.15 mol dm^{-3}, $[TiCl_4]$ = 0.015 mol dm^{-3}.

fairly constant over a large portion of the reaction; consideration of Fig. 3 shows that while the cyanate 2270 cm^{-1} peak has fallen by > 50% over the first 3 min, the complex peak at 2315 cm^{-1} has barely fallen at all, although in the later stages it falls to almost zero as expected of a reactive intermediate. When K[ArOCN] is set $\gg 1$, eqn. (2) reduces to (3).

$$-d[ArOCN]/dt = \frac{k'K[ArOCN]^2[TiCl_4]}{(K[ArOCN] + K_i[triazine])} \quad (3)$$

A further simplification can be made by neglecting the K_i[triazine] term; this is reasonable since during the early stages of the reaction (to which our kinetics relate) [triazine] is small. More formally, given (3), a plot of reciprocal rate 1/(d[ArOCN]/dt) against [triazine] would be linear with a slope of $K_i/K[ArOCN]v_{max}$ where v_{max} is the rate d[ArOCN]/dt in the absence of triazine; for **4** such a plot with a slope of 5.2×10^4 s mol^{-2} dm^6 gives $K_i/K[ArOCN] = 3.2$ and $K_i[triazine] < 0.016K[ArOCN]$, since in none of our 'initial rate' kinetic measurements does [triazine] rise above 0.005 mol dm^{-3}. Neglecting this term reduces (3) to (4) as observed, and the rate constant for reaction of cyanate with complex (k') is given by k the observed second order rate constant.

$$-d[ArOCN]/dt = k'[ArOCN][TiCl_4] \quad (4)$$

An alternative mechanism with rate-limiting transfer of Cl in the complex **16** to the cyanato carbon to give an imidoyl chloride-type intermediate (*e.g.* **17**, Y = $TiCl_3$)[9a] would give a rate zero order in cyanate under these conditions.* Indeed, we believe that no other reasonable mechanism is consistent with the kinetics and the observed behaviour of the complex.

The rate constants in Table 3 vary relatively little across the range of cyanates studied, with those having electron withdrawing substituents being faster. This small substituent effect has been observed for other cyanate cyclotrimerisations,[4,9a] and is consistent with nucleophilic attack by the nitrogen (remote from the substituent X) of **1** upon the electron deficient carbon (slightly less remote from X) of the complex **16**.

The activation parameters also show little variation with structure apart fom those for **7**, and the low enthalpy and high negative entropy values are consistent with Scheme 3 where cyanate reacts with a reactive pseudo-nitrillium ion **16** leading to an ordered transition state. The activation energies (E_{act}) for the thermal cyclotrimerisation of neat samples of **3**, **4** and **9** are known to be 53, 57 and 81 kJ mol^{-1}, respectively,[12a] and the dramatic rate increases seen for the $TiCl_4$-catalysed reaction appear to be due partly to a reduction in the activation enthalpy and partly due to an increase in the activation entropy.

Much research into cyanate cyclotrimerisation, particularly with repect to polymerisation of dicyanates, has centred on the search for dimeric intermediates.[13,18] In our work we found no evidence for such intermediates; the only material identified in the HPLC analysis of crude product mixtures of **4** was the phenol **19** (Ar = Ph–C$[CH_3]_2$–Ph–) and this is clearly derived from monomeric by-products (*vide supra*).

Our kinetic analysis shows that the reaction of the pseudo-nitrillium ion complex **16** with 'free' cyanate **1** is rate-limiting; a finding further supported by the lack of dimeric intermediates.

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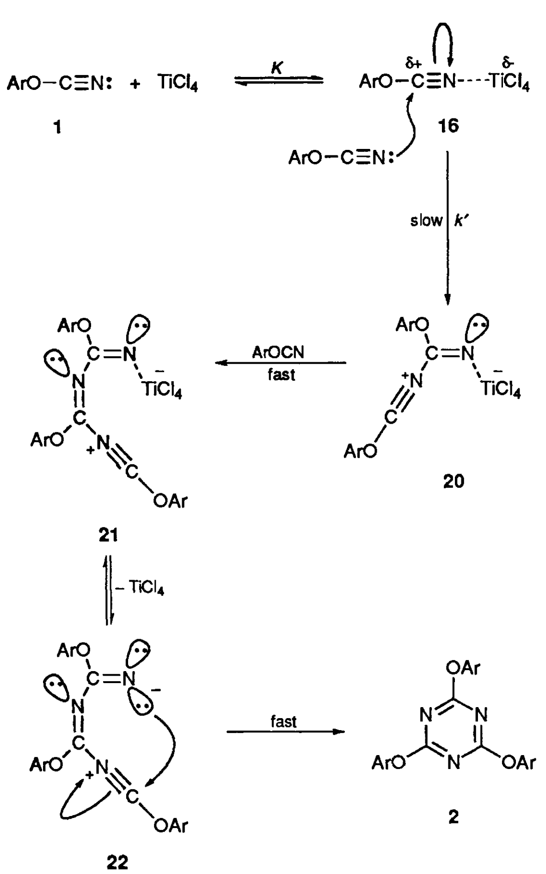
* If a structure of the form TiX_4L_2 is proposed for **16**, this mechanism would give rates either zero order (strong complex) or second order (weak complex) in cyanate.



Scheme 4

Given this we can only briefly speculate on the subsequent course of the reaction. However, that proposed in Scheme 4 is particularly attractive, since the dimeric product of the rate-limiting step **20** is a nitrillium ion[19] and would be expected to react with cyanate much more rapidly than the pseudo-nitrillium ion **16** to give the acyclic trimer **21**, also a reactive nitrillium ion. Moreover, nucleophilic addition to a nitrillium ion (and presumably to a pseudo-nitrillium ion) to give a *cis* arrangement of incoming nucleophile and nitrogen substituent (*trans anti* planar elimination of the lone pair), as shown for **16**⟶**20**, **20**⟶**21** and **21**↔**22**⟶**2**, is well established,[19] and would explain the efficient formation of the cyclic trimer.

Polymerisations of dicyanates are not normally carried out in solvent,[6] but the present reaction, catalysed by $TiCl_4$ in CH_2Cl_2 at room temperature, is a particularly clean and efficient one; the dicyanate **3** reacts rapidly and with complete loss of cyanate groups to give a resinous material. There may be applications for this method or a modification particularly for polymerisation of dicyanates bearing groups which are thermally labile.

Conclusions

The $TiCl_4$-catalysed cyclotrimerisation of aryl cyanates has been shown to proceed *via* a mechanism in which a pseudo-nitrillium ion cyanate–$TiCl_4$ complex undergoes nucleophilic attack by free cyanate. We propose that this attack is stereoselective, giving a nitrillium ion intermediate which reacts stereoselectively with further cyanate to yield the triazine product. We see no reason to invoke an imidoyl chloride intermediate as has been proposed by some, and suggest that this mechanism may prove to be common to many cyanate trimerisations catalysed by Lewis acids or electron-deficient metal ions.

Experimental

Materials.—$TiCl_4$, $TiCl_4$ in dichloromethane (1.0 mol dm^{-3}), 4-phenoxyphenol, 2,6-dimethylanisole, 2-allylphenol (Aldrich), 4-(1-methyl-1-phenylethyl)phenol (*p*-cumylphenol), and 2,2-bis(4-cyanatophenyl)propane (bisphenol A dicyanate) (Hi-Tek Polymers) were used as received.

Dichloromethane was dried by distillation from calcium hydride and stored over molecular sieves.

4-Phenylsulfonylphenol was prepared by the method of Szmant and Suld.[20] During this procedure it was found that initial reaction of benzenesulfonyl chloride with anisole yielded a mixture of *ortho-* and *para*-phenylsulfonylanisoles. However, treatment with HI yielded mainly the *para*-substituted phenol which was purified by recrystallisation.

4-Benzoyl-2,6-dimethylanisole and 4-Benzoyl-2,6-dimethylphenol.—To a mixture of 2,6-dimethylanisole (9.3 g, 0.067 mol) and aluminium trichloride (10.83 g, 0.082 mol) was added dropwise benzoyl chloride (9.41 g, 0.067 mol). The mixture was heated at 100 °C for 90 min and then poured onto ice, extracted into dichloromethane, dried, filtered, and concentrated *in vacuo*. Silica column chromatography using CH_2Cl_2–hexane gave 4-benzoyl-2,6-dimethylanisole[21] as a colourless oil (13 g, 81%); $\delta(CDCl_3)$ 2.32 (6 H, s, Me), 3.76 (3 H, s, MeO), 7.5–7.8 (7 H, m, ArH). Also isolated was 4-benzoyl-2,6-dimethylphenol as a colourless solid, m.p. 143 °C (lit.,[22] 141–142 °C); $\delta(CDCl_3)$ 2.28 (6 H, s, Me), 5.72 (1 H, s, OH), 7.4–7.8 (7 H, m, ArH).

4-Benzyl-2,6-dimethylanisole.[21]—4-Benzoyl-2,6-dimethylanisole (2.1 g, 0.0087 mol), potassium hydroxide (0.86 g, 0.015 mol), triethylene glycol (9 cm^3) and 99% hydrazine hydrate (0.88 cm^3) were heated to 195 °C for 4 h, during this time any water formed was removed by distillation. On cooling, the residue was extracted using ethyl acetate, dried and concentrated. Silica column chromatography of the residual yellow oil using CH_2Cl_2–hexane gave the product as a colourless oil (0.65 g, 35%); $\delta(CDCl_3)$ 2.20 (6 H, s, Me), 3.63 (2 H, s, CH_2), 3.81 (3 H, s, MeO), 6.80 (2 H, s, 3,5-H), 7.1–7.3 (5 H, m, ArH).

4-Benzyl-2,6-dimethylphenol.[21]—4-Benzyl-2,6-dimethylanisole (0.51 g, 0.0021 mol) and hydriodic acid (3.3 cm^3) were refluxed for 90 min. After cooling and addition of saturated aqueous Na_2CO_3 to pH 8, the mixture was extracted into CH_2Cl_2, dried and concentrated *in vacuo* to yield colourless needles after recrystallisation (0.16 g, 36%), m.p. 66 °C (from hexane) (lit.,[21] 68.5 °C); $\delta(CDCl_3)$ 2.19 (6 H, s, Me), 3.64 (2 H, s, CH_2), 4.45 (1 H, s, OH), 6.79 (2 H, s, 3,5-H), 7.1–7.3 (5 H, m, ArH).

Preparation of Cyanates.—A typical procedure was as follows.[1] To a solution of the phenol (0.0805 mol) in acetone (60 cm^3) was added cyanogen bromide (0.0805 mol). After cooling to −10 °C, triethylamine (0.0805 mol) was added dropwise and the reaction allowed to warm to room temperature over several hours. After dilution with dichloromethane (100 cm^3) and aqueous workup (except for the sulfonyl compound), the cyanate was purified by silica column chromatography using hexane–diethyl ether as eluent; the sulfonyl cyanate was further recrystallised from light petroleum.

Preparation of Triazines.—A typical procedure was as follows. To a solution of the cyanate (0.0015 mol) in dichloromethane (10 cm^3) at 25 °C was added a 1.0 mol dm^{-3} solution of titanium tetrachloride in dichloromethane (150 mm^3). After standing overnight the solution was washed with water, dried ($MgSO_4$), filtered and concentrated to leave the crude triazine which was purified by recrystallisation.

Equipment.—IR measurements and spectra were obtained using a Perkin-Elmer 841 or 1750 FT spectrophotometer; ^{1}H NMR spectra were obtained using a Bruker AC 300 instrument Analytical HPLC was carried out on a normal phase silica column fitted with a UV detector and using CH_2Cl_2 as solvent.

Kinetic Analysis.—Solutions of the cyanates, 0.05–0.15 mol dm^{-3} in dichloromethane (4 cm^3), were prepared in septum-capped vials and allowed to reach thermal equilibrium at 25 °C (thermostatted water bath). Reactions were initiated by injection of 10–60 mm^3 of 1.0 mol dm^{-3} titanium tetrachloride in dichloromethane solution, to yield reaction solutions 0.0025–0.015 mol dm^{-3} in titanium tetrachloride. The reactions were monitored by withdrawing at noted time intervals aliquots, typically 150 mm^3, and measuring the absorbance of the cyanate peak at 2237–2266 cm^{-1} using NaCl solution cells of 0.2 mm pathlength. Readings were corrected for cell and solvent absorbance by reference to an unchanging region of the spectrum around 2100 cm^{-1}. For repeated scans a similar procedure was used, except that spectra were recorded across the IR range using the FTIR instrument.

Values of $\mathrm{d}A/\mathrm{d}t_0$ obtained by this method showed standard deviations of $< \pm 6\%$ over at least three determinations. It should be noted that attempts to monitor the reaction *in situ* in NaCl solution cells gave much poorer reproducibility, probably due to the effect of atmospheric moisture, while the intense UV–VIS absorptions at the concentrations required for reasonable rates precluded *in situ* monitoring by UV–VIS spectroscopy.

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