ORGANOBORON COMPOUNDS

XXV *. KINETIC STUDIES OF THE AMINOBORATION OF PHENYL ISOCYANATE

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Summary

The rate constants, for the reaction between phenyl isocyanate and a series of aminoboranes have been determined using infrared spectroscopy. The relative rates for bis-amino-phenylboranes are $NHBu^n > NMe_2 > NHBu^t$, $NHBu^n > NHBu^i > NHBu^s$, and for $PhB \begin{smallmatrix} X \\ NMe_2 \end{smallmatrix}$ are $NMe_2 > NHBu^t > OMe > Br > F > Cl > Ph$.

We have recently obtained a relative migratory aptitude order for the reaction between phenyl isocyanate and bis-amino-phenylboranes using competition reactions [1]. The results were rationalised on the basis of the product of an insertion reaction (eq. 1) being thermodynamically controlled and this rationalisation was in agreement with previously published work [2].

$$Ph_2BNR_2 \quad + \quad PhNCO \quad \longrightarrow \quad Ph_2B \overset{\overset{\displaystyle Ph}{|}}{-} N \overset{\overset{\displaystyle O}{\|}}{-} C - NR_2 \quad (1)$$

In order to establish whether there is any correlation between rates of reaction and equilibria for these reactions the rate constants for the reaction of phenyl isocyanate and a series of bis-amino-phenylboranes have been determined. In addition we have also determined the rate constants for the insertion reaction between phenyl isocyanate and the dimethylamino group in a series of compounds of the type $PhB(NMe_2)X$ (where $X = F, Cl, Br, OMe, NMe_2, NHBu^t$ and Ph) in order to observe how the substituent X affects the rate of reaction.

The rate constants for the reaction between phenyl isocyanate and aminoboranes were evaluated by following the decrease of the $\nu(NCO)$ band of phenyl isocyanate in the infrared spectrum. Phenyl isocyanate has a very strong absorption peak at 2225 cm^{-1} which is not complicated by absorption peaks of the reaction products.

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* For part XXIV see Ref. 1.

Rate measurements

A calibration curve of peak height to concentration for the isocyanate absorption at 2225 cm^{-1} was determined over the concentration range 3.33×10^{-2} to 3.33×10^{-3} M. In a typical experiment a solution of a bis(dialkylamino)phenylborane in toluene (0.0333 M) was added to an equivalent quantity of a solution of phenyl isocyanate in toluene (0.0333 M). The mixture was then shaken for ten seconds and small quantities were removed at predetermined time intervals. The infrared spectrum of each sample was scanned in the 2450–2150 cm^{-1} region and the height of the 2225 cm^{-1} absorption band was determined. Using the calibration curve it was therefore possible to calculate the concentration, for each sample, of unreacted phenyl isocyanate.

Since the reaction under investigation follows second order kinetics and the concentrations of both reactants are the same the following equation for k, the second order rate constant, is applicable: $k = [x/at(a - x)]$ where x is the fractional concentration of phenyl isocyanate which has reacted in time t, a is the initial concentration of phenyl isocyanate and $(a - x)$ the fractional concentration of phenyl isocyanate remaining.

TABLE 1

PhB(NMe$_2$)$_2$ (0.0333 M) AND PhNCO (0.0333 M) IN TOLUENE AT 23°C

Time (min)	Height (mm)	$a - x$	x	$(x/a - x)$	k (1 M^{-1} min^{-1})
0	117	1.0	0	0	0
5	92	0.6	0.4	0.666	4.0
10	74	0.43	0.57	1.326	3.98
15	64	0.35	0.65	1.86	3.72
20	54	0.275	0.725	2.64	3.96
30	42	0.2	0.8	4.0	4.0
40	34	0.16	0.84	5.25	3.94
50	28	0.135	0.865	6.4	3.84
60	23	0.115	0.885	7.7	3.85
∞	0	0	1.0	∞	∞

TABLE 2

PhBNMe$_2$NHBu^i (0.0333 M) AND PhNCO (0.0333 M) IN TOLUENE AT 23°C

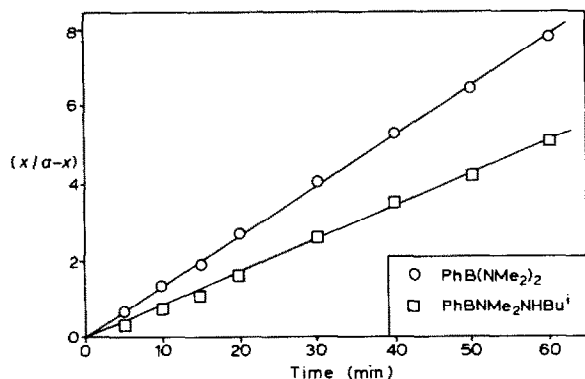| Time (min)	Height (mm)	$a - x$	x	$(x/a - x)$	k (1 M^{-1} min^{-1})
0	117	1.0	0	0	0
5	97	0.67	0.33	0.493	2.96
10	91	0.59	0.41	0.695	2.09
15	82	0.5	0.5	1.0	2.00
20	70	0.4	0.6	1.5	2.25
30	55	0.285	0.715	2.509	2.51
40	46	0.225	0.775	3.444	2.59
50	41	0.195	0.805	4.128	2.48
60	35	0.165	0.835	5.061	2.53
∞	0	0	1.0	∞	∞

Fig. 1. Kinetic plots of data in Tables 1 and 2.

Tables 1 and 2 record the kinetic data for two examples and Fig. 1 the kinetic plots, $[x/a - x]$ versus t, for each example. The slope (ak) of each graph was determined and hence the second order rate constant was calculated and the results are summarised in Table 3.

Discussion

Consideration of the values of the rate constants (Table 3) reveals that there is no dramatic change in the rate of the reaction as the amino group becomes more bulky, e.g. replacement of NMe_2 by NPr_2^i, although the rate of reaction is generally slower when the amino group is more hindered. Clearly the effect of steric hindrance could not in itself account for the relative migratory aptitude orders we have established for aminophenylboranes and it is more likely that the RMA orders are determined by thermodynamic control.

In contrast however a dramatic change in rate is observed in compounds of the type $PhB(NMe_2)X$ on changing the group X. For example when $X = NMe_2$ or $NHBu^t$ the rate is relatively fast, when $X = OMe$ the rate is slower and when $X = $ halogen the rate is very much slower. This observed behaviour correlates well with the degree of $p_\pi-p_\pi$ bonding between boron and the group X and the relative rate constants correlate with $G^\star$ values for the series $PhBNR_2X$. For example the value of $\Delta G^\star$, for the rotation about the B–N bond is generally about 10 kcal/mol for $X = NR_2$ [3,4], 16 kcal/mol for $X = OMe$ [5] and 20 kcal/mol for $X = $ halogen [5]. $\Delta G^\star$ can be taken as a measure of the degree of back donation from the group X and the relative rate constants appear to correlate with the degree of back donation from the group X. However a general correlation of $\Delta G^\star$ with rate constants is dangerous because although back donation from X increases k and decreases $\Delta G^\star$ increasing the size of NR_2 would both decrease $\Delta G^\star$ and k. However for the series $PhB(NMe_2)X$ (where X = F, Cl, Br, OMe and NMe_2) we would suggest that steric effects are relatively unimportant.

A speculative rationalisation of the observed results of the interaction between phenyl isocyanate and $PhB(NMe_2)X$ is as follows.

The mechanism of the reaction is envisaged as a nucleophilic attack of the nitrogen lone pair, of phenyl isocyanate, on boron with a concomitant nucleophilic

attack of the nitrogen lone pair of the amino group of the carbonyl carbon of phenyl isocyanate.
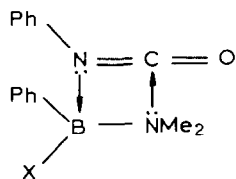
When the group X is a poor mesomeric donor (e.g. halogen) there is substantial back donation of the nitrogen lone pair towards boron resulting in a high barrier to rotation about the $B-NMe_2$ bond. Hence the NMe_2 group is therefore a less effective nucleophile and the rate of reaction is slow. However when the group X is a good mesomeric donor, e.g. NMe_2, back donation of the nitrogen lone pair to boron is reduced resulting in a lower barrier to rotation about the $>B-NMe_2$ bond. Since the delocalisation of the nitrogen lone pair on to boron is reduced it is therefore a better nucleophile and the rate constant is higher. The methoxy group shows intermediate behaviour.

A consideration of the rate constants in Table 3 suggests an order $NMe_2 > NHBu^t > Br > F > Cl > Ph$.

Experimental

The compounds used in the investigation were prepared by established methods namely dialkylaminophenylboranes [6], alkylaminodialkylaminophenylboranes [7], bis(dimethylamino)phenylborane [8], dialkylaminomethoxyphenylboranes [9,10], dimethylaminodiphenylborane [11,12] and dialkylaminohalophenylboranes [9,13,14].

TABLE 3

RATE CONSTANTS FOR THE INSERTION REACTION OF AMINOPHENYLBORANES WITH PHENYL ISOCYANATES (EQUAL INITIAL CONCENTRATIONS)

Compound	Concentration (M)	Temperature $(°C)$	k $(l\ M^{-1}\ min^{-1})$
$PhB(NMe_2)_2$	0.0333	23	3.9
$PhB(NHBu^n)_2$	0.0333	23	5.0
$PhB(NHBu^t)_2$	0.0333	23	2.4
$PhB(NMe_2)NHBu^n$	0.0333	23	4.2
$PhB(NMe_2)NHBu^i$	0.0333	23	2.6
$PhB(NMe_2)NHBu^s$	0.0333	23	2.7
$PhB(NMe_2)NHBu^t$ [a]	0.0333	23	2.3
$PhB(NMe_2)OMe$	0.0333	23	0.9
$PhB(NPr_2^i)OMe$	0.0333	23	0.45
$PhB(NMe_2)F$	0.0333	110	0.27
$PhB(NMe_2)Cl$	0.0333	110	0.21
$PhB(NMe_2)Br$	0.0333	110	0.36
$PhB(NMe_2)Ph$	0.0333	110	0.19
$PhB(NPr_2^i)Cl$	0.0333	110	0.15

[a] For this compound relative migratory aptitude is $NMe_2 > NHBu^t$ [1].

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