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THE KINETICS AND MECHANISM OF THE PHOSPHORUS-CATALYSED DIMERISATION OF ACRYLONITRILE

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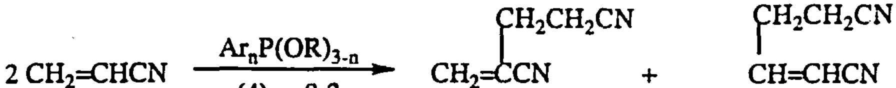
Abstract. The kinetics and mechanism of the phosphinite-catalysed dimerisation of acrylonitrile to 1,4-dicyanobut-1-ene and 2,4-dicyanobut-1-ene are presented and discussed.

INTRODUCTION

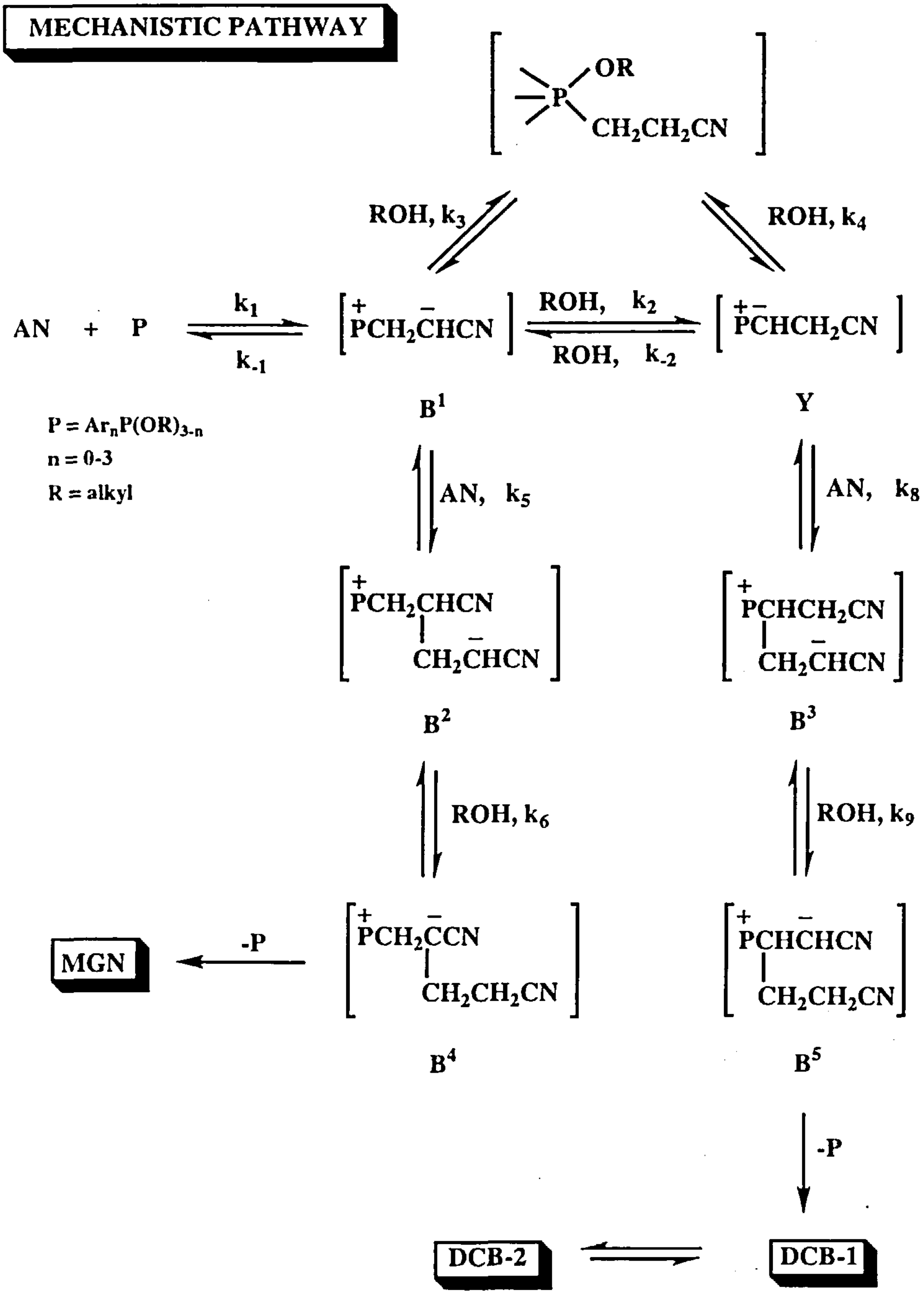
The dimerisation of acrylonitrile (AN,1) gives either 2,4-dicyanobut-1-ene (MGN, 2) or *cis/trans* 1,4-dicyanobut-1-ene (DCB, 3) as the principle products and hydrogenation of the latter leads to hexamethylene diamine, a vital intermediate en-route to Nylon. Thus the *selective*, catalysed dimerisation of AN and DCB is potentially a very important process which has been achieved using a variety of tricoordinate organophosphorus compounds (4) as homogeneous catalysts[1].



$$2\,CH_2{=}CHCN \xrightarrow[(4)\ n=0\text{-}3]{Ar_nP(OR)_{3-n}} CH_2{=}C(CN)CH_2CH_2CN + NCCH{=}CHCH_2CH_2CN$$

(1) (2) (3)

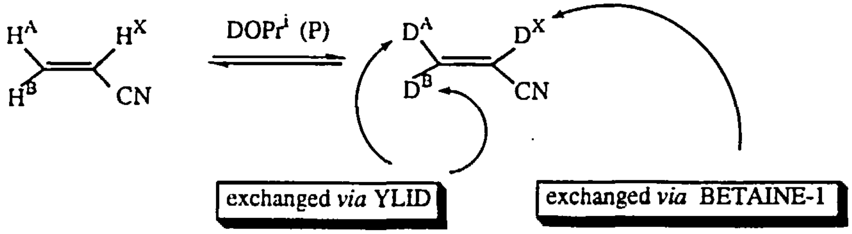
The successful exploitation of the dimerisation reaction as a commercial process, however, depends upon a knowledge of the optimum combination of rate, selectivity and turnover for the catalyst system. This paper describes the structural and kinetic studies to elucidate the mechanism of the reaction and hence define the operational window for maximum catalytic efficiency.


MECHANISTIC PATHWAY
OR
CH2CH2CN
ROH, k3
ROH, k4
AN + P
k1
k-1
+ − PCH2CHCN
ROH, k2
ROH, k-2
+− PCHCH2CN
P = ArnP(OR)3-n
n = 0-3
R = alkyl
B1
Y
AN, k5
AN, k8
+ PCH2CHCN − CH2CHCN
+ PCHCH2CN − CH2CHCN
B2
B3
ROH, k6
ROH, k9
MGN
-P
+ − PCH2CCN CH2CH2CN
+ − PCHCHCN CH2CH2CN
B4
B5
-P
DCB-2
DCB-1

Scheme 1

RESULTS AND DISCUSSION

The mechanistic pathway proposed for the formation of dimers (2) and (3) is shown in Scheme 1. In addition the reaction affords a number of by-products including 1,4-dicyanobut-2-ene, a variety of trimeric species and a crystalline hexamer $\{(CNCH_2CH_2)_2C(CN)CH=CHC(CN)(CH_2CH_2CN)_2\}$ in quantities dependent upon the reaction conditions and the catalyst used. Although no betaine (B) or ylid (Y) intermediates were observed by nmr, the intermediacy of the ylid species was established by trapping the latter with benzaldehyde[1b]. The kinetics of the reaction were studied by monitoring the rate of disappearance of AN and the rate of appearance of DCB or MGN by gas liquid chromatography (glc) on a capillary column which was also capable of analysing the reaction mixtures quantitatively for trimers. Any crystalline hexamer formed was filtered off and estimated gravimetrically. Independent experiments showed that hexamer was derived from either DCB-1 or DCB-2 and that the trimers (and oligomers) were derived in a consecutive fashion from dimers and AN rather than in a parallel manner from B^2 or B^3 plus AN (see Scheme 1). Thus it was possible to correct the concentrations of AN, DCB or MGN at any time, t, for the formation of hexamer or trimers. Thereafter, plots of ln f[AN], ln f {DCB] and ln f [MGN] *vs* time all gave excellent linearity ($r>0.99$) with slopes = $2k_1$ [P] where [P] is the concentration of catalyst used. Thus the reaction was shown to be first order in AN and first order in [P], - Table 1, which indicates the excellent agreement found between the three experimental parameters used to monitor the rate. The value of K_2k_8/k_5 was taken as the ratio of DCB/MGN found in the product and is seen to be essentially *independent* of the concentration of catalyst used. The value of K_2 was estimated independently from the ratio of H^A (or H^B) to H^X incorporated into unreacted D_3-AN or the incorporation of D into unreacted AN over a range of conversions from 2 to 40%. It was found to be about 2 for Ph_2POPr^i but to vary with



the nature of the catalyst (Table 2). Values for k_1 also varied with the catalyst (Table 2) and Hammett plots revealed ρ values (against σ) of -2.3 (for k_1) and +0.4 for K_2. These data, together with the activation parameters (Table 3) identify k_1 as the rate-limiting step of the reaction with K_2 controlling the selectivity to DCB as the substituents in the aryl groups are changed.

Table 1. k_{obs} *vs* [P] *via* [AN], f[MGN] and f[DCB] data
Temperature = 60°. 10 : 3 : 1 (v/v) toluene : AN : IPA, Ph_2POPr^i catalyst.

[CATALYST] mol l^{-1}	K_2k_8/k_5	10^5 x k_{obs} (s^{-1}) *via* [AN]	f[MGN]	f[DCB]
0.0426	18.9	1.06	0.904	0.904
0.0515	20.6	-	1.28	1.28
0.0618	18.9	1.52	1.67	1.67
0.0741	18.8	1.71	1.75	1.75
0.0754	20.8	2.18	1.91	1.91
0.124	19.9	3.23	3.19	3.19
0.146	18.9	3.72	3.57	3.57

Table 2. Average k_1 and K_2 values for a series of phosphinite catalysts $(XC_6H_4)(X'C_6H_4)POPr^i$ in 10 : 3 : 1 toluene : AN : IPA at 333K

CATALYST	K_2	k_8/k_5	10^4 k_1 (l mol^{-1} s^{-1})
X = X' = *p* -F	2.29	10.1	0.636
X = H' = H	2.02	9.4	2.57
X = X' = *m*-Me	1.55	9.9	4.85
X = H, X' = *p*-Me	1.65	10.1	5.34
X = H, X' = *p*-MeO	1.35	10.5	8.16
X = H, X' = *p*-Pr^iO	1.47	9.4	7.20
X = H, X' = *p*-Et_2N	1.01	7.5	77.1
X = X' = *o*-MeO	1.37	0.96	3.6

Table 3. Activation parameters for k_1 (10 : 3 : 1) at [CAT] = 0.073 M

CATALYST	10^4 k_1 (60°C) 1 mol^{-1} s^{-1}	E_A (kcal mol^{-1})	$\Delta S^\ddagger$ (cal mol^{-1} K^{-1}) (298 K)
(*p*-$Me_2NC_6H_4)_2$ $POPr^i$	2300	10.3	-33
(*p*-$MeOC_6H_4)_2POPr^i$	27.1	6.8	-52
(*p*-$MeC_6H_4)_2POPr^i$	3.91	6.0	-56
Ph_2POPr^i	2.57	5.0	-64

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