A Kinetic Study of the Reductive Coupling of 3-Bromo-propionitrile to Adiponitrile by Metals

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The kinetics of the iron metal-promoted reductive coupling of 3-bromopropionitrile (3-BrPN) to adiponitrile (ADN) and the reductive side reaction to a 1:1 molar mixture of propionitrile (PN) and acrylonitrile (AN) was investigated in the temperature range of 140 to 160 °C. AN and FeBr$_2$ were found to take part in the reactions. Without FeBr$_2$ initially present, the reaction system is characterized by an induction period and the presence of AN promotes the formation of adiponitrile. The kinetic data are most reasonably interpreted based on a reaction mechanism in which ADN and PN/AN are produced *via* kinetically independent pathways. The formation of ADN is believed to proceed through a soluble type of Fe(0)-complex. The average composition of the Fe(0)-complex was determined to be Fe(AN) (3-BrPN)$_5$.

The formation of PN and AN is believed to proceed *via* a classical Grignard reaction type pathway. In the presence of FeBr$_2$, the following metals were found to be active coupling agents: Cr, Mn, Co, Ni, Cu, Zn, Ag, Cd, In, Sn, Sb, Hg, Tl, Pb and Bi.

In the Fe metal-promoted coupling system, FeBr$_2$ could be substituted by other metal bromide salts.

The coupling of aliphatic as well as aromatic organic halides, as first reported by Wurtz,[1] Fittig[2] and Ullmann,[3] is formally a reductive process in which two electrons are consumed per molecule of coupled product (1):

$$2 R - X \xrightarrow{+2e^-} R - R + 2X^- \qquad (1)$$
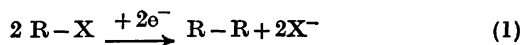
Numerous metals such as Na, K, (NaHg),[1,2] Mg,[4] Zn,[5,6] Fe,[7] Cu[3,8] and low valent metal compounds, *e.g.* Cr(II) salts,[9] Fe(CO)$_5$[10] and Ni(CO)$_4$[11,12] are known to be suitable chemical sources of electrons (coupling agents) for this type of reaction. Although sp-, sp^2- as well as sp^3-hybridized C atoms can be linked by this method, the reductive coupling reaction is known to proceed especially smoothly when the organic halide compound is of the allylic, vinylic or benzylic type. In particular, the mechanism of the allylic coupling reaction has been the subject of considerable study.[13]

The coupling reactions, which proceed *via* organocopper compounds, were recently reviewed by Kauffmann.[14] These reactions are classified as oxidative coupling reactions based on observations regarding the mechanism of the C/C linkage step (2):

$$[Cu - R] \longrightarrow \tfrac{1}{2} R - R + Cu \qquad (2)$$
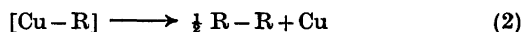
If we, however, consider the overall coupling process of an organic halide *via* this type of mechanism, this reaction is formally correctly classified as a *reductive* coupling reaction in which four electrons are being consumed per molecule of coupled product (3):

$$2R - X + 2CuX \xrightarrow[\text{(Mg, Li etc.)}]{+4e^-}$$
$$R - R + 2Cu + 4X^- \qquad (3)$$
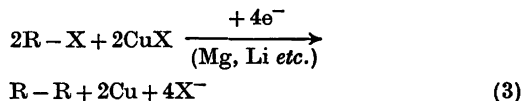
The copper salt is simply coreduced with the organic molecule during the process and, in being so, promotes the reaction. This type of coupling reaction is not limited to copper, but is also known to proceed with halides and such metals as Ag, Au, Hg, Co and Ni[15,16] as well as with thallium(I) halide.[17]
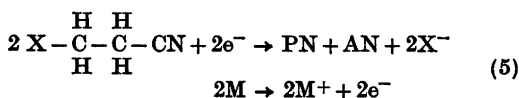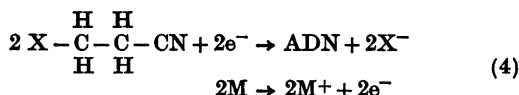
We have observed that organic compounds, containing a nitrile group (electron withdrawing group) attached to the β-carbon atom

relative to the halide, are efficiently coupled by a series of reductive coupling agents.[18] In particular, we wish to report on the mechanism of the iron metal-promoted reductive coupling of 3-bromoproprionitrile based on kinetic evidence. The reductive coupling of 3-chloropropionitrile using powerful reducing agents like NaHg in dipolar aprotic solvents is reported in the literature.[19]

RESULTS AND DISCUSSION

1. Stoichiometry and accountability

In addition to the main coupling product, adiponitrile (ADN), also propionitrile (PN) and acrylonitrile (AN) are formed in a molar ratio of PN/AN = 1/1. The formal stoichiometries of the redox reactions leading to these products are shown in eqns. (4) and (5).

$$2 X-\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{H}}{|}}{C}}-\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{H}}{|}}{C}}-CN + 2e^- \rightarrow ADN + 2X^-$$
$$2M \rightarrow 2M^+ + 2e^- \tag{4}$$

$$2 X-\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{H}}{|}}{C}}-\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{H}}{|}}{C}}-CN + 2e^- \rightarrow PN + AN + 2X^-$$
$$2M \rightarrow 2M^+ + 2e^- \tag{5}$$

X = Halide; M = One equivalent reducing agent. Assuming that the reactions (4) and (5) are the only electron-consuming reactions taking place in the system, *one* mol of (ADN + PN) is formed per every *two* equivalents of coupling agent (M) consumed. The molar ratio between the amounts of (ADN + PN) which are produced in a system and the theoretical amounts which are calculated on the basis given above, is defined as the accountability (Acc) of the coupling agent employed in the reaction.

Accountabilities in the order of 90 % were achieved in the iron metal-promoted coupling of 3-bromopropionitrile (3-BrPN) under certain conditions, but in most cases significantly lower accountabilities are observed. Normally, low accountabilities are taken as an indication of the possible occurrence of unknown organic side reactions. Such reactions were, however, not detected in the iron metal-promoted coupling reaction of 3-BrPN. The observation of low accountabilities (calculated from the

amount of iron converted and (ADN + PN) made) is well understood and was found to be a direct result of the overall coupling mechanism as formally outlined in eqn. (6).

$$2(XPN) + M \rightleftharpoons \boxed{M - (XPN) - \text{Complexes}} \rightarrow$$
$$ADN + MX_2 \tag{6}$$
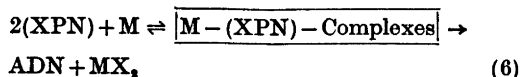
In accordance with eqn. (6), all systems which have not been reacted to completion (or close to) and in which the amount of intermediate complexes is significant relative to the amount of M converted, will show an apparent low accountability. By taking the amount of soluble intermediate complexes into account, the accountabilities for most of the systems investigated are in the order of 90 % of theory.

2. Kinetics of the iron metal-promoted coupling of 3-BrPN to ADN

The rate of reaction between Fe powder and 3-BrPN as well as the manner in which they react was found to be strongly influenced by the presence of FeBr₂ and AN. Since both compounds represent reaction products and naturally will be present in the reaction mixtures, it is necessary to take their effect into account in order to carry out a kinetic analysis.

2.1. The kinetic effect of $FeBr_2$. The rate effect of the initial absence of FeBr₂ is clearly demonstrated in Fig. 1 (curve a) and results
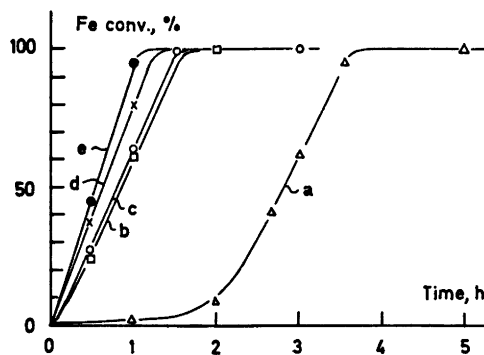

Fig. 1. The effect of FeBr₂ on the Fe conversion; time relationship at 150 °C. Feed composition: $[Fe]_0 = 100$ g l⁻¹, $[AN]_0 = 0.75$ mol l⁻¹ and $[3\text{-BrPN}]^0 = 10.9$ mol l⁻¹ $[FeBr_2]_0$ mol l⁻¹: a = 0, b = 0.23, c = 0.93, d = 1.16 and e = 1.39.
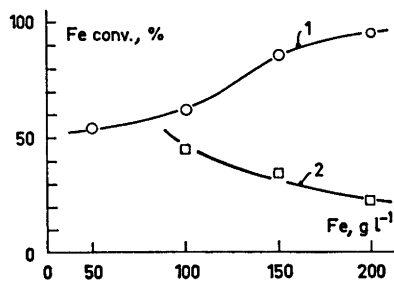
Fig. 2. The relationship between the Fe conversion and the concentration of Fe charged, in the absence (curve 1) and presence of initial $FeBr_2$ (curve 2). Temp: 150 °C, time: 3 h, $[AN]_0 = 0.75$ mol l^{-1}, $[3\text{-BrPN}]_0 = 10.9$ mol l^{-1} and $[FeBr_2]_0 = 1.39$ mol l^{-1} ($[FeBr_2]_0$ has reference to curve 2 only).
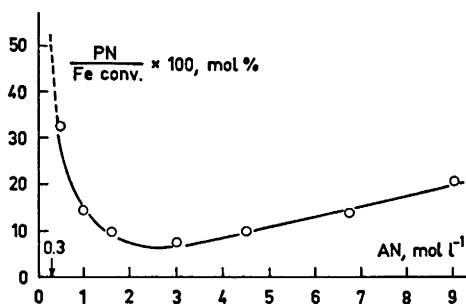

Fig. 3. The proportion of Fe used in the PN reaction as function of the AN-concentration. Temp: 150 °C, time: 1 h, $[Fe]° = 100$ g l^{-1} and $[FeBr_2]_0 = 1.39$ mol l^{-1}.

in the presence of an induction period (1 – 2 h). When $FeBr_2$ is added to the system, the disappearance of the induction period is observed (Fig. 1, curves b – e). From the shape of the curves, the following conclusions may be drawn: (a) Changing the concentration of $FeBr_2$ within the range $0 - 0.3$ (± 0.1) mol l^{-1} results in a dramatic effect on the rate of reaction, while the effect of increasing it above the level is minor. (b) With $FeBr_2$ present in a concentration exceeding 0.3 (± 0.1) mol l^{-1} the order of reaction with respect to Fe is close to zero up to Fe-conversions exceeding 95 %. It was furthermore observed, that two distinctly different relationships exist between the Fe-conversion and the amount of Fe charged to the reaction system depending upon whether or not $FeBr_2$ initially is present (Fig. 2, curve 1 *versus* 2). In the absence of $FeBr_2$, higher Fe-conversions are observed with increasing Fe-concentrations, while in the $FeBr_2$-promoted reaction system the reverse relationship is detected. The latter relationship is expected and in accordance with the zero order Fe kinetics, while the first one is best explained based on the observed $FeBr_2$-effect regarding the induction period. During the initial part of these reactions, $FeBr_2$ is formed at a rate which is dependent upon the amount of Fe present. The duration of the induction period is consequently reduced with increasing amounts of Fe present in the reaction mixture, and, as the overall result thereof, higher Fe-conversions are observed.

2.2. The kinetic effect of AN. It was initially observed that when "pure" 3-BrPN is reacted with $Fe/FeBr_2$, the initial reaction products formed are mainly PN and AN in accordance with reaction (5), until a certain amount of AN has been produced. Through the presence of AN in the reaction mixture the path of reaction, the relative rate of reactions (4) and (5),

Table 1. The effect of changing the concentrations of AN and 3-BrPN on the rate of Fe conversion and product composition. Temp.: 150 °C, time: 1 h. $[Fe] = 100$ g l^{-1} and $[FeBr_2]_0 = 1.4$ mol l^{-1}.

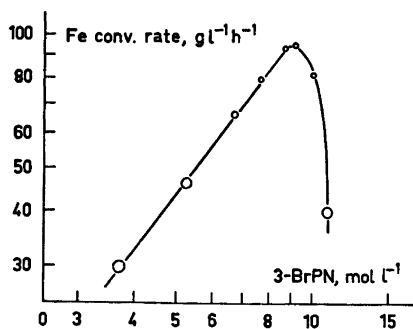| Feed, mol l^{-1}			Prod. composition, mol %		
AN	3-BrPN	Fe conversion,%	ADN	PN	Acc.mol %
0	11.5	81	5.0	95.0	32.5
0.75	10.9	95	76.7	23.3	62.4
1.51	10.3	93	83.1	16.9	59.5
3.01	9.06	79	80.2	19.8	52.0
4.52	7.88	66	74.4	25.6	39.7
6.78	6.05	46	71.2	28.8	45.5
9.05	4.21	30	67.1	32.9	63.8

Fig. 4. The relationship between the hourly Fe conversion and the concentration of 3-BrPN (log/log). Temp. 150 °C, time 1 h, $[Fe]_0 = 100 \text{ g l}^{-1}$ and $[FeBr_2]_0 = 1.39$ mol l^{-1}.
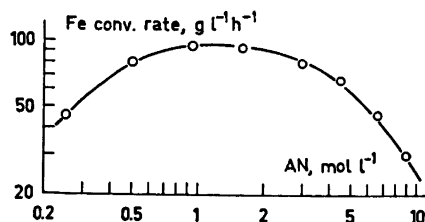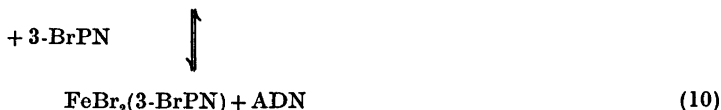

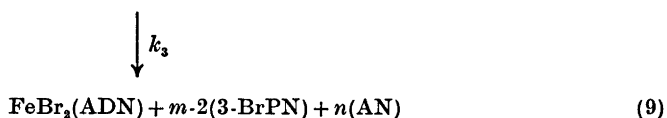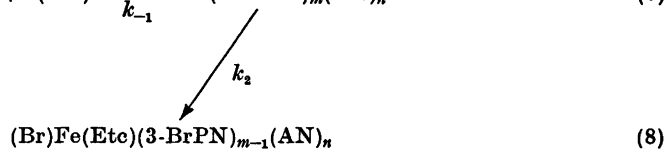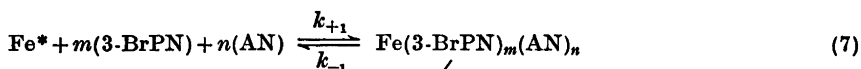*Fig. 5.* The relationship between the hourly Fe-conversion and the concentration of AN (log/log). Temp: 150 °C, time: 1 h, $[Fe]_0 = 100$ g l^{-1} and $[FeBr_2]_0 = 1.39$ mol l^{-1}.

is strongly influenced. The critical relative rate change was found to take place at relatively low AN concentrations as demonstrated in Fig. 3. At an AN concentration of approximately 0.3 mol l^{-1} (~ 1 wt.%) the relative rate of reactions (4) and (5) is in the order of one. At AN concentrations lower than 0.3 mol l^{-1}, the formation of PN and AN represents the main reaction, while with AN concentrations at a higher level the formation of coupled product, ADN, predominates (Table 1). Since AN represents an initial reaction product, closed reaction systems starting with "pure" 3-BrPN during the course of reaction undergo a critical change in the AN concentration with a corresponding change in the relative rate of reactions (4) and (5) and the composition of

products formed. A series of analogous experiments was carried out in the presence of constant initial amounts of Fe and FeBr$_2$ using different mixtures of 3-BrPN and AN in order to determine the overall kinetic effect of these two compounds on the rate by which Fe is converted. The conditions, as well as the data obtained, are reported in Table 1 and the relationships between the hourly conversion of Fe (rate) and the average concentration of 3-BrPN and AN during the run are shown in Figs. 4 and 5, respectively. Both relationships clearly demonstrate by the existing maxima that AN has to be considered as a true reactant in the system and not as an inert diluent. In particular, it appears that the kinetic influence is strong in the low AN concentration

$$Fe^* + m(3\text{-BrPN}) + n(AN) \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} Fe(3\text{-BrPN})_m(AN)_n \tag{7}$$

$$\downarrow k_2$$

$$(Br)Fe(Etc)(3\text{-BrPN})_{m-1}(AN)_n \tag{8}$$

$$\downarrow k_3$$

$$FeBr_2(ADN) + m\text{-}2(3\text{-BrPN}) + n(AN) \tag{9}$$

$$+ 3\text{-BrPN} \quad \Updownarrow$$

$$FeBr_2(3\text{-BrPN}) + ADN \tag{10}$$

Scheme 1. The formation of ADN. Fe* = Fe surface, Etc = $(-CH_2 - CH_2 - CN)$ and k = rate constant.

range (<1 mol l^{-1}) where a kinetic power of AN in the order of one is detected.

2.3. Formal reaction scheme and kinetics. As indicated previously, direct evidence was found to support the theory that the coupling of 3-BrPN to ADN occurred through soluble Fe-(3BrPN)-complexes. Such evidence is presented in the experimental data reported in Fig. 6, which demonstrates that significant amounts of ADN are formed after a complete conversion of the metallic Fe has been reached. Based on this information, as well as the experimental rate data (Figs. 4 and 5) and selectivity data regarding the formation of ADN, the reaction Scheme 1 [eqn. $(7-10)$] is discussed.

In the first reaction step [eqn. (7)], the Fe surface, 3-BrPN and AN are in equilibrium with a soluble type of an olefin $(AN) - Fe(0)$-complex, which in the second step [eqn. (8)] undergoes an irreversible oxidative rearrangement reaction leading to a Grignard type of organometallic Fe intermediate. This intermediate then in turn undergoes the C/C coupling reaction [eqn. (9)] which in Scheme 1 is formulated as a monomolecular reaction taking place within the organometallic complex. It is, however, not possible based on our kinetic data to exclude a bimolecular reaction step (between the complex and free 3-BrPN) since reaction (8) is believed to be the rate limiting step. Due to the relatively high complexing ability of ADN towards FeBr$_2$, it is likely that FeBr$_2$.ADN complexes are formed in the reaction mixture. (The composition of such complexes is given in Ref. 20). The relative amount of ADN in complex and free form is determined by equilibrium reactions with competing FeBr$_2$ complexing ligands present, *e.g.* 3-BrPN, as indicated by reaction (10) (Scheme 1). Under steady-state conditions in such systems wherein the formation of ADN represents the main reaction in the system, the rate of ADN formation is proportional to the rate by which Fe is converted. From the experimental data obtained under such conditions (the concentration of AN being above the critical level) it may be concluded that the formation reaction of ADN is zero order in Fe. This result is in agreement with the formulation of reaction (7) as a pre-established equilibrium reaction, the equilibrium being

maintained as long as Fe surface is present in the system (experimentally demonstrated for Fe concentrations as low as 5 g l^{-1}). Furthermore, it excludes the reaction taking place on the surface of Fe from being the rate controlling step in the formation of ADN. In accordance with reaction Scheme 1, two different types of ADN precursor complexes are involved, one containing Fe in the zero oxidation state and a Grignard type complex containing Fe in its oxidized form ($+2$ oxidation state). From the observation that practically no PN is made during (acid) hydrolysis of the effluent, the concentration of the Grignard type intermediate, which in reaction with H$_2$O would give PN, is considered to be low. On this basis, it is believed that the oxidative addition reaction (8) represents the rate determining step in the formation of ADN ($k_3 > k_2$). From the amount of ADN made after all the metallic Fe is reacted, the approximate concentration of the intermediate, Fe(3-BrPN)$_m$(AN)$_n$, can be calculated. For the system as reported in Fig. 6, (typical coupling experiment) it was determined to be 0.25 mol l^{-1}. It is noted at

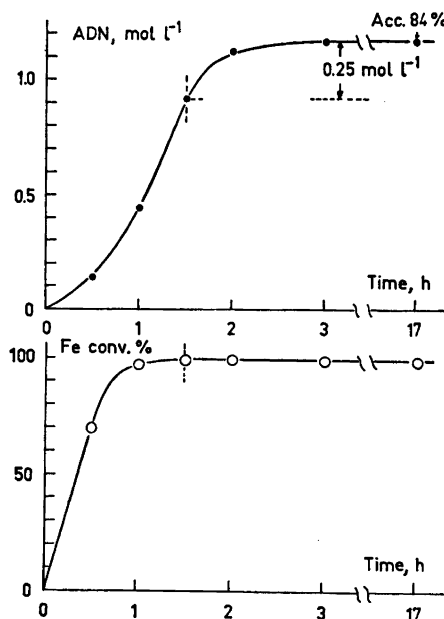*Fig. 6.* Bottom: Time-Fe conversion curve. Top: ADN concentration build-up as the function of time. Temp: 160 °C, [Fe]$_0 = 100$ g l^{-1}, [FeBr$_2$]$_0 = 1.39$ mol l^{-1}, [AN]$_0 = 0.75$ mol l^{-1} and [3-BrPN]$_0 = 10.9$ mol l^{-1}.
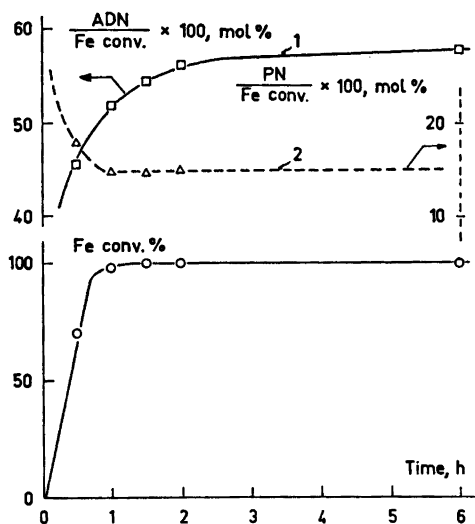
Fig. 7. Bottom: Time-Fe conversion curve. Top: The relative proportion of Fe reacted being accounted for by ADN (curve 1) and PN (curve 2). Temp. 160 °C, $[Fe]_0 = 100$ g l^{-1}, $[FeBr_2]_0 = 1.39$ mol l^{-1}. $[AN]_0 = 0.75$ mol l^{-1} and $[3\text{-BrPN}]_0 = 10.9$ mol l^{-1}.

this point, that practically no PN is made in the system after all the metallic form of Fe is converted (Fig. 7).

In order to understand and discuss the steady-state kinetics of the reaction leading to the formation of ADN, the system in which the following conditions are met;

$$[3\text{-BrPN}] \gg m[Fe(3\text{-BrPN})_m(AN)_n] \text{ and}$$
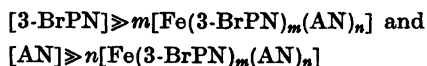
$$[AN] \gg n[Fe(3\text{-BrPN})_m(AN)_n]$$

will first be considered.

Under these conditions, the concentration of the intermediate is determined by eqn. (11) and since the rate of ADN formation is directly proportional to the concentration of the intermediate, $Fe(3\text{-BrPN})_m(AN)_n$, the overall dependence of $dADN/dt$ on the concentrations of 3-BrPN and AN is given by eqn. (12).

$$[Fe(3\text{-BrPN})_m(AN)_n] = \frac{k_{+1}}{k_{-1} + k_2} [3\text{-BrPN}]^m [AN]^n \tag{11}$$

$$\frac{-dFe}{dt} \approx \frac{d[ADN]}{dt} = \frac{k_{+1}k_2}{k_{-1} + k_2} [3\text{-BrPN}]^m [AN]^n \tag{12}$$

Through the application of an inspection method based on eqn. (12) and the experimental rate data (Fig. 4 and 5, Table 1), kinetic evidence for the values of m and n was computed. It was found that the only reasonable set of values for m and n which gave $k_{+1}k_2/k_{-1} + k_2 =$ constant over the entire range of different sets of 3-BrPN and AN concentrations examined, is

$$m = 5 \text{ and } n = 1$$

The kinetic values for $k_{+1}k_2/k_{-1} + k_2$ (150 °C) are reported in Table 2 and were found to be valid for systems in which the concentration of AN exceeds 1.0 mol l^{-1}. Accordingly, the average composition of the Fe(0)-intermediate complex based on the kinetic data is Fe(3-BrPN)$_5$(AN)$_1$, and the ADN formation rate in solvent free systems at 150 °C is given by eqn. (13).

$$\frac{d[ADN]}{dt} = 2.05 \times 10^{-5} [3\text{-BrPN}]^5 [AN] \tag{13}$$

The practical Arrhenius activation energy (E_A) for this reaction was calculated using eqn. (14) and found to be $E_A = 16 \pm 1$ kcal mol^{-1} based on rate data within the temperature range from 140 to 160 °C.

$$E_A = 1.986 \left(\ln \frac{k^1}{k^{11}} \right) \frac{T^1 T^{11}}{T^1 - T^{11}} 10^{-3}, \text{ kcal mol}^{-1} * \tag{14}$$

$k^1 =$ rate const. at the higher abs. temperature T^1.

From the shape of the curves (maxima) given in the Fig. 4 and 5 it can clearly be seen that the kinetics developed for systems in which $[3\text{-BrPN}] \gg 5[Fe(0)\text{-complex}]$ and $[AN] \gg$

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* 1 kcal = 4.184 kJ.

Table 2. Kinetic data related to eqn. 12. Temp.: 150 °C, $m = 5$ and $n = 1$.

[3-BrPN] (average) mol l^{-1}	[AN] (average) mol l^{-1}	dFe/dt mol l^{-1} h^{-1}	$\dfrac{k_1 k_2}{k_1 + k_2}$ l^5 mol^{-5} h^{-1} 10^5
5.2	6.8	0.83	2.3
6.7	4.5	1.18	2.0
7.7	3.0	1.43	1.8
8.6	1.6	1.83	2.1

2.05

[Fe(0)-complex] are not valid in 3-BrPN/AN systems in which the concentration of AN is less than ~ 1.0 mol l^{-1}. In order to understand and describe the reaction system at low AN levels, it is necessary to take the concentration of the intermediate into account. Steady state is then defined by eqn. (15), since the actual concentration of free AN in the reaction mixture is given by the difference between the total AN concentration, $[AN]_{tot}$, and the concentration of the intermediate Fe(0)-complex.

$$k_{+1}[3\text{-BrPN}]^5([AN]_{tot} - [Fe(3\text{-BrPN})_5(AN)]) = k_{-1} + k_2)[Fe(3\text{-BrPN})_5(AN)] \quad (15)$$

Rearrangement of eqn. (15) results in eqn. (16) and the rate by which ADN is formed in the system, accordingly is given by eqn. (17).
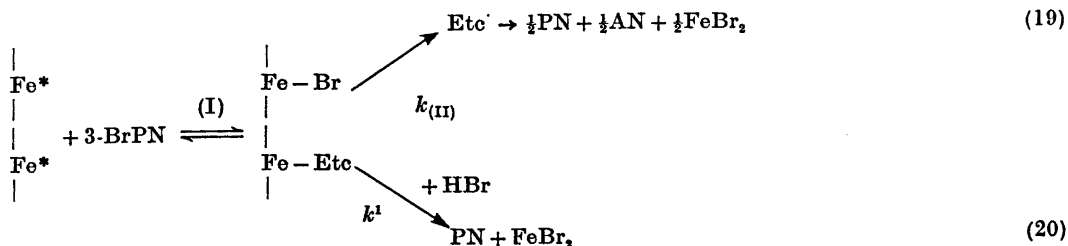
$$[Fe(3\text{-BrPN})_5(AN)] = \frac{k_{+1}[3\text{-BrPN}]^5[AN]_{tot}}{(k_{-1} + k_2) + k_{+1}[3\text{-BrPN}]^5} \quad (16)$$

$$\frac{d[ADN]}{dt} = \frac{k_{+1}k_2[3\text{-BrPN}]^5[AN]_{tot}}{(k_{-1} + k_2) + k_{+1}[3\text{-BrPN}]^5} \quad (17)$$

When high concentrations of 3-BrPN are used in conjunction with low AN concentrations, $k_{+1}[3\text{-BrPN}]^5 \gg (k_{-1} + k_2)$ and the rate of ADN formation becomes independent of the 3-BrPN concentration and first order with respect to the total concentration of AN in the system,

$$\frac{d\,ADN}{dt} \approx k_2[AN]_{tot} \quad (18)$$

The experimental observation of a rate maximum in the 3-BrPN/AN system (Figs. 4 and 5) and the observation that a direct relationship between the rate of reaction and the concentration of AN was found to exist at low AN levels is therefore clearly understood and consistent with the basic reaction Scheme 1.

Table 3. The relationship between Fe surface area and product composition. Temp.: 150 °C, $[Fe]_0 = 100$ g l^{-1}, $[AN]_0 = 0.75$ mol l^{-1}, $[3\text{-BrPN}]_0 = 10.9$ mol l^{-1} and $[FeBr_2]_0 = 1.4$ mol l^{-1}.

| Time, h | Fe con-version, % | Prod. composition, mol % | | |
		ADN	PN	Acc.mol %
3	100[a]	78.9	21.1	85.6
5	71[b]	87.1	12.9	59.5
5	18[c]	94.5	5.5	54.8

[a] Iron powder, Reagent (ROC/RIC) (200 mesh). [b] Ditto (40 mesh). [c] Iron nail, cut in $\sim 1 \times 1$ mm pieces (very low surface area).

With regard to the order of reaction in respect to the concentration of 3-BrPN it may be concluded that it is a function of the concentration of 3-BrPN itself and undergoes a change in value from five to zero.

2.4. Kinetics of the iron metal-promoted reduction of 3-BrPN to PN. If the byproduct, PN, was formed through the same intermediate Fe complexes as ADN, the basic kinetics regarding its rate of formation would be expected to follow that of ADN. The experimental data reported in Fig. 7 show, however, that this is not the case. The relative product composition is a function of the Fe conversion, PN being preferably made at low Fe conversions (high Fe concentrations). Also the fact that the formation of PN ceases at the moment all the metallic Fe is converted represents strong evidence for a reaction mechanism different from that reported for the formation of ADN. The assumption that the PN is made *via* a reaction taking place on the surface of Fe, therefore, appears reasonable based on these facts and is furthermore supported by the selectivity data reported in Table 3. While the formation of

$$Etc \rightarrow \tfrac{1}{2}PN + \tfrac{1}{2}AN + \tfrac{1}{2}FeBr_2 \quad (19)$$

$$
\begin{array}{ccc}
| & & | \\
Fe^* & & Fe-Br \\
| & (I) & | \qquad k_{(II)} \\
| + 3\text{-BrPN} \rightleftharpoons & & | \\
Fe^* & & Fe-Etc \\
| & & \qquad + HBr \\
& k^1 & \\
& & PN + FeBr_2
\end{array}
$$

$$(20)$$

Scheme 2. The formation of PN. $Fe^* = Fe$ surface, $Etc = (-CH_2 - CH_2 - CN)$.

ADN is zero order in Fe, the formation rate of PN appears to be related to the surface area of Fe present in the system. In order to discuss the kinetics, the reaction Scheme 2 is considered. In the first reaction step, 3-BrPN undergoes a homolytic splitting on the surface of Fe with the formation of one $Fe-Br$ bond and one $Fe-$carbon bond.

The $Fe-CH_2-CH_2-CN$ group then, because of its relative low thermal stability, either undergoes a homolytic splitting to an ethylcyano radical which disproportionates to PN and AN (pathway 19) or reacts with HBr (derived from 3-BrPN) to give PN directly (pathway 20). Both routes to PN will, because of the equilibrium reaction (21), give the same overall stoichiometry (5).

$$3\text{-BrPN} \xrightleftharpoons{K} \text{AN} + \text{HBr} \qquad (21)$$

$K =$ equilibrium constant.

Under conditions whereby the equilibrium between the Fe-surface and the 3-BrPN is established, the rates by which PN is made are given by the eqns. (22) and (23) for the two separate reaction pathways (19) and (20) respectively.

$$\frac{d[PN]}{dt} = 2k\text{Fe}^* \approx 2kf[\text{Fe}]^{2/3} \qquad (22)$$

$$\frac{d[PN]}{dt} = k^1\text{Fe}^*[\text{HBr}] \approx k^1Kf[\text{Fe}]^{2/3}$$
$$[3\text{-BrPN}][\text{AN}]^{-1} \qquad (23)$$

k and $k^1 =$ rate constants, $K =$ equilibrium constant (21), $\text{Fe}^* = $ Fe surface area and $f =$ conversion factor: Fe surface area/mass (assuming ball particles).

The overall rate for the formation of PN is accordingly given by eqn. (24) which rearranged for discussion of the kinetic data reported in Table 4 and Fig. 8 gives eqn. (25).

$$\frac{d[PN]}{dt} = (2kf + k^1Kf[3\text{-BrPN}][\text{AN}]^{-1}[\text{Fe}]^{2/3} \quad (24)$$

$$\frac{d[PN]}{dt}\left(\frac{1}{[\text{Fe}]^{2/3}}\right) = 2kf + k^1Kf[3\text{-BrPN}][\text{AN}]^{-1}$$
$$(25)$$

Based on the experimental PN data reported in Table 1, $(d[PN]/dt)(1/[\text{Fe}]^{2/3})$ values ([Fe] = the average conc. of Fe during the run in

[Fe] $g\ l^{-1}$	$[3\text{-BrPN}][\text{AN}]^{-1}$	$(d[PN]/dt)(1/[\text{Fe}]^{2/3})10^2$ $g^{1/3}\ l^{-1/3}\ h^{-1}$
59.5	20.0	16.90
52.5	9.60	9.50
53.5	5.50	6.55
60.5	2.50	2.98
67.0	1.50	4.06
77.0	0.78	3.06
85.0	0.41	3.68

g l^{-1}) corresponding to a series of molar 3-BrPN/AN ratios were calculated and are reported in Table 4. From the linear relationship between $(d[PN]/dt)(1/[\text{Fe}]^{2/3})$ and $[3\text{-BrPN}][\text{AN}]^{-1}$ (Fig. 8) it may be concluded that the experimental results are consistent with the basic kinetics developed based on the postulated reaction Scheme 2 [eqns. (19) and (20)]. The values for $(2kf)$ and (k^1kf) were graphically determined as indicated on Fig. 8 and found to be:

$$2kf = 2.6 \times 10^{-1} \ (150\ ^\circ\text{C})$$
$$k^1Kf = 0.61 \times 10^{-2} \ (150\ ^\circ\text{C})$$

Units: $d[PN]/dt$: g l^{-1} h^{-1}, [Fe]: g l^{-1}
[3-BrPN] and [AN]: mol l^{-1}

Using these values for the constants, the mol ratio of 3-BrPN/AN at which both reactions (19 and 20) give a 50 % contribution to the formation of PN was determined based on eqns. (22) and (23) and computed to be [3-BrPN]/[AN] = 4.25. Accordingly, in reaction mixtures having [3-BrPN]/[AN] > 4.25, the reaction (20) represents the main reaction route to PN. For [3-BrPN]/[AN] < 4.25, the
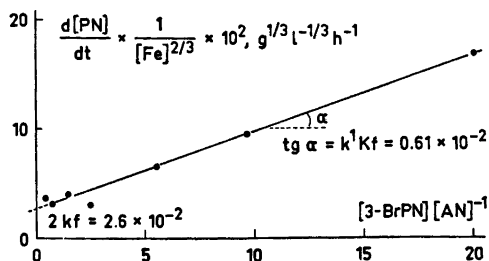

Fig. 8. Plot related to the kinetic evaluation of the PN reaction (Ref. eqn. 25).

Fig. 9. Kinetic relationship regarding the formation of PN.

bulk of PN is formed through reaction pathway (19). Under conditions whereby [3-BrPN]/[AN] $\ll 4.25$, the formation of PN should become independent of the 3-BrPN as well as the AN concentrations and only dependent upon the activity of Fe, *e.g.*, the thermal stability of the Fe − carbon bond o Fe − CH_2 − CH_2 − CN. Experimental results reported in Fig. 9 show that this in practice is the case for [3-BrPN][AN]$^{-1}$ < 2. On the other hand, when such concentrations of 3-BrPN and AN are employed that the mol ratio 3-BrPN/AN $\gg 4.25$, the rate of PN formation is directly proportional to the molar ratio between 3-BrPN and AN in the reaction system. At very low AN concentrations ([AN]→0) the value of 3-BrPN/AN limits infinity with a corresponding increase in the rate of PN formation *via* reaction (20) (step II). Under such conditions it is therefore likely that step I in the reaction Scheme 2, the addition of 3-BrPN to Fe*, becomes the rate controlling reaction step for the formation of PN.

2.5. *The mechanistic effect of FeBr$_2$ and AN.* The experimental data indicate two different types of FeBr$_2$ effects:

1. Activation of the Fe surface and thus catalyzing the equilibrium reaction (7).
2. Promotion of the oxidative addition reaction (8).

Oxidative addition reactions are known to take place on coordinative unsaturated species. Free coordination sites (as indicated by $\varDelta$) could be generated through a Lewis base dissociation reaction of the intermediate Fe-(0)-complex in which $FeBr_2$ acts as a Lewis base acceptor and accordingly promotes the reactions as indicated in eqn. (26). The coordinative unsaturated complex then in turn undergoes the oxidative addition reaction (27).

The complexes involved in these reactions (26 and 27) are stabilized by having AN as one of the ligands. The nature of the chemical bond between Fe and the olefinic function of AN is in accordance with the Dewer [21] and Chatt [22] binding model composed of a σ-type bond and a π-type electron back-donation bond. Because of the electron withdrawing effect of the electronegative nitrile group present in AN, it is reasonable to assume that the electron back-donation from Fe to AN is significant in these types of complexes and is to be made responsible for the overall stabilization of the Fe-(0)-complexes as well as the necessary thermal stability of the Fe-carbon bond in the

organometallic $(Fe-CH_2-CH_2-CN)$ interme-
diates. It is noted at this point, that data have
been obtained in our laboratories which clearly
indicate also the importance of AN as ligand
in Ni(0)-based coupling systems and that AN
in this type of system could be substituted by
the soft Lewis base, triphenylphosphine, which
of course is well-known to give the type of
stabilization effects discussed above.

3. The reaction promoting effect of salts different from FeBr₂

The promoting salt-effect was found not to
be limited to FeBr₂. A series of bromide salts
was tested in standard experiments and found
to be active. The data obtained with regard to
Fe conversion (1 h at 150 °C), selectivity to
ADN (mol ADN/mol Fe converted) and overall
accountability (mol (ADN + PN)/mol Fe con-
verted) are reported in Fig. 10, and indicate
that superior results are obtained using chro-
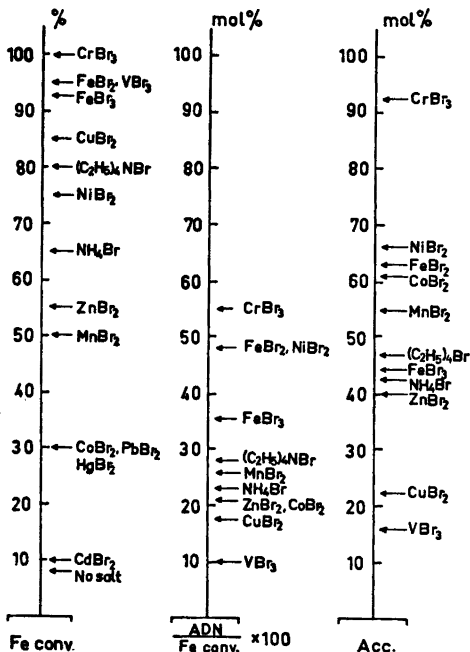mium, iron or nickel based promoters.

Fig. 10. The effect of bromide salts compared
with FeBr₂. Temp: 150 °C, time: 1 h. [Fe]₀ =
100 g l⁻¹ [AN]₀ = 0.75 mol l⁻¹, [3-BrPN]₀ =
10.9 mol l⁻¹ and [Bromide salt] = 1.39 mol l⁻¹.

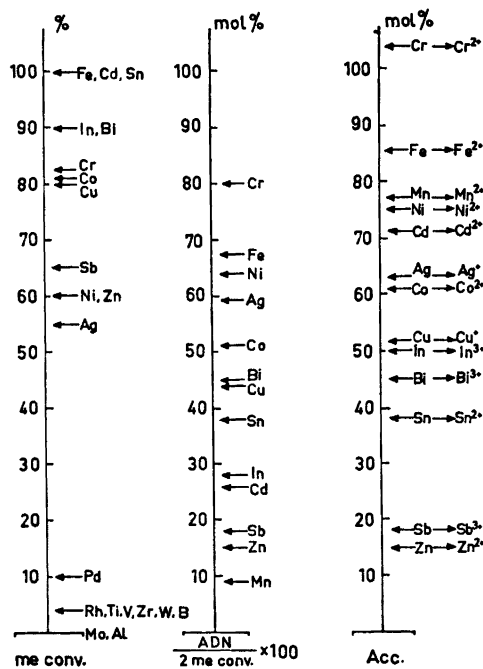*Fig. 11.* Reductive coupling of 3-BrPN pro-
moted by metals different from Fe. Temp:
150 °C, time: 3 h, [AN]₀ = 0.75 mol l⁻¹ [3-
BrPN] = 10.9 mol l⁻¹, [FeBr₂]₀ = 1.39 mol l⁻¹
and [me]₀ = 100 g l⁻¹.

4. Coupling agents different from Fe

In the presence of FeBr₂, the following metal
powders (100 – 200 mesh): Cr, Mn, Co, Ni,
Cu, Zn, Ag, Cd, In, Sn, Sb, Hg, Tl, Pb and Bi
were found to give ADN in reaction with
3-BrPN/A mixtures. The data reported in
Fig. 11 indicate how the different reducing
agents compare with Fe under the same condi-
tions (3 h at 150 °C). A characteristic feature
of the active coupling agents is that they all
show a standard oxidation potential between
+ 1.2 and − 0.8 V and together form a natural
grouping within the periodic table of the
elements. An interesting observation was made
by relating the selectivity of the coupling agent
to make ADN (Fig. 12) as well as the tendency
of the reducing agent to make PN (Fig. 13) to
the standard oxidation potential of the metal.
The results indicate that the systems mechanis-
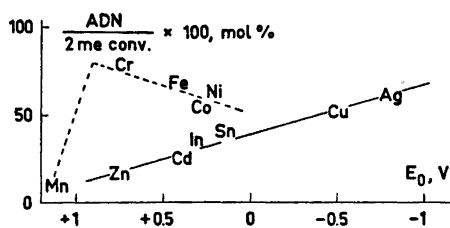tically fall into two different categories. The first

Fig. 12. The relationship between the standard oxidation potential and the tendency of metals to give ADN (conditions as reported in Fig. 11).

category being represented by the typical transition metals, Cr, Mn, Fe, Co and Ni while the second category is made up of the Mg-like elements, Zn, Cd, In and Sn and most likely also Cu and Ag. Characteristic for the reducing agents belonging to the first group is that they all are known to give relatively stable metal (0)-complexes. It is therefore possible that these coupling agents react *via* a mechanism which is similar to the one outlined for the Fe system. All elements of the second group are known to give stable metallorganic compounds of the Grignard type (M/C-σ bonds) and do not give metal(0)-complexes. The oxidative addition reaction of 3-BrPN with these metals is therefore believed to take place directly on the surface. Accordingly, equilibrium reactions analogous to the one shown in reaction 7 are not possible in these systems. The kinetics developed for the Fe system can therefore not be applied for this category of coupling agents.

EXPERIMENTAL

Chemicals

3-Bromopropionitrile (3-BrPN). The 3-BrPN obtained from Matheson, Coleman and Bell was dried over Molecular Sieve (Linde-type 5A) and fractionated through a 20 plate (25 mm I.D.) vacuum jacketed Oldershaw column under reduced pressure. The cut distilling between 76 and 78 °C at 10 mmHg was collected and stored in an atmosphere of argon at 5 °C. In all the experiments wherein the concentration of AN is higher than 1 % (rel. to 3-BrPN), a 3-BrPN stock solution containing 1 wt% AN was used. (AN acts as a stabilizer for 3-BrPN.)

Acrylonitrile (AN). Commercial, reagent grade AN was dried over a molecular sieve (Linde-type 5A) and fractionated at a reflux ratio of 10/1 through a 20 plate (25 mm I.D.) vacuum jacketed Oldershaw column at atmos-

pheric pressure. Argon (99.99 %) was used as inert atmosphere during the fractionation and the heart cut (80 % of charge) was mixed with 0.1 parts of hydroquinone per 100 parts AN in the receiver. The AN so obtained was stored in the dark under inert argon atmosphere at 5 °C. Samples were always withdrawn from the stock solution in argon counter flow, assuring the necessary exclusion of air and moisture.

Bromide salts. Anhydrous $FeBr_2$ (99 %) obtained from Research Organic/Inorganic Chemical Corp. was dried in a stream of HBr at 350 °C for 1 h. The anhydrous $FeBr_2$ was then cooled to room temperature in a stream of argon and stored under argon atmosphere at 25 °C. All the other metal bromides used were dried using analogous procedures.

Metal powders. The metal powders obtained from Research Organic/Inorganic Chemical Corp. were used without further treatment. In the kinetic experiments, 99 + % pure Fe powder (200 mesh) was used.

Experimental procedure and analyses

The coupling experiments were carried out in sealed thick wall (3 mm) glass ampoules of approximately 40 cm³ volume. The coupling agent and promoting salt were charged to the glass tube in a dry box. The ampoule was then evacuated to < 1 mmHg pressure and heated for 1 h at 100 – 120 °C. The ampoule was then filled with argon to atmospheric pressure and the desired amounts of 3-BrPN and AN charged to the ampoule in argon counter stream using argon flushed pipettes in order to exclude air and moisture. The reaction mixture was then cooled in a dry ice/acetone bath, evacuated to ~300 mmHg pressure and sealed on a gas flame. The ampoule was inserted into a steel container with screw top and the free space between the tube and the container filled with silicon oil for improved heat transfer. During the reaction, the ampoule was rotated and heated in a stirred and temperature controlled
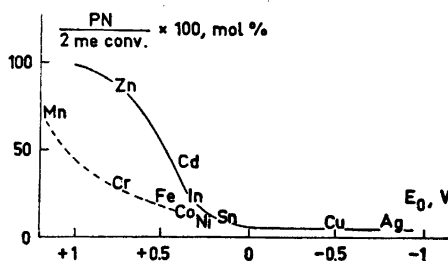

Fig. 13. The relationship between the standard oxidation potential and the tendency of metals to give PN (conditions as reported in Fig. 11).

oil bath. Independence between rate of reaction and rate of rotation was initially assured. After the reaction, the reaction mixture was cooled to room temperature. The amount of unreacted metal powder was determined by pressure filtration of the effluent. The ampoule and the filter cake were washed with water which was combined with the filtrate. The amount of water used was calculated to give an approximate 15 % salt concentration in the aqueous phase. The water phase was back extracted twice with 3-BrPN and the extracts combined with the orginal organics collected after the first hydrolysis step. The amount of ADN and PN made was determined based on GLC analysis of the organic mixture using a 2.4 m, OV-17 (20 %) packed column. The metal powder filter cake collected was washed with additional water and acetone, and dried in vacuum until constant weight. Based on the amount of Fe powder recovered, Fe rec., the Fe conversion was calculated using the following formula:

$$\text{Fe conversion} = \left(\frac{\text{Fe charged} - \text{Fe rec.}}{\text{Fe charged}}\right) \times 100 \text{ \%}$$

Control experiments using 3-BrPN, AN, ADN and FeBr$_2$ (heated for 3 h at 150 °C) and the workup and analytical procedure described above resulted in an average ADN recovery of 96.6 %.

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