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FORMATION OF PHENAZINE FROM AZOBENZENE OVER H-ZSM5: REACTION CONTROL BY A MOLECULAR CONSTRAINED ENVIRONMENT

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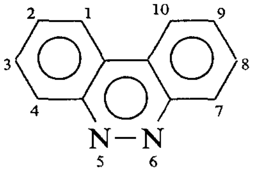
Azobenzene undergoes a unique reaction in the channels of H-ZSM5 zeolite at 593–673 K to give phenazine which is mainly retained within the zeolite. The yield of phenazine is increased by the addition to the reaction carrier gas of oxygen (1% vol.) which probably functions as a hydrogen acceptor. No reaction occurs when low acidity silicalite is used. On H-USY zeolite the yield of phenazine is low and the main product is a black, insoluble material which is probably polymeric. Benzo(c)cinnoline which is a known dehydrocyclization product from azobenzene under strongly acidic reaction conditions is never more than a trace product using H-ZSM5 or H-USY. A reaction scheme is proposed involving homolysis of the N ~ N bond in protonated *trans*-azobenzene, forming two radicals which, in a H-ZSM5 channel, are constrained in their mutual orientation so as to lead to the formation of phenazine.

1. Introduction

Azobenzene(I) is known to undergo internal dehydrocyclization to benzo(c)cinnoline(II) under strongly acidic conditions by the action of either (i) aluminium chloride at 333–393 K [1], or (ii) UV illumination in solution in sulphuric acid (ca. 92–98%) at room temperature [2]–reaction (1) **:

$$C_6H_5{-}N{=}N{-}C_6H_5 \xrightarrow{[-2H]} \qquad (1)$$

(I)



(II)

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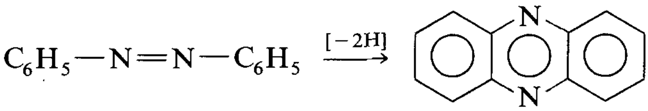
** The positional numbering of (II) in reaction (1) indicates the convention for the various diazaphenanthrenes: thus benzo(c)cinnoline would be 5,6-diazaphenthrene.

The immediate precursor to the dehydrocyclization step of reaction (1) is presumably the *cis* form of azobenzene, produced from the more stable *trans* form either thermally [1] when the temperature is high enough, or photochemically [2,3] at lower temperatures. In the photochemical reaction, at least some of the abstracted hydrogen is consumed by a hydrogen transfer reaction since hydrazobenzene and its rearrangement product benzidine were also observed [4].

In an attempt to replicate reaction (1) over the strongly acidic zeolite H-ZSM5, we observed, mainly in the reaction products trapped within the zeolite channels, the formation of phenazine (III) accompanied by only trace amounts of benzo(c)cinnoline. This unique conversion (reaction (2)) was observed both under oxygen-free conditions and in the presence of low concentrations of oxygen deliberately added as a possible hydrogen scavenger.



(2)

(III)

In order to help in understanding the mechanism of reaction (2), experiments were also undertaken with H-ZSM5 using the reactants 2-aminodiphenylamine, benzo(c)cinnoline, and aniline, and the reaction of azobenzene was also examined over non-acidic silicalite, and over the zeolites H-USY and H-mordenite.

2. Experimental

H-ZSM5 zeolite, prepared and characterized by standards methods [7], was as recently described [6] (SiO_2/Al_2O_3 molar ratio 46/1). Silicalite was prepared as previously described [8]. H-USY zeolite was obtained from Grace/Davison, Cat. No. Z-14 and was used as received (Al, 12.5 wt. %; Na^+, 2.6 wt. %; $[H^+] = 0.90$ mmol g^{-1}). The H-mordenite was prepared by exhaustive NH_4^+ exchange of Na-modenite (Zeolon 100, Norton; SiO_2 80.9 g wt.%, Na_2O 7.2 wt.%, Al_2O_3 11.8 wt.%), followed by washing, drying (373 K), and calcining at 773 K/16 h (giving $[H^+] = 0.85$ mmol g^{-1}).

Azobenzene, 2-aminodiphenylamine and benzo(c)cinnoline were from Aldrich. Aniline was purified by distillation immediately before use.

Reactions were carried out by passing carrier gas (20 cm^3 min^{-1}) containing reactant vapour through a bed of zeolite (0.5 g, 2–3 mm thick) contained in a down-flow reactor. Carrier gas was either high purity nitrogen ($\leqslant 10$ ppm impurity) or nitrogen/oxygen (99/1 (vol.)). Reactants solid at room temperature were introduced by passing the carrier gas over a heated bed of reactant (azobenzene, 453 K; benzo(c)cinnoline, 453 K; 2-aminodiphenylamine, 503 K) so that the reactant feed rate was ca. 0.5 g h^{-1}. Aniline reactant was fed into the carrier gas stream via a heated vapourizer using a motor-driven syringe (feed rate 0.27 cm^3 h^{-1}). Heated transfer lines were used.

At the end of the reaction, the products retained with the zeolite and (in some cases) those condensed from the effluent gases were analysed by GC-MS and GC. The retained products were recovered by acid dissolution of the zeolite followed by solvent extraction [5,6]. Because of the possibility of forming basic reaction products, the solvent extraction step was carried out from the aqueous phase under alkaline (excess sodium carbonate) and under acid conditions.

Before reactions, the catalyst was first pre-treated at 773 K *in situ* in a pure oxygen stream (20 cm^3 min^{-1}) for 2 h, then flushed in the working carrier gas stream at 773 K for 2 h, and cooled to the intended reaction temperature.

Components were identified from mass spectra and retention times with reference to authentic specimens and published mass spectra [9]. *

Total residue content of the treated zeolite was estimated by oxidative burn-off in the manner previously described [6].

3. Results and discussion

MAIN REACTION FEATURES

Compositions of retained residue (and reactor effluent condensate) from the reactions of azobenzene are given in table 1. The retained residue from H-ZSM5 treated with azobenzene (593 K/90 min) in the absence of added oxygen consisted almost exclusively of phenazine and unconverted azobenzene. However, addition of 1 vol.% O_2 to the nitrogen carrier gas (593 K, 673 K/120 min) resulted in the retained residue consisting almost entirely of phenazine. In all cases the reactor effluent consisted mainly of unconverted azobenzene accompanied by a very small amount ($\leqslant 2$ wt.%) of phenazine. In no case was benzo(c)cinnoline formed in other than trace amounts. Some black, insoluble, particulate matter (presumably polymeric) was also formed.

Use of silicalite, the non-acidic analogue of H-ZSM5, at 593 K/120 min in the absence or presence of added oxygen, gave no detectable conversion of azobenzene (c.f. table 1), from which we conclude that strong acidity is essential for the reaction to occur. We also ascribe the lack of any reaction with azobenzene over H-mordenite (593 K/90 min/N_2; c.f. table 1) to the absence of sufficiently strong acidic sites. **

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* Mass spectra of all the diazaphenanthrenes have been published (c.f. refs. [10,11]).

** For the H-mordenite, $[H^+] = 0.85$ mmol g^{-1} corresponds to about 37% protonation, assuming all of the Al is in the lattice.

Table 1
Composition of recovered residue from reaction of azobenzene on zeolites

zeolite and treatment conditions	total retained residue (wt. percent)	composition of retained residue [a]
H-ZSM5 [b]		
593 K/90 min/N_2	10.5	azobenzene, large [c] phenazine, large black insoluble polymer, small unknown (parent $m/e = 260$), v. small benzo(c)cinnoline, trace
593 K/120 min/N_2-O_2	7.6	azobenzene, v. small [c] phenazine, v. large black insoluble polymer, small unknown (parent $m/e = 260$), v. small benzo(c)cinnoline, trace
673 K/150 min N_2-O_2	9.1	azobenzene, v. small [c] phenazine, v. large black insoluble polymer, small unknown (parent $m/e = 256$), v. small benzo(c)cinnoline, trace
Silicalite		
593 K/120 min/N_2	~1	azobenzene, 100 wt.% [c]
593 K/120 min/N_2-O_2	~1	azobenzene, 100 wt.%
H-USY		
593 K/90 min/N_2	25.3	azobenzene, medium [c] phenazine, small black insoluble polymer, large benzo(c)cinnoline, trace other components [d], small (total)
H-mordenite		
593 K/90 min/N_2	1.4	azobenzene, 100 wt.% [c]

[a] trace < 1 wt.%, v. small 1–5 wt.%, small 6–10 wt.%, medium 11–30 wt.%, large 31–70 wt%, v. large > 70 wt.%; [b] reactor effluent ⩾ 98wt.% azobenzene, balance phenazine; [c] unreacted azobenzene in residue; [d] carbazole, diphenylamine, unidentified water soluble component (intense blue in acidified solution).

The retained residue from H-USY treated with azobenzene (593 K/90 min/N_2; c.f. table 1) was dominated by a large amount of black, insoluble, particulate matter (presumably polymeric): some phenazine was also formed but in relatively small amount, together with smaller amounts of carbazole, diphenylamine, and an unidentified water soluble component which gave an intense blue colour in an acidified solution. The residue also contained a substantial level of unconverted azobenzene. No more than a trace amount of benzo(c)cinnoline was present in the retained residue from H-USY.

In all cases, a careful search was made for benzidine, semidines (o-semidine, 2-aminodiphenylamine; p-semidine, 4-aminodiphenylamine), and hydrazobenzene in the product components, but none was found, even at trace levels.

The possibility that phenazine was formed from azobenzene via benzo(c)cinnoline was eliminated by treating H-ZSM5 with benzo(c)cinnoline (593 K/120 min/N_2) and noting that no reaction products could be detected either in the retained residue or in the reactor effluent. From measurement on molecular models we estimate the effective van der Waals dimensions of benzo(c)cinnoline to be about 0.62 × 1.04 nm *, so that its entry into the channels of H-ZSM5 should be just possible at the relatively high treatment temperature: in confirmation we recovered a substantial amount of unreacted benzo(c)cinnoline as retained residue from benzo(c)cinnoline-treated H-ZSM5. The treatment of H-ZSM5 with aniline (593 K/30–120 min/N_2) also yielded no reaction products.

Since one may postulate the conversion of 2-aminodiphenylamine (o-semidine) to phenazine by direct dehydrogenative ring closure, the treatment of H-ZSM5 by 2-aminodiphenylamine was examined (593 K/120 min/N_2). The main components in the retained residue were phenazine and unconverted reactant, together with lesser amounts of aniline, carbazole, diphenylamine, alkanes/olefins (C_{14}-C_{20}), and three components of uncertain identification (one with parent $m/e = 180$ having a mass spectrum suggesting a diazaphenanthrene but not benzo(c)cinnoline; two with parent $m/e = 184$ having mass spectra indicating isomers of diaminobiphenyl and/or aminodiphenylamine, but not reactant). The reactor effluent contained unconverted reactant and some phenazine.

REACTION THERMODYNAMICS

The value of ΔG_f^0 for azobenzene at 600 K is estimated at 739 ± 20 kJ mol^{-1} using data given by Benson [13,14]. The value of ΔG_f^0 for phenazine at 600 K is estimated at 558 ± 20 kJ mol^{-1} using thermodynamic data for pyrazine [15], and scaling the difference between pyrazine and phenazine to be the same as between benzene and anthracene [16]. The value of ΔG_f^0 for benzo(c)cinnoline is estimated at 613 ± 20 kJ mol^{-1} using thermodynamic data for pyridazine [15], and scaling the difference between pyridazine and benzo(c)cinnoline to be the same as between benzene and phenanthrene [16].

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* Molecular dimensions were obtained from measurement on Catalin models, with the application of a flat correction (reduction) of 0.04 nm to the Catalin values to obtain agreement with the known dimensions of a series of alkylbenzenes [12]. The value of 0.54 nm is the width of a benzene ring across the "flats".

Using the above data we obtain the following values for $\Delta G^0_{\text{react}}$:

azobenzene $\longrightarrow$ phenazine + H_2: $\Delta G^0_{\text{react},600} = -181 \pm 40$ kJ mol^{-1}

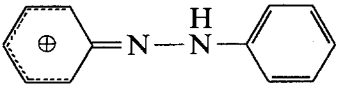
azobenzene $\longrightarrow$ benzo(c)cinnoline + H_2: $\Delta G^0_{\text{react},600} = -126 \pm 40$ kJ mol^{-1}

While both processes are thermodynamically favourable, it is clear that the formation of phenazine rather than benzo(c)cinnoline is a result of kinetic rather than thermodynamic control.

REACTION PATHWAY

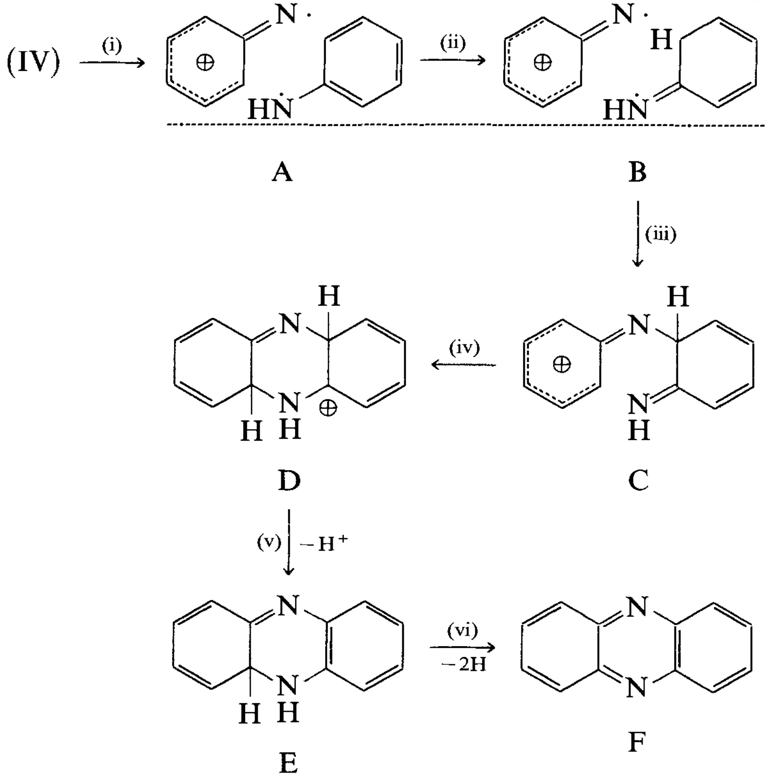
In the presence of hydrogen donors, azobenzene is known to undergo mineral-acid catalysed benzidine rearrangement at relatively low temperature [3,17], the reaction proceeding via hydrazobenzene. Nevertheless (not withstanding the observation that 2-aminodiphenylamine can yield some phenazine by reaction over H-ZSM5), the evidence suggests that benzidine rearrangement is not involved in the conversion of azobenzene to phenazine. No 2-aminodiphenylamine or benzidine was co-product of phenazine in the azobenzene conversion, and it would be difficult to reconcile a reaction pathway involving the conversion of azobenzene via hydrazobenzene with the observed increase in phenazine yield on addition of oxygen to the reaction mixture.

Azobenzene is known [3] under normal thermal reaction conditions (in the absence of a strong acid) to undergo free-radical decomposition at 673–773 K with the generation of N_2 and free-radical coupling products such as biphenyl and/or products resulting from attack of phenyl radicals upon other species [18]. The central problem in formulating a mechanism for the conversion of azobenzene to phenazine is how the –N=N– bond is broken. The conversion requires a very strong acid (e.g. H-ZSM5), and it is known that protonation of azobenzene occurs at the –N=N– group [19,20]. From the nature of the protonated species [19,20], one would expect considerable weakening of the –N=N– bond, particularly when the contribution of charge delocalization to a phenyl group is considered, involving a structure such as (IV) [19,20].



(IV)

We propose that this weakened N ~ N bond in the protonated structure can undergo homolysis to two "caged" radicals which react to yield phenazine by the pathway outlined in reaction (3). (The dotted lines in the upper sequence of reaction (3) have been drawn to indicate the constrained environment of a ZSM5 channel: it is to be understood that the remaining steps also take place within the zeolite).



(3)

With the probable exception of the dehydrogenation step (vi), all of the steps in reaction (3) are likely to be reversible. On the basis of this scheme, the effect of oxygen in increasing the phenazine yield would probably arise from it functioning as a hydrogen acceptor in step (vi).

REACTION CONTROL VIA A MOLECULARLY CONSTRAINED ENVIRONMENT

In its spacially most economical configuration, *trans*-azobenzene has van der Waals dimensions 0.54 × 0.54 × 1.25 nm (with the planes of the benzene rings approximately at right angles), while *cis*-azobenzene has 0.54 × 0.65 × 0.76 nm. *Trans*-azobenzene is thus able to enter the channels of H-ZSM5/or silicate), but *cis*-azobenzene is not Although *cis*-azobenzene could be accommodated in the channel intersections of H-ZSM5, examination of molecular models indicates that a *trans* → *cis* conversion would be sterically disallowed at that location (and would certainly be impossible within a channel). We conclude that azobenzene accommodated in the channel structure of H-ZSM5 would be exclusively in the *trans* form.

Trans-azobenzene in a channel of H-ZSM5 is severely constrained as are the radicals formed from homolysis of the corresponding protonated parent. Thus, referring to the two radicals represented at A in reaction (3), the H-ZSM5 channel size will allow the orientation shown, but will not allow further rotation of the radicals with respect to one another. The relative orientation of the radicals is thus constrained in the H-ZSM5 channel to that which would be expected to lead either to the formation of phenazine (by steps (ii)–(vi), reaction (3)), or to the reformation of parent (reverse of step (i), reaction (3)). The constraint of the H-ZSM5 channels also would hold the cationic intermediate C (reaction (3)) in a configuration favourable for ring closure in step (iv).

The zeolite H-USY has large cavities (diameter ~ 1.3 nm) with large windows (diameter ~ 0.8 nm), so that with this material the steric restrictions which the channels of H-ZSM5 places upon azobenzene and on its reaction intermediates would be largely removed. We suggest this is responsible for the dominance of the polymeric product formed from azobenzene with this catalyst, and the relative unimportance of the reaction pathway leading to phenazine.

Steric restrictions within the channels of H-ZSM5 are apparently not responsible for inhibition of the formation of benzo(c)cinnoline with this zeolite, since this product was also not formed with H-USY: under the present reaction conditions the removal of steric restrictions leads to the formation of polymeric product.

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