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MECHANISM OF REACTION OF AZOBENZENE FORMATION FROM ANILINE AND NITROSOBENZENE IN BASIC CONDITIONS. GENERAL BASE CATALYSIS BY HYDROXYIDE ION

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The reaction of nitrosobenzene with aniline, to give azobenzene, in basic conditions was studied. It was shown that the reaction exhibits general base catalysis by different buffers giving a Brønsted coefficient $\beta = 0{\cdot}318$. As in previous studies, a two-step process with a first step of attack of aniline on nitrosobenzene to give an addition intermediate and a second step of dehydration of this intermediate is proposed to interpret the mechanism of the reaction. The analysis of the Brønsted relationship and of the intermediate of the reaction led to the suggestion that hydoxide ion catalyses the reaction by a mechanism of general base catalysis in the dehydration step.

INTRODUCTION

Nitrosobenzene can be formed in biological systems and under physiological conditions can react with various nucleophiles. It therefore seems of interest to investigate the mechanism of the reactions of nitrosobenzene as models.

The mechanism of the reaction with aniline, to give azobenzene, in acidic media has been well studied.[1–4] The same condensation in alkaline media has also been reported.[5–7] However, the mechanism of azobenzene formation in alkaline media is controversial. Brown and Kipp,[6] using pyridine–water (80 : 20, v/v), in the presence of tetramethylammonium hydroxide (0·01 M), observed that the rate of azobenzene formation is increased by electron-donating substituents and decreased by electon-attracting substituents of aniline. In both cases the rate of the reaction satisfies the Hammett equation. They also showed that a linear relationship exists between the pseudo-second-order rate constant and the tetramethylammonium hydroxide concentration, postulating a mechanism in which the rate-determining step is the attack of the negatively charged nitrogen of the anilide ion, formed in a rapid pre-equilibrium between aniline and hydroxide ion, on the nitrogen of nitrosobenzene. We have interpreted[4] that the substituent effects observed by Brown and Kipp[6] are more consistent with a rate-determining step of dehydration of an addition intermediate formed between aniline and nitrosobenzene.

We carried out this study in order to elucidate the mechanism of this reaction in alkaline conditions and the mechanism of catalysis by hydroxide ion.

RESULTS AND DISCUSSION

The reactions were carried out in water–ethanol (97 : 3, v/v), where it is possible to obtain a homogeneous reaction mixture of aniline and nitrosobenzene giving principally azobenzene as the product. The concentration of aniline was in the required excess in order to obtain pseudo-first-order reaction conditions. The reaction was studied in the pH range 10–13.

The dependence of k_{obs} (pseudo-first-order rate constant) on pH is shown in Figure 1. All points have been extrapolated to zero buffer concentration. Equation (1) is consistent with the experimental results including terms for a pH-independent (k_0) and a base catalysis (k_{OH}) pathway:

$$k_{obs} = (k_0[PhNH_2] + k_{OH}[PhNh_2][OH^-]) \times ([H^+]/[H^+] + K_{ad}) \qquad (1)$$

The factor $[H^+]/[H^+] + K_{ad}$ was introduced considering the equilibria of formation of an adduct (K_{ad}) between the hydroxide ion and nitrosobenzene.[8] This

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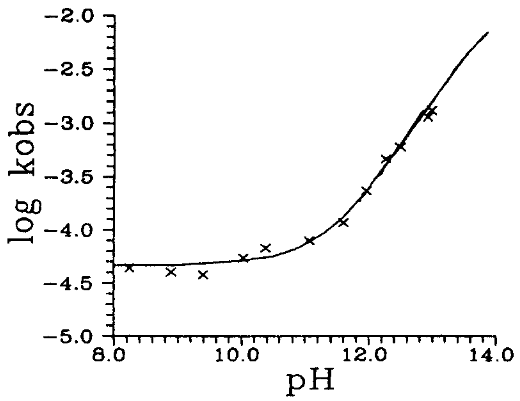

Figure 1. pH dependence of first-order rate constants for azobenzene formation in water–ethanol (97 : 3, v/v) at 25 °C and ionic strength 1·0 M (KCl). The solid line was computed from equation (1) utilizing individual rate constants given in Table 1

equation should tend to a plateau, which is not observed experimentally because $K_{ad} = 13{\cdot}8$.

It is important to note that between pH 12 and 13·5 nitrosobenzene undergoes an irreversible first-order reaction[8] in the absence of aniline. This reaction is also of first order with respect to the hydroxide ion concentration, but above pH of 13·5 this dependence is larger, as can be observed in Figure 2.

All the values of the observed rate constants for azobenzene formation were corrected for the values of the rate constants for the reaction of nitrosobenzene undergoing adduct formation with the hydroxide ion,[8] considering that they are first-order parallel reactions.[9] Working with different concentrations of aniline and extrapolating to zero aniline concentration on the plot of observed pseudo-first-order rate constants vs aniline concentration, the intercept gives the rate constant of the reaction of nitrosobenzene with hydroxide ion and the slope gives the second-order rate constant for azobenzene formation.[9]

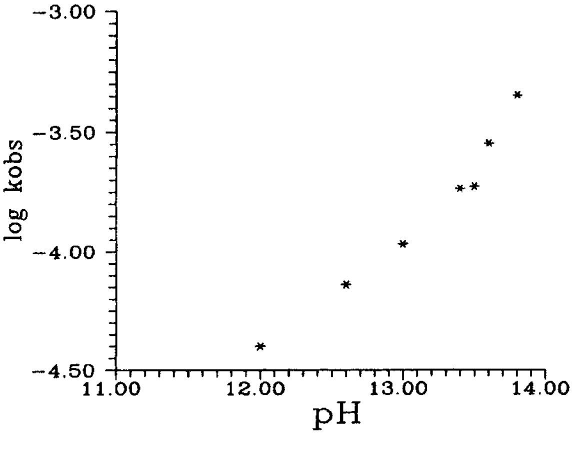

Figure 2. pH dependence of rate constants for nitrosobenzene decomposition in water at 25 °C and ionic strength 1·0 M (KCl)

The second-order rate constant is sensitive to the nature and concentration of the buffers used. Measurements of the catalytic effect as a function of the molar fraction of the base and acid components of carbonic acid–carbonate buffers of different concentrations established that the catalysis is of general base type.

The catalytic constants of general base catalysis (Table 1) follow the Brønsted relationship giving a Brønsted coefficient $\beta = 0{\cdot}318$ ($r = 0{\cdot}990$) (Figure 3). The value of catalytic rate constant for the hydroxide ion corresponds to that expected from the Brønsted

Table 1. Rate constants for general-base catalysed azobenzene formation from aniline and nitrosobenzene[a]

Catalyst	$pK_a + \log(p/q)$	k_c/lmol^{-1} s^{-1}	Log k_c/q
OH^-	15·74	0·18000	−0·744
$CF_3CH_2O^-$	12·37[b]	0·01960	−1·707
HPO_4^{2-}	10·92[c]	0·00834	−2·078
$N(CH_3)_3$	9·80[d]	0·00302	−2·520
HCO_3^-	9·00[e]	0·00103	−2·990
H_2O	−1·44	$8{\cdot}427 \times 10^{-6}$	−5·070

[a] In water–ethanol (97 : 3, /v) at 25 °C and ionic strength 1·0 (KCl).
[b] Ref. 10.
[c] Ref. 11.
[d] Ref. 12.
[e] Ref. 13.

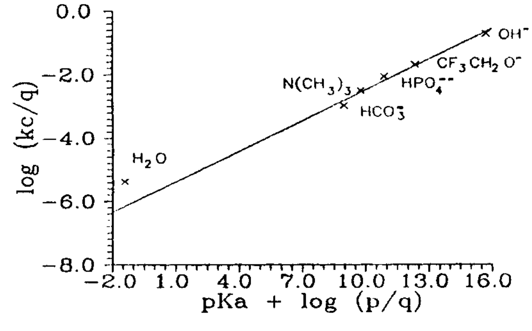

Figure 3. Brønsted plot for general base catalysis for reaction of azobenzene formation in water–ethanol (97 : 3, v/v) at 25 °C and ionic strength 1·0 M (KCl)

line, suggesting that the hydroxide ion participates in the reaction as a general base catalyst.

The reaction is of first order in aniline, nitrosobenzene and hydroxide ion. The kinetic equation consistent with the experimental results is

$$v = k_{\mathrm{OH}}[\mathrm{PhNH_2}][\mathrm{PhNO}][\mathrm{OH^-}] \qquad (2)$$

If the mechanism were that proposed by Brown and Kipp:

$$\mathrm{PhNH_2 + OH^- \rightleftharpoons PhNH^- + H_2O} \qquad (3)$$

$$\mathrm{PhNH^- + PhNO \rightarrow PhNHN(O^-)Ph} \qquad (4)$$

$$\mathrm{PhNHN(O^-)Ph \rightarrow PhN{=}NPh + OH^-} \qquad (5)$$

the rate law would be

$$v = k_2[\mathrm{PhNH^-}][\mathrm{PhNO}] \qquad (6)$$

and considering the acid dissociation of aniline, equation (6) leads to

$$v = k_2K_a[\mathrm{PhNH_2}][\mathrm{PhNO}][\mathrm{OH^-}]/K_w \qquad (7)$$

where K_a is the acid dissociation constant of aniline ($K_a = 10^{-27}$).[14]

From equation (7), k_2 can be calculated as

$$k_2 = k_{\mathrm{OH}}K_w/K_a = 1{\cdot}8 \times 10^{12}\ \mathrm{l\ mol^{-1}\ s^{-1}}$$

($k_{\mathrm{OH}} = 0{\cdot}180$, $K_a = 10^{-27}$)[14].

This value is larger than the diffusion-controlled limit,[15] indicating that the anilide ion is not an intermediate along the reaction pathway under the conditions used in this work.

It has been suggested[4] that the reaction between aniline and nitrosobenzene in ethanol–water 50:50, v/v) shows a change in the rate-determining step from attack of aniline on nitrosobenzene to the dehydration of an addition intermediate formed between aniline and nitrosobenzene as the pH becomes more basic. The change occurs between approximately pH 6 and 8.

The pH of the experiments and the Brønsted equation results suggest that in this case the hydroxide ion catalysis should occur in the dehydration step:

$$\mathrm{PhNO + PhNH_2 \rightleftharpoons PhN(OH)NHPh} \qquad (8)$$

$$\mathrm{PhN(OH)NHPh + OH^- \xrightarrow{slow} PhN{=}NPh + H_2O} \qquad (9)$$

In order to provide other evidence for this mechanism and to eliminate the possibility of the kinetically indistinguishible mechanism of specific base–general acid catalysis, we must consider the pK_a of the intermediate that would be formed in the first step of this mechanism:

$$\mathrm{PhNHN(OH)Ph + OH^- \rightleftharpoons PhN^-N(OH)Ph + H_2O} \qquad (10)$$

It can be calculated from the pK_a of the anilide ion (*ca* 27) considering the base-weakening effect of the —PhNHOH group. This group can be considered to be formed by the —NHOH and Ph groups, which have σ^* values[16] of 0·30 and 0·75, respectively. Applying the equation p$K_a = 0{\cdot}28 + 0{\cdot}87\sigma^*$, we obtain $-0{\cdot}54$ for the —NHOH group and $-0{\cdot}93$ for the Ph group. However, as the —NHOH group is directly bonded to the nitrogen, accepting a normal behaviour in this position, the value will be $-0{\cdot}54/0{\cdot}4 = -1{\cdot}35$. Then the p$K_a$ of the negatively charged intermediate would be $27 - 2{\cdot}28 = 24{\cdot}72$. According to Palmer and Jencks,[17] 'specific base or acid catalysis must exist and contribute to the observed rate whenever estable intermediate exists with a pK_a in the range $-1{\cdot}7$ to $+15{\cdot}7$,' hence the mechanism of specific base catalysis must not contribute to the observed rate of this reaction.

As we have indicated,[4] the substituents effects studied by Brown and Kipp[6] in pyridine 80–water (80:20 v/v) are more consistent with the dehydration of the addition intermediate proposed in equation (9) as the rate-determining step. Hence it is possible to conclude that the same mechanism should exist in water–ethanol (97:3, v/v), i.e. the conditions of this study, and in pyridine–water (80:20, v/v).

EXPERIMENTAL

Materials. Nitrosobenzene was synthesized and purified by sublimation. Commercial aniline was purified by vacuum distilation.

Kinetic procedure. The reactions were followed spectrophotometrically at 25 °C by monitoring the formation of azobenzene at 400 nm. The solvent used was water–ethanol (97:3, v/v) with ionic strength 1·0 M (KCl). The initial concentrations were $1{\cdot}0 \times 10^{-9}$ M for nitrosobenzene and 0·5–1·0 M for aniline. Reactions were followed for three half-times under these pseudo-first-order conditions.

Reactions of nitrosobenzene under the above conditions, but in the absence of aniline, were followed at 290 nm. Working in solutions degassed with nitrogen, to eliminate the oxygen, the value of the first-order rate constant did not change.

The yield of azobenzene, determined by high-performance liquid chromatography was 90%.

First-order rate constants were calculated with a computer and second-order rate constants were calculated by dividing the first-order rate constants k_{obs} by the concentration of aniline as free base.

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