

Kinetics and mechanism of dimerisation of benzylamine by hydrogen peroxide in the presence of ferrous sulphate as catalyst

IFTIKHAR AHMAD, KAMAL M. SAEED AND A. H. EL-NADI

Department of Chemistry, University of Khartoum, Khartoum, Sudan

ABSTRACT

The kinetics of dimerisation of benzylamine by hydrogen peroxide in the presence of Fe(II) ions have been studied. The reaction is first order with respect to both benzylamine and Fe(II) ions and zero order with respect to hydrogen peroxide. The energy of activation has been calculated to be 68.38 ± 0.01 kJ mol⁻¹. The rate law has been derived from our proposed reaction mechanism.

INTRODUCTION

Hydrogen peroxide in the presence of Fe(II) ions has been used to oxidise organic compounds (Merz & Waters 1949; Sosnovsky & Rawlinson 1970). Recently, Ashraf *et al.* (1979, 1980) studied the kinetics and mechanism of oxidation of amino acids by this reagent. Coffman *et al.* (1958) described the dimerisation of aliphatic amines (viz. propyl and *t*-butylamines) by hydrogen peroxide in the presence of ferrous sulphate. This study refers mainly to its reaction products, but no work appears to have been done on the kinetics and mechanism of dimerisation of amines by this reagent. Since the dimers of the amines are industrially important compounds, particularly in the polymer field, the kinetics and mechanism of the dimerisation of amines by hydrogen peroxide in the presence of ferrous sulphate as catalyst are reported in this paper.

EXPERIMENTAL SECTION

All the chemicals used were of Analar (B.D.H.) grade. The ionic strength of the reaction mixture was maintained by the addition of sodium perchlorate solution. The concentration of hydrogen peroxide in kinetic runs was measured colorimetrically as described elsewhere (Reichert *et al.* 1939). Measured quantities of benzylamine, ferrous sulphate, perchloric acid, sodium perchlorate (to maintain ionic strength) and distilled water were taken in a stoppered round-bottom flask and placed in a thermostatically controlled water bath. After the reactants had reached the required temperature, the reaction was started by the addition of temperature-equilibrated hydrogen peroxide. The kinetics were followed by examining 5 cm³ aliquots of the reaction mixture for hydrogen peroxide content. The aliquots were added to 5 cm³ of

titanium sulphate solution which turned yellow because of the formation of titanium oxysulphate; its optical density was measured at 410 nm. The concentration of hydrogen peroxide was calculated from the calibration graph.

IDENTIFICATION OF PRODUCTS

For the identification of products, another reaction mixture in which the concentrations of all the reagents were ten times those reported in Table 1, was heated at 40°C for about 30 hr. Twenty M sodium hydroxide was added in excess and the resulting ferrous hydroxide was filtered off. The filtrate was salted out and extracted with ether; the ethereal extract was dried over anhydrous magnesium sulphate and the solvent was removed by distillation on a water bath. The unreacted benzylamine was distilled off under reduced pressure. Pure 1,2-diphenylethylenediamine was collected as colourless needles, m.p. 90–92°C (literature m.p. 90–92°C). This was further confirmed by converting it to its picrate derivative by the standard method described by Vogel (1956). The picrate derivative was obtained as yellow needles of m.p. 200–202°C which is the same as reported in the literature.

RESULTS AND DISCUSSION

All the experiments have been carried out in the presence of aqueous perchloric acid. The concentration of the acid used in all experiments was 0.102 M which was sufficient to prevent the hydrolysis of Fe(II) ions and the self decomposition of hydrogen peroxide. The progress of the reaction was observed by measuring the disappearance of hydrogen peroxide in the presence of high concentration of benzylamine and very low concentration of catalyst (ferrous sulphate). The plots of concentration of hydrogen peroxide versus time were straight lines. This indicates zero order

Table 1. Pseudo-zero-order rate constants of the dimerisation of benzylamine

[HClO ₄] = 0.102 M; [FeSO ₄] = 5.00 × 10 ⁻⁴ M; [Benzylamine] = 7.50 × 10 ⁻² M; temp. 40°C		
[H ₂ O ₂] × 10 ³ (M)	<i>k</i> _{obsd} × 10 ⁷ (mol l ⁻¹ sec ⁻¹)	<i>k</i> ' × 10 ³ (l mol ⁻¹ sec ⁻¹)
2.50	1.25	3.33
3.00	1.25	3.33
3.50	1.26	3.36
4.00	1.26	3.36
4.50	1.26	3.36
5.00	1.25	3.33
5.50	1.25	3.33
6.00	1.26	3.36
6.50	1.24	3.31
7.00	1.26	3.36

$k' = (3.34 \pm 0.019) \times 10^{-3} \text{ l mol}^{-1} \text{ sec}^{-1}$

dependence of rate on hydrogen peroxide concentration. The slope of these lines yielded pseudo-zero-order rate constants (k_{obsd}). The results are shown in Table 1.

The order of reaction with respect to catalyst was determined by changing the ferrous sulphate concentration and keeping other variables constant. The plot of k_{obsd} against the concentration of ferrous sulphate was a straight line passing through origin (Table 2 and Fig. 1). This clearly indicates first-order dependence of rate on ferrous sulphate concentration and it also indicates that there is no reaction in the absence of ferrous sulphate. Similarly, the order of reaction with respect to benzylamine was determined by varying its concentration and keeping other variables constant. The value of k_{obsd} increases directly with the increase in benzylamine concentration (Fig. 2). This shows a first-order dependence of rate on benzylamine concentration.

Preliminary studies under our experimental conditions have clearly shown that neither ferrous sulphate nor hydrogen peroxide alone could bring about dimerisation of benzylamine in acid media. It is fairly well established (Merz & Waters 1949; Walling 1975) that hydrogen peroxide in the presence of Fe(II) ions produces the hydroxyl free radical ($^{\circ}\text{OH}$) which will very likely attack benzylamine and generate the free radical, $\text{Ph}-\dot{\text{C}}\text{H}-\overset{+}{\text{N}}\text{H}_3$, which will ultimately give the dimer of benzylamine. A possible mechanism of the dimerisation of benzylamine involving hydroxyl-free radical is represented in the following scheme:

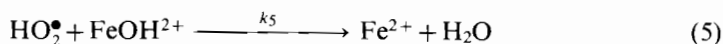
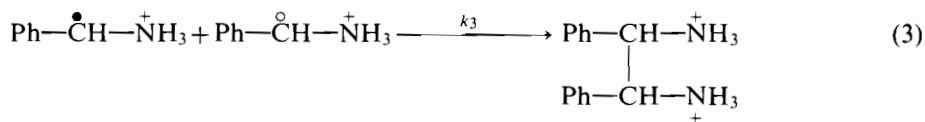
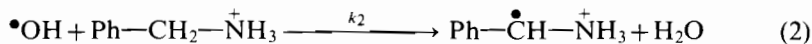


Table 2. First-order dependence of rate on ferrous sulphate concentration

[HClO ₄] = 0.102 M; [H ₂ O ₂] = 3.00 × 10 ⁻³ M; [Benzylamine] = 5.00 × 10 ⁻² M; temp. 40°C	
[FeSO ₄] × 10 ⁴ (M)	$k_{\text{obsd}} \times 10^7$ (mol l ⁻¹ sec ⁻¹)
1.00	0.25
1.50	0.38
2.50	0.67
3.75	0.95
4.30	1.05

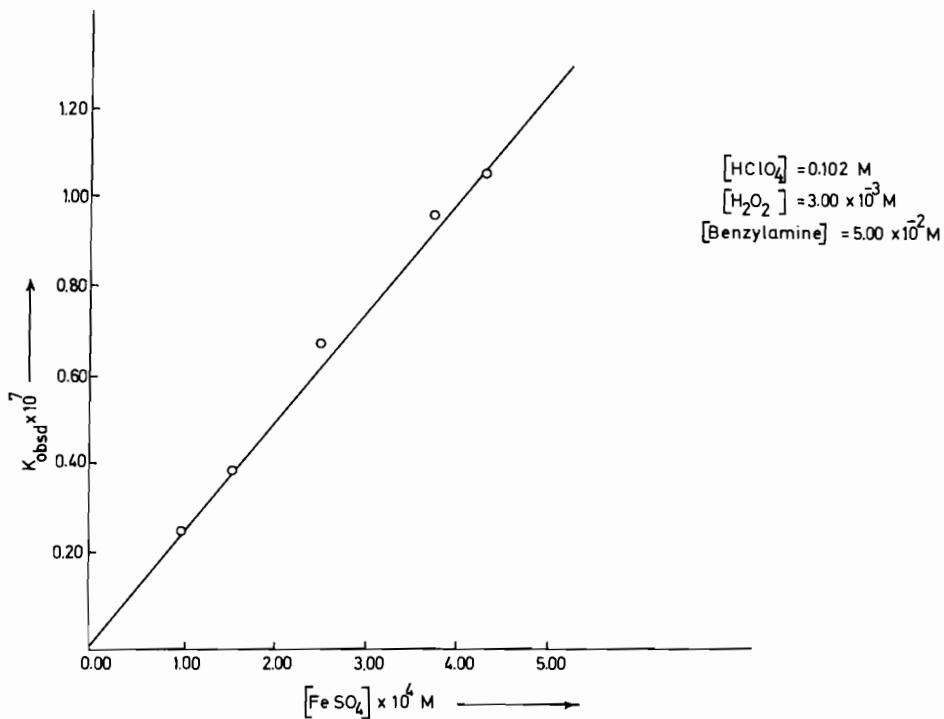


Fig. 1. Variation of reaction rate with ferrous sulphate concentration.

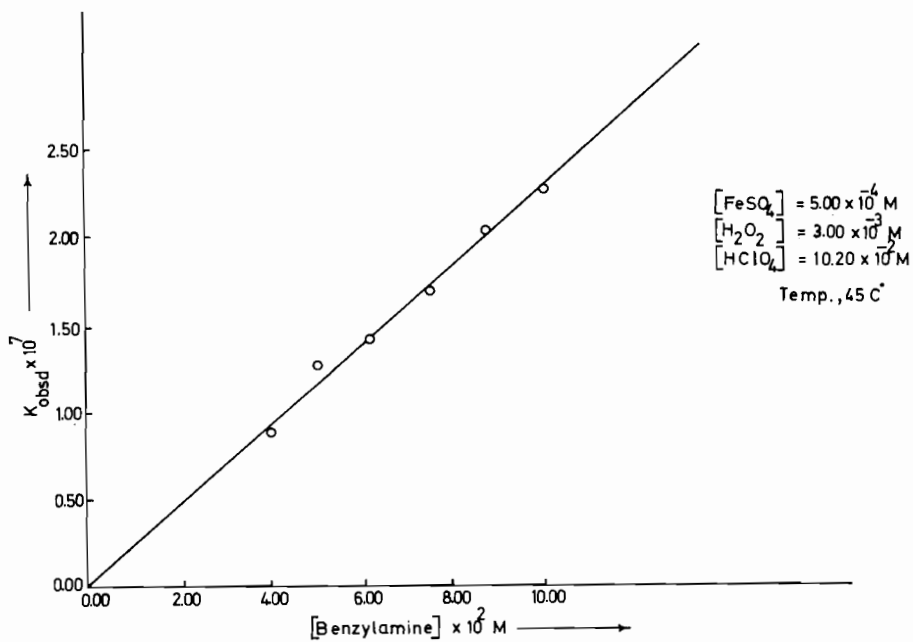
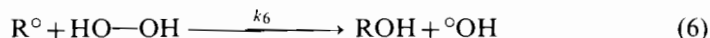


Fig. 2. Variation of reaction rate with benzylamine concentration.

The organic free radical of the type R° generated in step (2) may, in some cases, be able to react with molecular hydrogen peroxide (Walling 1975), as in the following step:



by a process which involves an electron-transference somewhat similar to reaction (1). But in our case, the organic free radical, $Ph-\overset{\circ}{C}H-NH_3^+$ may be too stable to attack the hydrogen peroxide molecule and in contrast, reaction (6) cannot occur. Then two organic radicals, $Ph-\overset{\bullet}{C}H-NH_3^+$, may become stabilised by dimerisation as in step (3).

$$\text{Rate of reaction} = \frac{d[\text{dimer}]}{dt} = k_3 [Ph-\overset{\bullet}{C}H-NH_3^+]^2 \quad (7)$$

Applying the steady-state approximations for the concentrations of $Ph-\overset{\bullet}{C}H-NH_3^+$ and ${}^\circ OH$, we obtain Equations (8) and (9).

$$[Ph-\overset{\bullet}{C}H-NH_3^+]^2 = \frac{k_2 [{}^\circ OH] [\text{Benzylamine}]}{2k_3} \quad (8)$$

$$[{}^\circ OH] = \frac{k_1 [Fe^{2+}] [H_2O_2]}{k_2 [\text{Benzylamine}] + k_4 [H_2O_2]} \quad (9)$$

Substituting the values of $Ph-\overset{\bullet}{C}H-NH_3^+$ from Equation (8) into Equation (7), we get,

$$\text{Rate of reaction} = \frac{k_2}{2} [{}^\circ OH] [\text{Benzylamine}] \quad (10)$$

Substituting the value of $[{}^\circ OH]$ from Equation (9) into Equation (10), we get,

$$\text{Rate of reaction} = \frac{k_1 k_2 [Fe^{2+}] (H_2O_2) [\text{Benzylamine}]}{2 (k_2 [\text{Benzylamine}] + k_4 [H_2O_2])} \quad (11)$$

In our experimental conditions the generation of the organic free radical, $Ph-\overset{\bullet}{C}H-NH_3^+$, is the rate-determining step (step 2). Hence,

$$k_2 [\text{Benzylamine}] \ll k_4 [H_2O_2] \quad .$$

Therefore, Equation (11) changes to

$$\frac{d[\text{dimer}]}{dt} = k' [Fe^{2+}] [\text{Benzylamine}] \quad (12)$$

where

$$k' = \frac{k_1 k_2}{2k_4} \quad . \quad (13)$$

Equation (12) can also be written as

$$\frac{d[\text{dimer}]}{dt} = k_{\text{obsd}} [H_2O_2]^0 \quad (14)$$

where

$$k_{\text{obsd}} = k' [Fe^{2+}] [\text{Benzylamine}] \quad . \quad (15)$$

Equation (12) explains the observed order of reaction with respect to benzylamine, Fe(II) ion and hydrogen peroxide concentrations.

Table 3. Dependence of rate on temperature

$[\text{H}_2\text{O}_2] = 3.00 \times 10^{-3} \text{ M}; [\text{FeSO}_4] = 5.00 \times 10^{-4} \text{ M};$ $[\text{HClO}_4] = 10.20 \times 10^{-2} \text{ M}; [\text{Benzylamine}] =$ $7.50 \times 10^{-2} \text{ M}$	
Temperature (K)	$k_{\text{obsd}} \times 10^7$ ($\text{mol l}^{-1} \text{ sec}^{-1}$)
303	0.42
308	0.87
313	1.24
318	1.67
323	2.50
328	3.78

The rate constant, k' , was calculated by substituting the concentrations of ferrous sulphate and benzylamine from Table 1, which is $(3.34 \pm 0.019) \times 10^{-3} \text{ l mol}^{-1} \text{ sec}^{-1}$. This value of k' is dependent on k_1 , k_2 and k_4 . k_1 and k_4 have been calculated by earlier workers (Walling 1975) and reported to be 76 and 1.2 to $4.5 \times 10^7 \text{ l mol}^{-1} \text{ sec}^{-1}$ respectively. In our calculations we used the average value of k_4 , i.e. $2.75 \times 10^7 \text{ l mol}^{-1} \text{ sec}^{-1}$. k_2 has been calculated by substituting these values of k_1 and k_4 , and found to be $2.42 \times 10^3 \text{ l mol}^{-1} \text{ sec}^{-1}$.

The reaction was studied at six different temperatures from 30 to 55°C ($\pm 0.1^\circ\text{C}$), and the results are given in Table 3. The plots of $\log k_{\text{obsd}}$ against reciprocal temperature gives a straight line and the energy of activation has been calculated from the slope of this plot and equals $68.38 \pm 0.01 \text{ kJ mol}^{-1}$.

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(Received 9 May 1983, revised 14 December 1983)

كيناتيكية البلمرة الثنائية لمركب بنزيل أمين
بوساطة فوق أكسيد الهيدروجين في وجود كبريتات الحديدوز
كعامل مساعد

افتخار أحمد وكمال سعيد وعبد الرحمن حسن النادي
قسم الكيمياء بجامعة الخرطوم ، الخرطوم ، السودان

خلاصة

في هذا البحث درست كيناتيكية البلمرة الثنائية لمركب بنزيل أمين بوساطة فوق أكسيد الهيدروجين بحضور ايون الحديد الثنائي . وقد وجد ان هذا التفاعل يتبع الدرجة الأولى بالنسبة لكل من مركب بنزيل أمين وأيون الحديد الثنائي ، كما يتبع الدرجة الصفرية بالنسبة لفوق أكسيد الهيدروجين وقد حسبت الطاقة التنشيطية وأعطيت القيمة $68,38 \pm 0,01$ كيلو جول لكل مول .

