A Kinetic Study of the Oxidation of 2,4-Dinitrophenylhydrazine with Acidic Bromate

Sreekantha Babu Jonnalagadda *† **and Gerald K. Muthakia**
Department of Chemistry, University of Nairobi, P.O. Box 30197, Nairobi, Kenya

The kinetics of the reaction of 2,4-dinitrophenylhydrazine with bromate ion in sulphuric acid solution have been studied by spectrophotometric techniques. In the fast initial step, 2,4-dinitrophenylhydrazine (dnph) is oxidised to the diazonium ion ($\text{dnp}\overset{+}{\text{N}}_2$). The reaction is of first-order with respect to dnph, bromate, and H^+. The stoicheiometric ratio of dnph to bromate ion is 1 : 1. The intermediate diazonium ion gives the final products, including 1,3-dinitrobenzene, in a slow reaction.

Diazotisation of a primary aromatic amine with nitrite ion is well known as a starting point for the preparation of various aromatic compounds. The formation of an azo compound through coupling of a diazonium ion with an aromatic substrate is also an important synthetic reaction.[1–4] A number of oxidative coupling reactions with various substrates and oxidising agents have been reported.[4–6]

A common method for the preparation of phenylhydrazines is the reduction of the corresponding substituted diazonium salts with $SnCl_2$ in the presence of HCl.[3] However no systematic study seems to have been done on the oxidation of phenylhydrazines. We now report a kinetic study of the oxidation of 2,4-dinitrophenylhydrazine by acidic bromate.[7–9]

Experimental

Reagents.—All the reagents employed were of Analar grade or of high purity. Solvents were distilled and laboratory grade 2,4-dinitrophenylhydrazine was twice recrystallised from butan-1-ol[10] prior to use. A 0.002M-solution of 2,4-dinitrophenylhydrazine (dnph) was freshly prepared every week by dissolving dnph (0.0991 g) in 20% v/v methanol–0.7M-sulphuric acid (50 dm^3). All the standard stock solutions were made in deionised distilled water.

Methods.—The reaction mixtures were stirred magnetically and solutions were maintained at constant temperature (25 ± 0.5 °C) by circulating water from a thermostat.

For the kinetic studies, stock solutions were mixed in the following order: requisite volume of water to make up the total volume, sulphuric acid (5.0M), dnph (0.002M), and then the other reagents as needed. The reaction was started by the separate addition of bromate solution (at 25 ± 0.5 °C). Kinetic runs were followed by monitoring absorbance at 323 nm (Pye-Unicam SP-150 or Cecil CE-272 Linear Radiant u.v. spectrophotometer). No interference of reactants or products was observed at the dnph 323 nm peak except for α-naphthylamine. When α-naphthylamine was added to the reactants as coupling agent, the same concentration of α-naphthylamine was used in the blank. In the concentration ranges of dnph employed Beer's law was obeyed.

Determination of $[HOBr + BrO_3^-]$. An iodometric method was used to determine $[HOBr + BrO_3^-]$. Samples of reaction mixture were added at intervals to a mixture of 0.1M-$HClO_4$ (10 ml) and 10% w/v potassium iodide solution (10 ml) with 10^{-6}M-molybdate catalyst. The solutions were incubated for 30—40 min, then titrated with 0.002M-sodium thiosulphate solution with starch as indicator.[11]

Determination of diazonium ion concentration. Concentrations of diazonium ion were determined by coupling the ion with α-naphthylamine to give a red azo compound. Samples (1 ml) of reaction mixture were added to 0.1% w/v α-naphthylamine solution (3 ml), and after 60 s the absorbance was measured at 504 nm (the absorption maximum of the azo compound). The actual concentrations were determined from a calibration curve.

Product analysis. About ten times higher concentrations than in the kinetic studies were used for the reaction (dnph 0.002M, H^+ 5.0M, and bromate ion 0.05M). After 14 h reaction at room temperature (about 18 °C), the mixture was filtered. The residue was washed with cold water and when crystallised from methanol gave an azo compound, possibly azobisdinitrobenzene, *m/z* 362 (33%, M^+), 195 (100), 93 (96), and 79 (96).

The aqueous filtrate was partitioned with diethyl ether. T.l.c. of the ether-soluble material showed a trace of dnph, and dinitrophenol and 1,3-dinitrobenzene as major products (compared with AnalaR standards). G.l.c.–mass spectrometric analysis of the methanol-crystallised compound showed *m/z* 168 (56%, M^+), 122 (24), 76 (86), 75 (93), and 50 (100), in agreement with identification as 1,3-dinitrobenzene (m.p. 89—90 °C; lit.,[12] 90.02 °C).

Stoicheiometry. The stoicheiometry of the reaction was determined by using 1:1 and 1:2 molar ratios of dnph and bromate ion in 0.56M-H_2SO_4 at room temperature. Concentrations of dnph and bromate were determined after 16, 24, and 40 h; it was found that dnph reacts with bromate ion in 1:1 molar ratio.

Preparation of the standard azo compound and determination of its extinction coefficient. To a mixture of dnph (0.002M; 50 dm^3), sulphuric acid (3.0M; 20 dm^3), and bromate (0.01M; 8 dm^3) (after 1 min reaction) a saturated solution of α-naphthylamine in 0.3M-NaOH was added. The precipitate was filtered off and recrystallised twice from methanol; m.p. 202—204 °C, *m/z* (VG-13-250 quadrapole instrument) 337 (15%; M^+) [as expected for 1-(α-naphthylazo)-2,4-dinitrobenzene], and 195 (33), 117 (13), 142 (100), and 75 (68). The azo compound has an extinction coefficient of 8.2×10^4 mol^{-1} dm^3 cm^{-1} for the absorption maximum at 504 nm which was also used for the calibration curve.

Results and Discussion

Preliminary investigations in which dnph concentration at 323 nm was monitored indicated that the depletion of dnph shows complicated kinetic behaviour involving a fast reaction to about 50% consumption followed by a slow one. Diazonium ion was detected in the reaction mixture.

Experiments were conducted using 2.0×10^{-4}M-dnph, 3.0×10^{-4}M-potassium bromate, and excess of H^+ (3.14M);

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† *Present address:* Department of Chemistry, University of Zimbabwe, Box MP 167, Harare, Zimbabwe.

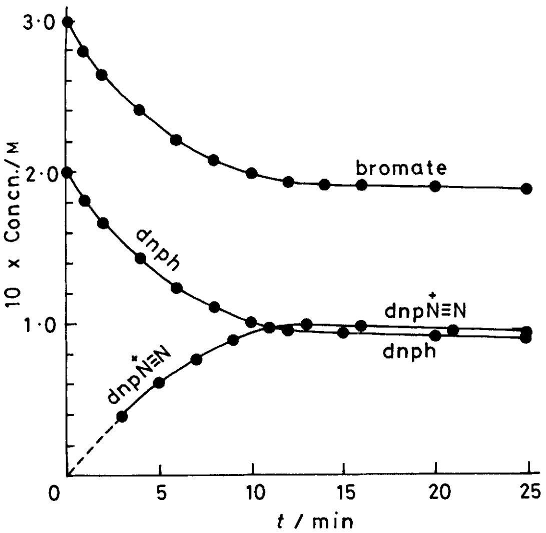

Figure 1. Concentration–time curves for dinitrophenylhydrazine (dnph), bromate ion, and dinitrobenzenediazonium ion ($dnp\overset{+}{N}_2$) (pseudo-second-order reaction); $[H^+]$ 3.14 mol dm^{-3}, [dnph] 0.0002 mol dm^{-3}, [bromate] 0.0003 mol dm^{-3}

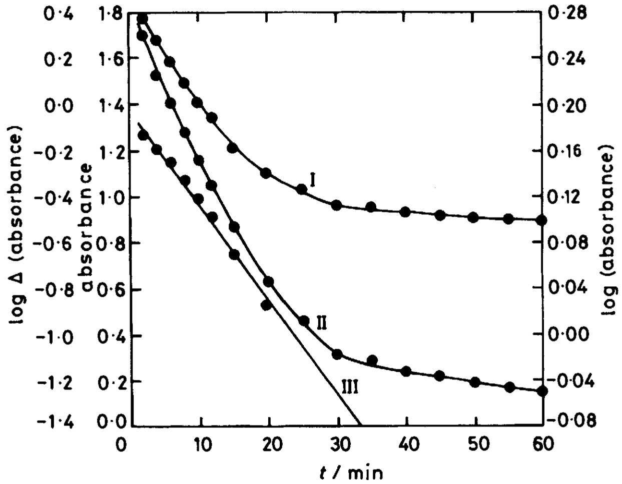

Figure 2. Kinetic curves; $[H^+]$ 0.64 mol dm^{-3}, [dnph] 0.0002 mol dm^{-3}, [bromate] 2.5×10^{-3} mol dm^{-3}; I, absorbance *versus* time; II, log absorbance *versus* time; III, log ($A_t - A_x$) *versus* time

it was found that diazonium ion formation was almost quantitative, accounting for about 95% of the dnph consumed up to the change of the fast depletion reaction into the slow one. Figure 1 shows the concentration–time profiles of dnph, bromate, and diazonium ion. The kinetic traces indicate that diazonium ion is the stable intermediate formed through a fast initial step, and then consumed slowly.

Order with Respect to dnph.—The depletion kinetics of dnph were monitored at 323 nm, with excess of potassium bromate and sulphuric acid. The kinetic data were analysed for dependence of the reaction rate on dnph concentration. In a typical experiment the absorbance (A_t) *versus* time and log A_t *versus* time plots showed a distinct break at about 50% depletion of initial dnph (Figure 2, curves I and II). The logarithm of the difference in absorbance values at time t (A_t) and at the transition (A_x)[log ($A_t - A_x$)] was then plotted against time. The curve obtained was a fairly straight line (gradient 0.000 85, corr. coefft. 0.99), if the point near the transition was excluded (Figure 2, curve III). This plot indicated the existence of an equilibrium and that dnph depletion followed pseudo-first-order kinetics. Pseudo-first-order rate coefficients (k_1'') were determined for different initial concentrations of dnph (Table 1). The fairly constant k_1'' values obtained confirm the first-order dependence on dnph concentration.

Table 1. Dependence of pseudo-first-order rate coefficient (k_1'') on dnph concentration[a]

$[H^+]$ 0.64 mol dm^{-3}; [bromate] 0.005 mol dm^{-3}

10^4 [dnph]/mol dm^{-3}	1.0	1.5	2.0	2.5
10^3 k_1''/s^{-1}	4.36	4.32	4.48	4.61

[a] Entries are the average values of three replicate experiments obtained by linear regression; the values had 5% average deviation.

Table 2. Effect of bromate ion concentration[a]

$[H^+]$ 0.64 mol dm^{-3}; [dnph] 0.0002 mol dm^{-3}

10^3 [bromate] / mol dm^{-3}	10^3 k_1'' / s^{-1}	k_1' / dm^3 mol^{-1} s^{-1}	k_1 / dm^6 mol^{-2} s^{-1}
2.50	1.96	0.784	1.225
3.25	2.76	0.849	1.327
5.00	4.48	0.896	1.400
6.25	5.19	0.830	1.298
7.50	6.24	0.832	1.300
10.00	8.57	0.857	1.339
Mean values		0.859	1.315

(where $k_1' = k_1''$/[bromate] and $k_1 = k_1''$/[bromate] $[H^+]$)

[a] Entries are the average values of three replicate experiments; values have 5% average deviation.

Table 3. Acid dependence of k_1''[a]

[dnph] 0.0002 mol dm^{-3}; [bromate] 0.005 mol dm^{-3}

$[H^+]$ / mol dm^{-3}	10^3 k_1'' / s^{-1}	k_1 / dm^6 mol^{-2} s^{-1}
0.39	2.72	1.395
0.64	4.48	1.400
0.89	6.38	1.434
1.14	8.63	1.514
1.39	10.21	1.469
Mean value		1.442

(where $k_1 = k_1''$/$[H^+]$[bromate])

[a] Entries are the average values of three replicate experiments obtained by linear regression fitting; values had 5% average deviation.

Order with Respect to Bromate Ion.—The k_1'' values for different initial bromate ion concentrations are given in Table 2. A plot of log k_1'' against log $[BrO_3^-]_0$ was a straight line with slope 0.98 (corr. coefft. 0.985), showing that the order with respect to bromate is unity. Pseudo-second-order rate coefficients (k_1') were calculated by dividing k_1'' values by initial bromate ion concentrations (Table 2).

Order with Respect to Hydrogen Ion.—log/log plots of k_1'' *versus* $[H^+]_0$ gave a line with gradient 1.06 (corr. coefft. 0.98), indicating first-order dependence on hydrogen ion concentration (Table 3). The overall rate coefficient (k_1) values were calculated by dividing k_1'' by the corresponding bromate and hydrogen ion initial concentrations. The k_1 values in the last columns of Tables 2 and 3 are fairly constant within the limits of experimental error.

The important reactions of bromate ion in aqueous sulphuric acid can be represented by equations (1)—(5).[7,11,12] With

$$BrO_3^- + 2H^+ + Br^- \rightleftharpoons HOBr + HBrO_2 \qquad (1)$$

$$HBrO_2 + H^+ + Br^- \rightleftharpoons 2HOBr \qquad (2)$$

$$2HBrO_2 \rightleftharpoons BrO_3^- + H^+ + HOBr \qquad (3)$$

$$BrO_3^- + H^+ + HBrO_2 \rightleftharpoons 2BrO_2 + H_2O \qquad (4)$$

$$HOBr + H^+ + Br^- \rightleftharpoons Br_2 + H_2O \qquad (5)$$

sufficient bromide ion in the system, a rapid equilibrium is established between the various species. Under the present experimental conditions, the order of dependence of reaction rate on the various reactants and the lack of any effect of added bromide ion suggest a direct reaction between bromate ion and dnph, similar to equation (1), but with dnph in place of bromide ion. Further, the observed sensitivity of the slow depletion step to added bromide ion suggest that HOBr is the species involved in that reaction step.[13]

From the kinetic data given in Figure 1, dnph and bromate values for different times were calculated and the pseudo-second-order rate coefficient k_1' was determined (5.28 $dm^3\ mol^{-1}\ s^{-1}$). Then the overall rate constant k_1 was obtained by dividing k_1' by 3.14M (the H^+ concentration). The k_1 value (1.68 $dm^6\ mol^{-2}\ s^{-1}$) agrees well with the k_1 values listed in Tables 2 and 3, supporting the proposal of reaction between dnph and bromate ion. An intermediate such as an imide (–N=NH) may be involved between dnph and $dnp\overset{+}{N}_2$. The possibility of formation of an imide as intermediate in the oxidation of arylhydrazines with Fehling's solution has been reported.[1,2]

$$dnpNH{-}NH_2 + H^+ + BrO_3^- \xrightarrow[slow]{k_1} dnpN{=}NH + HBrO_2 + H_2O \qquad (6)$$

$$dnpN{=}NH + HOBr \xrightarrow[fast]{k_2} dnp\overset{+}{N}_2 + Br^- + H_2O \qquad (7)$$

From the observation that the transition to slow depletion occurred earlier when the concentration of either H^+ or bromate ion was increased, initially it was supposed that a fast equilibrium exists between dnph and $dnp\overset{+}{N}_2$. However in a multistep oxidation reaction such an equilibrium between dnph and diazonium ion may not be feasible. In the light of the experimental findings, the break in the dnph depletion kinetics can better be explained by some reaction between dnph and $dnp\overset{+}{N}_2$, either forming a bisdiazo compound or a π-complex in equilibrium with dnph and $dnp\overset{+}{N}_2$, but well to the right [reaction (8)]. Increase in concentration of the stable intermediate $dnp\overset{+}{N}_2$ (k_1 step) could increase the possibility of complex formation with dnph, which is thus prevented from reaction with bromate. However, the slow reaction of HOBr, possibly with the complex, could then release dnph again, with formation of dinitrobenzene (dnb). Hence the rate of consumption of $dnp\overset{+}{N}_2$ (possibly complexed) or the rate of formation of dnb will be the limiting step for depletion of dnph also [equation (9)], similar to the reverse of equation (3).

$$dnp\overset{+}{N}_2 + dnph \rightleftharpoons (dnp\overset{+}{N}_2{\cdot}dnph) \qquad (8)$$

$$(dnp\overset{+}{N}_2{\cdot}dnph) + HOBr \xrightarrow[slow]{+BrO_3^-(k_3)} dnph + dnb + 2BrO_2 + N_2 \qquad (9)$$

If the prediction of complex formation inhibiting the oxidation of dnph is correct, then stopping the diazaonium ion from forming such a complex should allow continued fast depletion of dnph. Experiments were conducted with 0.0002M-dnph, 0.64M-H^+, and 0.025M- or 0.01M-bromate, with addition of α-naphthylamine (0.0005M) as coupling agent for diazonium ion. The reaction then went to completion without any transition, although the α-naphthylamine interfered to some extent in the kinetics. Hence it is reasonable to suggest the existence of some equilibrium reaction between dnph and diazonium ion inhibiting the depletion of dnph under normal conditions.

Rate Law.—For the oxidation of dnph, the rate law is expressed by equation (10). The consumption of diazonium ion can be expressed in terms of k_3, [HOBr], and the concentration of diazonium ion, its complex, or dnph.

$$-d[dnph]/dt = k_1[H^+][dnph][BrO_3^-] \qquad (10)$$

Acknowledgements

We thank Dr. P. G. McDowell (ICIPE, Nairobi) for running the mass spectra of the product samples, Drs. J. O. Midiwo and R. M. Munavu (Department of Chemistry, University of Nairobi) for discussions, and especially the referees for their suggestions on the mechanism of the reaction. One of us (G. K. M.) thanks D.A.A.D. (F.R.G.) for financial assistance.

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Received 7th October 1985; *Paper* 5/1723