Kinetics and Mechanism of Oxidation of 2,4-Dinitrophenylhydrazine, *p*-Nitrophenylhydrazine, and *p*-Tolylhydrazine with Potassium Hexacyanoferrate(III) in Acidic Perchlorate Media

Ashok K. Gupta, Bharati Gupta, Abhay K. Gupta, and Yugul K. Gupta *
Department of Chemistry, University of Rajasthan, Jaipur, India

The kinetics of oxidation of 2,4-dinitrophenylhydrazine (dnph), *p*-nitrophenylhydrazine (pnph), and *p*-tolylhydrazine (pth) with hexacyanoferrate(III) have been studied in acidic perchlorate solutions. The oxidation of pnph has no dependence on $[H^+]$ in the $[HClO_4]$ range 0.15—2.0 mol dm^{-3}. In the oxidation of dnph complex formation with $[Fe(CN)_6]^{3-}$ occurs, and the reaction is independent of $[H^+]$ in the $[HClO_4]$ range 0.025—2.5 mol dm^{-3}. The oxidation of pth in the $[HClO_4]$ range 0.01—1.6 mol dm^{-3} has been found to obey the rate law $-d[Fe(CN)_6{}^{3-}]/dt = 3[Fe(CN)_6{}^{3-}][pth]\{(k_1''/K_1''[H^+]) + k_2'' + k_3''K_2''[H^+]\}$, where K_1'' and K_2'' are the first and second protonation constants of pth, and k_1'', k_2'', and k_3'' are the second-order rate constants for the unprotonated, monoprotonated, and diprotonated species respectively. The oxidations occur *via* aryldiazene and diazonium ion intermediates, to produce substituted azobenzenes and anilines as final products. In the oxidations 2—3 mol of $[Fe(CN)_6]^{3-}$ are consumed by each mol of arylhydrazine, depending on the conditions; under specific conditions, the stoicheiometry is exact.

The oxidations of hydrazine[1] and phenylhydrazine[2,3] with hexacyanoferrate(III) have been reported; the effect on the rate of reaction of substitution in the aromatic ring and relationships between rate and structure are of interest. We have accordingly studied 2,4-dinitrophenylhydrazine (dnph), *p*-nitrophenylhydrazine (pnph), and *p*-tolylhydrazine (pth). Aryldiazenes and diazonium salts are reported to be intermediates[4,5] in such oxidations, and the spectral studies of Kosower and co-workers[6] and of Itano[7] have confirmed this. Moffalt and Lerch[8] have reported that the oxidation of dnph with dimethyl sulphoxide and dicyclohexylcarbodi-imide leads to *m*-dinitrobenzene, 2,4-dinitrophenyl methyl sulphide, and 2,2′,4,4′-tetranitroazobenzene *via* 2,4-dinitrophenyldiazene or 2,4-dinitrobenzenediazonium intermediates. In a kinetic study of the oxidation[9] of arylhydrazines with HNO_2, substantial amounts of diazonium ions were reported to be formed which also yield aryl azides. In kinetic studies[10,11] with thallium(III) the formation of phenols as the end products was reported *via* diazonium salt intermediates. These conflicting reports, and the paucity of kinetic studies on these systems prompted the present investigation of the stoicheiometry, end products, intermediates, kinetics, and mechanism of the oxidations of dnph, pnph, and pth with hexacyanoferrate(III) in acidic perchlorate solutions.

Experimental

Materials and Solutions.—Aqueous solutions of B.D.H. AnalaR grade potassium hexacyanoferrate(III) were prepared each day and protected from light.[12] The solutions were standardized iodometrically[13] and colorimetrically (ε 1 000 ± 10 dm^3 mol^{-1} cm^{-1}) with a 430-nm filter on a Coleman colorimeter. No decomposition of hexacyanoferrate(III) took place in acidic solutions.

2,4-Dinitrophenylhydrazine (dnph) (B.D.H. AnalaR) was recrystallized from dioxane and its purity checked by t.l.c. (light petroleum–acetone, 8 : 2). Solutions in dilute $HClO_4$ were estimated iodometrically.[14] *p*-Nitrophenylhydrazine (pnph) (Sisco) was recrystallized from ethanol, and its purity checked by t.l.c. as for dnph. *p*-Tolylhydrazine (pth) was a gift from Professor H. A. Itano, University of California, and was recrystallized from HCl (2.0 mol dm^{-3}). Solutions in water were estimated iodometrically.

The 70% perchloric acid used was Riedel grade. Solutions of $LiClO_4$ were prepared by neutralizing Li_2CO_3 (Merck) with 70% $HClO_4$ to pH 6.8. The solutions were boiled to remove CO_2 and cooled before use. Ionic strength was adjusted with these solutions. All other chemicals were either of B.D.H. AnalaR grade or Merck quality.

All solutions were prepared in doubly distilled (conductivity) water, the second distillation being from tetraoxomanganate(VII). Corning glass vessels were used.

Kinetic Procedure.—Measured quantities of the reductant, perchloric acid, and other components in a stoppered Erlenmeyer flask were placed in a thermostatted water-bath (±0.1 °C). Reactions were initiated by adding temperature-equilibrated hexacyanoferrate(III) solution. The order of mixing had no effect.

Reactions with pth were followed by removing aliquot portions (5 cm^3) at intervals and determining hexacyanoferrate(III) colorimetrically at 430 nm. Hexacyanoferrate(II) and other components were transparent at this wavelength. Concentrated solutions were suitably diluted before measuring the absorption, but the same concentrations of the other non-absorbing components were maintained.

In the reactions with dnph and pnph aliquot portions (5 cm^3) were withdrawn at intervals and added to an ice-cold HCl solution of such a concentration as to yield final solutions *ca.* 1.0 mol dm^{-3} in HCl. The unused hexacyanoferrate(III) was determined iodometrically[13] after complexing the hexacyanoferrate(II) with zinc sulphate. Iodine has been reported[15] to react slowly with hydrazine in the presence of acid, but in acidic solutions of 1.0—1.5 mol dm^{-3} and at low temperatures this reaction is not significant enough to interfere with the iodometric determination of hexacyanoferrate(III).

Concentrations of dnph of >10 mmol dm^{-3} and of $[Fe(CN)_6]^{3-}$ of >5 mmol dm^{-3} gave a precipitate within 1 or 2 min of mixing, and so concentration ranges of reactants which avoided this precipitation were used.

Rates of the Reaction and Precision.—Reaction rates were determined by the initial-rate method[16] and first-order plots

Table 1. Variation of initial rate, v_0, with $[Fe(CN)_6{}^{3-}]$ in the oxidation of arylhydrazines

(*i*) dnph (1.0×10^{-2} mol dm^{-3}), $[HClO_4]$ = 1.0 mol dm^{-3}, 30 °C

$10^4[Fe(CN)_6{}^{3-}]$/mol dm^{-3}	2.5	5.0	7.5	10	15	20	25	30
$10^7 v_0$/mol dm^{-3} s^{-1}	6.4	14	24	29	42	61	75	87

(*ii*) pnph (1.0×10^{-3}), $[HClO_4]$ = 1.0 mol dm^{-3}, 35 °C

$10^4[Fe(CN)_6{}^{3-}]$/mol dm^{-3}	10	15	20	25	30	35	40	45	50
$10^7 v_0$/mol dm^{-3} s^{-1}	13	21	31	37	47	56	62	70	78

(*iii*) pth (1.66×10^{-3}), $[HClO_4]$ = 0.5 mol dm^{-3}, 25 °C

$10^4[Fe(CN)_6{}^{3-}]$/mol dm^{-3}	1.66	3.30	4.96	6.60	8.26	9.9	11.56	13.2	16.5	18.16
$10^7 v_0$/mol dm^{-3} s^{-1}	4.5	8.5	13	17	21	27	30	32	38	42
$10^4 k$ */s^{-1}	27	26	26	25	—	—	—	—	—	—

* Pseudo-first-order rate constant.

were also used when conditions were appropriate. In colorimetric observations duplicate measurements were reproducible to ±5% while iodometric analyses yielded results to within ±10%.

Stoicheiometry.—Several mixtures with different concentrations of reactants were set aside for 12 h for completion of the reaction. Excess of hexacyanoferrate(III) was estimated iodometrically in the case of dnph and pnph, and colorimetrically in the case of pth. Excess of dnph was determined by indirect iodometry. Solid Na_2CO_3 was added to accelerate the reaction between iodine and dnph. With excess of dnph 2.02 ± 0.01 mol equiv. of $[Fe(CN)_6]^{3-}$ are required (six experiments), but with excess of $[Fe(CN)_6]^{3-}$ the stoicheiometry varies between 2 and 3 mol equiv.

Excess of pth and of pnph was determined iodometrically. From 13 experiments, 1 mol of pnph required 3.01 ± 0.1 mol of hexacyanoferrate(III). With excess of pth, from eight experiments 1 mol of pth was found to react with 3.01 ± 0.07 mol of hexacyanoferrate(III). With excess of $[Fe(CN)_6]^{3-}$ and particularly for low concentrations of reactants the stoicheiometry varied between 2 and 3 mol equiv. However, with sufficient excess of $[Fe(CN)_6]^{3-}$ 3.05 ± 0.06 mol of oxidant react with 1 mol of pth (10 experiments). The kinetic experiments used concentration ranges for which the reactions have a definite stoicheiometry.

Product Analysis.—From the reaction between dnph and $[Fe(CN)_6]^{3-}$ in $HClO_4$ (0.5 mol dm^{-3}) after about 3—4 h, a solid was obtained which was filtered off. The crude solid product was exhaustively extracted with acetone and the filtrate extracted with chloroform. The acetone and chloroform extracts were compared by t.l.c. and mixed. The solvents were distilled off and the crude residue chromatographed on a silica gel column with light petroleum and then benzene as eluant. Two components were isolated in pure form and identified as 2,2′,4,4′-tetranitroazobenzene {m.p. 219—220 °C (lit.,[17] 221 °C); R_f 76 in acetone–light petroleum (3 : 7); $\lambda_{max.}$(MeOH) 304 nm, ε 19 000 (lit.,[8] 18 900): ^{1}H n.m.r., δ 7.1 p.p.m. (aromatic H); *m/z* 362 (M^+), 195 [$M - C_6H_3(NO_2)_2$], 93, and 75}, and 2,6-dinitroaniline {m.p. 177—180 °C; R_f 62 in acetone–light petroleum (3 : 7); $\lambda_{max.}$(EtOH) 257 (ε 10 000; lit.,[18] 10 000 dm^3 mol^{-1} cm^{-1}) and 337 nm; *m/z* 183 (M^+), 167, 137, 107, 91, and 90}. The product from pnph was identified as 4,4′-dinitroazobenzene, m.p. 221 °C (lit.,[19] 221 °C), and that from pth as 4,4′-dimethylazobenzene, m.p. 143 °C (lit.,[20] 143 °C). Nitrogen was evolved in each case.

Spectrophotometry.—All spectrophotometric measurements were made on a Toshniwal u.v. instrument using 1-cm cells. The first protonation constant of dnph was determined at 30 °C by measuring the absorption at 360 nm of mixtures of dnph (5×10^{-5} mol dm^{-3}) and perchloric acid of different concentrations (2.5—10 mmol dm^{-3}); I = 1.0 mol dm^{-3}. Assuming that equation (1) represents the protonation equilibrium, equation (2) was employed to calculate K_1,

$$\text{dnph} + H^+ \overset{K_1}{\rightleftharpoons} \text{Hdnph}^+ \qquad (1)$$

$$\frac{1}{\varepsilon_1 - \varepsilon_0} = \frac{1}{(\varepsilon_1 - \varepsilon_2)K_1[H^+]} + \frac{1}{(\varepsilon_1 - \varepsilon_2)} \qquad (2)$$

where ε_0, ε_1, and ε_2 are the absorption coefficients of the mixture, free dnph, and protonated dnph respectively. The value of ε_1 was determined by extrapolating the decrease in absorbance of dnph with increasing $[H^+]$ to $[H^+] = 0$. A plot of $(\varepsilon_1 - \varepsilon_0)^{-1}$ *vs.* $[H^+]^{-1}$ in the range of $[H^+]$ = 5—100 mmol dm^{-3} (at 360 nm) gave a value of K_1 of 500 ± 200 dm^3 mol^{-1}. The second protonation constant could not be determined since the absorbance reaches a limiting value at $[HClO_4]$ = 100 mmol dm^{-3}. It appears that the absorption coefficient of the diprotonated species has the same value as that for the monoprotonated species. Similar measurements with pth and pnph did not lead to any definite conclusions.

pH-*Metric Titrations.*—pH Measurements were carried out on an EC digital pH meter with aqueous solutions of dnph and pth by titration against aqueous $HClO_4$. The first protonation constants were found to be 780 ± 5 dm^3 mol^{-1} at 30 °C for dnph and (2.5 ± 0.01) × 10^5 dm^3 mol^{-1} at 25 °C for pth, both at I = 1.0 mol dm^{-3} ($LiClO_4$). The agreement in the values of first protonation constant of dnph from spectrophotometric and pH measurements is not good. This is not of much consequence for explaining the kinetic results since the order of magnitude of the two values is the same. These first protonation constants are in the expected order, pth > phenylhydrazine > pnph > dnph as discussed later and shown in Table 5. This may also be true for the second protonation constant.

Results

Dependence on $[Fe(CN)_6{}^{3-}]$. The concentration of $[Fe(CN)_6]^{3-}$ was varied from 2.5×10^{-4} to 30×10^{-4} mol dm^{-3} for [dnph] = 1.0×10^{-2} mol dm^{-3} in $HClO_4$ (1.0 mol dm^{-3}). For pnph (1×10^{-3} mol dm^{-3}), $[Fe(CN)_6{}^{3-}]$ was varied from 1×10^{-3} to 5×10^{-3} mol dm^{-3} in $HClO_4$ (1.0 mol dm^{-3}). The results are given in Table 1. In both cases a plot of rate *vs.* $[Fe(CN)_6{}^{3-}]$ gives a straight line passing through the origin, showing the first-order dependence on $[Fe(CN)_6{}^{3-}]$. For pth

Table 2. Dependence of initial rate, v_0, on [arylhydrazine] in the reactions with $[Fe(CN)_6]^{3-}$

(*i*) dnph; * $[Fe(CN)_6{}^{3-}] = 5 \times 10^{-4}$, $I = 1.0$ mol dm^{-3}, 30 °C

10^3[dnph]/mol dm^{-3}	1.0	2.0	3.0	4.0	4.5	5.0	6.0	8.0	10.0	11.0	12.0
10^3k_1/s^{-1} ($[HClO_4] = 1.0$ mol dm^{-3})	0.67	1.10	1.50	1.75	1.90	2.0	2.20	2.50	2.65	2.70	2.85
($[HClO_4] = 0.5$ mol dm^{-3})	0.73	1.15	1.55	1.75	1.95	2.0	2.22	2.53	2.63	2.70	2.85
	(0.69)	(1.18)	(1.55)	(1.82)	(1.93)	(2.05)	(2.23)	(2.50)	(2.70)	(2.79)	(2.86)

(*ii*) pnph; $[Fe(CN)_6{}^{3-}] = 2.0 \times 10^{-3}$, $[HClO_4] = 1.0$, $I = 1.0$ mol dm^{-3}, 35 °C

10^4[pnph]/mol dm^{-3}	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20	25
10^7v_0/mol dm^{-3} s^{-1}	6.6	13	23	30	40	47	53	60	77

(*iii*) pth; $[Fe(CN)_6{}^{3-}] = 3.35 \times 10^{-4}$, $I = 1.0$ mol dm^{-3}, 25 °C

10^3[pth]/mol dm^{-3}	0.266	0.533	0.80	1.066
10^7v_0/mol dm^{-3} s^{-1} ($[HClO_4] = 0.05$ mol dm^{-3})	2.8	6.0	9.4	16
($[HClO_4] = 0.25$ mol dm^{-3})	1.4	2.5	3.7	5.5
($[HClO_4] = 1.0$ mol dm^{-3})	1.8	3.7	5.7	7.4

* k_1 is the pseudo-first-order rate constant. Figures in parentheses were calculated from equation (5) with values of k of 2.0×10^{-3} dm^3 mol^{-1} s^{-1} and K 210 dm^3 mol^{-1}.

Table 3. Dependence of rate * on concentration of pth in its reaction with $[Fe(CN)_6]^{3-}$ (3.35×10^{-4} mol dm^{-3}) at $I = 1.0$ mol dm^{-3} and 25 °C

10^3[pth]/mol dm^{-3}	1.33	1.66	2.0	2.33	2.66	3.0	3.33	3.66	4.0	4.33	4.66
10^3k/s^{-1} ($[HClO_4] = 0.05$ mol dm^{-3})	5.8	6.5	8.0	8.1	9.2	9.9	11.5	11.9	—	—	—
($[HClO_4] = 0.25$ mol dm^{-3})	2.0	2.4	2.9	3.4	3.9	4.6	5.0	5.8	6.2	6.7	7.1
($[HClO_4] = 1.0$ mol dm^{-3})	2.5	3.3	3.8	4.6	5.4	5.8	6.6	7.5	7.6	8.2	—

* k is the pseudo-first-order rate constant. Concentrations of pth are at least ten times that of the oxidant.

(1.66×10^{-3} mol dm^{-3}), $[Fe(CN)_6{}^{3-}]$ was varied from 1.66×10^{-4} to 18.16×10^{-4} mol dm^{-3} in $HClO_4$ (0.5 mol dm^{-3}). Again the order with respect to [oxidant] is one. Some pseudo-first-order plots yielded an average value of $(2.6 \pm 0.16) \times 10^{-3}$ s^{-1}. Slopes of the straight lines obtained from plots of initial rates *vs.* [oxidant] were $(3.0 \pm 0.05) \times 10^{-3}$ for dnph, $(1.5 \pm 0.05) \times 10^{-3}$ for pnph, and $(2.5 \pm 0.1) \times 10^{-3}$ s^{-1} for pth. If for comparison these values are divided by the concentrations of the respective arylhydrazines the observed second-order rate constants (dm^3 mol^{-1} s^{-1}) were found to be $(3.0 \pm 0.05) \times 10^{-1}$ for dnph at 30 °C and $I = 1.0$ mol dm^{-3}, 1.5 ± 0.05 for pnph at 35 °C and $I = 1.0$ mol dm^{-3}, and 1.5 ± 0.1 for pth at 25 °C and $I = 0.5$ mol dm^{-3}.

Dependence on [Arylhydrazine].—The results for the variation of arylhydrazine concentration at fixed $[Fe(CN)_6{}^{3-}]$ and $[HClO_4]$ are shown in Tables 2 and 3. For dnph the rate increases and tends to attain a limiting value with increase in [dnph] indicating some sort of complex formation. For pnph and pth a plot of initial rate *vs.* [arylhydrazine] yielded a straight line passing through the origin. Hence, the order with respect to [pnph] and [pth] is clearly one. The observed second-order rate constants (dm^3 mol^{-1} s^{-1}) were found to be 1.5 ± 0.08 for pnph in 1.0 mol dm^{-3} $HClO_4$ at 35 °C, and for pth 3.4 ± 0.1, 1.6 ± 0.1, and 1.9 ± 0.15, in 0.05, 0.25, and 1.0 mol dm^{-3} $HClO_4$ respectively, at 25 °C.

Effect of Ionic Strength and $[Fe(CN)_6]^{4-}$.—The ionic strength was varied in the range 0.05—2.0 mol dm^{-3} ($LiClO_4$), but no effect was observed. Similarly a variation in $[Fe(CN)_6{}^{4-}]$ from 0.5 to 2.5 mmol dm^{-3} had no effect on the rate.

Dependence on $[H^+]$.—The concentration of H^+ was varied by using different concentrations of $HClO_4$ at constant ionic strength adjusted with $LiClO_4$ (see Tables 4 and 5). The rate is independent of $[H^+]$ in the concentration range employed for dnph and pnph. Lower concentrations of $[H^+]$ could not be used since the solutions of dnph and pnph were made up in aqueous $HClO_4$. In the case of pth the rate first decreases, attains a minimum value, and then increases with increasing $[H^+]$. At low $[H^+]$ a plot of k (pseudo-first-order rate constant) *vs.* $[H^+]^{-1}$ yields a straight line with a non-zero intercept. Similarly at high $[H^+]$ a plot of k *vs.* $[H^+]$ yields a straight line with a non-zero intercept.

Effect of Ethylenediaminetetra-acetic acid (H_4edta), CN^-, *and* Cu^{2+} *on the Oxidation of* dnph.—Experiments with varying [dnph] had indicated complex formation and so we investigated the possible role of traces of metal ions in the reaction and the possibility of displacement of CN^- from $[Fe(CN)_6]^{3-}$. Experiments showed that H_4edta (10 mmol dm^{-3}), KCN (10 and 50 mmol dm^{-3}), and $CuSO_4$ (1 and 10 µmol dm^{-3}) had no effect on the rate.

Effect of $[Cl^-]$ *Variation on the* $[Fe(CN)_6]^{3-}$-pth *Reaction.*—*p*-Tolylhydrazine was in the form of its hydrochloride, but the variation of $[Cl^-]$ from 0.1 to 0.5 mol dm^{-3} had no effect on the rate.

Discussion

The first protonation constant of phenylhydrazine is reported[21] to be 1.86×10^5 dm^3 mol^{-1}. The first protonation constant of dnph may be taken as 640 dm^3 mol^{-1} (average): the second protonation constant is likely to be small.[22] Since 1.0 mol dm^{-3} $HClO_4$ was used, dnph will be present as the monoprotonated species.

Since the rate increases and becomes limiting with increasing [dnph], dnph must be involved either in complex formation with metal ions or the step involving dnph must be preceded by an equilibrium step. Investigations with traces of Cu^{2+}, $[Fe(CN)_6]^{4-}$, H_4edta, and CN^- show that there is no pre-equilibrium involving any of these species.

Table 4. Effect of $[\mathrm{H}^+]$ in the reaction of $[\mathrm{Fe(CN)_6}]^{3-}$ with arylhydrazines (v_0 = initial rate)

(*i*) dnph; $[\mathrm{Fe(CN)_6}^{3-}] = 2.0 \times 10^{-3}$, $[\mathrm{dnph}] = 4.0 \times 10^{-4}$, $I = 2.0$ mol dm^{-3}, 30 °C

$[\mathrm{H}^+]$/mol dm^{-3}	0.02	0.04	0.06
$10^7 v_0$/mol dm^{-3} s^{-1}	7.2	7.0	7.3

$[\mathrm{Fe(CN)_6}^{3-}] = 2.0 \times 10^{-3}$, $[\mathrm{dnph}] = 2.0 \times 10^{-3}$, $I = 2.0$ mol dm^{-3}, 30 °C

$[\mathrm{H}^+]$/mol dm^{-3}	0.1	0.2	0.3	0.5	0.8	1.0
$10^7 v_0$/mol dm^{-3} s^{-1}	22	20	20	21	20	21

$[\mathrm{Fe(CN)_6}^{3-}] = 2.5 \times 10^{-3}$, $[\mathrm{dnph}] = 1.0 \times 10^{-2}$, $I = 2.0$ mol dm^{-3}, 30 °C

$[\mathrm{H}^+]$/mol dm^{-3}	1.2	1.4	1.6	1.8	2.0
$10^7 v_0$/mol dm^{-3} s^{-1}	76	74	72	74	76

(*ii*) pnph (1.0×10^{-3} mol dm^{-3}); $[\mathrm{Fe(CN)_6}^{3-}] = 2.0 \times 10^{-3}$, $I = 2.0$ mol dm^{-3}

$[\mathrm{H}^+]$/mol dm^{-3}	0.15	0.3	0.4	0.6	0.8	1.2	1.4	1.6	1.8	2.0
$10^7 v_0$/mol dm^{-3} s^{-1} (35 °C)	32	33	32	33	32	30	30	31	32	32
(40 °C)	48	48	49	50	50	50	49	48	50	50

Table 5. Effect of $[\mathrm{H}^+]$ in the reaction of $[\mathrm{Fe(CN)_6}]^{3-}$ (3.3×10^{-4} mol dm^{-3}) and pth (1.66×10^{-3} mol dm^{-3}) at $I = 2.0$ mol dm^{-3} *

$[\mathrm{H}^+]$/mol dm^{-3}	0.01	0.02	0.04	0.06	0.08	0.1	0.2	0.3	0.4
$10^4 k$/s^{-1} (20 °C)	92	47	26	19	17	16	11	11	13
	(93)	(50)	(28)	(21)	(18)	(16)	(13)	(14)	(15)
$[\mathrm{H}^+]$/mol dm^{-3}	0.6	0.75	1.0	1.1	1.2	1.3	1.4	1.5	1.6
$10^4 k$/s^{-1} (20 °C)	16	20	25	24	31	33	35	37	39
	(19)	(22)	(27)	(29)	(31)	(33)	(35)	(38)	(40)
$[\mathrm{H}^+]$/mol dm^{-3}	0.01	0.02	0.04	0.06	0.08	0.01	0.2	0.3	0.4
$10^4 k$/s^{-1} (25 °C)	160	93	48	36	29	25	20	22	25
	(173)	(91)	(50)	(38)	(32)	(28)	(24)	(25)	(27)
$[\mathrm{H}^+]$/mol dm^{-3}	0.6	0.75	1.0	1.1	1.2	1.3	1.4	1.5	1.6
$10^4 k$/s^{-1} (25 °C)	30	36	44	50	52	57	63	68	72
	(33)	(38)	(47)	(51)	(55)	(58)	(62)	(66)	(70)

* Figures in parentheses are the pseudo-first-order rate constants calculated from equation (17).

On the basis of the various rate dependences we suggest the mechanism in equations (1), (3), and (4). Since $[\mathrm{H}^+] = 1.0$

$$\mathrm{dnph} + \mathrm{H}^+ \overset{K_1}{\rightleftharpoons} \mathrm{Hdnph}^+ \tag{1}$$

$$\mathrm{Hdnph}^+ + [\mathrm{Fe(CN)_6}]^{3-} \overset{K}{\rightleftharpoons} \text{Complex} \tag{3}$$

$$\text{Complex} \xrightarrow{k} \text{products} \tag{4}$$

mol dm^{-3} and $K_1 = ca.$ 640 dm^3 mol^{-1}, Hdnph^+ predominantly would be present. The rate law, after taking into consideration the stoicheiometry, may be expressed as in equation (5). A plot of rate^{-1} against $[\mathrm{dnph}]_T^{-1}$ or $[\mathrm{Hdnph}^+]_T^{-1}$

$$\frac{-\mathrm{d}[\mathrm{Fe(CN)_6}^{3-}]}{\mathrm{d}t} = \frac{2kK[\mathrm{Fe(CN)_6}^{3-}]_T[\mathrm{Hdnph}^+]_T}{(1 + K[\mathrm{Hdnph}^+]_T)} \tag{5}$$

for $[\mathrm{dnph}] > 5[\mathrm{Fe(CN)_6}^{3-}]$ yields a straight line with non-zero intercept, and from the intercept and slope k and K were found to be $(2.0 \pm 0.1) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} and 210 ± 20 dm^3 mol^{-1} respectively.

The first protonation constant of pnph is reported [22] to be 0.5×10^4 dm^3 mol^{-1} and as expected is smaller than that of phenylhydrazine.[2] The second protonation constant of pnph is also small.[22] Thus under the acidic conditions employed, pnph would wholly be present as the monoprotonated species. On the basis of the rate dependences on $[\mathrm{Fe(CN)_6}^{3-}]$ and [pnph], the mechanism in equation (6) and (7) appears to be

$$\mathrm{pnph} + \mathrm{H}^+ \overset{K_1'}{\rightleftharpoons} \mathrm{Hpnph}^+ \tag{6}$$

$$\mathrm{Hpnph}^+ + [\mathrm{Fe(CN)_6}]^{3-} \xrightarrow{k_1'} \text{products} \tag{7}$$

tenable, and the rate law, based on a stoicheiometry of 3 : 1, would be given by equation (8). However, $K_1'[\mathrm{H}^+] \gg 1$ and

$$\frac{-\mathrm{d}[\mathrm{Fe(CN)_6}^{3-}]}{\mathrm{d}t} = \frac{3K_1'k_1'[\mathrm{Fe(CN)_6}^{3-}]_T[\mathrm{pnph}]_T[\mathrm{H}^+]}{(1 + K_1'[\mathrm{H}^+])} \tag{8}$$

equation (8) reduces to (9). The second-order rate constant k'

$$-\mathrm{d}[\mathrm{Fe(CN)_6}^{3-}]/\mathrm{d}t = 3k_1'[\mathrm{Fe(CN)_6}^{3-}]_T[\mathrm{pnph}]_T = k'[\mathrm{Fe(CN)_6}^{3-}]_T[\mathrm{pnph}]_T \tag{9}$$

was found to be 0.50 and 0.80 dm^3 mol^{-1} s^{-1} at 35 and 40 °C, respectively.

A dependence on $[\mathrm{H}^+]$ was observed only in the case of pth. Hexacyanoferrate(III) has little tendency to become protonated [23,24] and hence this dependence is connected with the protonation of pth as shown in equations (10) and (11).

$$\mathrm{pth} + \mathrm{H}^+ \overset{K_1''}{\rightleftharpoons} \mathrm{Hpth}^+ \tag{10}$$

$$\mathrm{Hpth}^+ + \mathrm{H}^+ \overset{K_2''}{\rightleftharpoons} \mathrm{H_2pth}^{2+} \tag{11}$$

The value of K_1'' determined by pH measurements was found to be 2.5×10^5 dm^3 mol^{-1} at 25 °C and $I = 1.0$ mol dm^{-3}.

Table 6. Values of rate constants and protonation constants in the oxidations of arylhydrazines with hexacyanoferrate(III) in acidic perchlorate solution at $I = 2.0$ mol dm^{-3} except where indicated

	pth (25 °C)	Phenylhydrazine (30 °C)	pnph (35 °C)	dnph (30 °C)
Stoicheiometry [a]	3.0	4.0 [b]	3.0	2.0 [c]
Rate constant/dm^3 mol^{-1} s^{-1}	$0.033(k_1''/K_1'')$	$0.006\,7(k_1''/K_1'')$ [d]		
	$0\ 16(k_2'')$	$0.915(k_2'')$	$0.50(k')$	$2.0 \times 10^{-3}(k)$ [e]
/dm^6 mol^{-2} s^{-1}	$0.76(k_3''K_2'')$	$0.23(k_3''K_2'')$		
First protonation constant/dm^3 mol^{-1}	2.5×10^5 [f]	2.1×10^5 [f]	5.0×10^3 [g]	7.8×10^2 [f]
				5.0×10^2 [g,h]

[a] $[Fe(CN)_6^{3-}]/[\text{arylhydrazine}]$. [b] The product of oxidation was phenol. [c] Only with excess of dnph, 2—3 mol dm^{-3} otherwise. [d] $I = 3.5$ mol dm^{-3}. [e] Equation (5). [f] Determined by the pH metric method, $I = 1.0$ mol dm^{-3}. [g] Determined spectrophotometrically. [h] $I = 1.0$ mol dm^{-3}.

The second protonation constant K_2'' could not be determined, but its value would be small (*ca.* 10^{-5} dm^3 mol^{-1}) on the basis of the other second protonation constants for the other hydrazines.[22] If all the pth species are reactive as given in equations (12)—(14), the rate law in equation (15) is obtained.

$$[Fe(CN)_6]^{3-} + \text{pth} \xrightarrow{k_1''} \text{products} \qquad (12)$$

$$[Fe(CN)_6]^{3-} + \text{Hpth}^+ \xrightarrow{k_2''} \text{products} \qquad (13)$$

$$[Fe(CN)_6]^{3-} + \text{H}_2\text{pth}^{2+} \xrightarrow{k_3''} \text{products} \qquad (14)$$

$$\frac{-d[Fe(CN)_6{}^{3-}]}{dt} = \frac{3[Fe(CN)_6{}^{3-}]_T[\text{pth}]_T(k_1'' + k_2''K_1''[H^+] + k_3''K_1''K_2''[H^+]^2)}{(1 + K_1''[H^+] + K_1''K_2''[H^+]^2)} \qquad (15)$$

With the values of K_1'' and K_2'' mentioned above, the first and third terms in the denominator are insignificant and the rate law reduces to equation (16).

$$-d[Fe(CN)_6{}^{3-}]_T/dt = 3[Fe(CN)_6{}^{3-}]_T[\text{pth}]_T\{(k_1''/K_1''[H^+]) + k_2'' + k_3''K_2''[H^+]\} \quad (16)$$

$$\text{or } k = 3[\text{pth}]_T\{k_1''/(K_1''[H^+]) + k_2'' + k_3''K_2''[H^+]\} \quad 17)$$

The values of k_1''/K_1'' and k_2'' were found to be 1.8×10^{-2} (3.3×10^{-2}) s^{-1} and 0.10 (0.16) dm^3 mol^{-1} s^{-1} at 20 (25) °C respectively from plots of rate *vs.* $[H^+]^{-1}$ at low $[H^+]$. Similarly, from the plots of rate *vs.* $[H^+]$ at high $[H^+]$, the values of k_2'' and $k_3''K_2''$ were found to be 0.10 (0.16) (dm^3 mol^{-1} s^{-1}) and 0.42 (0.76) dm^6 mol^{-2} s^{-1} at 20 (25) °C respectively. The values of k_2'' from the two plots indicate good internal consistency. The calculated values of the pseudo-first-order rate constants from these rate constants on the basis of equation (17) are given in parentheses in Table 5; agreement between calculated and observed values is satisfactory.

Although the arylhydrazines were studied at different temperatures, the results may be compared with those for the oxidation of phenylhydrazine[3] (see Table 6). The values of the protonation constants decrease in the order pth > phenylhydrazine > pnph > dnph. The methyl group is electron-donating, increasing electron density in the hydrazine and thus facilitating protonation. The electron-withdrawing nitro-group would have the opposite effect. For a strict comparison of the rates, the rate laws in all four cases should be the same. However, since $[H^+] < 0.15$ mol dm^{-3} could not be used in the case of pnph and dnph and since the second protonation constants are small, the monoprotonated species would predominate. The various rate constants for pth and phenylhydrazine show that the major contribution to the rate is from the diprotonated species whereas for pnph and dnph, only the monoprotonated species appear to be reactive. The diprotonated species might be more reactive for pnph and dnph also, but since the second protonation constant is low the concentration of the diprotonated species is too small to make any contribution to the rate. Since hexacyanoferrate(III) is negatively charged the formation of the transition state will be facilitated by more positive reactants and so diprotonated species are likely to be more reactive. Thus eventually the rate behaviour should parallel the tendency for protonation. The observed rates are in the same order, *i.e.* pth > phenylhydrazine > pnph > dnph. The case of dnph is complicated by the formation of a complex of $[Fe(CN)_6]^{3-}$ and dnph, as indicated by the kinetic results. Complexes of $[Fe(CN)_6]^{3-}$ have also been reported with 2,2′-bipyridyl and 1,10-phenanthroline,[25] 8-hydroxyquinoline,[26] and nicotinoyl- and isonicotinoyl-hydrazines.[27]

Another study[11] of the oxidation of these phenylhydrazines with chloro complexes of thallium(III) indicated an order of reactivity of dnph > onph > phenylhydrazine > pnph > pth (onph = *o*-nitrophenylhydrazine). The rate-determining step in these reactions is the formation of a reactive complex of thallium(III) and the arylhydrazine and this would take place more readily for dnph and onph. Thallium(III) can co-ordinate to nitrogen of the hydrazine as well as to oxygen of the *o*-nitro-group in the case of dnph and onph.

References

1 E. J. Meehan, I. M. Kolthoff, and K. Mitsuhashi, *Suom. Kemistil. B*, 1969, **42**, 159.

2 A. M. A. Verwey, J. A. Jonker, and S. Balt, *Recl. Trav. Chim., Pays-Bas.*, 1969, **88**, 439.

3 A. K. Gupta, B. C. Joshi, and Y. K. Gupta, *Indian J. Chem., Sect. A*, 1981, **20**, 276.

4 F. D. Chattaway, *J. Chem. Soc.*, 1907, 1323.

5 A. Angeli and Z. Jolles, *Ber. Dtsch. Chem. Ges.*, 1929, **62**, 2099.

6 E. M. Kosower and P. K. C. Huang, *J. Am. Chem. Soc.*, 1965, **87**, 4645; P. K. C. Huang and E. M. Kosower, *ibid.*, 1968, **90**, 2362, 2367; E. M. Kosower, P. K. C. Huang, and T. Tsuji, *ibid.*, 1969, **91**, 2325.

7 H. A. Itano, *Proc. Natl. Acad. Sci. USA*, 1970, **67**, 485.

8 J. G. Moffalt and U. Lerch, *J. Org. Chem.*, 1971, **36**, 3861.

9 G. Stedman and N. Uysal, *J. Chem. Soc., Perkin Trans. 2*, 1977, 667.

10 V. S. Srinivasan and N. Venkatasubramanian, *Indian J. Chem., Sect. A*, 1977, **15**, 115.

11 U. S. Banthiya, B. C. Joshi, and Y. K. Gupta, *Indian J. Chem., Sect. A*, 1981, **20**, 43.

12 K. K. Girdhar and D. V. S. Jain, *J. Inorg. Nucl. Chem.*, 1965, **27**, 2653.

13 I. M. Kolthoff and R. Belcher, 'Volumetric Analysis,' Interscience, New York, 1957, vol. 3, p. 344.

14 W. C. Bray and E. J. Cuy, *J. Am. Chem. Soc.*, 1924, **46**, 858.

15 Tan Ah Bah and Mok Chup Mew, *J. Singapore Natl. Acad. Sci.*, 1977, **6**, 24; K. K. Sengupta and S. Sengupta, *Z. Phys. Chem. (Frankfurt am Main)*, 1965, **45**, 378.

16 M. Latshaw, *J. Am. Chem. Soc.*, 1925, **47**, 793.

17 A. S. Bailey, M. Moung, G. W. F. Orpwood, and J. E. White, *Tetrahedron*, 1966, **22**, 995.

18 W. A. Schroeder, P. E. Wilcox, K. N. Trueblood, and A. O. Dekker, *Anal. Chem.*, 1951, **23**, 1740.

19 I. M. Heilbron, 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1953, p. 365.

20 I. M. Heilbron, 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1953, p. 280.

21 H. H. Stroh and G. Westphal, *Chem. Ber.*, 1963, **96**, 184.

22 P. J. Brignell, C. D. Johnson, A. R. Katritzky, N. Shakir, H. O. Tarhan, and J. Walker, *J. Chem. Soc. B*, 1967, 1233.

23 J. Jordan and G. J. Erving, *Inorg. Chem.*, 1962, **1**, 587.

24 E. Coates, C. G. Marsdon, and B. Rigg, *Trans. Faraday Soc.*, 1969, **65**, 3032.

25 A. A. Schilt, *J. Am. Chem. Soc.*, 1960, **82**, 3000.

26 H. K. Saha and B. C. Saha, *J. Indian Chem. Soc.*, 1978, **55**, 101.

27 M. S. Frank and P. V. Krishna Rao, *Indian J. Chem., Sect. A*, 1980, **19**, 476.

Received 3rd May 1983; Paper 3/701