basis of hydrolysis of lost diborane.[6] Practically no loss of diborane was noted when a sample of gas was bubbled through concentrated and 100% sulfuric acids. Surprisingly, there was no appreciable increase in yield of diborane when the 100% sulfuric acid was used in the acid–borohydride reaction. The decrease in the amount of sulfur dioxide with decreasing concentration of acid may be due merely to increased solubility of the SO_2.

The experiment in which methanesulfonic acid replaced sulfuric acid was characterized by the complete absence of sulfur dioxide. The lower yield (76% B_2H_6) may have been due to the presence of moisture in the highly hygroscopic acid; however, only 91% of the diborane could be accounted for from hydrogen measurements calculated on the basis of hydrolysis of missing diborane.

When the reactions were carried out at one atmosphere pressure (nitrogen, hydrogen or helium atmospheres), the sodium borohydride burned as it was added to the sulfuric acid solution. This flaming caused a deposit of sulfur in the reactor, gave lowered yields of diborane and a product contaminated with hydrogen sulfide. A series of experiments, in which rate of addition of borohydride was varied, showed that the flaming increased with increased rate of addition. When a sulfur dioxide atmosphere was used, more intense flaming occurred. That diborane itself was not necessarily involved was shown by the fact that sodium hydride also gave flaming under these conditions. It was possible to avoid flaming, and thus to prepare diborane in good yields at atmospheric pressure, by cooling the acid and stirring vigorously while adding the sodium borohydride very slowly.

PASADENA, CALIFORNIA

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(6) H. G. Weiss and I. Shapiro, THIS JOURNAL, **75**, 1221 (1953).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Mechanism of Oxidation of Hydrazine by Ferric Ethylenediaminetetraacetate (FeY^-)[1,2]

BY H. MINATO, E. J. MEEHAN, I. M. KOLTHOFF AND C. AUERBACH

RECEIVED MAY 15, 1959

The stoichiometry and kinetics of the reaction between ferric ethylenediaminetetraacetate (FeY^-) and hydrazine in borax and phosphate buffers in the absence and presence of phenanthroline have been investigated. The oxidation product is mainly nitrogen; very small amounts of ammonia are formed, consistent with the reaction ratio, which is between 3.7 and 4.0 moles of FeY^- consumed per mole of hydrazine consumed. From the kinetic results it is established that the first step is reaction 1 of FeY^- and free base (not $N_2H_5^+$), $FeY^- + N_2H_4 \rightarrow FeY^{--} + N_2H_3\cdot + H^+$ (1). This reaction is reversible, and the $N_2H_3\cdot$ may reoxidize FeY^{--}, $FeY^{--} + N_2H_3\cdot + H^+ \rightarrow FeY^- + N_2H_4$ (−1) or be oxidized by FeY^-, $FeY^- + N_2H_3\cdot \rightarrow FeY^{--} + N_2H_2\cdot + H^+$ (2). The latter reaction leads eventually to the formation of nitrogen after two further oxidations of $N_2H_2\cdot$. Also, the $N_2H_3\cdot$ may dimerize, leading eventually to the formation of ammonia and nitrogen. By the addition of sufficient phenanthroline to form rapidly the stable complex with iron(II), the reaction (−1) may be practically eliminated, and the over-all reaction becomes first order both to FeY^- and hydrazine. The rate constant is thus found to be k_1 = 11 liter mole^{-1} min.$^{-1}$ at 40° and the activation energy 20 kcal. mole. When no phenanthroline is present, the occurrence of the back reaction leads to a rate which is approximately second order in FeY^-, first order in hydrazine, and inversely first order in FeY^{--}. The ratio of the rate constants k_{-1}/k_2 is found to be approximately 140 at *p*H 9 and 42 at *p*H 6.7, at 40°. The occurrence of the back reaction also is confirmed qualitatively by the pronounced acceleration of reaction rate caused by the EDTA complex of copper(II).

Introduction

This investigation originated in the discovery that the combination ferric ethylenediaminetetraacetate–hydrazine–organic hydroperoxide could be used for the initiation of emulsion polymerization of butadiene or styrene in alkaline medium at temperatures around 0°.[3] In this paper the complexes of Fe(III) and Fe(II) with ethylenediaminetetraacetate (EDTA) are denoted as FeY^- and FeY^{--}, respectively. Qualitatively it appeared that hydrazine reduced FeY^- to FeY^{--}, and that the latter substance was oxidized by hydroperoxide to re-form FeY^- and a free radical derived from the hydroperoxide. In order to arrive at an understanding of the kinetics and mechanism of this recipe, it was necessary to investigate the kinetics and mechanism of the reaction between FeY^- and hydrazine in the absence and presence of hydroperoxide. Results in the absence of hydroperoxide are presented in this paper.

Preliminary work on oxidation of hydrazine by FeY^- in borax and phosphate buffers was carried out in this Laboratory by Dr. C. Auerbach and Dr. P. K. Kapur in 1951–1952.[4] In general their results tended to support the view that the primary step was a bimolecular reaction leading to formation of $N_2H_3\cdot$. However, the unexpected result was found that the reaction, which was initially relatively rapid, came to a virtual standstill before completion. This was thought to be due to a back reaction between FeY^{--} and the hydrazyl radical. If so, the addition of phenanthroline, which forms a much more stable complex with iron(II) than does EDTA, would be expected to prevent or minimize the back reaction. It was found in fact that the addition of phenanthroline prevented the pronounced decrease in rate, so that the reaction proceeded to completion and was approximately first order in ferric Versenate. However, the order with respect to hydrazine

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(1) This investigation was carried out under a grant from the National Science Foundation.

(2) From the M.S. thesis of H. Minato, July 1958. For brevity many pertinent data given in the thesis are omitted from this paper.

(3) I. M. Kolthoff and E. J. Meehan, *J. Polymer Sci.*, **9**, 343 (1952).

(4) Reports to Office of Rubber Reserve.

TABLE I

STOICHIOMETRY AT 40°

All reaction mixtures 0.30 *M* in sodium sulfate; (Ph = phenanthroline)

Expt.	1	2	3	4	5	6[a]	7	8	9
FeY^-, *M*	0.05	0.075	0.0110	0.0100	0.0100	0.0100	0.0100	0.0100	0.0500
N_2H_4, *M*	0.004	0.004	0.0520	0.0025	0.0025	0.0025	0.0025	0.0025	0.004
Ph, *M*	0	0	0	0	0.03	0	0	0.03	0
Buffer[b]	B	B	B	B	B	B	P	P	P
*p*H (25°)	8.88		8.96	8.90	9.03	9.0	6.65		6.60
Reaction time (days)	3	3	3	3	3	2	10	10	10
FeY^{--} formed	0.0158	0.00637	0.01067[e]	0.00702	0.00935		0.00691	0.00956	
N_2H_4 left	0.0000	0.00228	0.0491	0.00065	(0)		0.00077	(0)	
NH_3 form.	1.52×10^{-4}	7.0×10^{-5}	3.93×10^{-4}	4.6×10^{-5}	6.6×10^{-5}	1.43×10^{-5}	0	1.4×10^{-5}	0
R[c]	3.95	3.70	3.67	3.79	3.74		3.99	3.82	
F[d]	0.038	0.041	0.136	0.025	0.038	0.057	0.000	0.006	0.00

[a] 0.0118 *M* cumene hydroperoxide. [b] B = 0.05 *M* borax; P = 0.05 *M* KH_2PO_4, 0.03 *M* NaOH. [c] *R* = moles FeY^- consumed/mole N_2H_4 consumed. [d] *F* = moles NH_3 formed/mole N_2H_4 consumed. [e] (FeY^-) remaining = 000035 *M* (polarographic).

appeared anomalous. The order appeared to be between one and one-half, depending upon the *p*H and the relative concentration of hydrazine and FeY^-.

Work before 1951 concerning mechanism and products of oxidation of hydrazine by a variety of oxidants has been summarized by Audrieth.[5] Based upon a survey of all work up to 1928, Kirk and Browne had proposed a comprehensive reaction mechanism.[6] In their mechanism the primary step in oxidation by a one-electron oxidant such as iron(III) is the formation of the hydrazyl radical, $N_2H_3\cdot$.

Recently work on kinetics of oxidation of hydrazine in acid medium has been reported by Powell,[7] Higginson,[8] and Rosseinsky.[9] This and other relevant work has been reviewed critically by Higginson.[10] The mechanisms of oxidation by iron(III) proposed by Powell and by Higginson are

$$\mathrm{Fe(III)} + N_2H_4 \longrightarrow \mathrm{Fe(II)} + N_2H_3\cdot + H^+ \qquad (1)$$

$$\mathrm{Fe(II)} + N_2H_3\cdot + H^+ \longrightarrow \mathrm{Fe(III)} + N_2H_4 \qquad (-1)^a$$

$$\mathrm{Fe(III)} + N_2H_3\cdot \longrightarrow \mathrm{Fe(II)} + N_2H_2 + H^+ \qquad (2)$$

followed by two rapid one-electron oxidations

$$2\mathrm{Fe(III)} + N_2H_2 \longrightarrow N_2 + 2\mathrm{Fe(II)} + 2H^+$$

$$2N_2H_3\cdot \longrightarrow N_4H_6 \qquad (3)$$

and then the fast reaction

$$N_4H_6 \longrightarrow 2NH_3 + N_2$$

$$2N_2H_3\cdot \longrightarrow N_2H_4 + N_2H_2 \qquad (4)^b$$

[a] Only in Higginson mechanism; [b] only in Powell mechanism.

The work described in this paper includes kinetic measurements at various concentrations of reactants and of FeY^{--}, in the absence and presence of phenanthroline, and determination of the stoichiometry. All the observations can be accounted for only if the back reaction (−1) is included in the mechanism. The anomalous reaction orders observed by Auerbach and Kapur[4] are explained by the fact that the reaction between FeY^{--} and phenanthroline is not instantaneous.

Experimental

Conductivity water was used in preparing solutions. These were deaerated when necessary with Linde high purity nitrogen. Disodium dihydrogen ethylene-diaminetetraacetate dihydrate ("Versene"), reagent grade, was obtained from Hach Chemical Co. 1,10-Phenanthroline monohydrate, reagent grade, was obtained from G. F. Smith Chemical Co. Hydrazine sulfate, reagent grade, was an Eastman product; solutions were prepared daily and adjusted to the desired *p*H by addition of sodium hydroxide. Other chemicals were analytical or reagent grade.

Experiments were carried out in borax and in phosphate buffers at temperatures from 0 to 40°. Sodium sulfate was added to bring the ionic strength to about unity except in a few experiments in which relatively large amounts of phenanthroline were present. The specified concentration of sodium sulfate includes that added with the hydrazine sulfate.

For the determination of stoichiometry the amounts of ferric iron and hydrazine consumed and of ammonia formed were determined. Calculated amounts of solution of FeY^-, buffer and sodium sulfate were put in a rubber-stoppered vessel and the mixture was deaerated. Deaerated hydrazine solution was added from a calibrated syringe. The compositions of the resulting solutions are in Table I. In all experiments the total volume was 80 ml. The reaction mixture was kept at 40° for 2–3 days (*p*H 9) or for 10 days (*p*H 6.7). Twelve and a half ml. of 8 *M* sulfuric acid was injected and the mixture was shaken for 30 sec. and then diluted to 100 ml. in a volumetric flask. Ten ml. of solution was mixed with 10 ml. of 8 *M* sulfuric acid and iron (II) was titrated with 0.01147 *N* ceric sulfate using two drops of 0.2% barium diphenylaminesulfonate as indicator. To this solution at the end-point was added 0.5 g. of potassium bromide and the remaining hydrazine was titrated amperometrically with 0.01033 *N* potassium bromate at +0.40 v. *vs.* SCE, using the rotating platinum wire electrode as indicator electrode. In a few instances residual FeY^- was determined polarographically (*vide infra*). Ammonia was determined in a separate 10-ml. portion of the reaction mixture to which were added 10 ml. of 6 *N* sulfuric acid and 0.5 g. of potassium bromide. Residual hydrazine was titrated as described above. When the cathodic current of bromine was observed, the titration was stopped and the solution was gradually heated to boiling to expel bromine. After cooling, the solution was put in a Kjeldahl flask and 30 ml. of 50% sodium hydroxide was added. Steam distillation was carried out for 30 min., the liberated ammonia being absorbed in 25 ml. of 1 *N* sulfuric acid. This solution was neutralized with sodium hydroxide, diluted to 60 ml., and made 0.2 *M* in sodium bicarbonate. Ammonia was titrated amperometrically with 0.0256 *M* sodium hypobromite at +0.20 v. *vs.* SCE using a rotating platinum wire electrode.[11]

For reaction rate studies, suitable amounts of FeY^-, sodium sulfate, buffer and phenanthroline if used were put in a polarographic cell at the desired temperature (thermostat) and the solution was deaerated. A deaerated hydrazine solution of the same *p*H and temperature was added while nitrogen bubbling was continued and the cell was shaken vigorously for 30 sec. The change in concentration of FeY^- was followed polarographically. In the absence of

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(5) L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951.

(6) R. E. Kirk and A. W. Browne, THIS JOURNAL, **50**, 337 (1928).

(7) J. W. Cahn and R. E. Powell, *ibid.*, **76**, 2568 (1954).

(8) W. C. E. Higginson and P. Wright, *J. Chem. Soc.*, 1551 (1955).

(9) D. R. Rosseinsky, *ibid.*, 4685 (1957).

(10) W. C. E. Higginson, Special Pub. of Chem. Soc., No. 10, 1957, p. 95.

(11) I. M. Kolthoff, W. Stricks and L. Morren, *Analyst*, **78**, 405 (1953).

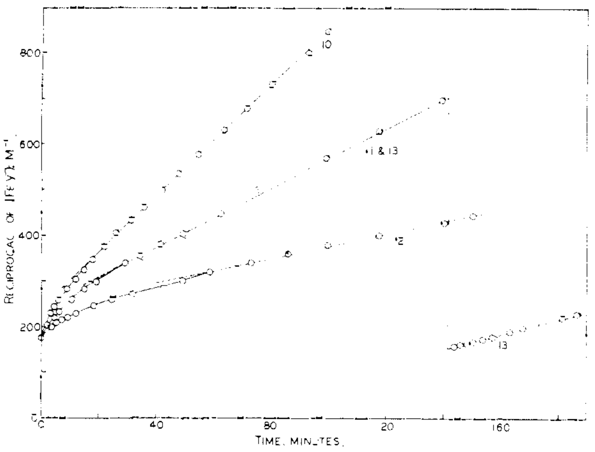

Fig. 1.—Hydrazine varied; phenanthroline absent; borax buffer, 40° (Table II).

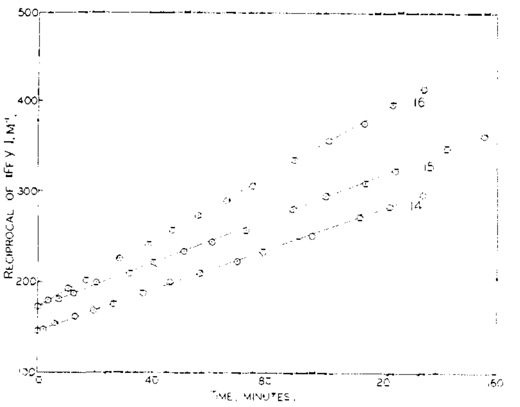

Fig. 2.—Hydrazine varied; FeY^{--} present initially; phenanthroline absent; borax buffer, 40° (Table II).

phenanthroline the cathodic diffusion current was measured at −0.9 v. *vs.* SCE using a Leeds and Northrup Electrochemograph Model E. Residual current was corrected for. The sensitivity corresponded to *ca.* 30 μa. for the diffusion current of 0.01 M FeY^-. In the presence of phenanthroline at *p*H 9 a well-defined diffusion current region near −1.0 v. *vs.* SCE was measured: sensitivity *ca.* 24 μa. for 0.01 M FeY^-. At *p*H 7 in the presence of phenanthroline irregular maxima were observed, but upon addition of 0.002% sodium *n*-dodecylamine sulfonate a diffusion current region was obtained near −0.3 v. *vs.* SCE. This current, corrected for residual current, was found proportional to the concentration of FeY^-. The electrode sensitivity was about the same as at *p*H 9. The polarographic method was applicable also in the presence of the EDTA complex with Cu(II), CuY^{--}, the diffusion current corresponding to the sum of CuY^{--} and FeY^-. Separate experiments showed that no appreciable reaction between CuY^{--} and hydrazine occurred in borax buffer in several hours. Since FeY^- rapidly oxidizes CuY^{---}, the assumption is justified that the current due to copper remains constant during the experiment and the contribution by the copper (II) may be subtracted from the observed current to yield that due to FeY^-.

Results

A. Stoichiometry.—Results are in Table I. At *p*H 9 the reaction R (moles FeY^- consumed per mole hydrazine consumed) is a little less than 4; at *p*H 6.7 R is practically 4. Only a small fraction of the hydrazine is converted to ammonia at either *p*H. If the only products of reaction are nitrogen and ammonia, R should be equal to $4 - 3f$, where f is the number of moles of ammonia formed per mole of hydrazine consumed. This relation is obeyed within experimental error. The presence of phenanthroline has only a slight effect on R at *p*H 9 (expts. 4, 5) and a somewhat larger effect on R at *p*H 6.7 (expts. 7, 8). At *p*H 6.7 no ammonia is formed in the absence of phenanthroline and R becomes equal to the value 4.00, when no side reactions occur. Addition of phenanthroline causes the value of R to become slightly less than 4, while a little ammonia is formed.

B. Rate of Reaction in Absence of Phenanthroline.—Rate measurements were made in mixtures of the compositions given in Table II. In all these experiments (except 21) the concentration of hydrazine was practically constant during reaction. Figure 1 (expts. 10–12) shows that the reaction is initially rapid, slows down markedly and becomes second order in FeY^-. The pseudo second-order rate constants K_2' derived from the slopes of the linear parts of the curves are given in Table II. The relative values of K_2' show that the reaction is first order in hydrazine. When FeY^{--} is present initially the reaction is second order in FeY^- during the entire reaction period (Fig. 2).

Table II

Rate Experiments, Absence of Phenanthroline, 40°

All reaction mixtures 0.30 M in sodium sulfate.

Expt.	Initial concn., M FeY^-	N_2H_4	FeY^{--}	*p*H[a] (25°)	K_2'[b]
10	0.0055	0.10	0	9.00	6.14
11	.0055	.05	0	8.95	3.26
12	.0055	.02	0	8.90	1.343
13[c]	.0055[c]	.05	0	8.90	1.713
14	.0068	.05	0.0107	8.85	1.122
15	.00553	.05	0.00947	8.83	1.226
16	.00566	.05	0.00434	8.90	1.835
17	.005	.05	0	8.95	4.11
18	.01	.05	0	8.86	1.87
19	.015	.05	0	8.85	1.12
20[d]	.005	.05	0	8.89	..
21[d]	.00576	.001	0.00243	8.82	..
22	.005	.05	0	6.52	0.683
23	.005	.2	0	6.70	2.71

[a] For buffer composition see Table I, footnote *b*. [b] Liter mole⁻¹ min.⁻¹; slope of linear portion, Fig. 1-2. [c] Continuation of expt. 11; at 142 min., more FeY^- was added so that FeY^- was 0.00694 M, FeY^{--} was 0.00396 M. [d] 0.001 M in CuY^{--}.

Qualitatively similar results are found in the phosphate buffer. The initially rapid reaction slows down and becomes second order in FeY^- and first order in hydrazine. At comparable reactant concentration (0.005 M FeY^-, 0.1 M hydrazine) the values of K_2' are 6.14 at *p*H 9 and 1.36 at *p*H 6.6, the ratio being *ca.* 4.5.

From the results of experiments 17 and 20, a pronounced acceleration due to CuY^{--} was established. In experiment 17 the FeY^- concentration decreased from 0.005 M to 0.0027 M in 20 minutes, while in the presence of 0.005 M CuY^{--} it decreased to 0.0016 M. However, no simple rate law was found to be obeyed.

C. Rate of Reaction in the Presence of Phenanthroline.—Preliminary experiments were carried out in borax buffer using 0.001 M FeY^-, 0.05 to 0.2 M hydrazine and 0.0056 M phenanthroline. No

TABLE III

RATE EXPERIMENTS, PRESENCE OF PHENANTHROLINE

Concentration of sodium sulfate 0.30 *M* except in expts. 35–37, 45–47.

Expt.	Initial concn., *M*			Ethanol, %	Methanol, %	Buffer[a]	*p*H (25°)	K_1'[b]
	FeY^-	N_2H_4	Ph					
			1. Experiments at 25°					
24[c]	0.0011	0.05	0.0056	2.2	0	P	6.79	0.0176
25[c]	.0011	.05	.0120	4.7	0	P	6.72	.0109
26[c]	.0011	.05	.0240	10.8	0	P	6.80	.0198
27[c]	.0011	.10	.0056	2.2	0	P	6.86	.0426
28[c]	.0011	.025	.0056	2.2	0	P	6.71	.0107
29	.0011	.05	.0056	2.2	0	B	9.12	...
30	.0011	.05	.012	4.7	0	B	9.14	...
31	.0011	.05	.028	10.8	0	B	9.20	.184
32	.0011	.05	.0056	10.8	0	B	9.38	...
33	.0011	.025	.028	10.8	0	B	..	.126
34	.0011	.0125	.028	10.8	0	B	..	.080
35[d]	.0011	.025	.0056	0	50	B	9.40	...
36[d]	.0011	.025	.1	0	50	B	9.40	.165
37[d]	.0011	.0125	.1	0	50	B	9.40	.097
38	.00102	.0093	.024	9.3	0	B	9.37	.0631
39	.0011	.0050	.024	9.3	0	B	9.38	.0377
40	.0011	.00375	.024	9.3	0	B	9.37	.0297
41	.0011	.0025	.024	9.3	0	B	9.37	.0216
			2. Experiments at 40°					
42[c]	0.001	0.01	0.0056	2.2	0	P	6.58	0.0195
43[c]	.001	.02	.0056	2.2	0	P	6.47	.0322
44	.000976	.00244	.0234	9.1	0	B	9.18	.102
			3. Experiments at 0°					
45[e]	0.0011	0.04	0.024	9.3	0	B	..	0.0115
46[e]	.0011	.02	.024	9.3	0	B		.00591
47[e]	.0011	.01	.024	9.3	0	B	9.39	.00344

[a] See Table I, footnote *b*. [b] Pseudo first-order rate constant, min.$^{-1}$. [c] 0.002% sodium *n*-dodecylamine sulfonate. [d] 0.025 *M* sodium sulfate. [e] 0.04 *M* sodium sulfate.

simple kinetic law was found to represent the reaction rate, which was between first and second order in FeY^-. It appeared desirable to use higher concentrations of phenanthroline. By adding a stock solution in water–ethanol, a concentration of 0.0280 *M* could be reached in the reaction mixture; such solutions were slightly supersaturated and some phenanthroline crystallized during the reaction. Alternatively, experiments were run in 50% methanol, which permitted the use of 0.1 *M* phenanthroline.

Rate measurements were made in mixtures having the compositions given in Table III. Results in phosphate buffers at 25° are given in Fig. 3. The three experiments (24–26) at the same reactant concentrations and varied concentrations of phenanthroline gave practically the same rate. (There is a minor effect due to ethanol v.i.) All the reactions were first order in FeY^-. The pseudo first-order rate constants K_1' ($K_1' = d \ln (FeY^-)/dt$) derived from Fig. 3 are given in Table III. Comparison of K_1' for experiments 24, 27, 28 shows that the reaction was first order in hydrazine.

The kinetic results and especially the fact that the rate of reaction is independent of phenanthroline concentration above 0.0056 *M* prove that the back reaction (−1) is eliminated completely by phenanthroline in the phosphate buffer. The results in borax were not so straightforward. Figure 4 gives experiments at varied concentrations of phenanthroline (and ethanol). Comparison of 31 and 32 shows the slight reduction of rate due to ethanol. At the higher concentrations of phenanthroline the reaction was much faster than in the absence of phenanthroline, and the rate became approximately first order in FeY^-. However, the rate increased with increasing concentration of phenanthroline, which shows directly that the back reaction (−1) was not completely sup-

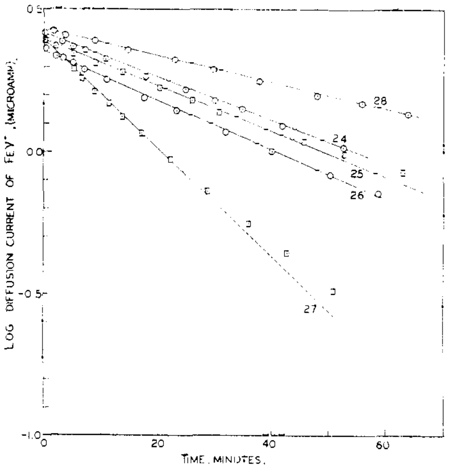

Fig. 3.—Hydrazine and phenanthroline varied; phosphate buffer, 25° (Table III).

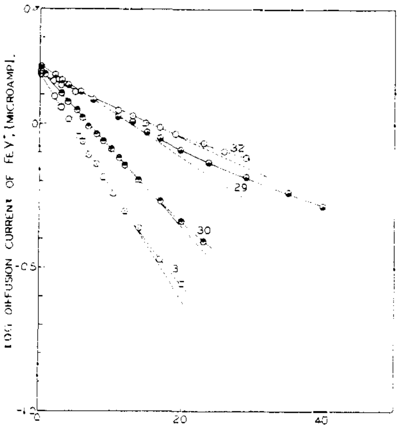

Fig. 4.—Phenanthroline varied; borax buffer, 25° (Table III).

pressed. The values of K_1' (expts. 31, 33, 34) correspond to an apparent order in hydrazine of 0.6. In 0.1 M phenanthroline, 50% methanol (expt. 36, 37) the order in hydrazine became 0.8, indicating a closer approach to suppression of reaction (−1).

Relatively slower reactions at lower concentrations of hydrazine (expts. 38–41, Fig. 5) gave orders in FeY^- and hydrazine of 1.0 and 0.82, respectively.

Finally, at 40°, phosphate buffer, 0.0056 M phenanthroline, the order in hydrazine was 0.9. The same order was found at 0° in borax buffer at 0.024 M phenanthroline. In both cases the order in FeY^- was unity.

Discussion

The mechanism given in the Introduction (reactions 1, −1, 2, 3, 4, plus the fast reactions) leads to expression 1 for the rate of reaction of FeY^- at constant $[H^+]$

$$-\frac{d(FeY^-)}{dt} = k_1(FeY^-)(N_2H_4) + 3k_2(FeY^-)(N_2H_3\cdot) - k_{-1}(FeY^{--})(N_2H_3\cdot) \quad (1)$$

An exact expression for the steady-state concentration of $N_2H_3\cdot$ based on the assumed mechanism would be very complex. However, the reaction ratio (*cf.* Table I) under all experimental conditions is nearly 4, which shows directly that reactions 3 and 4 must be of minor importance compared to (−1) and (2). Neglecting (3) and (4), a simple expression is found

$$(N_2H_3\cdot) = \frac{k_1(FeY^-)(N_2H_4)}{k_2(FeY^-) + k_{-1}(FeY^{--})} \quad (2)$$

which yields

$$-\frac{d(FeY^-)}{dt} = \frac{4k_1k_2(FeY^-)^2(N_2H_4)}{k_2(FeY^-) + k_{-1}(FeY^{--})} \quad (3)$$

Under conditions such that $k_{-1}(FeY^{--}) \gg k_2(FeY^-)$, this reduces to

$$-\frac{d(FeY^-)}{dt} = \frac{4k_1k_2(FeY^-)^2(N_2H_4)}{k_{-1}(FeY^{--})} \quad (4)$$

Thus when sufficient FeY^{--} is present, its concentration remains practically constant and the reaction should become second order to FeY^- and first order to hydrazine. Indeed this relation has been observed experimentally (Table II).

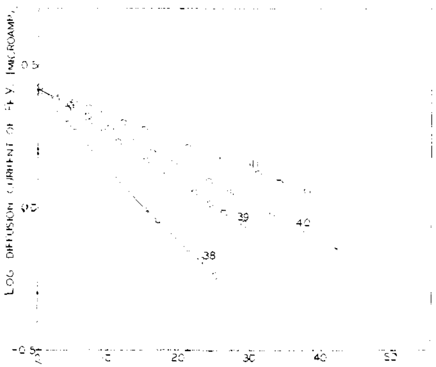

Fig. 5.—Low concentrations of reactants; phenanthroline present; borax buffer, 25° (Table III).

In the presence of phenanthroline sufficient to suppress completely reaction (−1), the rate of reaction becomes

$$-\frac{d(FeY^-)}{dt} = 4k_1(FeY^-)(N_2H_4) \quad (5)$$

Experimentally this relation was found true in phosphate buffer (*p*H 6.6) with 0.0056 M phenanthroline. Complete suppression of reaction −1 can be achieved only when the rate of the reaction

$$FeY^{--} + 3Ph + H^+ = FePh_3^{++} + HY^-$$

is much greater than that of reaction −1. Apparently this situation does not exist in the borax buffer. However, at the highest concentration of phenanthroline or at the lowest concentration of hydrazine, an approximation to eq. 5 was reached in that the order both to ferric Versenate and hydrazine approached unity.

Calculation of Rate Constants.—When reaction (−1) is suppressed, the bimolecular rate constant k_1 can be calculated from the values of K_1' (Table III) by means of equation 6; the results are in Table IV. This relation holds exactly in phosphate buffer

$$k_1 = \frac{K_1'}{4(N_2H_4)} \quad (6)$$

and only approximately in borax buffer. In the latter case experiments have been chosen in which the closest approach to suppression may be expected. The value of (N_2H_4) appearing in eq. 6 is that of the free base. The value of pK_B for hydrazine is 6.01 at 25° and zero ionic strength.[12] From the data[12] it is estimated that the values of pK_B at 0 and 40° are about 6.3 and 5.8, respectively. No data appear to be available at the ionic strengths and alcohol contents used in the present work. All the *p*H values given in Table III were measured at 25°. Based on these considerations the value $pK_B = 6.0$ has been used to estimate approximate percentages of hydrazine present as free base in the various experiments. The calculated percentages in borax buffer are relatively insensitive to the exact value of pK_B; those in phosphate buffer are very sensitive to pK_B.

(12) G. C. Ware, J. B. Spulnik and E. C. Gilbert, This Journal, **58**, 1605 (1936).

TABLE IV

EVALUATION OF k_1

Temp., °C.	Buffer[a]	Expt.	$C_{N_2H_4}$[b]	(N_2H_4)[c]	Alcohol, %	k_1[a]
25	P	27	0.1	0.00676	Ethanol, 2.2	1.6
25	P	28	.025	.00122	Ethanol, 2.2	2.2
25	P	26	.05	.00297	Ethanol, 10.8	1.7
25	B	41	.0025	.00240	Ethanol, 9.3	2.3
25	B	37	.0125	.00120	Methanol, 50	2.0
40	P	42	.01	.000366	Ethanol, 2.2	13
40	B	44	.00244	.00229	Ethanol, 9.1	11
0	B	47	.01	.00961	Ethanol, 9.3	0.0090

[a] See Table I, footnote *b*, [b] Total concentration, molar. [c] Present as free base, based upon $pK_B = 6.0$. [d] Liter/mole^{-1} min.$^{-1}$.

The calculated values of k_1 (in Table IV) are independent of *p*H, proving that reaction 1 involves the free base. From the values obtained in expts. 41, 44, 47 the activation energy of reaction 1 (in borax, 9.3% methanol) is found to be 20 kcal.-mole^{-1}.

Equation 3 upon integration yields an explicit expression for (FeY^-) as a function of time, k_1, the ratio k_{-1}/k_2, and (FeY^{--}). Unfortunately the magnitudes of the quantities involved are such that it is impractical to evaluate both k_1 and k_{-1}/k_2, or k_1 alone, from experiments in which reaction (−1) is occurring. However, an approximate estimate of k_{-1}/k_2 can be obtained from the values of K_2' (Table II). From eq. (4) it is found that

$$\frac{k_{-1}}{k_2} = \frac{4k_1(N_2H_4)}{K_2'(FeY^{--})} \tag{7}$$

The values are in Table V. In the calculation, the value of (FeY^{--}) was chosen as that at about the middle of the linear part of the curve of $(FeY^-)^{-1}$ *vs.* time.

TABLE V

CALCULATION OF k_{-1}/k_2 (40°)

Expt.[a]	K_2'[a]	N_2H_4[b]	FeY^{--}[c]	k_{-1}/k_2[d]
		Borax buffer		
10	6.14	0.0908	0.0030	219
11	3.26	.0449	.0034	180
12	1.343	.0178	.0035	168
13	1.713	.0444	.0055	209
14	1.122	.0438	.0132	132
15	1.226	.0436	.0112	141
16	1.835	.0444	.0068	157
17	4.11	.0449	.0035	138
18	1.87	.0439	.0068	153
19	1.12	.0438	.0096	181
		Phosphate buffer		
22	0.683	0.00160	0.0029	36
23	2.71	0.0100	0.0035	47

[a] See Table II. [b] Present as free base, calculated using $pK_B = 6.0$. [c] Value used in eq. 7, molar. [d] Based upon k_1 = 11 l./mole^{-1} sec.$^{-1}$.

The average of the ten values of k_{-1}/k_2 from experiments in borax buffer is 170 ± 24. The three experiments in which FeY^{--} was present initially (14–16) give an average of 140 ± 9, which is considered more reliable than the average of the ten. Two experiments in phosphate buffer yield $k_{-1}/k_2 = 42 \pm 6$. The difference in the ratio at the two *p*H's is due either to a relatively faster oxidation of FeY^{--} by $N_2H_3\cdot$ at *p*H 9 than at *p*H 7, or to a relatively faster reduction of FeY^- by $N_2H_3\cdot$ at *p*H 7 than at *p*H 9. There appears to be no way of deciding between the two alternatives. In any event, it appears that the relative importance of back reaction (−1) decreases with decreasing *p*H.

The pronounced acceleration by CuY^{--} corroborates the significance of the occurrence of the back reaction. Since the reaction between CuY^{--} and hydrazine is extremely slow, the acceleration is accounted for by the reactions

$$Cu(II) + N_2H_3\cdot \longrightarrow Cu(I) + N_2H_2 + H^+$$

$$Cu(I) + FeY^- \xrightarrow{\text{fast}} Cu(II) + FeY^{--}$$

in which the oxidation states of copper but not the composition are written. Thus the steady-state concentration of $N_2H_3\cdot$ is reduced by the addition of CuY^{--}, decreasing the importance of reaction (−1). If the back reaction did not occur, the addition of copper(II) could have little effect on the over-all rate of reaction, as pointed out by Higginson.[10]

It seems reasonable to infer from the measurable speed of the forward and backward reactions (1, −1) that the reduction potential of the system

$$N_2H_3\cdot + H^+ + e \rightleftarrows N_2H_4$$

is of the same order of magnitude as that of the system

$$FeY^- + e \rightleftarrows FeY^{--}$$

which is approximately 0.0 volt *vs.* NHE.

In connection with the study described in the present paper, it is of interest to consider briefly the reaction between ferricyanide and hydrazine. The kinetics of this reaction has been studied by Gilbert[13] at *p*H 6.0–6.5 at 20° and has been found first order in both reactants. Gilbert claims that the reaction is instantaneous in alkaline medium, but we found it possible to determine the order of the reaction at 0° at *p*H 9, using 0.001 *M* ferricyanide and 0.005–0.015 *M* hydrazine. The change with time of the diffusion current of ferricyanide was recorded at 0.0 volt *vs.* SCE, and the order was found to be unity in both reactants.

The puzzling fact that the reaction between ferricyanide and hydrazine is simply first order in both reactants at *p*H 6–9 may be accounted for by the plausible assumption that reaction 1 (writing ferricyanide instead of FeY^-) is practically irreversible, because ferricyanide can hardly reduce $N_2H_3\cdot$ to N_2H_4. Also, the rate of oxidation of $N_2H_3\cdot$ by ferricyanide (analogous to reaction 2) is very great. Thus the concentration of $N_2H_3\cdot$ is so small that no ammonia can be formed.

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(13) E. C. Gilbert, *Z. physik. Chem.*, **142A**, 139 (1929).