acetic acid) in 150 ml. of benzene. After the mixture had stood overnight at room temperature it was heated at 100° for an hour and then hydrolyzed in the usual way. The benzene layer was distilled to yield 18 g. (51%) of solid boiling at 130–140° (2 mm.). Crystallization from petroleum ether (b.p. 35–45°) gave colorless crystals of m.p. 58–59°; this was unchanged by mixture with authentic δ-phenylvaleric acid.

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RECEIVED OCTOBER 26, 1951

Exchange between the Tris-(5,6-dimethyl-1,10-phenanthroline) Complexes of Iron(II) and -(III)[1]

BY LOIS EIMER AND A. I. MEDALIA

Exchange reactions which proceed *via* transfer of an electron are of interest as a simple, symmetrical class of oxidation–reduction reactions. Uncertainties as to the states of complexing, which arise in studying simple ions, may be avoided by studying complexes of known structure, such as the phenanthroline complexes of iron(II) and -(III).

In undertaking such a study, an experimental survey was first made of seven commercially available phenanthrolines and analogs. It was established[2] that the most suitable compound for such a study, from the standpoint of the stability of both the ferrous and ferric forms in aqueous acid, is 5,6-dimethyl-1,10-phenanthroline, with which therefore all further work was conducted.

Experimental.—The 5,6-dimethyl-1,10-phenanthroline was used as obtained from the G. F. Smith Chemical Co. The red ferrous complex (designated as ferroin-5,6) was prepared by complexing of ferrous iron with 5–10% excess of the phenanthroline at *p*H 8.5–9.0; the blue ferric complex (ferriin-5,6), by oxidation of ferroin-5,6 with lead dioxide in 1 *N* sulfuric acid, followed by filtration through sintered glass to remove PbO_2 and $PbSO_4$. These compounds have been prepared with inactive iron; and with samples of radioactive iron of both low and high activity (Fe^{55}), which were obtained from Oak Ridge and then purified by extraction, fumed with sulfuric acid, and reduced with sulfur dioxide under the conditions suggested by Marti and Conde.[3] All water used was purified in a continuous quadruple Pyrex still.

Two methods of separation have been developed: (1) The ferroin-5,6 is precipitated as the perchlorate in 50% perchloric acid and is collected on a glass frit, the ferriin-5,6 remaining in solution. The precipitate is counted on the frit after drying 48 hours in a vacuum desiccator. (2) The ferroin-5,6 is extracted with a solution of camphorsulfonic acid (0.013 *f*) in chloroform, the ferriin-5,6 remaining in the aqueous phase.

The extraction method can be used at lower concentrations than the precipitation method; however, a lower limit is set by the reduction of ferriin-5,6 by impurities in the chloroform. Of several methods which were investigated for purification of the chloroform, the following gave the best results: analytical reagent grade chloroform was washed at 0° with several portions each of water, concentrated sulfuric acid, 0.1 *f* sodium bicarbonate, and water, in succession; then dried with potassium carbonate, and distilled over calcium hydride in a nitrogen atmosphere. The product was collected in a chilled receiver and stored under nitrogen at 5°. Ethylene dichloride showed some promise as an alternative solvent but its use was not fully investigated.

Ferriin-5,6 remaining in the aqueous phase after extraction has been reduced by passage of sulfur dioxide for 30 seconds; after addition of carrier (inactive ferroin-5,6, 5 × 10^{-4} *f*) the ferroin-5,6 was precipitated by addition of Na_2CdI_4 (0.02 *f*) at 0° and filtered through S&S #756 paper placed on a glass frit. The paper was dried at 110°, mounted and placed under an end-window G-M tube filled with 71.5 cm. of argon and 2.5 cm. of ethyl acetate, for counting.

Several methods have been investigated[2] for recovery of active iron from the chloroform extracts of ferroin-5,6. Satisfactory results were obtained by a procedure involving the following steps: evaporation of the extract in a silica dish, ignition at 500°, solution in boiling 0.6 *f* HCl, reduction with hydroxylamine hydrochloride, and re-formation of ferroin-5,6 in acetate buffer followed by addition of carrier, precipitation, filtration and counting as above.

Exchange Experiments with 4.2 × 10^{-4} *f* Solutions.—Mixtures were prepared at 0° of 2 cc. each of active and inactive ferroin-5,6 and ferriin-5,6 as shown in Table I. About five seconds were required for mixing. Six cc. of 70% perchloric acid at 0° was added and the mixture was shaken for one minute and then filtered. Filtration required approximately one minute. The precipitate was counted and in some cases the filtrate was treated with sulfur dioxide and the ferroin-5,6 thus formed was also precipitated as the perchlorate, filtered and counted. Results are given in Table I.

TABLE I

EXCHANGE OF 4.2 × 10^{-4} *f* SOLUTIONS IN 1 *N* SULFURIC ACID AT 0°

Total count on initially active species: 420 c./min.

Initially active species	c./min. ferroin-5,6 fraction	c./min. ferriin-5,6 fraction
Ferriin-5,6	198	...
Ferriin-5,6	204	...
Ferroin-5,6	185	183
Ferroin-5,6	194	249

Total activity of the ferroin-5,6 was determined by perchlorate precipitation; and of the ferriin-5,6 by reduction with sulfur dioxide followed by perchlorate precipitation. Completeness of precipitation of ferroin-5,6 and completeness of recovery of the ferriin-5,6 in the filtrate were checked spectrophotometrically.

It appears from the results in Table I that complete exchange took place in the experiments.

Exchange Experiments with 2.2 × 10^{-5} *f* Solutions.—Four cc. of a solution of camphorsulfonic acid (0.013 *f*) in chloroform was placed in a 30-cc. separatory funnel and chilled to 0°. To this were added simultaneously 2 cc. each of ferroin-5,6 and ferriin-5,6 at 0°, each 4.4 × 10^{-5} *f* before mixing. The separatory funnel was immediately stoppered and shaken for ten seconds; the chloroform was then drained off, and both phases were worked up as described above. Results are given in Table II.

TABLE II

EXCHANGE OF 2.2 × 10^{-5} *f* SOLUTIONS IN 1 *N* SULFURIC ACID AT 0°

Initially active species	c./min. in ferroin fraction	c./min. in ferriin fraction	Sum of fractions	Total on original ferroin solution	% of activity recovered
Ferroin-5,6	4350	4000	8350	8190	102
Ferroin-5,6	..	3820	..	8190	...
Ferriin-5,6	3980	3910	7890	8190	97
Ferriin-5,6	3780	3780	7560	8190	93
Blank (Ferriin-alone)	950	6720	7670	8190	94
Ferroin-5,6	4380	3400	7780	7750	100
Ferroin-5,6	4200	3890	8090	7750	104
Ferriin-5,6	3900	3880	7780	7750	100
Ferriin-5,6	3990	3720	7710	7750	100
Blank (Ferriin-alone)	620	6520	7140	7750	92

Reasonably good recovery was obtained in all experiments (between 92 and 104%). Reduction of ferriin-5,6 by the

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[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] L. Eimer and A. I. Medalia, BNL-1022.

[3] F. B. Marti and F. L. Conde, *Anal. Chim. Acta*, **3**, 547 (1949).

camphorsulfonic acid–chloroform amounted to about 10%. Within the over-all experimental error of about 10% the activity in both fractions was the same, and there was no definite evidence for greater recovery of activity in the initially active than in the initially inactive species. We therefore conclude that, using an extraction technique of separation, complete exchange is found between ferroin-5,6 and ferriin-5,6 within 15 seconds at 0°, at concentrations of $2.2 \times 10^{-5} f$ in each species.

We are grateful to Dr. R. W. Dodson for his guidance and stimulation.

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UPTON, LONG ISLAND, N. Y. RECEIVED NOVEMBER 21, 1951

The Ammonia Induced Decomposition of Nitric Oxide

BY CHARLES P. FENIMORE[1] AND JOHN R. KELSO

A means of catalyzing the sluggish decomposition of nitric oxide is suggested by reaction (A) which occurs in the thermal decomposition of nitrous oxide.[2]

$$O + N_2O \longrightarrow 2NO + 36.6 \text{ kcal.} \qquad (A)$$

The suggestion we draw from (A) is that its reverse might go if the unfavorable energy change could be overcome. If the oxygen atom could react with a particle, X, to form a labile oxide of dissociation energy, q, then the following scheme might permit the desired catalysis.

$$\begin{gathered} 2NO + X \longrightarrow N_2O + XO + (q - 36.6) \text{ kcal.} \\ XO + NO \longrightarrow NO_2 + X + (71 - q) \\ NO + N_2O \longrightarrow NO_2 + N_2 \\ 2NO_2 \longrightarrow 2NO + O_2 \end{gathered}$$

For if q lies between 37 and 71 kcal., the first two steps would be exothermal and, perhaps, relatively fast. The last two steps describe the catalytic decomposition of nitrous by nitric oxide and are known to be consistent with that process.[2] Since an N–O single bond possesses an energy in the desired range, we hoped that ammonia or some intermediate derived from ammonia might catalyze the decomposition of nitric oxide.

Experimental

Premixed ammonia and nitric oxide were heated in a spherical quartz vessel of 523-cc. volume. Both gases were distilled and were spectroscopically pure (infrared spectra). In a few runs in which hydrazine was used, the hydrazine was twice distilled from barium oxide.

The reacting gas was sampled by opening the quartz vessel to an evacuated bulb which was fitted with a manometer and a very small freezing appendix. The condensible gases, including oxygen in the presence of excess nitric oxide, were frozen with liquid nitrogen and the permanent gas measured. This was infrared inactive, hydrogen and oxygen free by analysis, and therefore all nitrogen.

A small amount of nitrous oxide was identified in the condensible portion by its infrared spectrum. The nitrous oxide was found only in partially reacted mixtures and disappeared toward the end of the catalytic decomposition.

Results

At temperatures at which pure nitric oxide is decomposed only very slowly, the ammonia induced decomposition of a constant initial pressure of nitric oxide, which is always in excess, is characterized by: (1) The yield of nitrogen, $(N_2)_\infty$, is proportional to the square root of the initial concentration of ammonia, $(NH_3)_0^{1/2}$.

(2) The half-time of the evolution of nitrogen is independent of $(NH_3)_0$.

TABLE I

DECOMPOSITION OF NO, NH₃ MIXTURES AT 700 MM. INITIAL PRESSURE[a]

T, °C.	(NH_3), %	$(N_2)_\infty/$ $(NH_3)_0^{1/2}$, mm.$^{1/2}$	½ time, min.
702	5	44	19
	2.5	41	17
	1.0	42	18
	0.5	43	18
725	2.5	34	9.0
	1.0	35	8.5
	0.5	35	9.0
740	2.5	28	4.4
	1.0	28	4.6
755	2.5	32	3.2
	1.0	30	3.2

[a] All pressures measured at reaction temperature.

These findings are proved by the data in Table I and illustrated by the typical curves in Fig. 1.

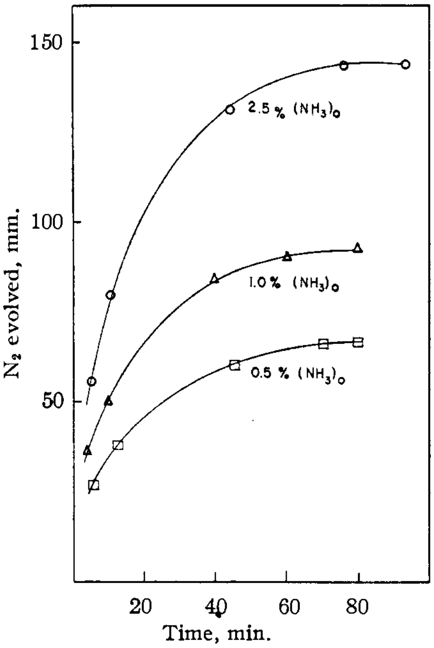

Fig. 1.—Evolution of N_2 from 700 mm. NO + NH_3 at 725°. Initial % of NH_3 is marked on each curve.

With varying initial pressures of nitric oxide, we find the data given in Table II, typical curves in Fig. 2.

(3) At 700 and 900 mm. pressure, the half-time of the evolution of nitrogen varies roughly inversely with the square of initial nitric oxide. On the initial reaction, rate varies roughly directly with this quantity.

(4) The yield of nitrogen at a fixed pressure is approximately independent of the initial nitric oxide concentration as long as this is in excess. This conclusion is not obvious from Fig. 2, but note in Table II that the low yield of nitrogen obtained

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[1] General Electric Research Laboratory, The Knolls, Schenectady, New York.

[2] F. F. Musgrave and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **135A**, 23 (1932).