The Kinetics and Mechanism of the Reaction of Potassium Ferrocyanide
and Nitrosobenzene catalysed by Mercuric and Mercurous Ions and
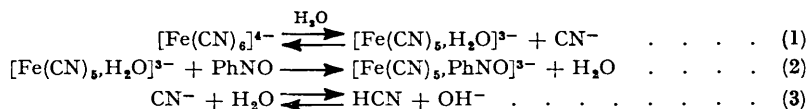Organic Mercuric Compounds.

By S. Ašperger and D. Pavlović.

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The reaction between potassium ferrocyanide and nitrosobenzene is
strongly catalysed by mercuric and mercurous ions and organic mercury
compounds except those in which mercury is bound with strong covalent
bonds. The catalytic effect was followed by spectrophotometric measure-
ments of the extinction of the violet product $[Fe(CN)_5,PhNO]^{3-}$. Catalytic
action relates to the dissociation of $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_5]^{3-}$, as does the
action of ultraviolet light. The mechanism of catalysis is discussed. Ions
of gold and platinum also act as catalysts. The order of action is $Pt^{4+} <$
$Au^{3+} < Hg^{2+} \approx Hg_2^{2+}$, corresponding to their arrangement in the Periodic
System. A method for determining traces of mercury in burnt mercury alloys
as well as for the identification of small amounts of pharmaceutical mercury
preparations is outlined on the basis of catalytic action.

CONTINUING earlier investigations on the kinetics of the decomposition of potassium
ferrocyanide in ultraviolet light (Ašperger, *Trans. Faraday Soc.*, 1952, **48**, 617) and on the
kinetics of the reaction of potassium ferrocyanide and nitrosobenzene in water (Ašperger,
Murati, and Čupahin, *J.*, 1953, 1041), we have studied the catalytic action of mercuric and
mercurous ions and of some organic mercuric compounds on the reaction which proceeds
according to equations 1—3. At low concentrations and at room temperature reaction

practically ceases, but in ultraviolet light or on the addition of mercuric ions in a concentration greater than 2×10^{-7}M the violet reaction product is formed.

$$[Fe(CN)_6]^{4-} \underset{H_2O}{\rightleftharpoons} [Fe(CN)_5,H_2O]^{3-} + CN^- \quad \ldots \ldots \quad (1)$$

$$[Fe(CN)_5,H_2O]^{3-} + PhNO \longrightarrow [Fe(CN)_5,PhNO]^{3-} + H_2O \quad \ldots \ldots \quad (2)$$

$$CN^- + H_2O \rightleftharpoons HCN + OH^- \quad \ldots \ldots \ldots \quad (3)$$

The kinetics of this reaction are easily studied by spectrophotometric determination of the violet complex. Our previous kinetic measurements largely had the practical purpose of determination of traces of mercuric ions in distilled bromine and chlorine water and of small amounts of mercury vapours in the atmosphere (Ašperger and Murati, *Analyt. Chem.*, 1954, **26**, 543). In the present work we studied the nature of the catalytic action itself.

EXPERIMENTAL

Materials.—Aqueous solutions of nitrosobenzene were prepared as described previously (*locc. cit.*). Molar concentrations given refer throughout to the monomeric form. The solutions of catalysts were prepared by dilution of more concentrated solutions immediately before measurement in order to avoid the influence of adsorption on glass. Jena or Pyrex glassware was used. Potassium ferrocyanide trihydrate and all inorganic mercury compounds were of analytical grade.

Apparatus.—A Unicam S.P. 500 quartz spectrophotometer was used for the spectrophotometric measurements (slit width : 0·01—0·02 mm.; corresponding spectral band width 12—18 Å; 10-mm. glass cells). The extinction was measured at 528 mμ, *i.e.*, at the absorption maximum of $[Fe(CN)_5,PhNO]^{3-}$, which is attributable solely to the violet complex : absorption of other components at 528 mμ is negligible (*J.*, 1953, 1042). Further, allowance was made for any possible influence by other components by use of controls.

Concentrations of Reagents.—If not otherwise indicated, potassium ferrocyanide was $5\cdot0 \times 10^{-4}$M and nitrosobenzene $4\cdot2 \times 10^{-4}$M. At these concentrations the control solutions, not containing catalyst, are stable for more than 30 min. at 20°. In all cases the extinctions were measured against freshly prepared control solutions.

Influence of pH.—The rate of formation of the violet product depends on the pH; it was highest when the pH of the mixture (aqueous nitrosobenzene and catalyst) was adjusted to 3·5 by adding a few drops of hydrochloric acid or potassium hydroxide before the addition of potassium ferrocyanide. (It was erroneously reported in *J.*, 1953, 1043, line 35, that the solution of potassium ferrocyanide was also adjusted to pH 3·5.) When potassium ferrocyanide was added in such an amount that its concentration in the final mixture was 5×10^{-4}M, it caused an increase of the pH from 3·5 to 4·1. Consequently the pH of all our solutions at zero time was 4·1.

Reaction catalysed by Mercuric Ions.—An aqueous solution of nitrosobenzene was prepared, a definite amount of mercuric chloride added, and the pH adjusted to 4·1. The pH of the solution of potassium ferrocyanide was also adjusted to 4·1. These solutions were mixed after thermal equilibrium had been reached at 20°. In the final mixture nitrosobenzene was $1\cdot05 \times 10^{-3}$M and mercuric chloride 1×10^{-5}M; the concentration of potassium ferrocyanide varied from $7\cdot5 \times 10^{-5}$ to 3×10^{-3}M. At intervals a portion of the solution was drawn off and the extinction measured at 528 mμ. Since in this series of measurements the concentration of potassium ferrocyanide varied, causing changes in the pH of the final mixture, it was necessary to adjust the pH of the solution of potassium ferrocyanide to 4·1. The results, given in Figs. 1 and 2, show that the velocity depends to a great extent on the concentration of potassium ferrocyanide. If reaction (1) is taken as the rate-determining stage, the velocity of formation of the violet product should not be influenced by variations in the initial concentration of nitrosobenzene above a certain point : Fig. 3 shows that this is so for a concentration of nitrosobenzene above 2×10^{-4}M.

Reaction (2), *i.e.*, the reaction between aquopentacyanide and nitrosobenzene, is much faster than reaction (1). Moreover reaction (2) is practically irreversible. If, for example, a mixture of ferrocyanide and nitrosobenzene is first exposed to ultraviolet light and then put in the dark, the extinction of the violet complex remains practically unchanged. On the other hand, reaction (1), *i.e.*, the dissociation of ferrocyanide into aquopentacyanide in the absence of nitrosobenzene, is reversible. The pH of the irradiated ferrocyanide solutions decreases in the dark until the initial pH value is almost regained.

Influence of Temperature.—In the first series of measurements the concentration of mercuric ions was 2×10^{-6}M (Fig. 4), in the second 7×10^{-6}M. If the logarithms of the initial reaction velocity are plotted against $1/T$, a straight line is obtained in each series (Fig. 5). The initial velocity was taken as the height of the ordinate at the intersection of the tangent to the curves

Fig. 1. *Dependence of the reaction velocity on the concentration* (M) *of potassium ferrocyanide.*
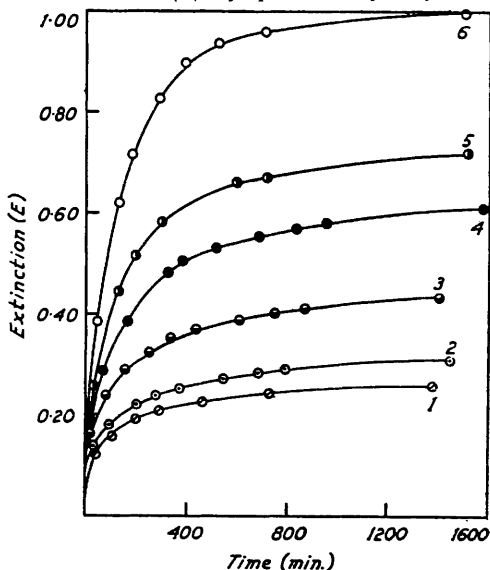
K$_4$Fe(CN)$_6$: 1, $7 \cdot 5 \times 10^{-5}$; 2, 1×10^{-4}; 3, $2 \cdot 5 \times 10^{-4}$; 4, 5×10^{-4}; 5, 1×10^{-3}; 6, 3×10^{-3}M; PhNO $1 \cdot 05 \times 10^{-3}$M; HgCl$_2$ 1×10^{-5}M; *initial* pH $= 4 \cdot 1$; $t = 20°$; $\lambda = 528$ mμ.

Fig. 3. *Dependence of initial reaction velocity* ($E_{10} = extinction$ *at* 10 *minutes*) *on concentration of nitrosobenzene.*
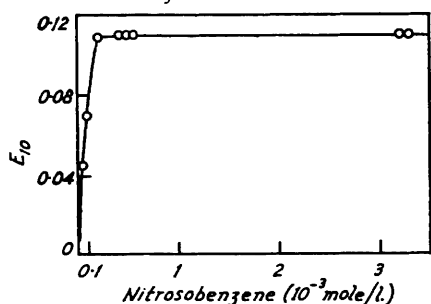
K$_4$Fe(CN)$_6$ 5×10^{-4}M; HgCl$_2$ 7×10^{-6}M; $t = 20°$; *initial* pH $= 4 \cdot 1$; $\lambda = 528$ mμ.

Fig. 2. *Dependence of the initial reaction velocity* ($E_{20} = extinction$ *at* 20 *minutes*) *on the concentration of potassium ferrocyanide.*
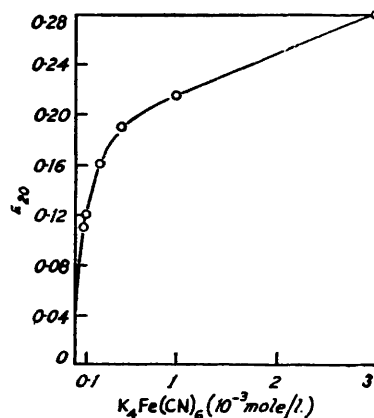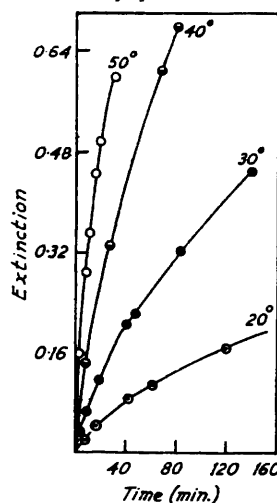

Fig. 4. *Influence of temperature on the velocity of reaction.*

K$_4$Fe(CN)$_6$ 5×10^{-4}M; PhNO $8 \cdot 38 \times 10^{-4}$M; HgCl$_2$ 2×10^{-6}M; *initial* pH $= 4 \cdot 1$; $\lambda = 528$ mμ.
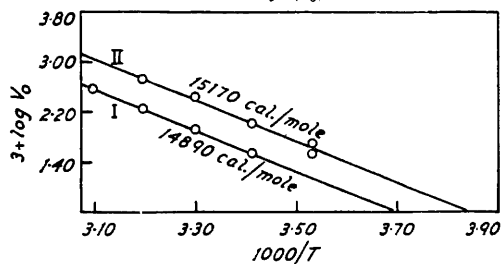
in Fig. 4 at $t = 0$, and the ordinate at $t = 10$. The constants of the straight lines were calculated by the least-squares method. The mean value of the activation energy (15 kcal./mole) is only approximate since, instead of rate constants, the initial velocities were used. The activation energy obtained relates to the slowest process, *i.e.*, the dissociation of [Fe(CN)$_6$]$^{4-}$ into [Fe(CN)$_5$]$^{3-}$; it is about 5 kcal./mole lower than that of the uncatalysed process (*J.*, 1953, 1044).

Salt Effect.—The velocity of the catalysed reaction decreases with the increase of ionic strength; *e.g.*, Fig. 6 shows the action of potassium chloride. The negative salt effect is in

agreement with Brönsted's theory, since the charges of ferrocyanide and mercuric ions are of opposite signs.
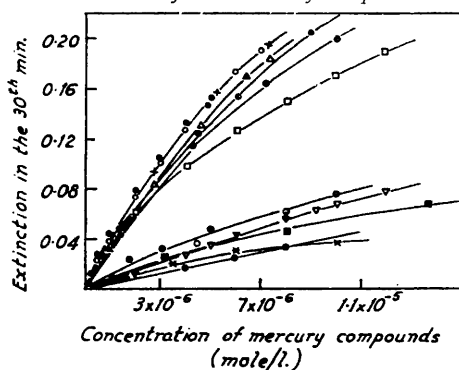
Catalytic Action of Different Mercury Compounds.—The dependence of catalytic action on the concentration of different mercury compounds is shown in Fig. 7. Extinction at 30 min. was taken as a measure of the catalytic action. It can be seen that the catalytic effects of mercuric chloride and bromide are equal; those of mercuric sulphate and nitrate are smaller. This can be ascribed to the salt effect since, in the preparation of the solutions of sulphate and nitrate, acid

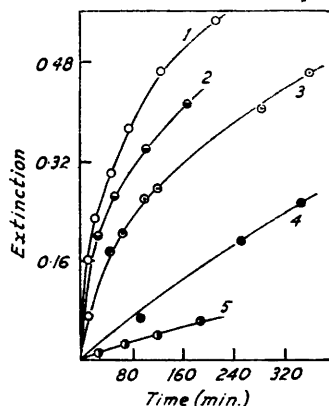FIG. 5. *Influence of temperature on the initial re-action velocity* (v_0).

Series I : HgCl$_2$ 2×10^{-6}M.   *Series II :* HgCl$_2$
7×10^{-6}M.

FIG. 6. *Influence of concentration of potassium chloride on the reaction velocity.*

KCl : 1,0·0; 2, 0·1; 3, 0·3; 4, 0·7; 5, 1·0M;
K$_4$Fe(CN)$_6$ 5 × 10^{-4}M; PhNO 1·05 × 10^{-3}M;
HgCl$_2$ 1 × 10^{-5}M; $t = 20°$; *initial* pH — 4·1;
$\lambda = 528$ μm.

FIG. 7. *Dependence of the reaction velocity on the concentration of some mercury compounds.*

Concentration of mercury compounds
(mole/l.)

○ HgCl$_2$, × HgBr$_2$, ● Hg$_2$(NO$_3$)$_2$, △ HgSO$_4$,
◑ Hg(OBz)$_2$, ◐ Hg(NO$_3$)$_2$, □ Hg(CN)$_2$, ◔
Ph·Hg·OAc, ▽ Me·HgBr, ■ mercuri-*o*- and
-*m*-hydroxybenzoate, ◑ MeHgI, ✱ mercuribis-succinimide. K$_4$Fe(CN)$_6$ 5 × 10^{-4}M; PhNO 4·2 ×
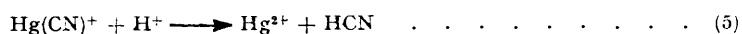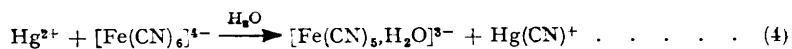10^{-4}M; $t =20°$; *initial* pH = 4·1; $\lambda = 528$ mμ.

FIG. 8. *Catalytic action of mercuric chloride (curve 1) and diphenylmercury (curve 2) on the reaction velocity in 73·2% (vol.) methanol.*

Concentration of mercuric compounds
(mole/l.)
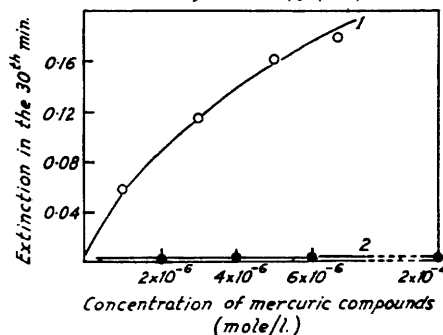
was added to suppress hydrolysis. The catalytic action of mercuric benzoate is very strong, that of mercuric cyanide weaker. It is interesting that the action of mercurous nitrate is equal to that of mercuric chloride, *i.e.*, the catalytic action of both Hg^{2+} and Hg$_2^{2+}$ is the same. The effect of phenylmercuric acetate, methylmercuric bromide, mercuri-*o*- and -*m*-hydroxybenzoate

$\left(\text{HO·C}_6\text{H}_3\overset{\text{Hg}}{\underset{\text{CO}_2}{<}} \right)$, methylmercuric iodide, and mercuribis-succinimide [Hg(N·C$_4$H$_4$O$_2$)] is much

smaller. This is consistent with the view that the catalysis is due to mercuric or mercurous ions for in all these compounds one or both of the mercury bonds are more or less covalent. Diphenylmercury was not expected to exhibit any catalytic action. Since this compound is insoluble in water, alcoholic solutions were prepared containing 73·2% (vol.) of methanol. Under the same conditions measurements were carried out with mercuric chloride. From Fig. 8 it may be seen that diphenylmercury has no catalytic action, even at a concentration 2 × 10^{-4}M, 100 times greater than the mean concentrations of mercuric chloride used.

DISCUSSION

Reaction between ferrocyanide and nitrosobenzene takes place much faster in ultra-violet light than in the dark; thus we can talk of the catalytic action of light. Our earlier spectrophotometric measurements (*J.*, 1953, 1042) have shown that the same violet product is formed regardless of whether the reaction is catalysed by ultraviolet light or by mercuric ions. The light energy of wavelengths shorter than 400 mμ causes the dissociation of one cyanide group from the hexacyanide ion and accelerates the otherwise very slow thermal reaction. The catalytic action of mercuric ions must relate to the slowest process, shown in the previous section to be the decomposition of $[Fe(CN)_6]^{-4}$ to $[Fe(CN)_5]^{3-}$. Moreover, the action of the mercuric ion was expected to relate to the dissociation of the ferrocyanide ion, as in the case of ultraviolet light. The product of reaction between mercuric and ferrocyanide ion is very probably the intermediate $Hg(CN)^+$, which in a relatively fast reaction with a hydrogen ion regenerates a mercuric ion according to the scheme :

$$Hg^{2+} + [Fe(CN)_6]^{4-} \xrightarrow{\text{H}_2\text{O}} [Fe(CN)_5,H_2O]^{3-} + Hg(CN)^+ \quad . \quad . \quad . \quad . \quad (4)$$

$$Hg(CN)^+ + H^+ \longrightarrow Hg^{2+} + HCN \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By this mechanism catalytic action of mercuric ions will not be possible in basic solutions since $Hg(CN)^+$ reacts with the hydroxyl ion, giving $Hg(CN)\cdot OH$ (Borelli, *Gazzetta*, 1908, **38**, I, 361) and mercuric ions are then not regenerated. The catalytic action of all mercuric compounds in basic solutions is actually very small. In an acid solution regeneration is possible and catalytic action does not cease [Pinter, *Farm. Vjesnik*, 1940, 3 (Zagreb, Croatia)]. In fact the action of hydrogen ions is more complicated than might be expected from equation (5). In acid solutions of potassium ferrocyanide we have the following equilibria : $H^+ + [Fe(CN)_6]^{4-} \rightleftharpoons [HFe(CN)_6]^{3-}$ and $H^+ + [HFe(CN)_6]^{3-} \rightleftharpoons [H_2Fe(CN)_6]^{2-}$. According to Nekrasov and Zotov (*J. Appl. Chem. U.S.S.R.*, 1941, **14**, 264), the first two dissociation constants of $H_4Fe(CN)_6$ are very large. The dissociation constants of the third and fourth stages are approximately 10^{-3} and 5×10^{-5} respectively. Assuming the first two dissociations to be complete, we can compute the concentration of ions present in a solution of potassium ferrocyanide. The approximate concentrations of ions in 5×10^{-4}M-potassium ferrocyanide at pH 4·1 are : $[Fe(CN)_6]^{4-}$ 1·8 $\times 10^{-4}$, $[HFe(CN)_6]^{3-}$ 2·9 $\times 10^{-4}$, $[H_2Fe(CN)_6]^{2-}$ 2·3 $\times 10^{-5}$; and at pH 2 : 2·3 $\times 10^{-7}$, 4·5 $\times 10^{-5}$, and 4·5 $\times 10^{-4}$ respectively. We see that, in fairly acid solutions of potassium ferro-cyanide, $[H_2Fe(CN)_6]^{2-}$ predominates. It might be expected that the smaller the number of protons in the complex ion, the easier would be the loss of the cyanide ions from it. Consequently, in very acid solutions of potassium ferrocyanide the reaction velocity should decrease, as is in fact the case. The two effects of hydrogen ions, suppression of the dissociation of $H_4Fe(CN)_6$ and regeneration of the catalyst, are in opposition, and this must lead to an optimum pH. Actually the maximum reaction velocity is observed when the pH of the final reaction mixture at zero time is 4·1, or the pH of the reaction mixture before adding ferrocyanide is 3·5 (*J.*, 1953, 1041). The negative salt effect, the decrease in activation energy of the decomposition of $[Fe(CN)_6]^{4-}$ into $[Fe(CN)_5]^{3-}$ in the presence of mercuric ions, and the fact that purely covalently bonded mercury gives no catalytic action, are in accordance with the above *general* scheme.

It may be expected that ions of some other heavy metals, which have a close affinity for the cyanide ion and can be regenerated in acid solutions, will also exhibit catalytic action. Gold and platinum ions show catalytic action; on the other hand, none was observed for silver. The increasing order of catalytic action corresponds to the arrangement of these metals in Periodic Table, $Pt^{4+} < Au^{3+} < Hg^{2+} \approx Hg_2^{2+}$

Further Use of the Reaction in Analysis.—A method for the determination of small amounts of mercury in burnt mercury alloys remaining in the smelting plants of mercury mines has been developed. About 1 g. of the alloy was heated in an air-stream at 1100°. The mercury vapour liberated was mixed with bromine vapour according to Moldawskii (*J. Appl. Chem. U.S.S.R.*, 1930, **3**, 955; cf. Stock, *Ber.*, 1938, **71**, 550). The mercuric bromide remains in the absorption vessel. The determination of these small amounts of mercuric bromide was performed

according to our earlier procedure (*loc. cit.*, 1954), 23 samples containing 0·002—0·007% of mercury being analysed.   The error was about 5%.

Pharmaceutical preparations containing ionic mercury could be identified as mercury compounds even in extremely small quantities.   Determination is also possible on the basis of a calibration curve.

INSTITUTE OF INORGANIC, ANALYTICAL, AND PHYSICAL CHEMISTRY, FACULTY OF PHARMACY,
    UNIVERSITY OF ZAGREB, CROATIA, YUGOSLAVIA.