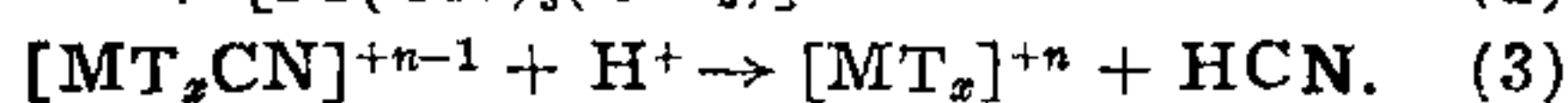
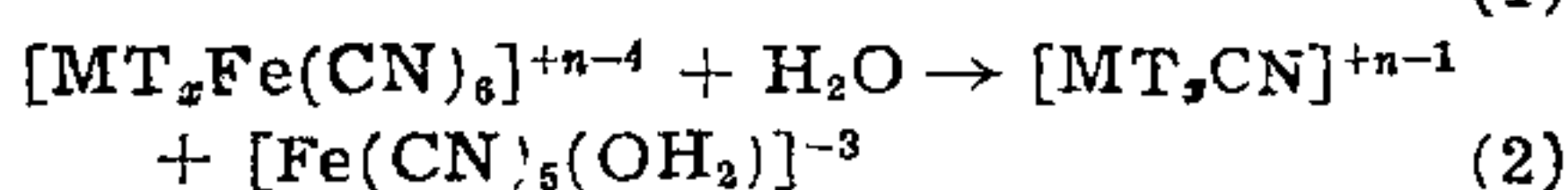
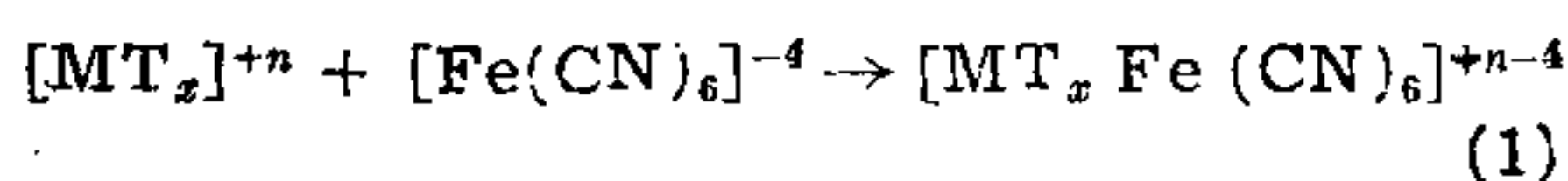


CATALYSED DECOMPOSITION OF FERROCYANIDE ION BY SULPHUR LIGATED 'CLASS b' METAL IONS

It is well known¹ that the hexacyanoferrate (II) and pentacyanoaquoferrate (II) ions are highly stable in aqueous solution. In acid medium² very slow decomposition of ferrocyanide solutions has been reported. We have observed that the decomposition of ferrocyanide solution, however, is strongly catalyzed by the presence of S-ligated 'class b' metal ions. The decomposition then occurred to the maximum extent in the pH range 2 to 5 when working with 10⁻³ to 10⁻⁵ molar concentrations of both ferrocyanide and the metal complexes. The S-ligands employed were thiourea (T), thio-glycolic acid and various dithiocarbamates; the metal ions found most effective were Hg(II), Ag(I) and Cu(I). These metal ions in the absence of S-ligands affected decomposition of ferrocyanide solutions only to a limited extent. The final product of the decomposition carried out in air was confirmed to be Prussian blue (absorption maximum 690 mμ).

The decomposition apparently results by progressive removal of cyanide ions from the co-ordination site of Fe²⁺ ions, for example, by 'class b' metal-thiourea complexes, [MT_x]⁺ⁿ, as follows:



Initially, formation of a loose complex as in (1) is envisaged between the Fe(II)-cyanide complex (hexacyano to start with and later lower cyano complexes with progress of reaction) which changes over by cyanide transfer as in reaction (2), to a mixed thiourea-cyano complex of the 'class b' metal M, [MT_xCN]⁺ⁿ⁻¹. The complex [MT_xCN]⁺ⁿ⁻¹ will lose CN⁻ by reaction (3), regenerating [MT_x]⁺ⁿ which can effect further decyanation of Fe²⁺. The ultimate Fe(II) species will be [Fe(OH₂)₆]²⁺ which on aerial oxidation gives [Fe(OH₂)₆]³⁺. This would react with undecomposed ferrocyanide to yield Prussian blue. In absence of S-ligands the metal ions M⁺ⁿ, though they may initially displace part of cyanide ions from ferrocyanide, do not further act as catalysts, because these metal cyanide complexes are quite stable. Though no direct evidence was obtained in the present studies

for complexes of type [MT_xCN]⁺ⁿ⁻¹ in solution phase, their formation is supported by the well-known existence of many mixed complexes of thiourea and halide and pseudo-halide ions, with 'class b' metal ions such as HgT₂Cl₂, AgT₂Cl, CuTCl, CuT₃Cl; HgT₂(SCN)₂, AgT₃.SCN, CuT.SCN, etc. Cyanide ion being a typical pseudohalide ion may be expected to behave similarly. It was possible in some cases to isolate solid complexes, containing ferrocyanide and S-ligated 'class b' metal groups. For example, when solutions of HgT₃(NO₃)₂ and potassium ferrocyanide were intermixed a sparingly soluble yellow complex of composition [HgT₃]₂[Fe(CN)₆] was obtained. (Analyzed Hg 37.1%, Fe 5.38%, S 18.69% required for [HgT₃]₂[Fe(CN)₆] Hg 37.49%, Fe 5.22%, S 17.98%).

Even in the solid state on exposure to air, this complex changed to Prussian blue and other products on keeping for several days in darkness.

The 'class a' metal ions such as Co²⁺, Ni²⁺, Zn²⁺ and the border ones such as Cd²⁺ did not catalyze the decomposition of aqueous ferrocyanide solution in presence and absence of S-ligands. This is to be expected from the low stability known for the S-complexes of these ions.^{3,4}

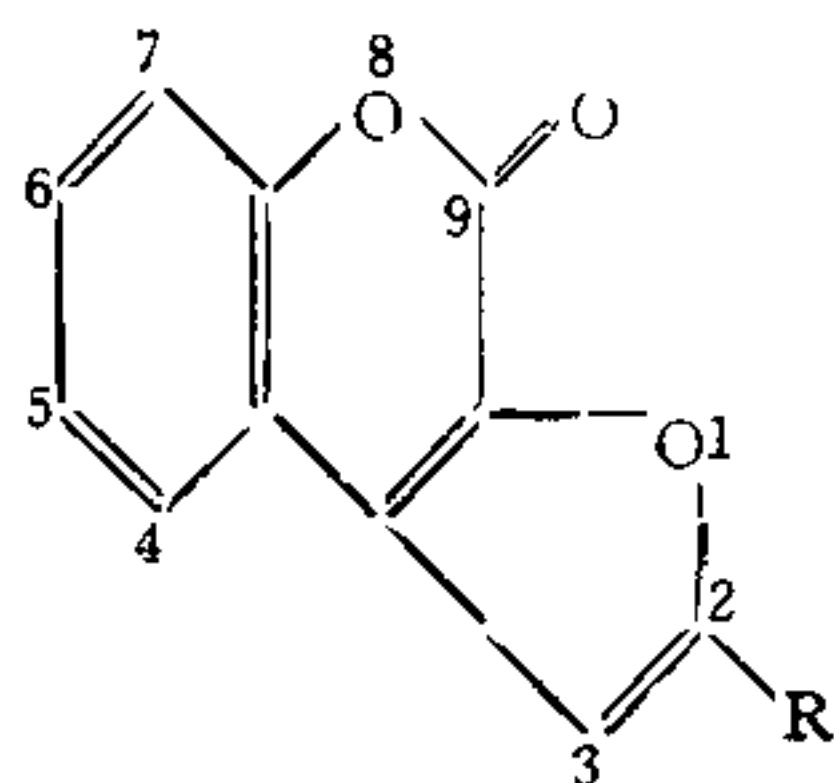
Dept. of Chemistry, M. RAMAKRISHNA UDUPA.
Indian Institute of Technology, G. ARAVAMUDAN.
Madras-36, May 2, 1969.

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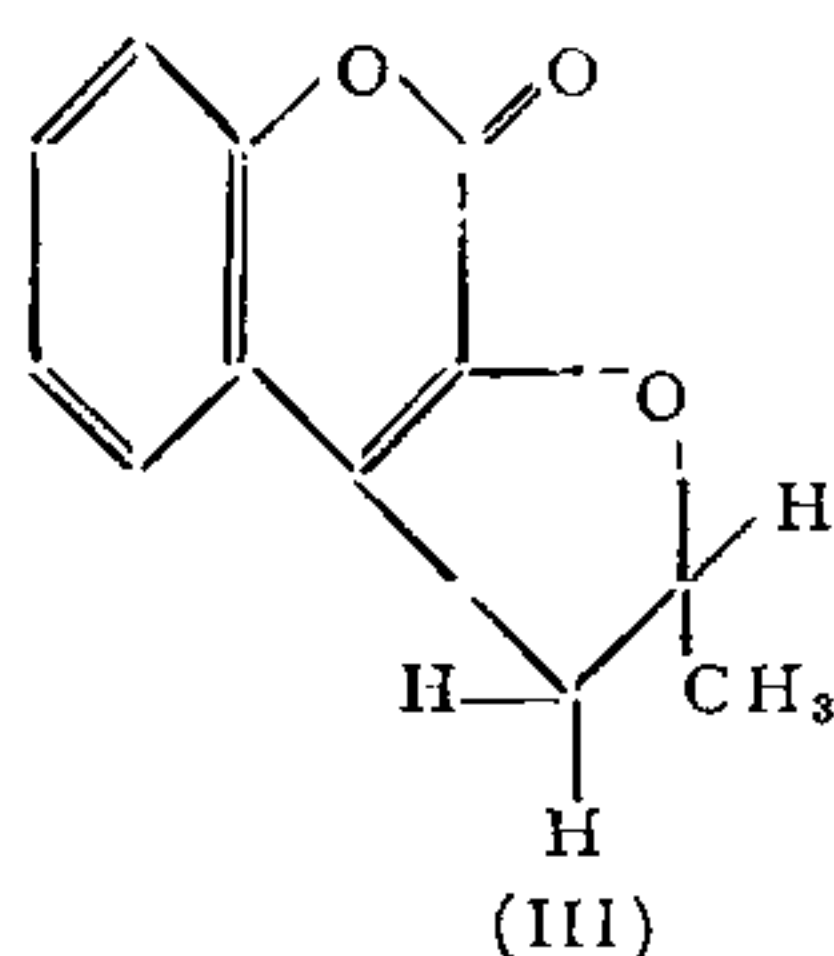
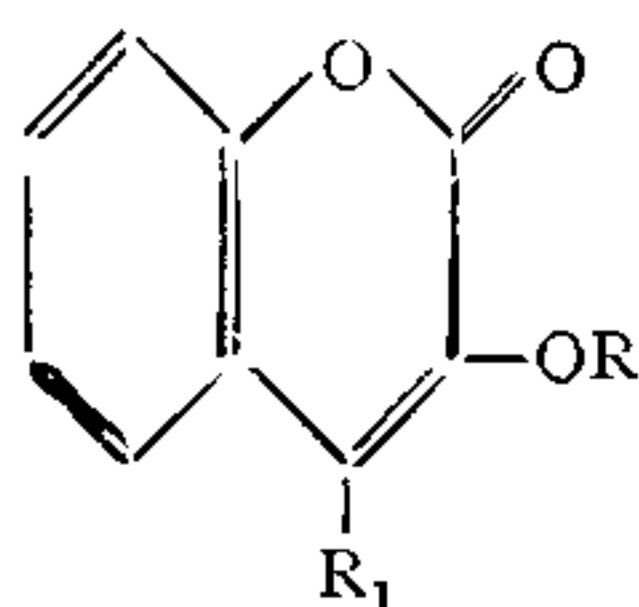
SYNTHESIS OF 2-METHYL-9H-FURO (2, 3-C) BENZOPYRAN-9-ONE, A FUROCOUMARIN DERIVED FROM 3-HYDROXYCOUMARIN

DHOLAKIA AND TRIVEDI¹ synthesised 4H-Furo (3, 2-C) benzopyran-4-one from 4-hydroxycoumarin. An attempt to prepare 9H-Furo (2, 3-C)-benzopyran-9-one(Ia) by this procedure met with failure as 3-hydroxycoumarin failed to condense with malic acid or ethyl acetoacetate in the presence of concentrated sulphuric acid or anhydrous aluminium chloride. It was, therefore, thought of interest to build up furan ring on 3-hydroxycoumarin by a different route.

3-Hydroxycoumarin (II a), on allylation with allylbromide and potassium carbonate in refluxing acetone, gave 3-allyloxycoumarin (II b) m.p. 98° C., which underwent Claisen rearrangement to give 4-allyl-3-hydroxycoumarin (II c), m.p. 149° C., when refluxed with dimethyl aniline under nitrogen atmosphere. The ring closure of (II c) to (III), m.p. 111° C., was accomplished by trituration with concentrated sulphuric acid for 10 minutes at room temperature. This method was found superior to earlier



I a: R = H
I b: R = -CH₃



II a: R = H; R₁ = H
II b: R = -CH₂-CH=CH₂; R₁ = H
II c: R = H; R₁ = -CH₂-CH=CH₂

methods² which used hydrobromic acid or pyridine hydrochloride. The compound (III) was dehydrogenated by refluxing it with diphenyl ether in the presence of palladised charcoal (10%) to 2-methyl-9H-furo(2,3-c)-benzopyran-9-one (I b), m.p. 159° C. All compounds described above gave satisfactory analytical results. Furocoumarins of this type having different substituents like Br, OCH₃, etc., in the benzenoid part of the furocoumarin ring have been synthesized by this procedure and will be published elsewhere.

Thanks are due to Professor S. Sethna for his keen interest in this work and to Dr. S. S. Lele for micro-analyses of the compounds.

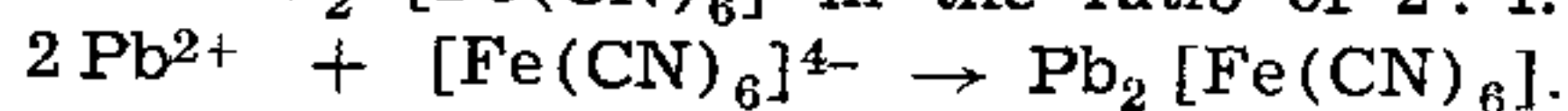
Chemistry Department, Y. A. SHAIKH.
Faculty of Science, K. N. TRIVEDI.
M.S. University of Baroda,
Baroda-2, May 15, 1969.

TITRIMETRIC DETERMINATION OF FERROCYANIDE

FERROCYANIDE is mainly determined by oxidation or precipitation methods. Following the application of 4-(2-pyridylazo)-resorcinol (PAR) as complexometric¹ and spectrophotometric³ reagent, and its application for complexometric determination³ of Pb²⁺, Pb²⁺.PAR chelate was used as end-point detection in determination of several anions.^{2,4} The present study has revealed the possibility of direct titration of [Fe(CN)₆]⁴⁻ with Pb²⁺, using Pb²⁺.PAR chelate for end-point detection. Due to slight solubility of Pb₂ [Fe(CN)₆], reddish colour developed from the start of titration, which made end-point detection rather difficult. Hence, isopropyl alcohol has been added to titrating mixture. Data obtained with isopropyl alcohol concentration maintaining from 10% to 40% gave fairly accurate and reproducible results.

Lead nitrate solution is standardised⁵ as usual whereas standard solution of ferrocyanide is prepared from pure sample of potassium ferrocyanide (BDH AnalaR). ~0.02 M solution of PAR is prepared by dissolving 0.5 g. of its monosodium salt in 100 ml. of water.

Aliquots of ferrocyanide solution are taken in 250 ml. conical flask, appropriate volume of isopropyl alcohol added, ~0.2 g. of hexamine added, pH adjusted to 6.5-8.0 by dilute acetic acid, 1 or 2 drops of dyestuff added, and titrated with standard lead nitrate solution, with constant stirring of solution, until the colour change from yellow/orange-yellow to brilliant rose-red is permanent. The colour change is quite sharp in presence of hexamine. The reaction between Pb²⁺ and ferrocyanide is found to be stoichiometric, with the formation of Pb₂ [Fe(CN)₆] in the ratio of 2:1.



Results are returned in Table I.

TABLE I

Vol. of alcohol + water ml.	Amount of ferrocyanide			
	Taken mg.	Found mg.	Diff. mg.	Error %
5 + 9	2.645	2.614	0.031	-1.20
10 + 15	5.290	5.325	0.035	+0.60
5 + 25	10.59	10.56	0.03	-0.30
10 + 20	21.19	20.91	0.28	-1.30
20 + 60	42.38	41.62	0.76	-1.70
20 + 48	52.97	53.51	0.54	+1.08

Interfering cations, e.g., Cu (II), Hg (I, II), Sb (III), Fe(III), Ni(II), Zn(II), Th(IV),

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