## EVIDENCE FOR EXISTENCE OF + 2 OXIDATION STATE OF IRON IN $KF_e\,Cr(CN)_6$ BY MÖSSBAUER SPECTROSCOPY

THE Mössbauer effect has been extensively used to study a wide variety of ionic ferrous compounds[1]. The physical quantities isomer shift ($\delta$) and quadrupole splitting ($\Delta E_Q$ or $\Delta$) give a direct picture of the environment around the nucleus. The displacement of resonance line from zero velocity gives the isomer shift and as the position of the resonance line is governed by the *s*-electron density of the iron, isomer shift value is representative of the oxidation state of the sample under investigation. In the present communication studies of the oxidation state of iron in $KF_e\,Cr(CN)_6$ with mössbauer spectroscopy has been reported.

*Experimental*

The mössbauer spectrum was recorded at IIT, Kanpur, employing an ND-512 multichannel analyzer. The source used was 2·0 m Ci $^{57}Co$ in copper matrix. The IR spectrum of the compound was recorded with a Beckman IR 20 spectrophotometer (range 4000–350 $cm^{-1}$).

The sample was prepared by mixing aqueous solutions of potassium hexacyanochromate (III) and ferrous ammonium sulphate (B.D.H., A.R.) in their molar proportions. The orange coloured precipitate was filtered and washed with distilled water, alcohol and finally with ether. The sample was dried in vacuum over anhydrous calcium chloride. The dried sample was then ground to a fine powder and a 50 $mg/cm^2$ thick layer was sandwiched between the folds of an aluminium foil and mounted on the sample holder of the instrument.

*Analysis of the Data.*—The instrument was calibrated using enriched iron (99·99% pure). The count rate was plotted against channel number to obtain the mössbauer plot (Fig. 1).

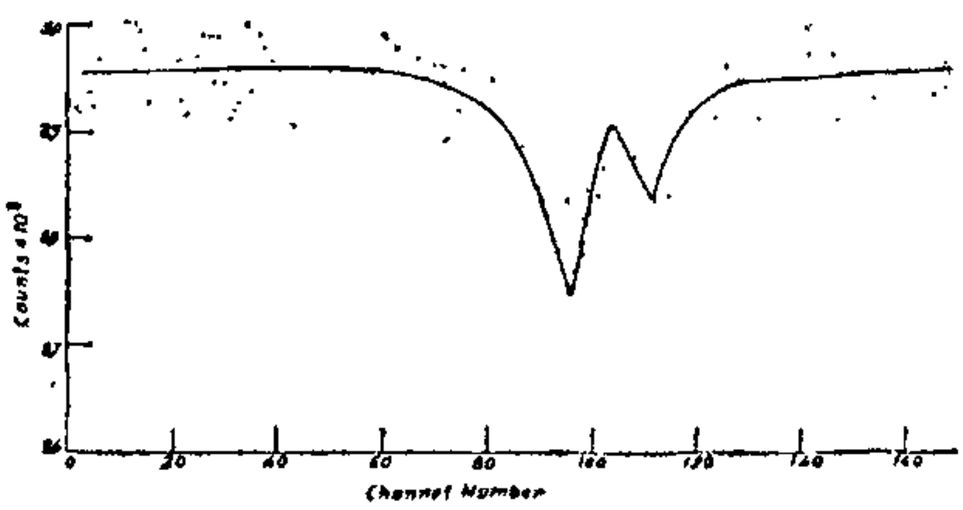


FIG.1.-Mössbauer spectrum of $KFeCr(CN)_6$.

The velocity at a particular channel was determined using a previously worked out computer programme.

*Results and Discussion*

The infra red spectra of the compound showed two $C \equiv N$ stretching bands at 2160 $cm^{-1}$ and 2085 $cm^{-1}$ as reported by Shriver *et al.*[2], and Cr — C stretching band at 600 $cm^{-1}$.

The mossbauer spectrum of $KF_e\,Cr(CN)_6$ shows dips at channel numbers 96 and 112. The velocity corresponding to these channel numbers comes out to be 0·0 mm/sec. and 1·71 mm/sec.

Thus

isomer shift ($\delta$) : 0·85 mm/sec.

and

quadrupole splitting ($\Delta$) : 1·71 mm/sec.

Identification of iron as high spin ferrous or ferric can be easily carried by mössbauer spectroscopy[3,4] as each state of iron gives a distinctive pattern. Thus two lines appearing in the mössbauer spectrum of $KF_e\,Cr(CN)_6$ with a quadrupole splitting value of 1·71 mm/sec. show that iron in this compound is in ionic and + 2 oxidation state.

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## REACTION OF DIETHYL-γ-OXO-PIMELATE WITH ALDEHYDES. A TYPE OF STOBBE CONDENSATION

THE reaction of diethyl-γ-oxo-pimelate and anisaldehyde in the presence of potassium tert.-butoxide was observed to yield an acid in 90% yield. The equivalent weight and the analytical values suggested that it was an ester-acid[1] and this was supported by the spectral data [uv : $\lambda_{max}^{EtOH}$ 226 nm (log ε 4·16), 304–308 nm (log ε 3·40) ; ir : 1685 $cm^{-1}$ (an extended aryl conjugated α, β-unsaturated carbonyl), 1718 $cm^{-1}$ (saturated carboxyl), 1735 $cm^{-1}$ (saturated ester)].

The formation of *β-arylidene-γ-oxo-ω-carbethoxy hexanoic acid* takes place in preference to the β-ketoester which could be obtained by an internal self condensation corresponding to Dieckmann Cyclisation, or an acyclic diester by a Claisen reaction. The formation of the ester-acid could be explained by assuming that a carbanion, formed from the more acidic keto-methylene, condenses with the aldehyde to yield the oxyanion[2]. This could cyclise to a γ-lactone as in the Stobbe reaction[1], and the lactone then cleaves to the ester-acid[1].

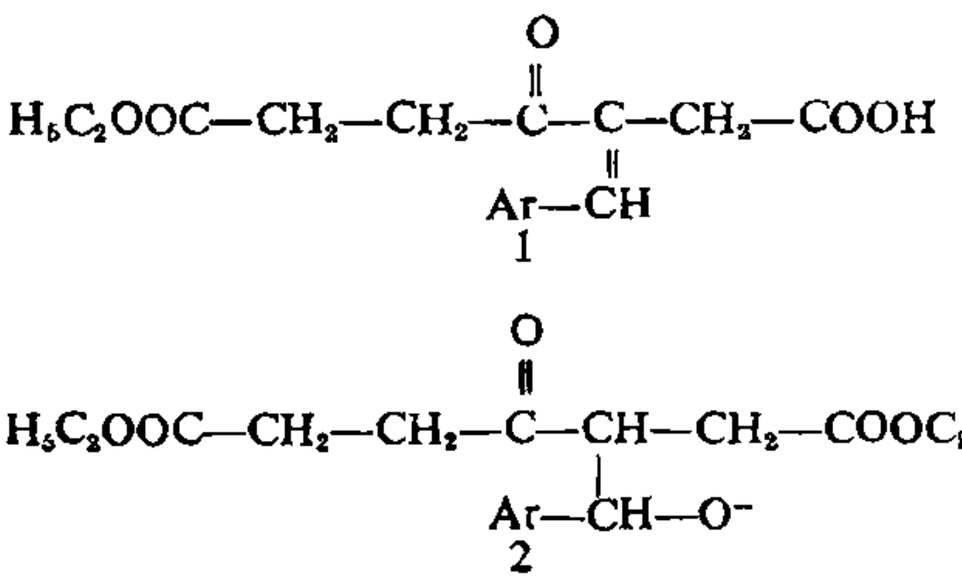
TABLE I

*Reaction of Diethyl-γ-oxo-pimelate with Aryl aldehydes*

| Sl. No. | Ar | mp | Yield (%) | $\lambda_{max.}^{EtOH}$ (nm) | log ε | IR ($cm^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|
| 1. | $C_6H_5$ | 103–5° | 85 | 276 | 3·77 | .. | .. | .. |
| 2. | $4\text{-}CHO_3C_6H_4$ | 87–9° | 90 | 226 | 4·16 | 1685 (s) | 1718 | 1735 |
| | | | | 304–308 | 3 40 | | | |
| 3. | $3:4\,(O\cdot CH_2\cdot O)C_6H_3$ | 73–6° | 100 | 226 | 4·42 | 1680 | 1715 | 1733 |
| | | | | 290 | 4·06 | | | |
| | | | | 300 | 4 07 | | | |
| 4. | $3:4\,(OCH_3)_2C_6H_3$ | 83° | 95 | 226 | 4·50 | 1860 (s) | 1716 | 1735 |
| | | | | 286 | 4·18 | | | |
| | | | | 312 | 4·19 | | | |
| 5. | $2ClC_6H_4$* | .. | 70 | 268 | 3·92 | 1682 | 1710–1730 | .. |
| 6. | $4ClC_6H_4$ | 64–5° | 80 | 214 | 3·85 | 1675 | 1705(s) | 1730 |
| | | | | 286 | 3·91 | | | |

* This compound is viscous.

The reaction proceeded equally well with sodium ethoxide as the catalyst. Condensation with other aldehydes yielded the corresponding acids (Table I).



*Experimental*

*Condensation of diethyl-γ-oxo-pimelate and anisaldehyde in potassium tert.-butoxide.*—A mixture of diethyl-γ-oxo-pimelate (5 g) and anisaldehyde (3·0 g) was added to potassium tert.-butoxide (from 1 g of potassium and 30 ml of tert.-butanol) and stirred for 45 minutes under inert anhydrous condition at room temperature. The reaction mixture was acidified with 6 N hydrochloric acid and the tert.-butanol removed under reduced pressure. The residue was taken up in ether and the ethereal phase was repeatedly washed with ice-cold sodium carbonate solution. The alkaline phase on acidification gave *β-arylidene-γ-oxo-ω-carbethoxy hexanoic acid* (6·3 g, 90%). m.p. 103–5° ; Found : eq. wt., 317 ; C, 63·5 ; H, 6·4, reqd. for $C_{16}H_{20}O_6$ ; eq. wt., 320 ; C, 63·75 ; H, 6·25%.

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## MEASUREMENT OF FORMAL POTENTIAL OF THE IODOBENZENE DICHLORIDE/IODOBENZENE COUPLE IN GLACIAL ACETIC ACID

A SOLUTION of iodobenzene dichloride in dry acetic acid has been employed for the determination of a variety of reductants in non-aqueous and partially aqueous media[1-3]. In such media, iodobenzene dichloride ($PhICl_2$) acts as a moderately strong oxidizing agent, the electron transfer reaction being

$$PhICl_2 + 2\,e^- \rightarrow PhI + 2\,Cl^- \qquad (1)$$

It is of practical importance to determine the redox potential of the couple. But the measurement of *standard* redox potential is difficult due to the involvement of various factors such as activity coefficients, liquid junction potentials, etc., and also since the medium is not aqueous. It is, however, possible to determine the *formal* potential. Lingane[4] also considers that the formal potential is a "kind of practical standard potential".

Iodobenzene (Koch-Light) was redistilled and used ; iodobenzene dichloride was prepared as described earlier[1]. Glacial acetic acid was purified by the usual procedure. Standard solutions of both iodobenzene dichloride and iodobenzene in dry acetic acid were separately prepared ; the strength of the former was checked by the iodometric method[2]. A Toshniwal CL 06—Titration Potentiometer with magic eye detector was used. A bright platinum strip was used as indicator electrode while an aqueous saturated calomel electrode (SCE) served as the reference one.

Mixed solutions of various compositions containing iodobenzene dichloride and iodobenzene were kept in a thermostat at 35 ± 0·02° C. After ensuring the attainment of thermal equilibrium, the e.m.f. was determined for the following cell :

| Hg | $Hg_2Cl_2$ (s) | KCl aq. satd. || KCl agar bridge || $PhICl_2$/PhI in acetic acid | Pt |
|---|---|---|---|---|---|