aldehydes have been studied extensively[1]. However, similar studies on 2-hydroxyketoxime complexes have not been made. This prompted us to study the isotopic exchange of Co(II) complexes of the oximes of resacetophenone and 5-nitroresacetophenone.

Resacetophenone oxime was prepared by the method suggested by Dey and Sitaraman[2]. 2-Hydroxyacetophenone (Fluka) was used to prepare its oxime. 5-Nitroresacetophenone oxime was prepared according to the method developed by Omer *et al.*[3].

Cobalt(II) solution in water was adjusted to *p*H 7·5 using acetate-borax buffer. Stoichiometric amount of the reagent to form a 1:2 complex in aqueous ethanol was added to the cobalt(II) solution in cold under nitrogen atmosphere. The precipitate was allowed to settle, filtered, washed with warm water and finally with 20% ethanol and dried at 110°. The composition of the complex was ascertained by estimating cobalt gravimetrically. Methyl ethyl ketone, the solvent used in the exchange study was purified by the method recommended by Walden[4]. Cobalt(II) perchlorate (BDH Analar), sodium perchlorate (E. Merck) were used as such.

Solutions of cobalt(II) perchlorate labelled with ^{60}Co and of the complexes were prepared in methyl ethyl ketone. Sodium perchlorate was used to maintain the ionic strength. Predetermined volumes of the complex and labelled cobalt(II) solutions were mixed and the ionic strength of the mixture adjusted to the desired value. The mixture was kept in a thermostat bath at $30{\cdot}0 \pm 0{\cdot}01°$. The course of the exchange was followed by measuring the activity appearing in the initially inactive complex with time after separation from the reactants in the following manner. A 2 ml aliquot of the reaction mixture was withdrawn and treated with 2 ml of water and 0·5 ml of chloroform. Most of the complex was extracted into the methyl ethyl ketone-chloroform layer while cobalt remained in the aqueous phase. The organic phase was separated and washed with the same volumes of water-chloroform and an accurately measured aliquot was transferred to a counting tube. The activity of the samples was measured under the 1·3 MeV photopeak of ^{60}Co using a gamma ray spectrometer type GRS 20B with a single channel analyser and $3{\cdot}6 \times 5{\cdot}9$ cm NaI(Tl) crystal with $1{\cdot}6 \times 3{\cdot}9$ cm well (Trombay Electronic Instruments).

The details of the procedure employed for the calculation of the exchange rates has been reported earlier[5]. The half-times and rates obtained for the exchange of cobalt between the complex and the free cobalt(II) ion for the complexes studied are given in Table 1.

In all the three complexes the exchange reaction was found to obey the second order kinetics. The energy of activation of the exchange process was determined in the case of bis-2-hydroxyacetophenone oxime Co(II) complex from the exchange rates at 30° and 40° and the value was found to be 16·55 kcal. These factors indicate that the most probable mechanism for the exchange is the collision between the cobalt ion and the molecule of the complex, similar to that suggested by Calvin and Duffield for the salicylaldoxime derivatives[6].

TABLE 1 — EXCHANGE DATA OF THE Co(II) COMPLEXES

{[Co(II] = $1{\cdot}68 \times 10^{-3}M$; [complex] = $0{\cdot}5 \times 10^{-3}M$; [NaClO$_4$] = $0{\cdot}2M$; temp. 30°}

Complex	Half-time of exchange (min)	Rate of the exchange reaction $\times 10^6$ mole litre^{-1} min^{-1}
Bis-2-hydroxyacetophenone oxime Co(II)	48·9 (16·1)	5·47 (13·20)
Bis-resacetophenone oxime Co(II)	31·2	8·68
Bis-5-nitroresacetophenone oxime Co(II)	20·4	13·10

Values in parentheses were obtained at 40°.

As the rates of exchange for the three complexes were determined under identical conditions of temperature, ionic strength and solvent, the differences in the rates of exchange observed could be attributed to the effect of substituents in the ligand. In the case of the bis-resacetophenone oxime Co(II) complex the hydroxyl group in the *para* position will decrease the electron density due to resonance effect on the chelating nitrogen atom and hence the metal-ligand bonds in this complex would be weaker and the cobalt is expected to exchange faster than that containing unsubstituted ligand. This conclusion is in accordance with the experimental observation. Similar arguments hold good for the bis-5-nitroresacetophenone oxime Co(II) complex. The observed exchange rate is hence in order.

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Determination of Hexacyanoferrate(III) Using a Mercury Reductor

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The method consists in reducing hexacyanoferrate(III) in 0·5-1·5*M* hydrochloric acid in a mercury reductor and titrating the ferrate(II) formed with cerium(IV) sulphate (in 0·2-1·0*M* hydrochloric acid medium) using ferroin as indicator. A mixture of hexacyanoferrate(III) and ferrate(II) can also be analysed by this method using the same oxidant. The method is accurate and convenient.

NUMEROUS methods are available[1-36] for the titrimetric determination of hexacyanoferrate(III) both in acid and alkaline media. In most of these methods, hexacyanoferrate(III) is either titrated with a variety of reducing agents including metal and metal amalgam reductors or it is treated with an excess of a reducing agent and the excess back titrated with a standard oxidant. In yet another category of methods, hexacyanoferrate(III) in acid solution is treated with excess of potassium iodide and the iodine liberated determined either with hypo[37-39], arsenite[40], or sodium sulphite[41] employing a potentiometric or starch end-point method.

Apart from the low accuracy involved, most of these methods suffer from the disadvantage that the preparation and preservation of the reductants or metal reductors are tedious. Further, the titrations have to be often carried out in an inert atmosphere. The only satisfactory method appears to be that of Kolthoff[37] which consists in treating an acid solution of hexacyanoferrate(III) with potassium iodide and titrating the liberated iodine with standard hypo. We have now developed an accurate and convenient method for the determination of hexacyanoferrate(III) using a mercury reductor. The present method has the further advantage that it enables the determination of both hexacyanoferrate(III) and ferrate(II) using the same oxidant.

An approximately 0·05M solution of cerium(IV) sulphate was prepared and standardized[42]. A 0·05M aqueous solution of potassium hexacyanoferrate(III) (BDH, AR) was prepared and standardized[37]. A 0·01M solution of ferroin was employed. All other chemicals used in the present investigation were of analytical grade.

Procedure — To 5-25 ml of hexacyanoferrate(III) taken in a mercury reductor enough water and 6M hydrochloric acid were added to give an overall hydrochloric acid concentration of 0·5-1·5M when diluted to about 50 ml. A rapid stream of carbon dioxide was passed into the solution for about 5 min to displace the air present, the reductor stoppered immediately and shaken vigorously for 3-4 min. The supernatant solution was first decanted into a 250 ml beaker and then filtered into a 500 ml suction flask through a G_4 filter. The reductor was washed four times (each time using about 15 ml water and swirling for about 5 sec) and the washings collected into the previous filtrate. Finally, the beaker and filter disc were washed twice with 15 ml portions of N hydrochloric acid and the washings collected into the same filtrate. The reduced solution was titrated immediately with cerium(IV) sulphate using four drops of ferroin as indicator. The hydrochloric acid concentration, during the titration should be 0·2-1M to get reproducible results. A constant blank correction of 0·14 ml of 0·05M cerium(IV) sulphate was found to be necessary; of this 0·04 ml corresponded to the indicator correction and the remaining 0·1 ml to a small amount of hydrogen peroxide formed in the reductor.

To determine hexacyanoferrate(III) and ferrate-(II) in a mixture, an aliquot of the mixture was titrated directly with cerium(IV) sulphate using ferroin as indicator. This gives hexacyanoferrate(II) content in the mixture. Another aliquot was reduced as above and titrated as usual. The difference between the two titres gives the ferrate(III) content.

TABLE 1 — DETERMINATION OF HEXACYANOFERRATE(III)

$K_3[Fe(CN)_6]$ (mg)		$K_3[Fe(CN)_6]$ (mg)	
Taken	Found	Taken	Found
121·3	121·3	300·0	300·0
144·3	144·2	360·9	360·6
163·9	163·9	409·6	409·8
189·3	189·3		

TABLE 2 — DETERMINATION OF HEXACYANOFERRATE(III) AND FERRATE(II) IN A BINARY MIXTURE

$K_4[Fe(CN)_6]$ (mg)		$K_3[Fe(CN)_6]$ (mg)	
Taken	Found	Taken	Found
105·3	105·3	81·91	81·96
105·3	105·3	327·7	327·8
421·0	421·1	81·96	81·96
292·1	292·2	180·3	180·3
210·6	210·6	164·1	163·9
134·8	135·0	204·8	204·6
193·7	193·5	98·35	98·35

Solutions containing known amounts of hexacyanoferrate(III) were analysed ten times according to the recommended procedure. Averages and relative standard deviations were: 82·03 mg, 0·04% (82·04 mg taken); 164·08 mg, 0·06% (164·1 mg taken); 328·21 mg, 0·03% (328·2 mg taken).

Some typical results obtained for the determination of ferrate(III) and for ferrate(III) and ferrate(II) in a mixture are recorded in Tables 1 and 2 respectively.

The hexacyanoferrate(II) solution obtained by this method is stable only for 15 min. Afterwards, a blue colour develops slowly resulting in a gradual decrease in the titre. This blue colour which gradually intensifies with time is probably due to the mercuric ion (formed in traces during the course of reduction)[43] catalysed formation of prussian blue[44], $KFe[Fe(CN)_6]$. However, if required, the solution can be kept stable for 1 hr by increasing the hydrochloric acid concentration in the filtrate to 1·5M or above.

Phosphate and nitrate ions up to overall concentrations of 0·01 and 0·02M respectively (in the reductor) and sulphate, acetate and perchlorate ions do not interfere in this method. The interference of these ions is studied using the corresponding acids.

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Polarographic Reduction of Some Substituted Phenylthioureas

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Polarographic reduction of substituted phenylthioureas in Britton-Robinson buffers and in 0·1*M* NaOH gives one well-defined, diffusion-controlled, partially irreversible, two-electron transfer oxidation waves. Below *p*H 5·0 ill-defined waves are obtained. The $E_{1/2}$ shifts towards more negative value with the increase in *p*H and towards more positive potential with the increase in [depolarizer]. Phenylthioureas do not undergo direct oxidation but form mercurous complex with mercury at d.m.e. This is further supported by the effect of substituents on $E_{1/2}$.

POLAROGRAPHIC investigations on thiols and sulphydryl compounds have been carried out by a number of workers[1,2]. Two aspects have been generally studied: (i) practical applicability of the double waves of these compounds for diagnostic purpose; and (ii) anodic depolarization. In the latter case the general electrode process is represented by the reaction

$$\text{R-SH}+\text{Hg}\rightarrow\text{R-S-Hg}+\text{H}^{+}+e$$

Generally the electrode process is irreversible but in a few cases reversibility has also been claimed. Another class of compounds which could exhibit one of the above mentioned polarographic behaviour may be the thioureas. Detailed studies on the polarography of these compounds especially on phenylthioureas have not been undertaken so far. In this communication we report our results on the polarographic behaviour of substituted phenylthioureas.

Phenylthiourea and 2-methyl-, 3-methyl-, 4-methyl-, 4-chloro-, 4-bromo-, 4-methoxy- and 4-ethoxy-phenylthioureas were synthesized in the laboratory by the action of ammonium thiocyanate on the hydrochloride of the corresponding amine[3,4].

0·01*M* solution of each of the above mentioned thioureas was prepared in dimethylformamide (AR). The polarograms were recorded on a Cambridge pen recording polarograph. The capillary characteristic was 3·75 mg$^{2/3}$ sec$^{-1/2}$. The temperature coefficient was calculated by using Nejedly's method[6] and the value of n, the number of electrons involved in the electrode process was calculated by the method of DeVries and Kroon[7] using a mercury pool cathode and calomel electrode as a reference.

The cell containing 10 ml of buffer was deoxygenated by bubbling it with purified nitrogen for 30 min prior to the recording of the polarogram. Similarly the polarograms of different thioureas were recorded in Britton-Robinson buffer[5] and in NaOH. Each limiting current was corrected for the residual current.

All the substituted phenylthioureas gave a single well-defined oxidation wave at d.m.e. in buffers and in the alkaline solution. In the case of B.R. buffers, well-defined waves were obtained at higher *p*H.

The nature of the oxidation waves was found to be diffusion-controlled as revealed by the linear dependance of wave height to $h^{1/2}$. The temperature coefficients of these thioureas were found to lie in the range 1·20% deg^{-1} to 1·60% deg^{-1}. The half-wave potential was found to shift towards more positive potential with increase in [depolarizer], suggesting thereby complex formation[8] rather than oxidation. Since the plots of $E_{\text{d.e.}}$ vs $[\log (i/i_d-i)]$ were not linear, the waves were analysed for irreversible nature, employing Koutecky's equation[9] for irreversible cathodic wave

$$E_{\text{d.e.}}=E^{\circ}_{1/2}+0{\cdot}0542/(1-\alpha)n\ [\log i/(i_d-i)-0{\cdot}546 \log t]$$

where

$$E^{\circ}_{1/2}=-0{\cdot}2412-0{\cdot}05915/(1-\alpha)n\ \log\ 1{\cdot}349K^{\circ}_{b,h}/D_0^{1/2}$$

The plots of $E_{\text{d.e.}}$ vs $[\log (i/i_d-i)-0{\cdot}546 \log t]$ are linear and the value of α and $K^{\circ}_{b,h}$ calculated from

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