

i.e., $+ 32 \pm 5 \text{ cm}^{-1}$, in agreement with the change predicted for bridge formation¹⁸. However, from the present results we are not sure whether nitrogen end of CN^- is coordinated to cobalt atom of $\text{Co}(\text{salen})\text{CH}_3$ moiety or to $\text{Co}(\text{dmgh})_2\text{CH}_3$ moiety. In this respect it may be mentioned that linkage isomerisms of a bridging cyanide group is possible in $(\text{NH}_3)_5\text{Co NC Co}(\text{CN})_5\text{H}_2\text{O}$ and $(\text{NH}_3)_5\text{Co CN Co}(\text{CN})_5\text{H}_2\text{O}$ ¹⁹. Labilizations of trans ligand (here water molecule) by σ -bonded methyl group might help to form the cyano-bridged complexes (IV) and (V).

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Redox Reactions in Non-aqueous Media. Determination of Alkyl/Arylammonium Alkyl/Aryldithiocarbamates with Iodine and Iodine Halides

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NON-AQUEOUS solvents are important for the redox determination of those compounds which are slightly soluble in water or react with it through hydrolysis or oxidation, or are decomposed by the media of aqueous redox titrations. The problems associated with the redox determination in aqueous media of dithiocarbamates, firstly because of their tendency to undergo decomposition with acids which serve as the media of aqueous redox titrations and secondly because of the interference of their insoluble oxidation products (thiuram disulphides), can be avoided if non-aqueous redox methods are used for the purpose. However, most of such work has been reported for water soluble dithiocarbamates. Verma and Kumar^{1,2} have recently described the use of iodine, iodine halides and N-bromosuccinimide (in acetonitrile) for the determination of these compounds in acetonitrile medium. Paul *et al.*^{3,4} carried out the determination of these compounds potentiometrically with iodine cyanide in alcohol, alcohol-chloroform or acetone medium; and with bromide cyanide in alcohol or acetonitrile medium.

Monoalkyl/arylammonium monoalkyl/aryldithiocarbamates and dialkyl/arylammonium dialkyl/aryldithiocarbamates which are prepared^{5,6} through the reactions of primary and secondary amines with carbon disulphide in organic solvents, have been put to various uses⁷. These compounds, unlike sodium/potassium salts of dithiocarbamic acid, are only sparingly soluble in water and hence the determination of these compounds by non-aqueous redox methods has the added advantage. No effort in this direction appears to have been made.

The present communication reports the direct visual and potentiometric non-aqueous redox determination of these compounds with iodine and iodine halides using acetonitrile as a solvent both for the preparation of oxidant solution as well as media of titration. The potentiometric titrations have been performed using a bright platinum wire as indicator electrode and modified -calomel or antimony electrode as reference electrode. The proposed method for the determination of alkyl/arylammonium alkyl/aryldithiocarbamates are simple, rapid, accurate and widely applicable.

Experimental

Reagents and Equipment; Acetonitrile of BDH quality was distilled twice over phosphorus pentoxide (5 g/l).

NOTES

Iodine monobromide (solid) was prepared by the Method of Popov and Skelly⁷. Iodine and Iodine trichloride were of BDH 'AnalaR' grade. Iodine monochloride was of E. Merck quality. Each oxidant solution (0.05N in acetonitrile) was prepared by dissolving a little more than the calculated amount in the solvent. Iodine solution was standardised by titration against standard aqueous sodium thiosulphate. Iodine halides solutions were however standardised iodometrically in aqueous acidic medium.

Alkyl / arylammonium alkyl / arylthiocarbamates were prepared by reported methods^{6,8}. The compounds were kept in vacuum desiccators.

All other chemicals used in this investigation were of guaranteed quality.

Potentiometric titrations were performed with TOSHNIWAL titration potentiometric (type CLO6A), using bright platinum wire indicator electrode and modified-calomel (methanol saturated with potassium

chloride used instead of aqueous potassium chloride) or antimony electrode as reference electrode.

Microburette, 10 ml capacity, graduated in 0.01 ml divisions, was used.

Procedure :

Aliquots of solutions in acetonitrile of each compound were taken in a conical flask (for visual titrations) or a beaker (for potentiometric titrations) and the volume made to 30-35 ml with the solvent. The solution was cooled to room temperature ($\sim 25^\circ$) in each case and titrated visually and potentiometrically with standard (0.05 N) iodine and iodine halides (monobromide, monochloride or trichloride) solutions (in acetonitrile) run from a microburette provides with a guard tube for the protection of oxidant solution from atmospheric moisture. In visual titrations, the end-point was signalled by the yellow tint imparted to the solution by the first drop of oxidant in excess. A sharp jump in potential was observed at the equivalence point in each potentiometric titration.

TABLE 1—TITRATIONS OF ALKYLAMMONIUM ALKYLDITHIOCARBAMATES WITH STANDARD (0.05N) IODINE MONOBROMIDE IN ACETONITRILE.

Compound	Values are means of ten determinations with standard deviations (\pm)								Inflection point ^{††} mV	Potential jump ^{††} per 0.05 ml of 0.05N IBr mV
	Amount found*, mg				Amount found*, mg					
	Visual method	Potentiometric method	Visual method	Potentiometric method	Visual method	Potentiometric method	Visual method	Potentiometric method		
Dithiocarbamates (Mono/dialkylammonium salts)										
Methyl	10.01, 0.037	10.00, 0.031	40.06, 0.078	40.02, 0.058	—(165 to 200)	260 to 325				
Ethyl	10.02, 0.033	9.99, 0.032	40.12, 0.069	40.03, 0.062	—(170 to 215)	265 to 320				
Isopropyl	10.00, 0.039	9.97, 0.025	39.98, 0.082	40.00, 0.048	—(160 to 210)	270 to 330				
n-Propyl	9.99, 0.034	9.99, 0.031	39.94, 0.069	39.92, 0.047	—(165 to 200)	270 to 315				
Isobutyl	9.99, 0.035	10.00, 0.032	40.05, 0.076	40.03, 0.056	—(160 to 200)	265 to 320				
Sec.-butyl	10.04, 0.040	10.00, 0.033	40.11, 0.077	40.04, 0.046	—(175 to 205)	260 to 310				
n-Butyl	10.04, 0.037	9.99, 0.035	40.12, 0.081	40.05, 0.054	—(160 to 195)	240 to 285				
n-Amyl	10.05, 0.035	10.01, 0.029	40.08, 0.074	40.09, 0.041	—(170 to 200)	245 to 295				
n-Hexyl	9.98, 0.031	9.99, 0.031	39.91, 0.072	39.90, 0.042	—(165 to 190)	250 to 295				
β -Hydroxyethyl	10.01, 0.028	9.99, 0.024	39.94, 0.078	39.96, 0.058	—(180 to 220)	285 to 320				
Morpholyl	9.97, 0.036	9.97, 0.028	39.88, 0.082	39.90, 0.061	—(185 to 210)	260 to 325				
Piperidyl	9.96, 0.035	9.96, 0.029	40.02, 0.069	39.98, 0.054	—(180 to 215)	260 to 320				
Pyrrolidyl	10.04, 0.032	10.01, 0.024	40.08, 0.071	40.05, 0.047	—(170 to 190)	245 to 315				
Dimethyl	10.03, 0.034	10.00, 0.025	40.12, 0.068	40.06, 0.057	—(175 to 200)	250 to 315				
Diethyl	10.01, 0.036	10.00, 0.026	40.03, 0.074	40.00, 0.049	—(170 to 195)	260 to 315				
Di-n-propyl	10.02, 0.041	9.99, 0.036	39.96, 0.078	39.96, 0.056	—(160 to 190)	270 to 320				
Di-n-butyl	10.00, 0.035	9.99, 0.025	39.95, 0.073	39.96, 0.053	—(165 to 190)	270 to 325				
Benzyl	9.96, 0.033	9.94, 0.027	39.93, 0.073	39.95, 0.051	—(170 to 195)	260 to 310				
β -Phenylethyl	9.98, 0.035	9.98, 0.026	40.02, 0.076	39.97, 0.047	—(175 to 200)	240 to 300				

*Amount taken, 10 mg

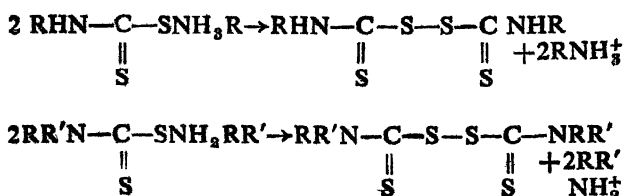
*Amount taken, 40 mg

††Range of ten determinations.

From the volume of iodine or iodine halide solution used corresponding to the equivalence point in visual and potentiometric titrations, the amount of each compound was calculated. The results of determination of the compounds with iodine monobromide (as a representative of these oxidants) are given in Table 1. Since the results obtained by potentiometric titrations using platinum-modified calomel electrode assembly agree closely with those obtained with platinum-antimony electrode assembly, hence for sake of convenience, only the former are recorded in the Table. The inflection points and potentials jumps corresponding to each compound are also recorded in the Table.

Results and Discussion

The determination of alkyl / arylammonium alkyl / arylthiocarbamates with iodine or iodine halides is based on their oxidation to the corresponding substituted thiuram disulphides.



R, R' = alkyl or aryl group (same or different)

The results obtained for the determination of these compounds with iodine and iodine halides agree so well among themselves that it would be appropriate to mention the results with one of the oxidant only. Results with iodine monobromide are recorded in Table 1. The overall standard deviation calculated from the pooled data of all the visual and potentiometric titrations performed with 10 mg of each dithiocarbamate have been found to be 0.035 and 0.029 respectively. The same for 40 mg samples are 0.075 and 0.052 respectively. The potential jump at the equivalence point in titrations of dithiocarbamates with iodine monobromide in acetonitrile medium using platinum-modified calomel electrode assembly have been found to be of the order of 240 to 330 mV with the addition of 0.05 ml of 0.05 N oxidant solution. Using platinum-antimony electrode assembly, the jump in potential is of the order of 270 to 375 mV with the addition of 0.05 ml of 0.05 N oxidant solution.

The effect of some typical compounds in the titrations of alkyl/arylammonium alkyl/aryldithiocarbamates with iodine and iodine halides was studied by the recommended procedure in the usual way. No interferences were found from alkyl isothiocyanates, isocyanates, urea and carbon disulphide even when present in upto 6-fold amounts relative to dithiocarbamate. Amines, thioacetamide and mercaptans interfered.

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Solvent Extraction and Spectrophotometric Determination of Zinc with Thiobenzoylacetone

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ACETYLACETONE¹⁻³ proved to be an inefficient extractant for zinc, while benzoylacetone and dibenzoylmethane⁴ extracted it from highly alkaline media. 2-Thenoyltrifluoroacetone⁵ and thiothenoyltrifluoroacetone⁵ and thenoyltrifluoroacetone in presence of tributyl phosphate⁶ were also used for the extraction of zinc. Thiothenoyltrifluoroacetone⁷ and thiodibenzoylmethane⁸ when used as extractants, improved the selectivity to some extent. This paper presents a better method for the extractive spectrophotometric determination of zinc with thiobenzoylacetone.

Experimental

Apparatus: Spektromom-204 spectrophotometer with matched 10 mm quartz cells. Digital pH meter (ECIL, India), pH-822 model with glass and calomel electrodes. Wrist action flask shaker (Toshniwal and Co., India).

Reagents: Thiobenzoylacetone (HSBA) was synthesised from benzoylacetone (Fluka, England) as per the procedure described earlier⁹. A 5×10^{-4} M solution in benzene was used and was always preserved in a refrigerator.

A stock solution of zinc was prepared by dissolving 5.50 g. of zinc sulphate heptahydrate (BDH, AnalaR) in 250 ml. of distilled water. The solution on standardization complexometrically¹⁰ was found to contain 5 mg./ml. of zinc. A dilute solution containing 2 µg./ml. of zinc was prepared by appropriate dilution.