Determination of Thiocarbamides‡

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NEWLY synthesised thiocarbamides[1], 1-phenyl-3-benzoyl thiocarbamide (PBT), 1-*p*-tolyl-3-benzoyl thiocarbamide (TBT), 1-*p*-chlorophenyl-3-benzoyl thiocarbamide (CBT) and 1-pyridyl-3-benzoyl thiocarbamide (PYBT), have been found to be useful potential reagents for different analytical studies[2]. However, their quantitative estimation has not been attempted. Therefore in this paper determination of thiocarbamides in acetone medium has been carried out by enthalpimetric, conductometric and potentiometric titrations and results are compared.

Experimental

Reagents :

(1) Acetone-Acetone C.P. grade, purified by usual methods[3] was used.

(2) Titrants-Three titrants, Tetra-*n*-butyl ammonium hydroxide ($TBuNH_4OH$), potassium-hydroxide in isopropyl alcohol (Alc.KOH) and potassium tertiary butoxide in tertiary butyl alcohol (tert.BuOK), were prepared by standard methods and preserved as described earlier[4]. They were protected from atmospheric moisture and carbon dioxide.

(3) Thiocarbamides-4 different thiocarbamides were prepared by the action of benzoyl isothiocyanate on corresponding amine[1] at 0°. The product was recrystallized from ethyl alcohol. The melting points and molecular weights were found to be.

	m.p. °C	Mol. Wt.
(1) 1-phenyl-3-benzoyl thiocarbamide (PBT)	155	256.5
(2) 1-*p*-tolyl-3-benzoyl thiocarbamide (TBT)	157	270.0
(3) 1-*p*-chlorophenyl-3-benzoyl thiocarbamide (CBT)	121	290.0
(4) 1-pyridyl-3-benzoyl thiocarbamide (PyBT)	143	258.0

Instruments and Procedure :

All titrations were carried in nitrogen atmosphere. The end points were always determined graphically. Results of enthalpimetric, conductometric and potentiometric titrations of thiocarbamides were compared.

Results and Discussion

Effect of titrants : In order to select the proper titrant, three titrants TB_uNH_4OH, Alc. KOH and tert-B_uOK were tried by three different techniques. Results obtained show that Alc.KOH gives the best results in enthalpimetric, conductometric and potentiometric titrations of PBT. It also gives minimum errors in the estimation of TBT, CBT and PyBT by different methods. Hence Alc.KOH is selected as the most suitable titrant for further investigation.

Effect of concentration : Experiments were performed to find out the effect of concentration on the estimation of thiocarbamides and the limits of estimation by different techniques under present experimental conditions were determined. Comparison of results obtained, show that potentiometric titrations gave the best results in the estimation of thiocarbamides. Maximum errors, for PBT, TBT, CBT and PyBT were 1.1%, 1.3%, 0.9% and 0.9% respectively. The method was found to be most accurate for estimation of 1 to 20 mg of thiocarbamides under experimental conditions. However, titrations required longer time and very often end point had to be determined by plotting a graph for $\frac{E}{V}$ against volume of base added.

In conductometric titrations graph for conductance vs volume of Alc.KOH did not show sharp break and location of end point was difficult. Errors in estimation were also relatively larger (Maximum errors for PBT, TBT, CBT and PyBT were 2.9%, 2.3%, 2.5% and 2.8% respectively). However, the method can be used for determination of 1 to 20 mg of the compounds.

Enthalpimetric titrations show peculiar behaviour. Smaller weights of thiocarbamides (less than 14 mg) gave sufficiently accurate results. Maximum errors were 1.5%, 2.0%, 1.7% and 1.7% for PBT, TBT, CBT and PyBT respectively. But for larger amounts of compounds (14 mg or more) the results obtained were lower. This is probably due to the fact that volume of solvent used in enthalpimetric titrations was smaller (5 ml) as compared to those for potentiometric and conductometric titrations (25 ml). Under these conditions incomplete ionisation of weakly acidic solute gives lower results for higher concentrations of the solute. However, for lower concentrations, liberation of proton and subsequent reaction with alkali (Alc.KOH) is complete and hence the results are satisfactory.

It is seen that enthalpimetric titrations can be precisely used for the estimation of 1 to 12 mg of PBT and TBT, and 1 to 14 mg of CBT and PyBT.

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The method has an added advantage that it is quicker and simpler as compared to conductometric and potentiometric methods and hence is recommended for quick analysis of thiocarbamides upto 10 mg.

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References

1. G. V. K. NAIR, *J. Indian Chem. Soc.*, 1963, **40**, 953.
2. (Miss) H. B. PATHAK, Project Report, Nagpur University, Nagpur, 1978.
3. J. KUCHARSKY and L. SAFARIK, 'Titration in Non-aqueous Solvents', 2nd ed, Elsevier Publishing Co., New York, 1964.
4. D. S. SABDE and R. B. KHARAT, *J. Indian Chem. Soc.*, 1980, **57**, 53.

Analytical Applications of DEAPG as Gravimetric Reagent III : Estimation of Au(III)

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P-DIETHYLAMINOANIL of phenylglyoxal (abbreviated as DEAPG) precipitates gold(III) quantitatively and gives grey coloured complex in the *p*H range 5.0 ± 1.0 by adding double to triple theoretical quantity of the ligand. It can be used for the gravimetric estimation of Au(III) either alone or in the presence of foreign ions.

A perusal of literature on gravimetric analysis of metals reveals that many organic compounds have been used in the inorganic quantitative estimations but ketoanils[1-3] have been rarely employed as precipitating reagents. Moreover gravimetric estimations of noble metals[4-8], viz., Au(III) etc have not been carried out to good extent. Some references[9-10] on the gravimetric estimation of Au(III) are available but no attempt has been made in the quantitative estimation of this ion by employing ketoanil (DEAPG) as precipitating reagent so far. However, estimation of Hg(II) and Pt(IV) with this ligand have been done by authors[11-12]. The present paper aims at using the same ligand for the gravimetric determination of Au(III). The work incorporated in this paper describes the suitable conditions for the precipitation of metal ions by the ligand.

Experimental

Stock solution of metal chloride (J. M. C., London) was prepared by dissolving pure compound in alcohol and was used after standardisation by standard methods[13]. Standard solution of ligand was prepared by dissolving its directly weighed quantity in the same medium. All the reagents and chemicals used were of either B.D.H. or E. Merck, A. R. and G. R. grades respectively. Ligand was prepared by method reported by Verma[14].

The *p*H of the solution was adjusted by using hydrochloric acid and sodium hydroxide. A Phillips *p*H meter with glass and saturated calomel electrodes was used for *p*H measurements. G4-sintered glass crucibles (JENA) were used for gravimetric estimations.

In the gravimetric estimations Au(III) chloride solution was diluted with double distilled water ten times to the initial volume before adding the precipitant. Reagent solution was added very slowly with constant stirring to the metal chloride solution till in slight excess. The quantitative reaction was ensured by adjusting *p*H with alcoholic solution of acid and alkali. Reaction mixture was left for four hours and was collected on sintered glass crucible. The precipitate of the complex was washed with ether till free from excess reagent and was dried to constant weight.

Au(III) – DEAPG complex was found soluble in acetone alcohol and methyl cyanide but insoluble in benzene, petroleum ether, carbon-tetrachloride and ether. It was decomposed by conc. nitric and sulphuric acids.

Results and Discussion

Effect of pH, reagent concentration and temperature :

The effect of *p*H, ligand concentration and temperature has been observed with 4.0 ml of metal chloride solution containing 19.126 mg metal. A perusal of data reveals that the weights of the precipitate were almost corresponding to the theoretical values of Au(III) – DEAPG complex at *p*H 5.0 ± 1.0 in the temperature range of 100-110° by the addition of double to triple theoretical quantity of the ligand. Grey coloured complex [Au(DEAPG)Cl. H_2O]Cl_2 was found stable above 180°

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