3400 © *1989 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.,* ***62,*** *3400—3402 (1989)* [Vol. 62, No. 10

Extraction and Spectrophotometric Determination of Rhenium(VII) with Thiocyanate and Amides

Neera Mishra, S. K. Sinha, K. S. Patel,* and R. K. Mishra
Department of Chemistry, Ravishankar University, Raipur-492010, M. P., India

(Received October 20, 1988)

Synopsis. A new spectrophotometric method for determining rhenium with thiocyanate and organic reagents such as amides, thioamide and hydrazide over 2.0—6.0 mol dm^{-3} H_2SO_4 is described. The molar absorptivity of the complexes in the organic solvents are (2.57—3.01)$\times 10^4$ l mol^{-1} cm^{-1} at absorption maximum. Of these, *N*-phenylacetamide (PAA) has been chosen for detailed studies. The detection limit of the method with PAA is 0.03 μg Re cm^{-3}. The effect of kinds of acids, solvents or reagents and of diverse ions is discussed.

Several spectrophotometric methods for the determination of rhenium have been reported.[1-8] Of these, the classical thiocyanate method is one of the most popular method for the spectrophotometric determination of the metal but it suffers from some experimental difficulties.[1] Thiourea[2] and hexamethylphosphoric triamide[3] were proposed to enhance the selectivity of the classical thiocyanate method, however they require a prolonged heating or extraction and involve the interference of some metals. Oximes were employed as sensitive reagents too but they lack selectivity.[4-6] The sulfur containing reagents like 5,6-diphenyl-3-hydroxy-1,2,4-triazine-3(2*H*)-thione[7] and di-2-pyridyl ketone 2-furyl(thiocarbonyl)-hydrazone[8] were reported for the extraction and spectrophotometric determination of the metal and subject to serious interference from the metal ions. The purpose of this work is to develop a selective and sensitive extraction-spectrophotometric method for rhenium(VII) with a series of commonly available reagents such as *N*-(alkyl or aryl)acetamides, *N*-(2-pyridyl)-thiobenzamide ($C_6H_5CSNHC_5H_4N$), and *N′*-phenylacetohydrazide ($CH_3CONHC_6H_5$) in presence of thiocyanate ion. Of ten compound reported, the simplest one, *N*-phenylacetamide ($CH_3CONHC_6H_5$) was chosen for detailed studies in the present investigation. The method is applicable over wide acidity range, and removes most of interferences of classical thiocyanate method with improved sensitivity.

Experimental

Reagents. A standard solution of rhenium(VII) was prepared by dissolving (0.5 g) accurately weighed potassium perrhenate in double distilled water. Amides, thioamide, and hydrazide were synthesized as described in the literature.[9] Solutions of amides (1.2—2%) in benzene, and solutions of *N*-(1-naphthyl)acetamide, *N*-(2-pyridyl)thiobenzamide, or *N′*-phenylacetohydrazide (2—3.8%) in chloroform were employed for extraction work. All chemicals and reagents used were of analytical grade (E. Merck). In the case of benzene, all solutions employed were presaturated with benzene.

Procedure. A tin(II) chloride solution (2 cm^3) and 5 cm^3 of 10 mol dm^{-3} H_2SO_4 were added to a perrhenate solution (5—90 μg Re) in a 100-cm^3 separatory funnel, the mixture was reacted with 2 cm^3 potassium thiocyanate solution and diluted to 15 cm^3 with distilled water. The metal complex was extracted with 15 cm^3 benzene solution of the organic reagent for 2 min. The absorbance of the complex was measured at λ_{max} against reagent blank. In the case of *N*-(2-pyridyl)thiobenzamide, *N′*-phenylacetohydrozide, or *N*-(1-naphthyl)acetamide the metal complex was extracted with 15 cm^3 chloroform solution of the reagent and washed with 3$\times$2 cm^3 fresh portions of chloroform. All the dried extract was transferred into a 25-cm^3 volumetric flask and diluted with chloroform to the mark. The absorbance of the complex was measured at λ_{max} against reagent blank.

Results and Discussion

Absorption Spectra. Figure 1 shows the absorption spectra of Re(IV)-SCN$^-$-PAA complex and the reagent blank in benzene. All the complexes of Re(IV) with amides and hydrazide exhibit an absorption maximum around 435 nm while with thiobenzamide at 438 nm. As the reagent shows an absorption at the λ_{max} of the complex, the reagent blank was used as a reference for all measurements.

Choice of Solvents. The extraction of Re(IV)-SCN$^-$ with PAA into various solvents like 1-pentanol, isobutyl methyl ketone, ethyl acetate, chloroform, carbon tetrachloride, benzene, and toluene was performed. The complex was quantitatively extracted in these solvents except carbon tetrachloride (the maximum extraction of the complex require a triple extraction) showing the value of molar absorptivity to be in the range of (2.43—2.70)$\times 10^4$ dm^3 mol^{-1} cm^{-1} at λ_{max} 430—435 nm. Of these, benzene was used for further experimental work due to the most sensitive

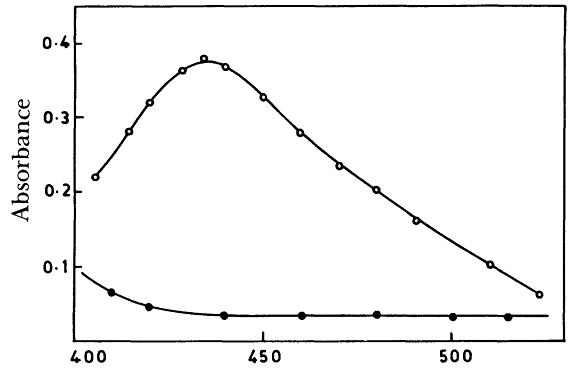

Fig. 1. Absorption spectra of *N*-phenylacetamide (PAA) blank and [ReO(SCN)$_2$(PAA)$_2$] in benzene. [H_2SO_4]=4 mol dm^{-3}; [Sn^{2+}]=0.03 mol dm^{-3}; [$S\bar{C}N$]=0.26 mol dm^{-3}. (—○—), [ReO(SCN)$_2$-(PAA)$_2$], [Re^{7+}]=1.43$\times 10^{-5}$ mol dm^{-3}; (—●—) 0.1 mol dm^{-3} PAA in benzene after equilibration.

color reaction in it.

Effect of Acidity. The effect of acids like HCl and H_2SO_4 (10 mol dm^{-3}) on the extraction of Re(IV)-SCN$^-$ with PAA in benzene was studied. With H_2SO_4 in aqueous solution, the rate of extraction was relatively fast and the color intensity of the complex in organic solvent was higher than with HCl. The modified property in hydrochloric acid media is due to further reaction of the thiocyanato or chloro complex species with excess of tin(II) ions.[10] The optimum acidity range was found to be 2.0—6.0 mol dm^{-3} H_2SO_4 with PAA in benzene.

Effect of Reagents and Other Variables. The effect of amount of reagents on the extraction of the metal was examined at 4 mol dm^{-3} H_2SO_4. The reduction of Re(VII) into Re(IV) was made by tin(II) ions and 0.015—0.05 mol dm^{-3} tin(II) ions was adequate for the extraction of the metal. At least 0.15 mol dm^{-3} KSCN and 0.06 mol dm^{-3} PAA (in benzene) were necessary for the maximum color development of the complex in the organic solution, and the addition of more KSCN and PAA up to 0.6 and 0.19 mol dm^{-3}, respectively, caused no adverse effect. The order sequence of addition of reagents was not critical. The variation in volume ratio of the organic to the aqueous phase from 3 : 1 to 3 : 5 did not affect the distribution of the metal. The extract was stable for at least 4 h at room temperature (≈27 °C). The effect of electrolytes i.e. KCl and $(NH_4)_2SO_4$ in extraction of the metal was examined and absorbance of the complex was intact up to 1 mol dm^{-3} KCl or $(NH_4)_2SO_4$.

Stoichiometry of Extraction. The mechanism involved in the reduction of ReO_4^- with tin(II) chloride in the presence of thiocyanate was studied by various workers.[10—12] The formation of $[ReO(SCN)_5]^{2-}$, $[Re(SCN)_6]$, or $[Re(SCN)_6]^-$ has been reported, and the addition of excess Sn^{2+} leads to formation of $[Re(SCN)_6]^{2-}$, exclusively. According to Pavlova[10] the most probable reduced state of rhenium participating in the extraction is Re(IV). In the present investigation, the ratio of variables in the complex was evaluated by plots of logarithm distribution ratio of the metal versus logarithm thiocyanate concentration in the aqueous solution and PAA concentration in the organic solution at equilibrium. Figure 2 shows the slope of these plots to be 1.9 and 2.0, respectively. Since these values are close to 2, the possible reaction mechanism can be written as:

$$ReO^{2+} + n\,SCN^- + n'PAA_o \rightleftarrows [ReO(SCN)_n(PAA)_{n'}]_o$$

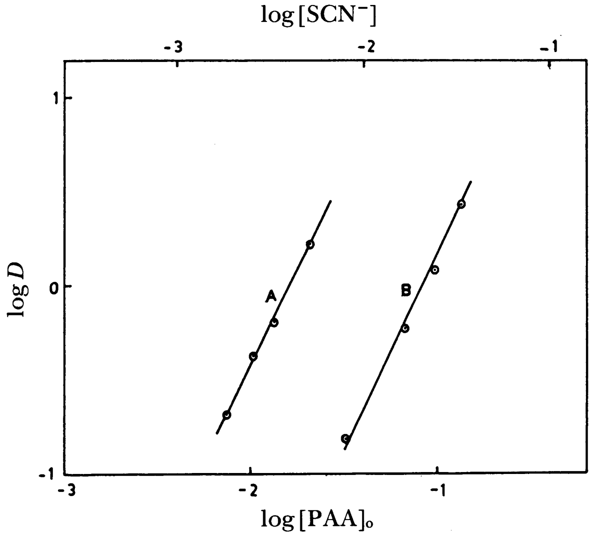

Fig. 2. Determination of the values of the variables in $[ReO(SCN)_n(PAA)_{n'}]$ in benzene. $[H_2SO_4]=4$ mol dm^{-3}; $[Sn^{2+}]=0.03$ mol dm^{-3}; $[Re^{7+}]=1.43\times10^{-5}$ mol dm^{-3}. (A), log (distribution ratio of the metal) versus $\log[PAA]_o$; $[S\bar{C}N]=0.26$ mol dm^{-3}. (B), log (distribution ratio of the metal) versus log $[S\bar{C}N]$; $[PAA]_o=0.1$ mol dm^{-3}.

For the simplest system, where the metal species in the aqueous phase is ReO^{2+} only and that of the complex is $[Re(SCN)_n(PAA)_{n'}]$ $\log D=\log K+n\log[SCN^-]+n'\log[PAA]_o$.

In present investigation, the value of D (distribution ratio of the metal) was evaluated by spectrophotometric method using the formulae, $D=A/A_{max}-A$. The distribution ratio of PAA in the organic solution is not very high, hence the effective concentration of the amide in the organic phase was determined by following equation.

$$[PAA]_o=\frac{Kd[PAA]_t}{1+Kd}$$

Where, o, Kd, D, K, $[PAA]_o$, $[PAA]_t$, A_{max}, and A represent the organic phase, distribution ratio of the reagent, distribution ratio of the metal, equilibrium or extraction constant, concentration of the reagent in the organic solution at equilibrium, total analytical concentration of the reagent in the organic solvent before equilibrium, maximum absorbance of the complex when the reagent is present in constant excess and absorbance of the complex when the reagent is in equilibrium, respectively.

Amides, Thioamides, and Hydrazide as Extraction Reagents. In the present investigation, the extraction potentiality of various amides, thioamides, and hydrazide towards Re(IV) in the presence of thiocyanate was examined. In amide series, acetamides derived from aliphatic or aromatic amines (except amines containing electron-withdrawing groups e.g. Cl, OH, etc.) are capable of extracting the metal. Chloroform is an adequate diluent for the extraction of the complex with *N*-(1-naphthyl)acetamide, *N*-(2-pyridyl)thiobenzamide, and *N'*-phenylacetohydrazide. The potentiality of all compounds tested towards Re(IV) are approximately the same, and show the molar absorptivity of $(2.57—3.01)\times10^4$ dm^3 mol^{-1} cm^{-1} at λ_{max} 435—438 nm in the organic solvent. The detection limit of the method is 0.013 μg Re cm^{-3} and it follows Beer's law over 0.5—6.0 μg Re cm^{-3} with PAA in benzene. The relative standard deviation of the method was found to be ±1.4% for 10 measurements each containing 40 μg Re/15 cm^3.

Effect of Diverse Ions. The effect of diverse ions on the determination of 40 μg of Re(VII) was studied with 0.1 mol dm^{-3} PAA in benzene as above. In this method, Nb(V) and Mo(V) seriously interfere in the determination of the metal, and W(VI) is tolerated only in equal amount. The interference of Mo is removed by prior extraction with 0.1 mol dm^{-3} PAA in benzene from aqueous solution containing 4 mol dm^{-3} H_2SO_4 +0.1 mol dm^{-3} ascorbic acid +0.4 mol dm^{-3} KSCN. The interference of niobium is masked by sodium oxalate (3% solution 3 cm^3). The tolerance limit of various diverse ions (in mg) in the determination of rhenium causing an error less than ±2% is shown in parenthesis as; W (0.04); Pd, Mo (0.1); Cu(0.5); Al, Cr, Co, Zr, F^- (20); U (30); oxalate (40); Zn (75); Cd (100); AsO_4^{3-} (150); tartrate (220); or PO_4^{3-} (250).

We are thankful to Council of Scientific & Industrial Research, New Delhi for partial financial support of this work.

References

1) Z. Marczenko, "Spectrophotometric Determination of Elements," Ellis Horwood, Chichester (1976).

2) C. P. Savariar and T. R. Hariharan, *Mikrochim. Acta*, **I**, 477 (1975).

3) M. Mitra and B. K. Mitra, *Talanta*, **25**, 597 (1978).

4) F. Trusell and R. J. Thompson, *Anal. Chem.*, **36**, 1870 (1964).

5) E. N. Pollock and L. P. Zopatti, *Anal. Chim. Acta*, **32**, 418 (1965).

6) D. Thierig and F. Umland, *Z. Anal. Chem.*, **240**, 19 (1978).

7) A. K. Majumdar and B. Datta, *Anal. Chim. Acta*, **97**, 129 (1978).

8) A. Kettrup, T. Seshadri, and F. Jakobi, *Anal. Chim. Acta*, **115**, 383 (1980).

9) K. S. Patel and K. H. Lieser, *Anal. Chem.*, **58**, 1547 (1986).

10) M. Pavlova, *Zh. Anal. Khim. (English Transl.)*, **25**, 99 (1970).

11) R. A. Bailey, T. W. Michelsen, and W. N. Mills, *J. Inorg. Nucl. Chem.*, **33**, 3206 (1971).

12) A. Davison, A. G. Jones, L. Muller, R. Tatz, and H. S. Trop, *Inorg. Chem.*, **20**, 1160 (1981).