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Studies on the synthesis of 5-(*p*-aminobenzylidene)-rhodanine and its properties

E. Tang, Guangyu Yang*, Jiayuan Yin

Department of Chemistry, Yunnan University, Kunming 650091, People's Republic of China

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Abstract

A new analytical reagent 5-(*p*-aminobenzylidene)-rhodanine (ABR) was synthesized. The acidic dissociation constant of ABR has been determined. The properties, the acid–base behavior of ABR and the reactions of ABR with metallic ions have been studied. The color reactions of the reagent with Pd(II), Au(III), Ag(I), Ru(III), Hg(II) and Cu(II) are studied in detail. The composition of Pd(II)–ABR, Au(III)–ABR and Ag(I)–ABR complexes were discussed. \bigcirc 2002 Published by Elsevier Science B.V.

Keywords: 5-(p-Aminobenzylidene)-rhodanine; Color reaction; Synthesis; Acidic dissociation constant

1. Introduction

Nencki [1] noted that rhodanine precipitated certain metal ions from aqueous solution when he first characterized the compound, but Feigl [2] was the first to suggest a rhodanine derivative as an analytical reagent. He recommended 5-iso-nitrosorhodanine as a precipitant for mercury and silver ions. Shortly afterwards, Feigl and Pollak [3] introduced rhodanine itself as a selective microgravimetric precipitant for silver ion. The use of rhodanine derivatives as colorimetric reagents has stemmed directly from Feigl's introduction of chromophoric groups into the rhodanine molecule [4]. Some derivatives of rhodanine were found to have higher sensitivity and selectivity for the spectrophotometric analysis of some noble metal ions and heavy metal ions [5-9]. In order to furtherly develop and utilize the derivatives of rhodanine, in this work, a new analytical reagent 5-(*p*-aminobenzylidene)-rhodanine (ABR) was synthesized. The acidic dissociation constant of ABR has been determined, and the properties, the acid-base behavior and the reactions of ABR with metallic ions have been studied. In the presence of surfactant, ABR has higher sensitive, selective and stable color reactions with Au(III), Ag(I), Ru(III), Hg(II) and Cu(II). Satisfactory results will be obtained if appropriate samples are chosen. The composition of Pd(II)-ABR, Au(III)-ABR and Ag(I)-ABR complexes were also discussed initially.

^{*} Corresponding author. Tel./fax: +86-871-831-6812

E-mail address: huquifena@163.com (G. Yang).

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2. Experimental

2.1. Apparatus

The absorption spectra at the visible region was recorded with a 722 spectrophotometer (Shanghai, China). The pH measurement was made with a model pHs-2 pH meter (Shanghai, China). Elemental analysis was carried out with CARLO ERBI STRUMENTAZIONE Elementa (Italy). FTS-40 Fourier transform infrared spectrophotometer (Bio-Rad, USA), FX-90 Q NMR spectrometer (Switzerland) and MS VG Autostec 3000 mass spectrometer (UK) were used for recording IR, NMR and MS spectra. The splitting patterns for ¹H-NMR spectra were designated as follows: s, singlet; d, doublet and m, multiplet.

2.2. Syntheses of ABR

Acetic acid (15μ l) was added to the sample of 1.3 g of rhodanine and 1.2 g of p-aminobenzaldehyde, and the mixture was heated gently to dissolve rhodanine and *p*-aminobenzaldehyde completely. The solution was refluxed for about 1.5 h, about 1 ml of concentrated sulfuric acid was added dropwise. After the color of the solution turned red, the refluxing was stopped and the sample was poured into 200 ml of distilled water. After the red solids precipitated from the solution, a small amount of aqueous ammonia was added. Then the precipitants were separated by filtration. The precipitants were recrystallized twice from absolute alcohol and the yield was 70% (m.p. 242-244 °C). The structure has been verified as shown in Fig. 1 by elemental analysis, IR, ¹H-NMR and MS. Elemental analysis was shown as following: calculated: 50.83% C, 3.41% H, 11.85% N; found: 50.59% C, 3.39% H, 11.80% N. IR (KBr) (cm⁻¹):



Fig. 1. The structure of ABR.

3470, 3450, 3355 (v_{N-H}); 3060, 3020 ($v_{=C-H}$); 1628 (δ_{N-H}); 1681 ($v_{C=O}$); 1566, 1548, 1515, 1450 ($v_{C=C}$); 1292 (v_{C-N}); 1171 ($v_{C=S}$); 825 (δ_{Ar-H}); 806 ($\delta_{C=C-H}$). ¹H-NMR (solvent: DMSO-d₆) (δ , ppm): 7.46 (1H, s, C=C-H); 7.26, 7.35 (2H, d, $J \approx 9$ Hz, H-2 and H-6); 6.62, 6.72 (2H, d, $J \approx 9$ Hz, H-3 and H-5); 3.36 (2H, w, $-NH_2$). MS (EI) (m/z): 236 (M⁺), 149 (B, M⁺-87, S=C=CH-C₆H₄-NH₂⁺).

2.3. Reagent and chemicals

All chemicals used were of analytical reagent grade and doubly distilled water was used throughout. ABR solutions $(1.0 \times 10^{-4} \text{ mol } 1^{-1} \text{ and } 0.05\%)$ were prepared by dissolving ABR in absolute ethanol. All metal ion solutions were standardized. Surfactant, TritonX-100 solution (2.0% v/v), Emulsifier OP solution (2.0% v/v) and Tween-80 solution (2.0% v/v) were used. Buffer solutions, pH 4.0 and 7.0 were prepared from HAC-NaAC and NH₄AC.

2.4. Procedures

2.4.1. Spectrophotometric determination of dissociation constants

ABR solution (1.0 ml), $(1.0 \times 10^{-4} \text{ mol } 1^{-1})$ in absolute ethanol was placed in a 25 ml standard flask and 5 ml of 0.5 mol 1^{-1} potassium chloride was added to five and ionic strength of 0.1. The pH values were adjusted with sodium hydroxide solution and hydrochloric acid and the solution was diluted with water to the mark. The absorbance was measured at the appropriate wavelengths against water as blank (1 cm cells). The dissociation constants were determined by the methods of Hilldebrand and Reilley [10].

2.4.2. Reactions of ABR with metal ions

The reactions of numerous ions with ABR were tested in a certain medium. The solutions were prepared in 25 ml standard comparison tubes, to which 10 μ g of metal ions, 1 ml ABR (dissolved in ethanol), 2 ml surfactant prevents the precipitation of the complex), 5 ml of buffer solution were added and diluted to the volume with distilled

water; the spectrum from 200 to 700 nm was measured against a reagent blank.

3. Results and discussion

3.1. Properties of ABR

ABR is red grains. It dissolves readily in N,Ndimethylformamide and methylsulfoxide. It is soluble in polar solvents such as ethanol, acetone and alkaline aqueous solution and insoluble in low polar solvents such as carbon tetrachloride and petroleum ether. Its solubility increases and color deepens with small amount of alkali added.

ABR is stable in absolute ethanol for about over 2 weeks. The stability in the ethanol-aqueous medium shows a pH dependence; so, it is stable for at least 100 h in acid and neutral media (pH 1.5-7), but in alkaline medium (about pH 12) the absorbance of the maximum decreases. This behavior may be attributed to the hydrolitic breakdown of the bond $\frac{H-N-C=0}{L}$ analogous to hydantoin derivatives [11].

3.2. Acid-base behavior of ABR

The acid-base behavior of ABR can be explained by the existence of tautomeric forms of therhodanine molecule [12], but the derivatives at C-5 of rhodanine exhibit only three tautomeric forms (four for rhodanine alone), since the keto-enol tautomerism between C-5 and C-4 atoms is eliminated by the double bond at C-5. Besides, because of the greater acidity of the thiomidol group, formed between C-2 and N-3 atoms, in front of the imidol group formed between the N-3 and C-4, thio-enol form is probably the form mainly present in solution. This is in accord with



Fig. 2. Absorbance spectra of ABR at different pH.



Fig. 3. Effect of the pH on the absorbance of ABR.

the stabilization of -CO- by conjugation effect. The absorbance spectra of ABR and effect of the pH on the absorbance of ABR is showed in Figs. 2 and 3, respectively. Typical spectral curves corresponding to the appearance of individual hydrogen complexes of ABR is presented in Scheme A. The equilibria are marked by shifts, of the absorption spectra and the isosbestic points, which consequently appear. The overall equilibrium of ABR involves two hydrogen ions and Scheme A encloses Equilibrium 1 plus Equilibrium 2.





Fig. 4. The partial charge of atoms in ABR.

The dissociation constants of ABR obtained by spectrophotometric methods [13] is 3.0 (p K_{a1}) and 7.4 (p K_{a2}). In the absorption spectra of ABR, as showed in Fig. 2, the isosbestic points are 388 nm (pH 2.2–3.8, complex H₂R⁺, HR) and 426 nm (pH 6.1–9.2, complex HR, R⁻). The characteristics of the partial charge of atoms in ABR shown in Fig. 4 and the spectral characteristics of the reagent in solution at different pH values support the hypothetical scheme A assumed before.

3.3. Reaction ability of ABR

The reactions of some metallic ions with ABR were tested and the results are summarized in Table 1. According to the experiment, it is concluded that in the presence of surface active reagents, ABR gives good reactions only with Pd(II), Au(III), Ag(I), Ru(III) and Cu(II) to form stable complexes, and the color of ABR changes from yellow to orange or red. The reaction behavior of ABR is determined not only by the metal ions, but also by the pH of solution and the reaction medium. For example, ABR reacts with Pd (II) in strong acid solution, and in (1+1) HCl, the best result was obtained, but with Ru(III), the better medium is (1+10) H₃PO₄. Besides, nonionic surfactant such as TrionX-100, Tween-80 and Emulsifier OP can enhance the water solubility of the complexes. Furthermore, they can raise the absorbance of complex systems, the sensitivity of the systems are also raised. At the same time, it is found that large amount of alkali metal ions and alkali earth metal ions in the solution do not interfered with the determination of these metal ions. As to the determination of

Table 1

Photometric characteristics of the complexes in solution

Cation	Reaction conditions	λ_{\max} (nm) (Reagent blank)	λ_{\max} (nm) (Complex)	$\Delta\lambda$ (nm)	$\varepsilon \times 10^4 \text{ (l mol}^{-1} \text{ cm}^{-1}\text{)}$
Pd(II)	(1+1) HCl, 2% (v/v) TritonX-100 solution	360	475	115	9.35
Au(III)	pH 3-4, 2%(v/v) Emulsifier OP solution	430	510	80	7.2
Ag(I)	pH 7.0 Ammonium acetate buffer solution, $2\%~(v/v)$ Tween-80 solution	420	495	75	5.93
Ru(III)	(1+10) H ₃ PO ₄ , 2% (v/v) Emulsifier OP solution	360	500	140	2.53
Hg(II)	pH 6-7, 2% (v/v) Emulsifier OP solution	420	460	40	2.33
Cu(II)	pH 5, 2%(v/v) Emulsifier OP solution	420	540	120	2.99

Pd(II), a certain amount of other noble metal ions and heavy metal ions are permitted in the solution. Although the metallic ions, Pd(II), Au(III) and Ag(I), interfered with each other in the determination of these ions, some simple and effective methods have been used to eliminate the interferences. The mixture of (1+1) HCl solution, 10 g 1^{-1} diacetyldioxime ethanol solution and trichloromethane can easily extract palladium(II) out of the hydrochloride acid solution of samples which contain palladium(II) and other noble metals. The method was used in the determination of palladium(II) ion and to eliminate the interference of palladium in the determination of other metallic ions. As to the elimination of Ag(I), it can be eliminated by the pretreatment of samples with hydrochloride acid solution. And as to Au(III), it can be eliminated by the extraction with ethyl acetate. More than 2-fold Ru(III) and Cu(II) were not interfered with the determination of Pd(II), Au(III) and Ag(I) (the tolerance limit was taken as the maximum concentration of Ru(III) and Cu(II) causing about a $\pm 5\%$ error in the determination). But, if a sample contains only one of the five metallic ions was analyzed, ideal results would be obtained. So, the selectivity of the reagents is high and ABR can used to determine palladium in the samples containing a certain amount of other noble metals and heavy metals. A new analytical method has been applied to the determination of palladium in Jingbao mountain sulfonium alloys successfully. Other new analytical methods have also been applied to the determination of other ions like silver (I) ion and gold(III) ion in the samples which do not contain palladium and the results were satisfying.

3.4. Composition of the complexes

The absorption spectra showed that the maximum absorption wavelength of the reagent blank shifted remarkably after Pd(II), Au(III), Ag(I), Ru(III) and Cu(II) were added, respectively. Which indicates that the complexes between ABR and these metal ions were formed after metal ions were added. In the IR spectra of the solid Pd(II)–ABR, Au(III)–ABR and Ag(I)–ABR complexes (prepared by the general procedure, but omit the surface active reagents),the absorption intensity of all the vibration bands, as showed in Table 2, weakened or disappeared compared with that of ABR.

From Table 2, it is indicated that the nitrogen atom in the rhodanine ring, the sulfur atom in the thio-carbonyl group and the oxygen atom in the carbonyl group were involved in the co-ordination of the metal ions, which is also well supported by the partial charge of oxygen atom and nitrogen atom in the ring of rhodanine in Fig. 4. The new



Fig. 5. The possible structures of Pd(II)-ABR, Au(III)-ABR and Ag(I)-ABR complexes.

Table 2			
Comparison of IR	spectra of ABR	and its the	ree complexes

Reagent and complexes	$v_{\rm N-H} \ ({\rm cm}^{-1})$	$v_{C=O} (cm^{-1})$	$v_{C=S} (cm^{-1})$	$v_{\rm C-N} \ ({\rm cm}^{-1})$
ABR	3355 (m*)	1681 (s)	1171 (s)	1292 (m)
Pd(II)-ABR	_	1626 (w)	1167 (s)	1322 (m)
Au(III)-ABR	_	1671 (w)	1172 (s)	1322 (m)
Ag(I)-ABR	-	1634 (m)	1168 (s)	1297 (m)

*, s, strong; m, medium; w, weak.

peaks appeared at 428 and 310 cm⁻¹ in the IR spectra of the complex indicating the existence of N–M and S–M bonds in the complex [14,15], which also proved the involvement of nitrogen and sulfur atoms in the triazene group in the complex formation with Pd(II), Au(III) and Ag(I).

The composition of the complexes was determined by Job's method of continuous variation and the molar ratio method. Both indicated that the molar ratios of Pd(II), Au(III) and Ag(I) to ABR were 1:1, 1:2 and 1:1, respectively.

Based on the molar ratios and IR spectra, the possible structures of the complexes might be deduced as showed in Fig. 5.

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