1,2-DITHIOLIUM SALTS

III. EXAMINATION OF THE ANALYTICAL PROPERTIES OF 4-(p-TOLYL)-1,2-DITHIOLIUM HYDROGEN SULFATE*

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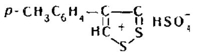
4-(p-Tolyl)-1,2-dithiolium hydrogen sulfate (I) is not a specific analytical reagent for the majority of anions, and it is not very selective, only in a few cases attaining pD = 5 (MoO_4^{2-}, $[Hg(CNS)_4]^{2-}$, and $[PtCl_6]^{2-}$). All strongly colored anions give colored salts with I. Among the weakly colored anions, the $[Fe(CN)_6]^{4-}$ anion is worthy of special note, since it forms a deeply colored salt with I. This anion can be detected with I in the presence of Cl^-, Br^-, I^-, CNS^-, ClO_4^-, IO_4^-, and ReO_4^-, which form fairly readily soluble salts with I. Compound I is also a fairly selective reagent for Pd^{2+} in acid solution (pD = 5).

It has been shown previously [1] that the 1,2-dithiolium cation forms crystalline, brightly colored salts with the anions of many inorganic, hetero-organic, and organic acids. These salts are readily obtained by metathesis from the readily water-soluble 1,2-dithiolium hydrogen sulfates [2,3] with aqueous solutions of salts of the appropriate acids. It is also known [4] that 4-aryl-1,2-dithiole-3-thiones can be used as analytical reagents for copper, mercury, platinum, and palladium.

It was therefore of interest to examine the analytical properties of 1,2-dithiolium salts, in particular the readily accessible 4-(p-tolyl)-1,2-dithiolium hydrogen sulfate (I).



At pH > 2 (on treament with alkali and salts of weak acids) [1], I is converted into bis-3-[4-(p-tolyl)-1,2-dithiolium] oxide (see also [5]).

With salts of strong acids, I gives the corresponding salts. We have determined the limiting concentrations of anions at which it is possible to detect them with I in aqueous solution. The results obtained, and the colors of the resulting 4-(p-tolyl)-1,2-dithiolium salts, are given in Table 1. We see that I is not a specific reagent for the majority of anions, and does not possess high selectivity. Only in MoO_4^{2-}, $[Hg(CNS)_4]^{2-}$, and $[PtCl_6]^{2-}$ was pD = 5. All strongly colored anions gave colored salts with I. Among weakly colored anions, $[Fe(CN)_6]^{4-}$ is noteworthy, since it forms with I a dark-brown salt (at low concentrations, dark-brown rhombic crystals). This occurs also in the presence of Cl^-, Br^-, I^-, CNS^-, ClO_4^-, IO_4^-, and ReO_4^-, which form comparatively readily soluble salts with I. Therefore, I can be recommended as a reagent for the detection of the $[Fe(CN)_6]^{4-}$ anion.

At pH ≤ 2, I reacts with the Pd^{2+} ion to form a reddish-brown compound which is soluble in chloroform.

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* For part II, see [1].

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TABLE 1. Results of the Examination of the Analytical Properties of 4-(p-Tolyl)-1,2-dithiolium Hydrogen Sulfate

Anion	Limiting concentration, g-ion/liter	Color of precipitate	Time to the initial appearance of a precipitate at the limiting concentration, sec	Anion	Limiting concentration, g-ion/liter	Color of precipitate	Time to the initial appearance of a precipitate at the limiting concentration, sec
Cl^-	$1 \cdot 10^{-1}$	Light yellow	0	$[BeF_4]^{2-}$	$1 \cdot 10^{-3}$	Light yellow	5—10
Br^-	$1 \cdot 10^{-2}$	Light yellow	~10	$[Hg(CNS)_4]^{2-}$	$1 \cdot 10^{-5}$	Light yellow	0
I^-	$1 \cdot 10^{-3}$	Orange	~10	$[ZrF_6]^{2-}$	$2{,}5 \cdot 10^{-2}$	Light yellow	~10
CNS^-	$5 \cdot 10^{-3}$	Bright yellow	~5	$[SnCl_6]^{2-}$	$1 \cdot 10^{-4}$	Light yellow	5—10
ClO_4^-	$1 \cdot 10^{-2}$	Light yellow	2—3	$[Fe(CN)_5NO]^{2-}$	$1 \cdot 10^{-3}$	Light brown	3—5
IO_4^-	$5 \cdot 10^{-3}$	Light yellow	~60	$[RuOHCl_5]^{2-}$	$2 \cdot 10^{-4}$	Reddish-brown	0
ReO_4^-	$2 \cdot 10^{-3}$	Light yellow	0	$[IrCl_6]^{2-}$	$5 \cdot 10^{-5}$	Brown	0
VO_3^-	$1 \cdot 10^{-3}$	Yellow	0	$[PtCl_6]^{2-}$	$1 \cdot 10^{-5}$	Light yellow	0
$C_6H_2(NO_2)_3O^-$	$1 \cdot 10^{-4}$	Bright yellow	~30	$[MoCl_6]^{3-}$	$1 \cdot 10^{-3}$	Light brown	~10
$S_2O_3^{2-}$	$5 \cdot 10^{-4}$	Orange	0	$[Fe(CN)_6]^{3-}$	$1 \cdot 10^{-4}$	Yellow	10—15
$S_2O_8^{2-}$	$5 \cdot 10^{-4}$	Light yellow	20—30	$[OsBr_6]^{3-}$	$1 \cdot 10^{-4}$	Dark brown	0
$Cr_2O_7^{2-}$	$1 \cdot 10^{-4}$	Orange	0	$[Fe(CN)_6]^{4-}$ *	$5 \cdot 10^{-4}$	Dark brown	~60
MoO_4^{2-}	$1 \cdot 10^{-5}$	Yellow	15—20				

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* May be observed in the presence of anions which give weakly colored precipitates.

The limiting concentration for the detection of the Pd^{2+} ion is $1 \cdot 10^{-5}$. Thus, I can be recommended as a reagent for the palladium ion.

Determination of the Limiting Concentration of anions for Detection by I. A saturated aqueous solution of I [1-3] was used, and dilute aqueous solutions of the salts containing the corresponding anions. These were mixed in a 1:1 ratio by volume. In order to obtain an 0.001 M solution of the given salt (0.001 g-ion/liter) in the final volume of 2 ml, 1 ml of its solution in a concentration of 0.002 g-ion/liter was added to 1 ml of the saturated aqueous solution of I. In order to obtain a final concentration of 0.0001 g-ion/liter, solutions containing 0.0002 g-ion/liter of the salts were prepared.

Determination of the Limiting Concentration of Pd^{2+}. A 0.001 M solution of $PdCl_2$ with a pH ≈ 1 was used. It was diluted as described above. The reagent was a saturated aqueous solution of I. One ml of each solution was mixed, and the mixture was extracted with 2 ml of chloroform during a period of 3 min. After separation, the color of the chloroform layer was noted. The limiting concentration was 1.10^{-5} g-ion/liter of Pd^{2+}, and this gave the extract an orange-yellow color.

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