1-Hydroxy-1, 2, 3-benzotriazoles as Analytical Reagents. I. 4-Nitro-1-hydroxy-1, 2, 3-benzotriazole as a Specific Reagent for Silver

By H. L. SHARMA and S. K. MUKERJI

(Received September 16, 1964)

Comparatively few organic reagents afford precipitates with silver which can be directly weighed for estimation of the metal. Only *p*-dimethylaminobenzalrhodamine and some other compounds containing the grouping >NOH have been reported.[1-7] Out of the few hydroxybenzotriazoles, which are under investigation for analytical purposes by one of the authors (H. L. S.), the use of 4-nitro-1-hydroxy-1, 2, 3-benzotriazole (R) in the gravimetric estimation of silver is described in the present communication.

The aqueous-ethanolic (1 : 4 v/v) solution of this reagent R gave a scarlet red precipitate with silver ions. The precipitation was quantitative between pH 2.8—4.3 and the precipitate was stable enough to be dried at 110—125°C to a stoichiometric composition of $AgC_6H_3O_3N_4$.

The chief advantage of the reagent R over existing ones for estimation of silver is that the estimation of silver, when present singly or even in the presence of other metal ions, is fairly rapid and takes only one hour. Filtration of the precipitate is easy and quick and variation of the interval between precipitation and filtration does not affect the results.

The advantages over the recently reported reagent I[7] are that our reagent is specific for silver and that the reagent R is more soluble than I.* Moreover the precipitation of the silver salt could be well effected with reagent R in alcoholic solution, and finally it could also be dried completely whereas the precipitate of silver salt, with the reagent I, cannot be freed from $^1/_2\,C_2H_5OH$ even when dried at 120°C.**

Experimental

Preparation and the Solubility of the Reagent R.—The reagent R, viz. 4-nitro-1-hydroxy-1, 2, 3-benzotriazole was prepared by the method reported earlier.[9] The results in Table I show that the average solubility of reagent R per 100 g. of water at 30°C is 0.21344 g. but an 0.4% solution of R in aqueous ethanol (1 : 4 v/v) was used for all estimations.

---

1) F. Ephraim, *Ber.*, **63**, 1928 (1930).

2) G. Denigés, *Bull. Soc. Pharm. Bordeaux*, **70**, 101 (1932).

3) D. C. Sen, *J. Indian Chem. Soc.*, **15**, 473 (1938).

4) J. F. Flagg and N. H. Furman, *Ind. Eng. Chem., Anal. Ed.*, **12**, 529 (1940).

5) K. J. Keuning and J. V. Dubský, *Rec. trav. Chim.*, **59**, 978 (1940).

6) P. Wenger, R. Duckert and M. L. Busset, *Helv. Chim. Acta*, **24**, 889 (1941).

7) D. S. Deorha, N. K. Kulshrestha and B. B. Varma, *Indian J. Appl. Chem.*, **27**, 4 (1964).

* The recently reported reagent, 6-chloro-4-nitro-1-hydroxy-1, 2, 3-benzotriazole (I) by Deorha et al.,[7] appears to be more than 0.8—1% soluble as 1% aqueous solution of the reagent I was used by them for all estimation. In comparison to I, we selected R as the reagent with an assumption that it should be more soluble than I. Surprisingly R was found to be only 0.2134% soluble at 30°C, a result under controversy. As such I was also prepared by the method reported earlier[8] and was found to be only 0.0708% soluble at 30°C.

8) S. S. Joshi and D. S. Deorha, *J. Indian Chem. Soc.*, **29**, 548 (1952).

** Deorha et al.,[7] also report that when precipitation was done with an alcoholic solution of the reagent I, the precipitate corresponds to the composition $AgC_6H_2O_3N_4Cl\cdot 1/2C_2H_5OH$, and that the precipitate could not be freed from alcohol even when dried at 120°C. However, such abnormality was not observed in our case.

9) W. Borsehe and D. Rantscheff, *Ann.*, **379**, 152 (1911).

Table I

Temp.: 30

Wt. of the solvent (water) used., g.	Wt. of the solute R after evaporation, g.	Solubility g./100 g. at 30°C
10	0.02134	0.21340
20	0.04271	0.21355
40	0.08536	0.21340
60	0.12804	0.21340
80	0.17074	0.21342
100	0.21348	0.21348

Silver Nitrate Solution.—Stock solution of N/20 silver nitrate was prepared and estimated by the usual classical methods. In order to get concordant results, estimations were made in duplicate.

Composition of the Precipitate.—The scarlet red precipitate obtained by mixing an excess of the solution of R with a solution of silver nitrate was washed with alcohol to remove excess of the adsorbed reagent R and was analysed after drying at 110°C. It was noted that the precipitate explodes whenever heated in a silica crucible over a flame. So the silver was estimated by obtaining silver as silver chloride from the precipitate by decomposing it with 50% hydrochloric acid. The triazole thus liberated was removed by washing the combined precipitate repeatedly with ethanol until the filtrate gave a negative test for chloride ions.

Found: N, 19.18; Ag, 37.578. Calcd. for $AgC_6H_3N_4O_3$: N, 19.52; Ag, 37.59% (Conversion factor for silver being 0.3759).

Procedure for Estimation of Silver.—An aliquot quantity of silver nitrate was diluted to about 100 ml. and the pH was adjusted to about 3—4. Excess of the solution of R was then added with constant stirring. The precipitate was digested on a boiling water bath for about half an hour, filtered through a sintered crucible (No. G3), washed with cold 0.06% solution of the reagent and then with 95% ethanol. It was then dried at 110—120°C to a constant weight. Table II summarizes the results of some experiments.

Table II

pH: 3—4 (approx.)

Ag taken mg.	Wt. of the ppt., mg.	Ag Found mg.	Error mg.
5.394	14.31	5.379	−0.015
8.091	21.60	8.119	+0.028
10.788	28.76	10.810	+0.022
13.485	33.22	13.470	+0.015
16.182	43.10	16.201	+0.019
18.879	50.20	18.870	−0.009
21.576	57.33	21.550	−0.026

Table III

Ag : Taken 8.091 mg.; pH: 3—4 (approx.)

Ag: Reagent (mol. ratio)	Wt. of the ppt., mg.	Ag Found mg.	Error mg.
1 : 1.00	20.80	7.818	−0.273
1 : 1.50	21.29	8.003	−0.088
1 : 2.00	21.55	8.100	+0.009
1 : 2.50	21.55	8.100	+0.009
1 : 3.00	21.55	8.100	+0.009
1 : 3.50	21.56	8.104	+0.013

Table IV

Ag: Taken 8.091 mg.

pH value	Ag Found mg.	Error mg.
2.2	7.88	−0.211
2.5	7.89	−0.201
2.8	8.06	−0.031
3.1	8.04	−0.051
3.4	8.07	−0.021
3.7	8.08	−0.011
4.0	8.09	−0.001
4.3	8.09	−0.001
4.6	8.03	−0.061
4.9	7.88	−0.211
5.2	7.87	−0.221
5.5	7.86	−0.231

Table V

pH: 3—4; Ag: Taken 8.091 mg.

Ag+Metal present (mg.)	Ag Found mg.	Error mg.
Na^+ Excess	8.10	+0.009
K^+ Excess	8.08	−0.011
Pb^{2+} (8.208)	8.08	−0.011
Pb^{4+} (16.416)	8.09	−0.001
Hg^+ (8.02)	8.08	−0.011
Hg^{2+} (8.02)	8.10	+0.009
Bi^{3+} (10.45)	8.11	+0.019
Au^{3+} (6.573)	8.08	−0.011
Cu^{2+} (6.354)	8.07	−0.021
Cd^{2+} (11.24)	8.09	−0.001
As^{3+} (7.49)	8.07	−0.021
Sb^{3+} (6.088)	8.11	+0.019
Sn^{4+} (11.87)	8.08	−0.011
Fe^{2+} (15.95)	8.09	−0.001
Fe^{3+} (31.90)	8.07	−0.021
Cr^{3+} (10.40)	8.09	−0.001
Al^{3+} (8.99)	8.06	−0.031
Zn^{2+} (13.07)	8.10	+0.009
Mn^{2+} (9.015)	8.09	−0.001
Ni^{2+} (13.04)	8.12	+0.029
Co^{2+} (13.09)	8.12	+0.029
Ba^{2+} (13.736)	8.07	−0.021
Sr^{2+} (8.763)	8.09	−0.001
Ca^{2+} (13.36)	8.06	−0.031
Mg^{2+} (6.776)	8.12	+0.029
Be^{2+} (4.506)	8.11	+0.019
Tl^{3+} (10.219)	8.08	−0.011
Ti^{4+} (4.79)	8.09	−0.001
Ce^{3+} (7.006)	8.06	−0.031
Ce^{4+} (7.006)	8.08	−0.011
UO_2^{2+} (11.903)	8.07	−0.021
Th^{4+} (11.60)	8.08	−0.011
Zr^{4+} (9.122)	8.11	+0.019

Effect of Reagent Concentration.—By keeping the amount of silver constant and varying that of the reagent, it was found that the precipitation of silver with the reagent R was not complete unless double the stoichiometrically required amount of the latter was used. Refer Table III.

Effect of pH.—Table IV shows that the most suitable pH range for the precipitation is between 2.8—4.3. The negative error increases as we go above pH 4.6 and below pH 2.8. It has been found that the precipitate is soluble in dilute alkalies.

Effect of Diverse Metal Ions.—A known amount of a standard solution of silver was taken in a beaker and diluted to 100 ml. with distilled water. Solutions of diverse metal ions were prepared by using nitrates and acetates of the metals. Difinite quantities of these solutions were added to the beaker. Estimation of silver was carried out as described earlier. Hydrolyses of Bi^{3+}, Sb^{3+}, Sn^{4+} and Ti^{4+} were prevented by using sodium potassium tartarate. In the case of cerium, a small amount of ammonium sulphate was added to keep the cerium salt in solution as the double sulphate.

The results of Table V clearly indicate that there is no interference by other metal ions.

Summary

4-Nitro-1 - hydroxy - 1, 2, 3 - benzotriazole (R) has been used as a reagent for the gravimetric estimation of silver. The precipitation of the metal by this reagent is complete between pH 2.8—4.3, and after drying at 120°C the composition of the precipitate corresponds to the formula $AgC_6H_3O_3N_4$. The presence of other metal ions does not interfere in the estimation. For complete precipitation of the metal, double the stoichiometrically required amount of R was used and it was found that variation of the interval between the precipitation and filteration does not effect the result. The solubility of R is 0.2134 g./100 g. of water at 30°C.

The authors' sincere thanks are due to Professor Dr. R. C. Mehrotra, Head of the Chemistry Department, University of Rajasthan, Jaipur, Shri B. B. Mathur (H. M.), and Shri P. D. Goswami (S. I.) for providing facilities and to Mrs. Sushama Sharma for carrying out nitrogen estimations.

Chemistry Laboratories
Darbar Multipurpose Higher Secondary School
Jaipur (Rajasthan), India

Department of Chemistry
University of Rajasthan
Jaipur (Rajasthan), India