

Preparation and characterization of hydrazinium derivatives

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Abstract. A number of simple and complex hydrazinium derivatives have been prepared by the reaction of hydrazine hydrate with ammonium salts. The products were characterized by chemical analysis and infrared spectra.

Keywords. Hydrazinium derivatives; hydrazinates.

1. Introduction

Preparation of simple hydrazinium salts is easily accomplished either by neutralization of aqueous hydrazine with corresponding acids, or by double decomposition of hydrazine sulfate with corresponding barium salts (Audrieth and Ogg 1951; Hudson *et al* 1967 and Mellor 1927). Anhydrous hydrazine is known to react with ammonium salts giving corresponding hydrazinium derivatives (Audrieth and Ogg 1951). However, only few hydrazinium salts have been prepared using anhydrous N_2H_4 ; e.g. $N_2H_5N_3$ (Muller 1937), $N_2H_5ClO_4 \cdot 0.5 H_2O$ (Stern 1964), H_2N_5F (Glavic and Slivnik 1967) and $N_2H_5NO_3$ (Saad and Detweiler 1969). The use of anhydrous hydrazine in the preparation of hydrazinium derivatives has not been pursued, probably because of its hazardous nature. An attempt was therefore made to prepare hydrazinium derivatives from ammonium salts using hydrazine hydrate. Further, it was thought interesting if this method could be extended to ammonium alums and double salts since, hydrazinium metal sulphates of the general formula; $(N_2H_5)_2M(SO_4)_2$ where $M=Mn, Fe, Co, Ni, Zn$ and Cu have been described as antiferromagnetic materials and were prepared by cocrystallisation of metal sulphates with $N_2H_6SO_4$ (Nieuwpoort and Reedijk 1973).

2. Experimental

All ammonium salts used in this study were of analytical grade. Hydrazine hydrate (99–100%) was commercially available and was used as such. Stoichiometric quantities of ammonium salts and hydrazine hydrate were mixed and allowed to react. Ammonium salts dissolved completely with the evolution of ammonia. The resulting solution was allowed to crystallize in a vacuum desiccator over P_2O_5 . Conversion of ammonium salt to hydrazinium salt was quantitative. Metal ($M=Fe^{2+}, Co^{2+}$,

Ni^{2+} and Al^{3+}) ammonium alums when treated with hydrazine hydrate yield corresponding hydrazinium metal sulphate hydrazinates. The products were characterized by their melting points, infrared spectra and compositions were fixed by hydrazine content as well as metal analyses. Infrared spectra were recorded as nujol mulls and KBr pellets using Carl-Zeiss UR-10 spectrophotometer. Hydrazine content was determined by volumetric analysis using standard (0.05 M) potassium iodate solution under Andrews conditions (Vogel 1951). Metal contents were determined by EDTA titrations (Welcher 1958).

3. Results and discussion

Hydrazine hydrate is an aqueous solution of hydrazine. Hydrazine and water form a constant boiling mixture with a maximum boiling point at 120.5°C (771 mm pressure) corresponding to a mixture containing 58.5% hydrazine. Reaction between hydrazine and water is represented by the equilibrium:



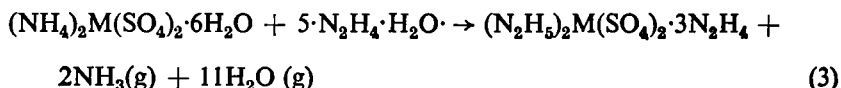
The solutions of hydrazine in water are basic and act as reducing agents. The stoichiometry of the reaction of hydrazine hydrate with ammonium salts and alums could be represented by eqs (1) to (4):



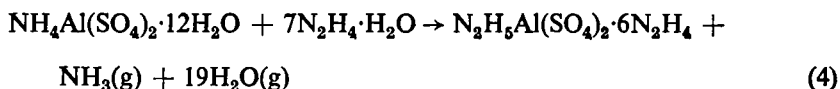
where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{ClO}_4$ and N_3



where $\text{Y} = \text{SO}_4, \text{C}_2\text{O}_4$



where $\text{M} = \text{Fe}, \text{Co}$ and Ni



Simple hydrazinium derivatives are quite hygroscopic and need handling in dry atmosphere. Analytical data of all the compounds prepared are presented in table 1. The observed melting points of the simple hydrazinium salts are in good agreement with the literature values. The hydrazine contents correspond to the formulae. The compositions of the hydrazinate complexes were fixed by the hydrazine contents and metal analysis. It is interesting to observe that in metal ammonium alums in addition to substitution of NH_4^+ ions by N_2H_5^+ ions the water of crystallisation was

Table 1. Analytical data of hydrazinium derivatives

Compound	MP* °C	% Hydrazine		% Metal		I.R. Absorption ν N-N cm^{-1}
		Observed	Theoretical	Observed	Theoretical	
$\text{N}_2\text{H}_5\text{F}$	120 (—)	61.11	61.53			980,960
$\text{N}_2\text{H}_5\text{Cl}$	90 (89)	47.0	46.72			970
$\text{N}_2\text{H}_5\text{Br}$	80 (80)	28.07	28.32			965
$\text{N}_2\text{H}_5\text{I}$	125(124-126)	20.60	20.51			970,965
$\text{N}_2\text{H}_5\text{NO}_3$	62 (62-91)	33.61	33.66			960
$\text{N}_2\text{H}_5\text{N}_3$	75 (75.4)	42.50	42.62			960
$\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$	—	22.38	22.61			960
$(\text{N}_2\text{H}_5)_2\text{SO}_4$	85 (85)	39.36	39.45			970,965
$(\text{N}_2\text{H}_5)_2\text{C}_2\text{O}_4$	150 (148)	41.50	41.54			970,965
$(\text{N}_2\text{H}_5)_2\text{Fe}(\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$	—	38.63	39.04	13.60	13.63	1010,995
$(\text{N}_2\text{H}_5)_2\text{Co}(\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$	—	39.92	38.74	14.25	14.27	1000,990
$(\text{N}_2\text{H}_5)_2\text{Ni}(\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$	—	38.78	38.74	14.25	14.28	1000,990
$\text{N}_2\text{H}_5\text{Al}(\text{SO}_4)_2 \cdot 6\text{N}_2\text{H}_4$	—	51.00	50.44	6.12	6.08	1020,990

*Melting points in the parentheses are from Lange's Hand Book of Chemistry 11th Edition 1973 (New York: McGraw-Hill Book Company) p. 4-57.

also quantitatively replaced by hydrazine molecules. The number of hydrazine molecules is half the number of water molecules in the alums. In reactions (3) and (4) although ammonia and water are formed, there was no evidence of the hydrolysis of the metal ions.

Infrared spectra has been useful in identifying N_2H_4 , N_2H_5^+ and $\text{N}_2\text{H}_6^{+2}$ which show characteristic absorption of ν N-N \sim 880, 960 and 1025 cm^{-1} respectively (Braibanti *et al* 1968). Hydrazinium derivatives show characteristic absorption of N_2H_5^+ \sim 965 cm^{-1} (table 1). The hydrazinium metal sulphate hydrazinate show a doublet \sim 1000 cm^{-1} which could be assigned to ν N-N of N_2H_5^+ similar to that observed in $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2$ (Nieuwpoort and Reedijk 1973) as well as ν N-N the coordinated hydrazine (Sacconi and Sabatini 1963).

4. Conclusions

(a) Hydrazine hydrate reacts with simple ammonium salts to yield corresponding hydrazinium derivatives.

(b) Hydrazine hydrate reacts with metal ammonium alums substituting NH_4^+ ions by N_2H_5^+ ions and replacing water of crystallisation by hydrazine molecules.

This method of preparation of hydrazinium derivatives is simple and safe.

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