

Note

MASS SPECTRAL AND pH-METRIC STUDIES ON *p*-NITROBENZALDEHYDE SEMI- AND THIOSEMI-CARBAZONES AND THEIR URANYL COMPLEXES

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Due to carcinostatic properties of the substituted semi- and thiosemi-carbazones, and their metal complexes, the subject rightly engages the attention of scientists today. Sawhney et al. [1–4] have studied some of the metal complexes of such complexing agents. This note highlights mass spectral studies leading to the fragmentation patterns of *p*-nitrobenzaldehyde semi- and thiosemi-carbazones, and pH-metric studies on the stability and thermodynamics of UO_2 -*p*-nitrobenzaldehydesemicarbazone and UO_2 -*p*-nitrobenzaldehydethiosemicarbazone systems.

EXPERIMENTAL

All the chemicals used were of analytical grade. Reaction of equimolar solutions of semicarbazide hydrochloride/thiosemicarbazide (water base) and *p*-nitrobenzaldehyde (acetone base) was carried out at 40°C with constant stirring. On completion of the reaction the precipitate was filtered, washed repeatedly with warm water and kept overnight in an oven (40°C) for drying. *p*-Nitrobenzaldehydesemicarbazone (a dull yellow powder) and *p*-nitrobenzaldehydethiosemicarbazone (a yellow powder) were subjected to TLC study for purity. Developers were chosen so as to ensure an R_F value between 0.4 and 0.7.

Mass spectra were recorded on a Kratos MS-Model with a DS-55 Data System. The filament current was 300 μA and the EI mode of fragmentation at 70 eV was maintained. A direct insertion probe was used because of the solid nature of the samples. Source/probe temperature was 250/150°C. Scan interval was 3 s per decade.

pH-metric study

Reagents: 0.1 M NaOH (50% acetone in water); 1 M KNO_3 (aq.); 0.1 M HNO_3 (aq.); 0.01 M *p*-nitrobenzaldehydesemicarbazone (*p*-N-BENZ-SC) (acetone); 0.01 M *p*-nitrobenzaldehydethiosemicarbazone (*p*-N-BENZ-THIO-SC) (acetone); 0.01 M $\text{UO}_2(\text{II})$ (aq.).

Sets: (1) 2 ml HNO_3 + 5 ml KNO_3 + 18 ml water + 25 ml acetone; (2) 2 ml HNO_3 + 5 ml KNO_3 + 18 ml water + 10 ml ligand + 15 ml acetone; (3) 2 ml HNO_3 + 5 ml KNO_3 + 16 ml water + 10 ml ligand + 2 ml $\text{UO}_2(\text{II})$ + 15 ml acetone.

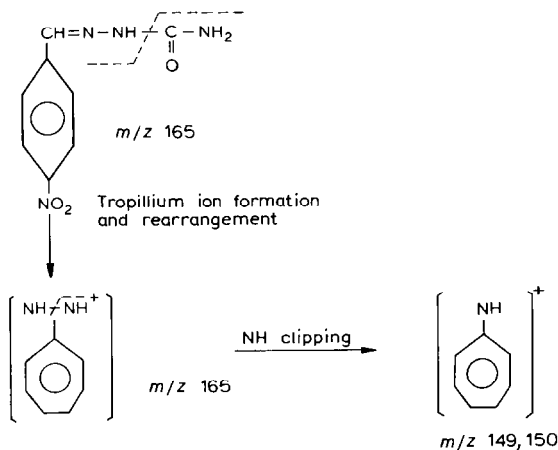
The above sets were pH-metrically titrated with NaOH ; the graphs (corrected pH vs. NaOH added) were usual in shape.

RESULTS AND DISCUSSION

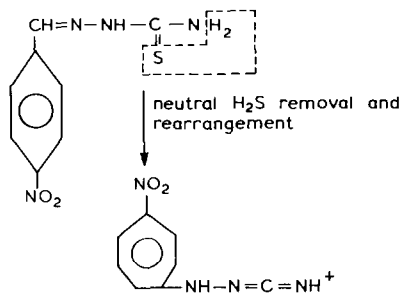
Mass spectral analysis

Since they are nitrogen, sulphur and oxygen containing compounds, it is difficult to interpret the exact fragmentation paths of the substituted semi- and thiosemi-carbazones. In both cases the molecular peaks are clearly visible, i.e., m/z 208 and m/z 224. Due to the even number of nitrogen atoms present, the peak is also even. These compounds belong to the category in which the heteroatom forms part of the aromatic ring. More than one heteroatom substituent in an aromatic compound and the relative positions in the aromatic ring are of great importance since they modify the fragmentation paths.

Peaks at m/z 149, 150 and 165 may be due to the following paths.



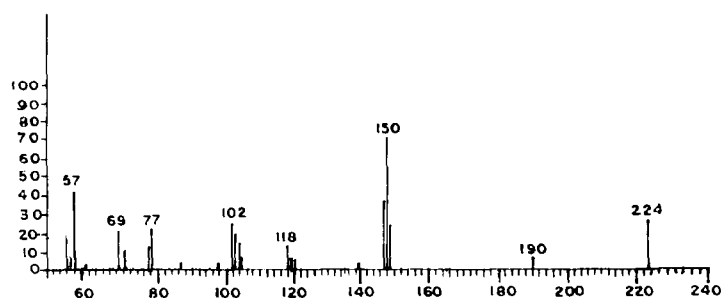
Further clipping of $-\text{NH}$ from the m/z 150 fragment may yield the m/z 135 fragment. Peaks at m/z 92 and m/z 65 are indicative of tropillium ion formation. In the case of *p*-nitrobenzaldehydethiosemicarbazone, removal of the H_2S neutral radical may account for m/z 190 as another parent ion peak.



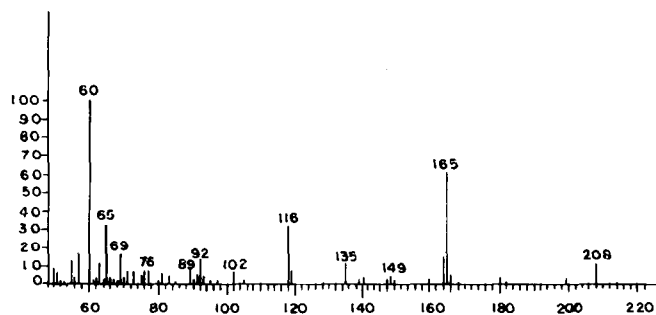
Further clipping and cleavage of the two double bonds may yield m/z 150 and $(M - 1)$ m/z 149 peaks.



In Fig. 1 are shown the mass spectra of *p*-N-BENZ-THIO-SC and *p*-N-BENZ-SC.



P - N - B E N Z - T H I O - S C



P - N - B E N Z - S C

Fig. 1. Mass spectra of *p*-nitrobenzaldehydethiosemicarbazone and *p*-nitrobenzaldehydesemicarbazone.

pH-metric studies

Titration of solutions with varying ratios of uranyl ion to either *p*-N-BENZ-SC or *p*-N-BENZ-THIO-SC, i.e., 0 : 1, 1 : 1, 1 : 2 and 1 : 3 displaying separation, indicated a pH drop on the addition of uranyl ion to the ligand solution in question suggesting the displacement of weak acidic protons of *p*-N-BENZ-SC (OH) and *p*-N-BENZ-THIO-SC (SH) by the uranyl ion; separation of curves further hinted at the participation of an anionic form of these ligands. With limiting conditions being reached with a ratio of 1 : 2 for both systems, the curves then overlapped, establishing the maximum liberation of two protons per uranyl ion.

Work near infinite dilution and at constant ionic strength (0.1 M KNO₃) has been done: under these conditions the formation constant at a certain concentration becomes the thermodynamic formation constant as all the activity coefficients are equal to unity with these experimental conditions. To avoid hydrolysis of the uranyl ion during titration, sets containing a five-fold concentration of ligand to that of uranyl ion in addition to other ingredients were prepared.

For formation constants, the Bjerrum half integral method [5] was followed; the data were within the conditions necessary for its justification ($\log k_1/k_2 \geq 2.50$). The formation curves (\bar{n} vs. pL) under experimental conditions did not extend beyond $\bar{n} = 1.5$. At $\bar{n} = 0.5$, the value of $\log k_1$

TABLE 1

Stability and thermodynamic data on UO₂(II)-*p*-nitrobenzaldehydethiosemicarbazone and UO₂(II)-*p*-nitrobenzaldehydesemicarbazone systems

Parameters	Temp. (°C)	System	
		UO ₂ - <i>p</i> -N-BENZ-THIO-SC	UO ₂ - <i>p</i> -N-BENZ-SC
log k_1	25	7.70	6.80
	35	7.50	7.10
log k_2	25	4.10	3.20
	35	3.10	3.30
log k_{av}	25	5.90	5.00
	35	5.30	5.20
log k_1/k_2	25	3.60	3.60
	35	4.40	3.80
log β_2	25	11.80	10.00
	35	10.60	10.40
ΔG^0 (kcal mol ⁻¹)	25	-15.93	-13.50
	35	-14.79	-14.52
ΔH^0 (kcal mol ⁻¹)	35	-49.41	16.47
ΔS^0 (cal deg ⁻¹ mol ⁻¹)	35	-113.51	101.61

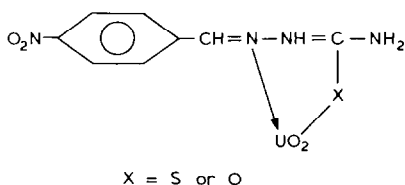
was read; for $\log k_2$, the following relation was used

$$2 \log k_{av} = \log k_1 + \log k_2$$

where $\log k_{av}$ equals pL at $\bar{n} = 1.00$. Table 1 gives the values of the constants and thermodynamic data of the systems in question.

Values of $\log k_1$ and $\log k_2$ of the UO_2 -*p*-N-BENZ-THIO-SC system showed a decreasing trend making lower temperature a favourable for complexation because of the decreasing number of collisions with decreasing kinetic energy of the molecules, and as a result the stability of the system is lowered. On the contrary, the reverse was true for values of these constants of the UO_2 -*p*-N-BENZ-SC system. Negative ΔG^0 values for both systems testified the spontaneity of the reactions; the feasibility of the former reaction lessened as ΔG^0 became less negative at higher temperature. The reaction of UO_2 with *p*-N-BENZ-SC was found more feasible at higher temperature. ΔH^0 values for these systems pointed to the exothermic and endothermic natures of these reactions, respectively, giving credence to the preceding conclusions on the systems. A high value of $-\Delta H^0$ indicated the possibility of the presence of considerable covalency in the UO_2 -*p*-N-BENZ-THIO-SC system, and suggested the reaction to be enthalpy controlled. A negative ΔS^0 value did not favour complex formation; for the UO_2 -*p*-N-BENZ-SC system this value was positive.

The subsequent structure is based upon earlier data [6-8] and the present conclusions.



The high stability of UO_2 -*p*-N-BENZ-THIO-SC compared to that of UO_2 -*p*-N-BENZ-SC is attributed to the less polar nature of S-H in the former system in comparison to the latter one containing an O-H bond (the electronegativity value for sulphur on the Pauling scale is 2.3 compared to 3.5 for oxygen) rendering sulphur comparatively a weaker hydrogen-bonding donor in solution.

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