Chapter 3

SPECTRAL AND EXTRACTION CHARACTERISTICS OF DIPHENYL CARBAZONE

Introduction -

Diphenylcarbazone, \( \text{C}_6\text{H}_5 - \text{NH} - \text{NH} - \text{CO} - \text{N} = \text{N} - \text{C}_6\text{H}_5 \), is found in orange-red needles which melt at 157\(^\circ\)C with decomposition. It is not soluble in water but dissolves in alcohol, chloroform, benzene and isobutyl methyl ketone.

Cazeneuve\(^{408}\) and Bamberger\(^{409,410}\) reported that diphenylcarbazone can split off only one proton to form the monosodium or potassium salt, which would prove diphenylcarbazone to be a monobasic acid. From its behaviour on neutralization with sodium hydroxide, it has been reported that diphenylcarbazone is a monobasic acid.\(^{411}\) However, Hisahiko Einaga et al\(^{22}\) established that diphenylcarbazone is a monobasic acid.

Two series of salts are possible for diphenylcarbazone, one is derived from the keto form and the other is derived from the enol modification. Its ketonic and enolic forms are present in tautomeric equilibrium in solution.

\[
\text{C}_6\text{H}_5 - \text{NH} - \text{NH} - \text{CO} - \text{N} = \text{N} - \text{C}_6\text{H}_5 \Leftrightarrow \text{C}_6\text{H}_5 - \text{NH} - \text{N} = \text{C}(\text{OH}) - \text{N} = \text{N} - \text{C}_6\text{H}_5 .
\]

keto form.  Enol form.
The sodium salt of diphenylcarbazone is strongly coloured; Bamberger\textsuperscript{409} takes this fact to indicate that diphenylcarbazone is present in the enolic form in this compound. Infra-red spectra of the solid 1:1 complexes of mercury (I), mercury (II) and cadmium (II) (in potassium bromide discs) do not show any absorption at 5.85 $\mu$, the characteristic wavelength for C = O bond in diphenylcarbazone. This is an indication of metal-oxygen bonding in these complexes with the carbazone in the enolic form.\textsuperscript{412} S. Balt and E. Van Dalen\textsuperscript{20} determined the compositions of the diphenylcarbazone complexes of the metal ions - manganese (II), nickel (II), zinc (II), mercury (I), lead (II), iron (II), cobalt (II), copper (I), copper (II), iron (III), cadmium (II), mercury (II) and tin (II) by Job's method;\textsuperscript{19} the general formula was proved to be $M(\text{HD})_n$ where $n$ is the valence of the cation ($H_2\text{D} = \text{Diphenylcarbazone}$). They found that for the bivalent cations, the ratio of metal to carbazone at the maximum was 1:2, for copper (I), it was 1:1 and for iron (III), it was 1:3.

Experimental -

Reagent -

Diphenylcarbazone, 0.02 per cent ($8.32 \times 10^{-4}M$) solution in isobutyl methyl ketone -

The diphenylcarbazone used to prepare this solution was obtained from B.D.H. and was purified before use by extraction
with diethyl ether so as to remove any diphenylcarbazide and was finally recrystallized from ethanol.

Adjustment of the pH was carried out by using 0.2M sodium acetate - 0.2M acetic acid or 0.05M sodium borate - 0.1M hydrochloric acid or sodium hydroxide solution.

Apparatus -

Absorption spectra and absorbances at the specified wavelength were obtained with a Beckmann DK-2 spectrophotometer in matched quartz cells of 1.0 cm optical path. The pH of the equilibrated aqueous phase was measured with a pH meter.

Procedure -

Measurements of extractibility (percentage extraction) and absorption characteristics of diphenylcarbazone in the isobutyl methyl ketone - water system were obtained by the following procedure.

To 10 ml of an aqueous solution at various pH values, 10 ml of 0.020% diphenylcarbazone solution in isobutyl methyl ketone was added and the mixture was shaken for 3 minutes. After separation of the phases, the organic phase was used to determine the concentration of diphenylcarbazone by measuring the absorbances at 450 nm (a calibration graph was constructed by using
Fig. 1. Absorption characteristics of diphenylcarbazone in the isobutylmethylketone-water system.

1 to 4, Absorption spectra of organic phase, pH value of equilibrated aqueous phase: 1, 1.7; 2, 5.6; 3, 9.7; and 4, 11.3; 5, absorption spectrum of aqueous phase, pH 9.7.
purified diphenylcarbazone). The separated aqueous phase was used for measurement of hydrogen ion concentration. The concentration of diphenylcarbazone in the aqueous phase was obtained as the difference between the initial concentration and that in the organic phase.

Results and discussion -

The spectral and extraction characteristics of diphenylcarbazone are shown in Figs. 1 and 2 respectively. The absorption spectrum of this reagent did not vary with change in pH of the equilibrated aqueous phase below pH 8, and had an absorption maximum at 450 nm, which showed, however, a gradual bathochromic shift when the pH was increased and reached a constant value above pH 11 ($\lambda_{\text{max}} = 505$ nm at pH 11.3).

The distribution of the reagent from the organic to aqueous phase became appreciable when the pH was above 8. With increasing pH above 8, the distribution of the reagent from the organic to aqueous phase gradually increased and at pH 12, the amount of the reagent in the organic phase was negligible. The aqueous phase containing diphenylcarbazone showed an absorption maximum at 490 nm which was independent of pH.

Diphenylcarbazone is present in the organic phase in both ketonic and enolic forms in tautomeric equilibrium.
Fig. 2. Dependence of distribution ratio on pH.
The ketonic form exhibits maximum absorption at 450 nm and the enolic form shows maximum absorption at 505 nm. Below pH 8, the ketonic form predominates. But when the pH of the aqueous solution is above 8, the tautomeric equilibrium is gradually shifted in favour of the enolic form. The enolic form is then distributed into the aqueous phase. In aqueous phase, it dissociates into a proton and the anion, HOD, where HOD represents the undissociated diphenylcarbazone. The equilibria can be expressed as follows -

\[ \text{H}_2^+ \text{D}_{\text{keto,org}} \rightleftharpoons \text{H}_2^+ \text{D}_{\text{enol,org}} \rightleftharpoons \text{H}_2^+ \text{D}_{\text{enol,aq}}. \]

\[ \text{H}_2^+ \text{D}_{\text{enol,aq}} \rightleftharpoons \text{HOD}^- + \text{H}^+ \]

where the subscript keto represents the ketonic form, enol the enolic form, org the organic phase and aq. the aqueous phase.

The distribution of the reagent from the organic to aqueous phase is very negligible below pH 8 but above pH 8, it gradually increases and becomes appreciable with increasing pH. At pH 12, the amount of reagent present in the organic phase is negligible. Fig. 2 shows the dependence of the distribution ratio of diphenylcarbazone on hydrogen ion concentration.