

THE STRUCTURE OF CYCLOHEXANONE OXIME HYDROCHLORIDES

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(Received 19 June 1964)

Cyclohexanone oxime (I) forms two kinds of salts with hydrogen chloride; one is monohydrochloride (II)*, a colorless powder and the other is dihydrochloride (III)** , a brown oily matter. The latter is unstable and easily releases one mole of hydrogen chloride at room temperature, while the former is very stable.

In this report we present the molecular structure of these hydrochlorides studied by infrared, ultraviolet and NMR spectroscopy.

Cyclohexanone oxime monohydrochloride was prepared by introducing hydrogen chloride to carbon tetrachloride solution of cyclohexanone oxime and drying the precipitate thus obtained under dry nitrogen atmosphere.

The oily dihydrochloride was prepared by introducing hydrogen chloride to dried monohydrochloride.

* Anal Found : C, 48.00; H, 8.05; N, 9.33; Cl, 24.11.
Calc : for $C_6H_{11}NO \cdot HCl$ C, 48.18; H, 8.03; N, 9.37; Cl, 23.72.

** Actually 1.9 mole of hydrogen chloride is found to add to 1 mole of I by titration.

TABLE I Comparison of IR Spectra of Cyclohexanone Oxime and its Hydrochlorides *1

	cyclohexanone oxime			cyclohexanone oxime - d	
	*2 oxime (I)	oxime mono- hydrochloride (II)	oxime dihydro- chloride (III)	oxime-d (IV)	oxime-d-mono deuteriochloride (V)
$\nu(\text{OH})$ assoc.	3260	3360	3170, 2980	-	-
$\nu(\text{OD})$ assoc.	-	-	-	2336	2630
$\nu(\text{N}^+\text{H})$	-	2645	2680	-	-
$\nu(\text{N}^+\text{D})$	-	-	-	-	2000
$\nu(\text{C}=\text{N})$	1659	-	-	1649	-
$\nu(\text{C}=\text{N}^+)$	-	1690	1690	-	1656
$\delta(\text{OH})$ assoc.	1480	-	1480	-	-
$\delta(\text{OD})$ assoc.	-	-	-	1088	1016
$\nu(\text{NO})$ assoc. $\text{ON}\cdots\text{H}$	961	-	-	958	-
$\nu(\text{N}^+\text{O})$ $\text{ON}^+\text{-H}$	-	978	978	-	976
$\delta(\text{OD})$ assoc.	-	-	-	575	556
$\delta(\text{OH})$ assoc.	791	772	769	-	-
Peaks characteristic to oxime	994	-	-	996	-
Peaks characteristic to hydrochlorides	-	1055, 1075	1055, 1075	-	1047, 1069
	-1	901	882	-	-

* 1 All samples except III were measured by Nujol paste method and III was obtained by liquid film method.

* 2 followed by Kimura and his coworker's result (1).

Infrared spectra were taken with a Perkin-Elmer 125 spectrometer. The spectra of hydrochlorides were analysed by referring to the assignment of cyclohexanone oxime, cyclohexanone oxime-d(1), and quaternary ammonium chloride (2, 3), and by comparison with the spectra of cyclohexanone oxime-d deuterochloride (V). The results are listed in Table I.

New bands appear at 2645 and 2680 cm^{-1} in II and III, and at 2000 cm^{-1} in V and they are assigned to the $\text{N}^+ - \text{H}$ and $\text{N}^+ - \text{D}$ stretching, respectively. The $\text{C} = \text{N}$ stretching bands are shifted to higher frequency in these compounds and they are assigned to the $\text{C} = \text{N}^+$ stretching (3). From these observations it is concluded that hydrogen chloride in II, III and V is not added to $\text{C} = \text{N}$ double bond but proton attacks nitrogen atom to form a dative bond. The $\text{N}^+ - \text{O}$ stretching is also shifted to higher frequency as compared with $\text{N} - \text{O}$ stretching.

In II, the $\text{O} - \text{H}$ stretching frequency is shifted to higher and the $\text{O} - \text{H}$ in-plane and out-of-plane bending frequencies are shifted to lower regions in comparison with those of I. This shows that hydrogen bond is weakened in monohydrochloride. This is because in II no lone pair electrons exist and the formation of hydrogen bond of the type $\text{C} = \text{N} \cdots \text{HO}$ is prohibited. The same tendency is observed for $\text{O} - \text{D}$ vibrations in V. The structure of monohydrochloride is concluded to be the one illustrated in Fig. 1.

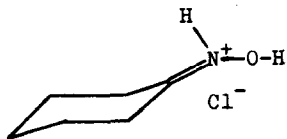


FIG. 1

In the case of the dihydrochloride, there is no remarkable difference from the monohydrochloride except the following points. First, the OH stretching is shifted to lower frequency and it suggests the presence of $O^+ - H$ bond on the analogy with the relation between $N - H$ and $N^+ - H$ stretching frequencies. Second, the $O - H$ out-of-plane bending is shifted to lower frequency than that of monohydrochloride probably because the formation of $OH \cdots O$ hydrogen bond is prohibited. The structure of the dihydrochloride proposed is illustrated in Fig. 2.

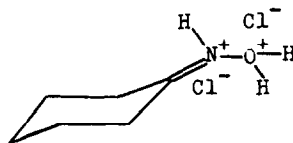


FIG. 2

Ultraviolet spectrum of I in isoöctane solution gives absorptions at $192 \text{ m}\mu$ ($\epsilon = 6,900$) and $310 \text{ m}\mu$ ($\epsilon = 15$). The former is assigned to $\pi \rightarrow \pi^*$ transition and the latter to $n \rightarrow \pi^*$ transition. As $n \rightarrow \pi^*$ transition of II and III in methylene dichloride solution disappears, it is concluded that protonation to lone pair electrons both or either of the nitrogen and oxygen atoms occurs*¹.

The NMR spectra of I, II and III are shown in Figs. 3, 4 and 5, respectively. The α -methylene proton signal of I appears as doublet. It was confirmed from the measurements at both 60 and 100 MC that this is due to chemical shift. In II and III these two peaks coalesce into a single peak, the chemical shift from TMS of which being at lower field

1 The $\pi \rightarrow \pi^$ transition cannot be observed due to absorption by solvent itself.

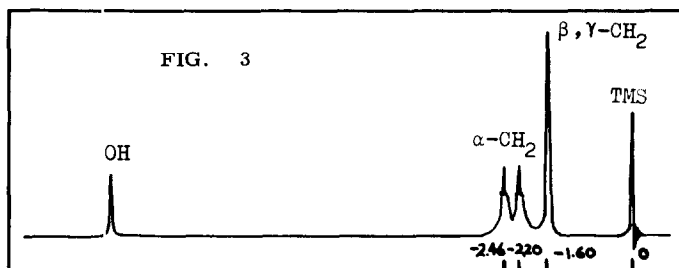


FIG. 3 NMR spectrum of cyclohexanone oxime (CCl₄ solution/100MC)

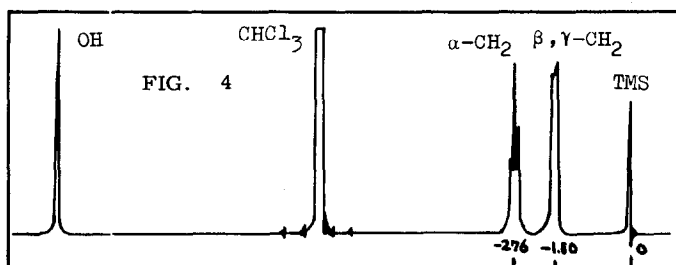


FIG. 4 NMR spectrum of cyclohexanone oxime monohydrochloride (CHCl₃ solution/100 MC)

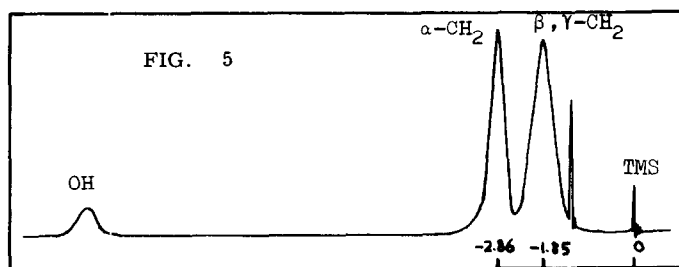


FIG. 5 NMR spectrum of cyclohexanone oxime dihydrochloride (pure/100 MC)

than those of I. From the theoretical considerations, it is concluded that the difference of chemical shifts between two α -methylene groups in I is due to the magnetic anisotropy effect of lone pair electrons in nitrogen atom on anti- and syn-methylene protons. In II and III, those lone pair electrons disappear and accordingly magnetic anisotropy effect is eliminated to give an unsplit peak. Detailed discussions will be reported elsewhere.

REFERENCES

- (1) M. Kimura, Y. Kuroda, O. Yamamoto and M. Kubo, Bull. Chem. Soc. Japan, 34, 1081 (1961).
- (2) cf. L. J. Bellamy, "The Infrared Spectra of Complex Molecules" p. 260, Methuen, London (1954).
- (3) J. Goulden, J. Chem. Soc. 1953, 997.