

THE ULTRAVIOLET ABSORPTION SPECTRA OF OXIMES

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Oximes are stable, photosensitive (3), easily prepared derivatives of ketones and aldehydes. Surprisingly, there is a paucity of reliable spectroscopic data for these compounds. Conflicting reports on the position of the $n \rightarrow \pi^*$ band in these compounds (3a,4) prompt us to present some of our own observations.

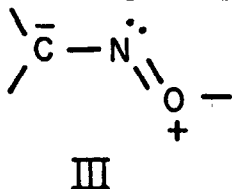
Careful investigation of the accessible absorption spectra (above 186 $m\mu$) of several saturated and α, β -unsaturated oximes and O-methyl oximes in several solvents revealed no distinct low intensity band or shoulder that could be attributed to a forbidden $n \rightarrow \pi^*$ transition similar to that of carbonyl compounds or azomethines. Except in the close vicinity of the moderately intense bands discussed below, bands of molar absorptivity of 0.5 would easily have been seen. This is in agreement with several other reports (3a,4b); it is probable that previously reported weak maxima near 300 $m\mu$ (4a) were due to carbonyl compound impurities. Considering that attachment of an ether oxygen to a carbonyl group results in a hypsochromic shift of the $n \rightarrow \pi^*$ band of ca. 35 kcal./mole (5), it is not surprising that the $n \rightarrow \pi^*$ transition observed near 250 $m\mu$ in azomethines (6) should be shifted to very short wavelengths (ca. 190 $m\mu$) in saturated oximes.

Any weak $n \rightarrow \pi^*$ band occurring near 190 $m\mu$ would be swamped by the moderately intense transition that saturated oximes show in this region. The position and intensity of this band for several oximes and related compounds are presented in Table I. This transition is far too intense ($\epsilon \sim 8 \times 10^3$) for

a forbidden transition and is probably a $\pi \rightarrow \pi^*$ band involving the π -orbital that is localized mainly on oxygen. This assignment is strongly supported by the great similarity of the transitions (in energy, intensity, and response to solvent polarity) of cyclohexanone O-methyloxime (I) and cyclohexenyldenyl



methyl ether (II). As shown by the data in Table I, this transition of saturated oximes exhibits a "blue shift" with increase in solvent polarity. Considering the nature of the transition, it is likely that the excited state has a large contribution from the polar resonance form III. This should result in considerable diminution and possibly even reversal of the ground



state dipole moment. It should also result in a considerable decrease in basicity of the oxygen atom. Either sort of change between ground and excited state should result in a "blue shift" (7).

As a further test for the buildup of positive charge on oxygen during the transition, one may compare the spectra of cyclohexanone oxime and O-methyloxime (I). Substitution of methyl for hydrogen should decrease the transition energy as it does when a methyl group is attached to the β -position of α, β -unsaturated esters (8) and related compounds. The red shift of the transition of I with respect to that of IV (7 kcal./mole in isooctane) is almost exactly the same as the energy difference between the $\pi \rightarrow \pi^*$ transitions of methyl acrylate and trans-crotonate in the identical solvent (1917 Å vs. 2017 Å) (8).

Conjugation of the oximino group with a carbon-carbon double bond results in the appearance of a high intensity band near 240 μ . This transition shows a normal modest red shift with increasing solvent polarity, and is probably related to the $\pi \rightarrow \pi^*$ transitions of α, β -unsaturated ketones, aldehydes, and esters.

TABLE I
 $\pi \rightarrow \pi^*$ Bands of Oximes and Related Compounds

Compound ^a	$\lambda_{\text{max.}}, \overset{\text{O}}{\text{A}} (\epsilon_{\text{max.}})$		
	Isooctane	Acetonitrile	Other
Cyclohexanone oxime	1928 (7,800)	1905 (8,700)	1892 (7,800) ^b
2-Methylcyclohexanone oxime (m.p. 42.5-44°)	1925 (8,300)	1901 (9,000)	1888 (sat.) ^b
2,6-Dimethylcyclohexanone oxime (<u>trans</u>)	1945 (8,500)	1896 (9,300)	-
Menthone oxime (m.p. 82-88°)	1942 (8,000)	1908 (8,600)	-
Testosterone oxime (m.p. 221-222°)	-	2382 (23,100)	2412 (22,600) ^c
Cyclohexanone O-methyloxime	2021 (7,000)	1998 (8,100)	1967 (7,500) ^b
Δ^2 -Cyclohexenone O-methyloxime	2363 (13,700)	2366 (14,300)	2378 (13,700) ^c
Cyclohexenyliденyl methyl ether	2104 (7,200)	2036 (7,400)	1976 (8,400) ^d
Methylenecyclohexane	1909 (10,500)	1915 (10,600)	-

^aAll oximes had m.p.'s agreeing with literature values. In addition, they were recrystallized until no ketone carbonyl bands could be observed in the IR and UV. The other compounds, all liquids, had b.p.'s agreeing with literature values, and except for cyclohexenyliденyl methyl ether were gas chromatographically pure and showed no carbonyl band in the IR. The latter compound contained a few per cent cyclohexanone but the absorption due to this was subtracted from the UV spectra to obtain the data in Table I. ^bWater.

^cMethanol. ^d2,2,3,3-Tetrafluoropropanol.

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