

ROTATIONAL BARRIERS IN O-(N,N-DIMETHYLCARBAMOYL)-OXIMES

C. Hackett Bushweller and Michael A. Tobias
Mobil Chemical Company, Edison, New Jersey, U.S.A.

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Resonance effects are important in causing high barriers to rotation about single bonds (1,2,3,4,5), and unusually low barriers to rotation about double bonds (6). Amides and formamides (7,8,9) have been studied extensively as examples of resonance contributing to an increased rotational barrier about the central C-N bond.

However, there have been few reports concerning hindered rotation about the carbonyl carbon-nitrogen bond in carbamates (10,11,12,13,14) and no reports related to O-(N,N-dimethylcarbamoyl)-oximes. This report concerns the measurement of the rotational barrier in some O-(N,N-dimethylcarbamoyl)-oximes using variable temperature nuclear magnetic resonance (nmr) spectroscopy (15).

At 35°, the N-(CH₃)₂ proton resonance (δ 2.88) of O-(N,N-dimethylcarbamoyl)-acetone oxime (20% by weight in CS₂) is a sharp singlet. As the temperature is lowered, the N-(CH₃)₂ signal broadens and separates into two resonances (Δν = 3.2 Hz) of equal area (FIG. 1).

The rate constant for rotation was calculated at coalescence from the expression $k = \pi \Delta\nu_{\max} / \sqrt{2}$ where Δν_{max} is the chemical shift between the two N-CH₃ resonances under conditions of slow exchange (7).

Similar behavior was observed for the N-(CH₃)₂ resonance (δ 3.03) of O-(N,N-dimethylcarbamoyl)-cyclohexanone oxime (5% by weight in CS₂) and the N-(CH₃)₂ resonance (δ 3.06) of O-(N,N-dimethylcarbamoyl)-fluorenone oxime (4% by weight in CS₂). Kinetic and NMR parameters for all three compounds are compiled in Table 1.

FIG. 1

The Temperature Dependence of the $N-(CH_3)_2$ Resonance
of $O-(N,N\text{-Dimethylcarbamoyl})\text{-Acetone Oxime}$

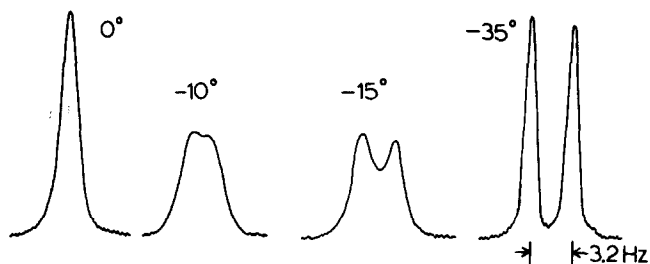
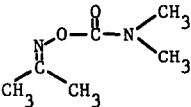
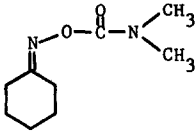
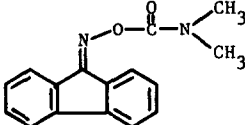


TABLE 1

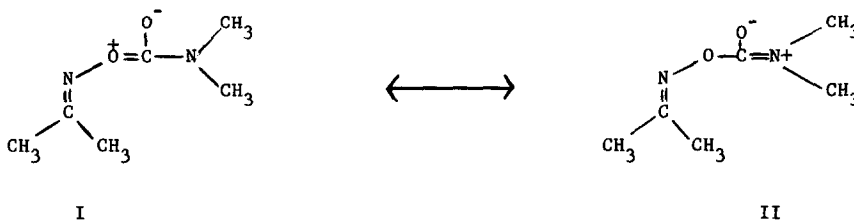
Kinetic and NMR Parameters for Rotation about the
Carbonyl Carbon-Nitrogen Bond in $O-(N,N\text{-Dimethylcarbamoyl})\text{-Oximes}$

Compound	T_c ($^{\circ}K$)	$\Delta\nu_{max.}$ (Hz)	ΔF^{\ddagger} (kcal/mole)
	$264^{\circ} \pm 2^{\circ}$	3.2	14.4 ± 0.2
	$262^{\circ} \pm 2^{\circ}$	2.7	14.3 ± 0.2
	$270^{\circ} \pm 2^{\circ}$	8.9	14.2 ± 0.2

Because of inherent difficulty in measuring temperature very accurately (15), no meaningful Arrhenius energy of activation (E_a) could be obtained, but free energies of activation at the temperature of coalescence (T_c) are listed in Table 1.

The substantial reduction in the barrier to rotation in the dimethylcarbamoyl-oximes reported here and in simple carbamates (13,14) ($\Delta F^{\ddagger} = 14\text{-}16$ kcal/mole), as compared to simple amides (8,9,12) and formamides ($\Delta F^{\ddagger} = 19\text{-}22$ kcal/mole), is remarkable. It would seem that

canonical structures such as I (9,10) assume significant importance in dimethylcarbamoyl-oximes at the expense of forms such as II important in amides.



The similarity in the barriers for all three dimethylcarbamoyl-oximes is noteworthy especially in light of the widely diverging concentrations.

The O-(N,N-dimethylcarbamoyl)-oximes were prepared by reacting the appropriate oxime with an equimolar amount of N,N-dimethylcarbamoyl chloride in pyridine at 0°. Details of the preparations will be reported in due course.

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15. The NMR spectra were recorded on a Varian A-60 NMR spectrometer equipped with a V-6040 Variable Temperature Controller.