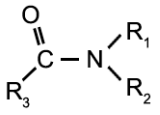
Colorado State University

CHEM 477
Physical Chemistry Laboratory - 2

Notes for
Determination of Rotational Barrier via Nuclear Magnetic Resonance (NMR)

The following is a set of short notes to outline the experiment in question and to provide helpful guidance to those executing the experiment.

A. Nuclear Magnetic Resonance (NMR) is capable of probing chemically distinct species in a molecule and to provide information on the molecular dynamics of those species.

B. In substituted amido compounds 

, the C–N bond is not strictly an sp^3 bond exhibits substantial sp^2 behavior (why?) including an elevated (relative to sp^3) potential energy barrier to rotation. At low temperatures the thermal energy available to the molecule is insufficient to surmount the rotational barrier and the nitrogen substituents, R_1 and R_2, are found to be co-planar with the carbonyl group where they experience different chemical environments and exhibit individual NMR signals with different chemical shift values. At higher temperatures sufficient thermal energy is available to induce fast rotation about this bond resulting in (motional) averaging of the environments experienced by the nuclei and motional averaging of the NMR signals into a single one with a weighted chemical shift.

C. The compound N,N-dimethylacetamide is an excellent exemplar of this type of system and suitable for study via solution NMR spectroscopy. Examination of the details of the shapes of the NMR signals (lines) can, through the use of sophisticated modeling, provide the rotation or exchange rate at individual temperatures. Analysis of these rates can be used to determine the activation energy of the process which, in turn, gives the magnitude of the potential energy barrier.

D. This process and system have been studied with moderately low field NMR (1.4 T or 60 MHz for ^1H resonance) and are in the literature. At the higher field available in this laboratory (8.4 T or 360 MHz for ^1H resonance or even higher), the minimum rotation rate necessary for coalescence and the temperature required for the attainment of this rate is significantly higher than at low field. Adjustment must be made for the difference in field.

E. The observation of these various signals is the experimental target of this experiment. The simulation and analysis of these signals using NMR processing software followed by

the interpretation of this analysis in terms of suitable thermodynamic variables will be performed. The theoretical explanation of the origin of the rotational barrier will be discussed in the Laboratory Report.

F. The dynamic analysis to be performed requires accurate knowledge of the sample temperature throughout the experiment and a separate calibration of this experimental variable is required.

G. The elevated temperatures required by this experiment will necessitate sealing of NMR tubes containing samples.