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Cautionary note: Linewidth effect in dynamic NMR

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In using NMR spectroscopy to evaluate the effects of kinetic processes taking place in the solute molecules being studied, one must estimate the inherent width w of each line, which is hidden from view throughout the kinetic thermal region due to the line-width broadening effected by the processes. We have herein built a self-consistent model function $w(T)$ to attempt to evaluate the variation in the Arrhenius activation energy obtained with the model parameters present in $w(T)$. As it turns out, a sizable number of such line-width parameters yields excellent spectral fits, and these lead to a considerable range of possible activation energies.

1. Introduction

The spectral fitting over some appropriate temperature range of AB-type proton (or ^{13}C) NMR spectra to obtain kinetic parameters such as the Arrhenius activation energy ΔE_A and pseudo-thermodynamic parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$ obtainable from the former via equations in [3]) is well known. By "kinetic", we mean herein the intramolecular dynamic phenomenon being evaluated. We and many others have published the relevant mathematical apparatus, stemming from density-matrix considerations: for example, see [10]. This assumes a line-shape function $V(\Gamma)$, where Γ denotes a parameter set, as described below. Our latest paper using this formalism appeared very recently [2]. The 'fixed' parameters to be used in the fitting are the inherent line width w of the absorption curve (full width at half-height, inversely proportional to the relaxation time ι_2), the picryl chemical-shift difference $\delta_{AB} = \nu_A - \nu_B$, the nuclear spin–spin coupling parameter J_{AB}, and the measurement frequency ν_o; all four appear in frequency units (e.g., Hz = s^{-1}). These parameters often are measurable at temperatures T below the kinetic region, but become hidden as the latter phenomenon takes over. Thus $w(T)$ [and $\delta_{AB}(T)$, and much less important: $J_{AB}(T)$], become guesswork in the kinetic analysis. Of course the primary fitting parameter is the 1st-order rate constant $k(T)$, which is the inverse of the mean lifetime τ of the two states A and B. The course of events observed by NMR spectroscopy as the temperature is raised, passing through the kinetic region, is summarized in Appendix A.

Recently, we took it on ourselves herein to investigate the effect of empirically varying the width w analytically and quantitatively within the kinetic region, establishing the effect of this on the activation energies attained, in a suitable model system related to an actual physical situation: the spectra of 2,2′-diphenyl-1-picrylhydrazine (denoted by DH herein; see Fig. 1) dissolved in liquid benzene-d$_6$, in its hindered-rotation thermal region, for ν_o = 500 MHz proton NMR.

2. Programs and devices used

WinDNMR v7.1.13 [8], Excel 2007 [5], Origin 7.5 [6], Light Table: Porta-Trace [7] were used for visual spectral fitting of NMR spectra.

3. Width functions

The choice of the width test function is somewhat arbitrary. Such a function $w(T)$ could be linear in T, quadratic in T, exponential, etc. Physically, it is highly probable that w will increase with increasing T. In most chemical systems, one can explore the thermal region situated just below onset of the kinetic phenomena (broadening, kinetic coalescence and then narrowing: for example, see Fig. 4 of [2]) to derive some idea of $w(T)$. The choice of $w(T)$ is of course highly limited in that one must be able to successfully fit the line shapes throughout the dynamic range.

In our work, we found simple visual comparison of the experimental and simulated spectra sufficiently sensitive and accurate, so that we did not resort to automatic computer-based comparisons.

From experience, with various hydrazines related to DH and with various solvents, we know that, as T decreases, $w(T)$ levels off to a fixed value [1, Fig. 3]. For DH in benzene, w is ca. 6.5 Hz when measured with 500 MHz NMR just above the melting point.

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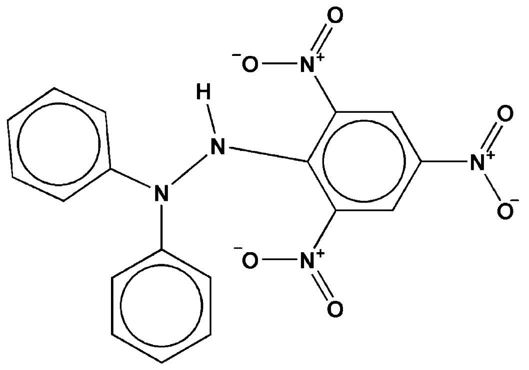

Fig. 1. DH molecular model.

Probably this value is set by relaxation times and field inhomogeneity.

To obtain the latter width, 6.5 Hz at 285 K, we used WinDNMR v7.1.13 to simulate the experimental spectrum. The fixed parameters were taken to be: $\nu_A = 4072.7$ Hz, $\nu_B = 3799.8$ Hz, $J_{AB} = 2.6$ Hz. We assumed k_{AB} equals 0 Hz, and then used the program to obtain the line width w at this temperature. Result: $w = 6.5$ Hz. This value is too great to permit resolution of the J splitting; thus only two lines (and not four) are observable in benzene (see Appendix A).

At the temperatures above the kinetic coalescence value (Appendix A), the width of the single line decreases with T. From the values measured above T_{coa}, one can best-fit $w(T)$ to obtain the estimated high-T limit w_∞, which in our DH case is 45.19 Hz. To do so accurately may be made difficult by several factors: possible fragility of the NMR probe, the boiling point of the solvent, changes in the solute/solvent interaction, and possible onset of other dynamic effects in the solute.

3.1. *Sigmoid width function*

We found it convenient and satisfactory for our present purposes to adopt the logistic sigmoid function

$$w = w_a + \left(\frac{w_b}{1 + e^{-b(T - T_o)}}\right) \tag{1}$$

as our primary empirical test function. This is seen to feature 4 adjustable parameters. Three are to be adjusted to values yielding functions $w(T)$ appropriate for our specific physical problem, and were kept constant throughout all our fitting runs, while the fourth (T_o) was assigned different values for our various runs. Here the T range is taken to be $-\infty$ to $+\infty$. Note that $w_{-\infty} = w_a$, and $w_\infty = w_a + w_b$. Here the three fixed parameters were taken to be $w_a = 6.5$ and $w_b = 38.692$ Hz, and $b = 0.5\ \mathrm{K}^{-1}$.

We note that the high-T leveling off of $w(T)$ is of course an artifact, but this approximation does not affect our kinetic results significantly.

In Fig. 2, we present members of the set of sigmoid functions which permitted high-quality fits of our NMR spectra.

3.2. *Linear width function*

As a simplest approach, for comparison, we also took w to be linear in T, utilizing the expression

$$w = w_a + bT \tag{2}$$

with $w_a = -206.5 \pm 3.0\ \mathrm{s}^{-1}$, $b = 0.75 \pm 0.01\ \mathrm{s}^{-1}\,\mathrm{K}^{-1}$ (see Fig. 2), obtained by fitting 3 estimated points.

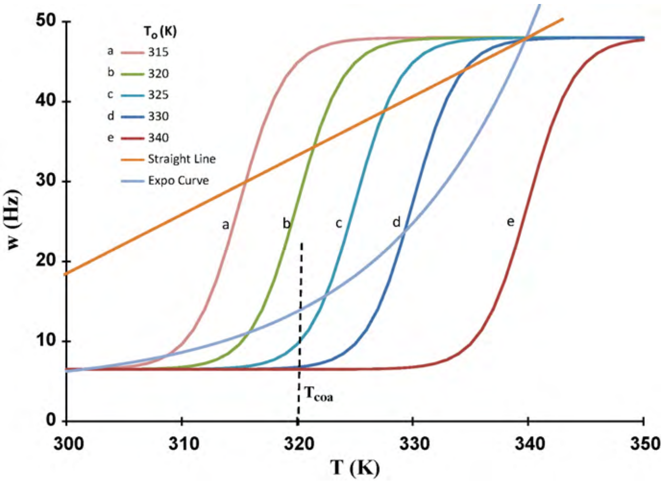

Fig. 2. Width vs. T plots.

3.3. *Exponential width function*

As a further simple function, as we had used in past papers, we used the exponential function

$$w = w_a + w_b\, e^{bT} \tag{3}$$

with $w_a = 4.2 \pm 0.1\ \mathrm{s}^{-1}$, $w_b = (2.0 \pm 5.7) \times 10^{-10}\ \mathrm{s}^{-1}$, $b = 0.077 \pm 0.008\ \mathrm{K}^{-1}$ (see Fig. 2), obtained by fitting 6 estimated points.

4. NMR behavior of molecules DH

The hindered rotation (interconversion between atropisomers) in DH has been studied by NMR in the past, beginning ca. 45 years ago [4], at various frequencies and in various solvents. A tutorial description has been published [3].

Detailed runs for DH in toluene (MP/BP = 180/384 K) have been recently published [2]. Here T_{coa} is 318 K (@ 500 MHz), so that one can easily follow the kinetic phenomenon throughout the most sensitive range (ca. 300–340 K), and one can estimate $w(T)$ and $\delta_{AB}(T)$ from measurements made below that range.

With DH in benzene (MP/BP = 279/353 K), which has $T_{coa} = 320$ K, it is difficult to attain much feeling for $w(T)$ and $\delta_{AB}(T)$ since the available region below the kinetic onset is so limited. This then also causes the published values of ΔE_A to be suspect.

The values of $\delta_{AB}(T)$ utilized in this modeling were calculated with the equation

$$\delta = \delta_0 + \varepsilon T \tag{4}$$

with $\delta_0 = 157.158$ Hz and $\varepsilon = 0.406\ \mathrm{Hz\,K}^{-1}$, obtained by linear fitting of (scant) chemical-shift-difference data measured at low temperatures (285–294 K). The resulting values of δ_{AB} in the kinetic region varied from 280 to 291 Hz, and we assumed that $J_{AB} = 2.6$ Hz throughout.

In Table 1, we compare estimates of the inherent widths w of the picryl proton lines of DH in our two solvents. We see that the widths in benzene tend to be double those in toluene, which may

Table 1
Comparison of various inherent linewidths of the picryl proton peaks of DH in benzene-d$_6$ and toluene-d$_8$ at various temperatures.

Solvent	w (Hz) at 250 K	w (Hz) at 285 K	w_{coa} (Hz)	w_∞ (Hz)
Benzene	–	6.5[a]	13.7	48
Toluene	1.4[a]	3.2	6.9	20

[a] Just above the melting temperature.