

Evaluation of the Rotational Barrier in the Bis-(dimethylamido) Phosphenium Cation by Spin Saturation Transfer and ^1H and ^{13}C Complete Bandshape Analysis

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Abstract

The barrier to rotation about the phosphorus–nitrogen bond in the bis(dimethylamido) phosphenium cation has been determined by ^{13}C and ^1H DNMR complete bandshape analysis and spin saturation transfer methodologies. Arrhenius activation energies for this simple two-site exchange process as derived from the three techniques are 11.2, 11.0 and 12.7 kcal mol $^{-1}$, respectively. Corresponding activation enthalpies are 10.7, 10.5 and 12.2 kcal mol $^{-1}$. Activation energies and enthalpies derived from these methods are thus in agreement within 1.7 kcal of one another.

Introduction

Since their first reported synthesis and isolation in 1968 by Fleming *et al.* [1] and independently by Maryanoff and Hutchins [2], dicoordinate phosphenium ions have been the subject of much interest [3]. Phosphenium ions are planar ions containing dicoordinate phosphorus and typically a N–P–N π system which in the case of $(\text{Me}_2\text{N})_2\text{P}^+$ (Fig. 1) renders the two methyls attached to each nitrogen chemically inequivalent at low temperatures [4]. These ions form a novel series of coordinatively unsaturated cations of the main group elements in that the lone electron pair on phosphorus allows it to behave as a ligand for low valent transition metal complexes [5], while its positive charge and empty π^* orbitals make it the quintessential π acid. The transfer of electron density into orbitals which are antibonding with respect to the N–P–N π bond results in a lowering of the barrier to rotation about the P–N bonds, making the phosphenium cation an ideal candidate as a charge density probe for transition metal centers. Activation parameters for rotation about the P–N bond in the amidophosphenium cation were first determined by Thomas [6] using ratio intensity [7, 8] and peak separation [9] methods, both of which are currently considered to be inaccurate and unreliable

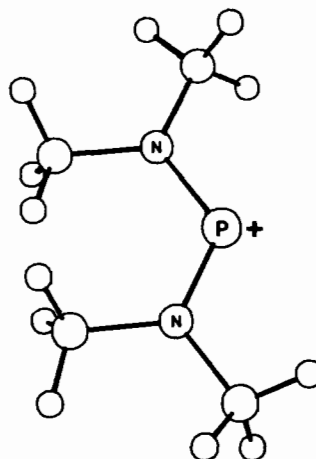


Fig. 1. The conformation of the bis(dimethylamido) phosphenium cation at temperatures below coalescence.

[10, 11]. An obvious prerequisite to the use of this ligand as such a probe involves an accurate determination of the rotational barrier about the P–N bond in the uncoordinated phosphenium ion. In this report we present the results of the measurement of the rotational barrier about the phosphorus–nitrogen bond in the tetrachloroaluminate salt of the bis-(dimethylamido) phosphenium cation using ^1H and ^{13}C complete bandshape analysis (CBS) and ^1H saturation transfer, currently the methods of choice in dynamic NMR.

Experimental

$[(\text{Me}_2\text{N})_2\text{P}]^+[\text{AlCl}_4]^-$ was prepared according to the method previously described by Thomas [6]. All NMR spectra were recorded on a Bruker WM-250 MHz spectrometer operating in the FT mode, with ^1H and ^{13}C chemical shifts referenced with respect to CH_2Cl_2 and standardized to TMS. The bandshape simulation program DNMR3 of Klier and Binsch [12] was utilized to provide calculated dynamic spectra. Due to the sensitivity of the phosphenium cation to moisture and oxygen, it was necessary to prepare sealed-tube samples. Temperatures were measured by

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an Omega Chromel/Alumel thermocouple placed inside a dummy sample tube of identical sample concentration utilized in the above studies, with the tube positioned at the level of the receiver coil.

^{13}C NMR

^{13}C NMR spectra were recorded in the temperature range 220–300 K in increments of ten degrees with NOE-suppressed gated decoupling ($PW = 90^\circ$, acquisition time = 1.4, relaxation delay = 6 s), with the decoupler being turned on only during the acquisition. Typically, 64 scans were recorded per spectrum.

^1H NMR

^1H NMR spectra were recorded in the temperature range 220–310 K in increments of ten degrees (five degrees around coalescence) with the following conditions: $PW = 90^\circ$, acquisition time = 3.3 s, relaxation delay = 3 s. No ^{31}P broad band decoupling was utilized. Only eight scans were necessary to obtain sufficient sensitivity.

^1H Saturation Transfer

Spectra were recorded in the temperature range 240–250 K. With respect to the pulse sequence in this system, a selective 180° decoupler pulse of 180 ms was utilized followed by a nonselective 90° observation pulse of 4.6 μs with a variable delay time in between. In order to observe varying amounts of exchange, this variable delay time is altered according to the times (see below Fig. 4). The pulse delay between the 90° observation pulse and the next selective 180° pulse was set at 10 s (approximately $5 \times T_1$) in order to insure that fully relaxed spectra were obtained.

Results and Discussion

Proton decoupled ^{13}C NMR spectra of the AlCl_4^- salt of the bis(dimethylamido) phosphonium cation are displayed on the left in Fig. 2, with the corresponding theoretical spectra calculated by the bandshape analysis program DNMR3 [12] on the right. The spectrum at 220 K contains two sharp doublets at 43.0 and 40.8 ppm (TMS) resulting from the two inequivalent methyl resonances coupled to the phosphorus nucleus. Bandshape perturbations due to chemical exchange appear above 220 K, with coalescence occurring between 267 and 290 K. ^1H NMR spectra of the cation and their theoretical bandshapes are shown in Fig. 3. The proton NMR spectra qualitatively parallel the ^{13}C spectra, exhibiting two doublets at 1.98 and 2.15 ppm (TMS) at 220 K. In this case bandshape perturbations appear between 220 and 260 K, with coalescence occurring between 270 and 290 K.

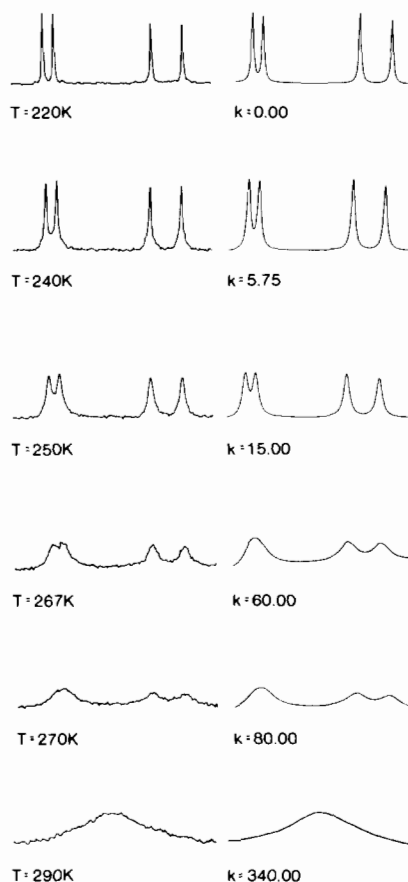


Fig. 2. ^{13}C NMR experimental spectra and computed line-shapes of the methyl resonances of $[(\text{Me}_2\text{N})_2\text{P}]^+[\text{AlCl}_4]^-$.

In the selective pulse modification of the saturation transfer experiment, the resonance due to nucleus A is inverted with a selective 180° pulse which is followed by a nonselective 90° observation pulse for the entire system. If exchange is occurring between nucleus A and nucleus B the intensity of the peak, I_B , will be reduced as a result of the transfer of magnetization as A exchanges with B. By varying the time between the selective 180° degree pulse and the nonselective 90° degree observational pulse the excess magnetization equilibration into site B due to chemical exchange can be observed as a function of time. This time dependency is represented conveniently as sum and difference spectra, related by the following exponential functions [13]:

$$I_A' + I_B' = -2M_0 e^{-t/T_1} \quad (1)$$

$$I_A' - I_B' = -2M_0 e^{-t(1/T_1 + 2k_{AB})} \quad (2)$$

where M_0 is the degree of magnetization of both sites in the absence of the selective inversion of resonance A, k_{AB} is the rate constant for exchange between sites A and B, T_1 is the longitudinal (spin-lattice)

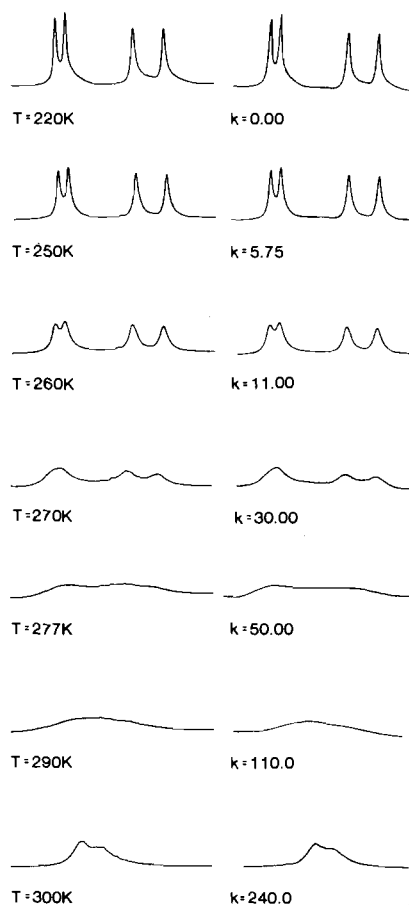


Fig. 3. ^1H NMR experimental spectra and computed lineshapes of the methyl resonances of $[(\text{Me}_2\text{N})_2\text{P}]^+[\text{AlCl}_4]^-$.

relaxation time, t is the delay time between the 180 and 90 degree pulses, and I' is the difference between the perturbed and nonperturbed (90°) intensities of each site. A plot of $\ln(I_A' + I_B')$ versus t yields a line with a slope equal to $1/T_1$, while a plot of $\ln(I_A' - I_B')$ versus t produces a line with slope $1/T_1 + 2k_{AB}$. The difference between the two slopes divided by 2 provides a direct measurement of the exchange rate constant, with experiments at several different temperatures yielding activation parameters from the corresponding Arrhenius and Eyring plots. Spectra for the saturation transfer experiment are displayed with intensities recorded with the normal 90° acquisition pulse subtracted from intensities observed when the resonance at one site is subjected to a 180 degree inversion pulse followed by a delayed non-selective 90° degree pulse:

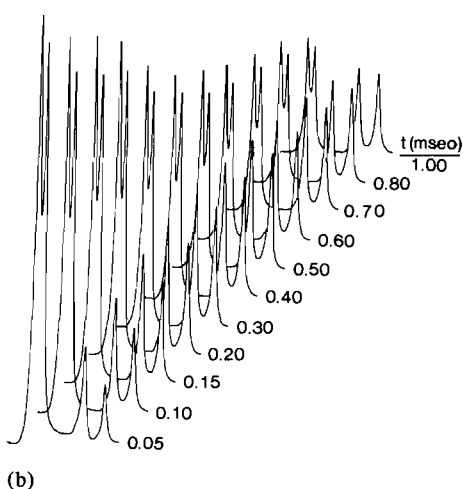
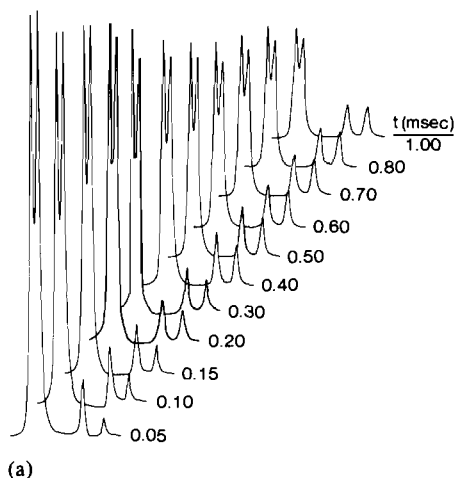
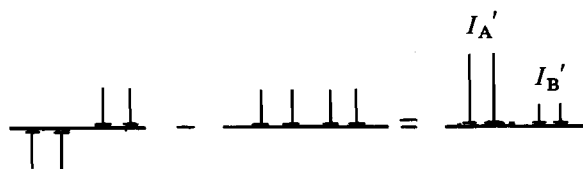


Fig. 4. ^1H NMR saturation transfer spectra obtained at (a) 240 K and (b) 250 K, with the corresponding delay times between ν_{180} (selective) and ν_{90} .

As the delay time is increased more magnetization is transferred from the 'selected' site to the other, resulting in a decrease in the difference peak of the selected nucleus and an increase in the difference peak of the other nucleus.

In this study the saturation transfer phenomenon was observed between 240 and 250 K in 2–3 degree increments. Difference spectra and their respective delay times obtained at 240 and 250 K for the proton resonances of the exchanging methyl groups of the phosphenium cation are shown in Fig. 4. Use of eqns. (1) and (2) resulted in a determination of exchange rate constants over the temperature range.

Activation parameters related to the rotational barrier about the P–N bond in the amidophosphenium cation are tabulated in Table I. Even with a potential for disparity between the rate constants determined via different techniques [14], activation energies and enthalpies determined with all three

TABLE I. A Comparison of the Values of E_a and ΔH^\ddagger for $[(\text{Me}_2\text{N})_2\text{P}]^+$ as Determined by Several Methods

Technique	E_a (kcal/mol)	ΔH^\ddagger (kcal/mol)
^{13}C CBS	11.2	10.7
^1H CBS	11.0	10.5
^1H saturation transfer	12.7	12.2
Ratio method ^a	12.8	12.2
$\nu_A - \nu_B$ method ^b	12.1	11.6

^aRef. 6, p. 37. ^bRef. 6, p. 37.

methods agree within $1.7 \text{ kcal mol}^{-1}$. Excellent agreement between the activation parameters obtained by complete bandshape analysis of both ^{13}C and ^1H nuclei is observed, with differences of 0.2 kcal/mol for the parameters of interest.

While peak separation and ratio intensity methods are techniques not currently favored in dynamic studies, as indicated in Table I the values obtained by these approximation methods are in good agreement with those reported in this work. It should also be noted that the results obtained from saturation transfer and complete bandshape analysis studies are closer to the theoretical barrier computed for rotation of one P–N bond in $(\text{Me}_2\text{N})_2\text{P}^+$ by the MNDO method [15]. Cowley has previously reported barriers to exchange of $11.6 \text{ kcal mol}^{-1}$ for rotation about the two equivalent P–N bonds in the bis(diisopropylamido) phosphonium cation and 11.5 and $12.6 \text{ kcal mol}^{-1}$, respectively, for rotation about the two inequivalent P–N bonds in the (diisopropyl)(dimethylamido)phosphonium cation [16]. The values were determined by a ^1H DNMR study of the above compounds, but experimental details of the method utilized were not reported.

The two types of methods considered in this work are subject to different errors due to dependencies in one case on T_1 (saturation transfer) and in another, T_2 (bandshape analysis). Nevertheless the barriers to rotation derived from ^{13}C and ^1H bandshape analysis, spin saturation transfer, and even intensity ratio and peak separation methods all produce activation energies and enthalpies for rotation about the P–N

bond in the bis(dimethylamido) phosphonium cation which agree within 2 kcal mol^{-1} . Although many more studies of a similar nature must be performed before any general conclusions can be drawn, the experiments described herein suggest that either the errors in relaxation times and temperature measurement tend to cancel one another, or that the determination of thermodynamic barriers to exchange is relatively insensitive to these errors.

Acknowledgement

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