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A NMR STUDY OF BARRIERS TO INTERNAL ROTATION IN 3-DIAZO-2-BUTANONE

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It is recognized that in α -diazoketones free rotation about the central C-C bond might be hindered through positive overlap of the carbonyl π -system with the p orbital on the α -carbon part of the CNN fragment.^{1,2}

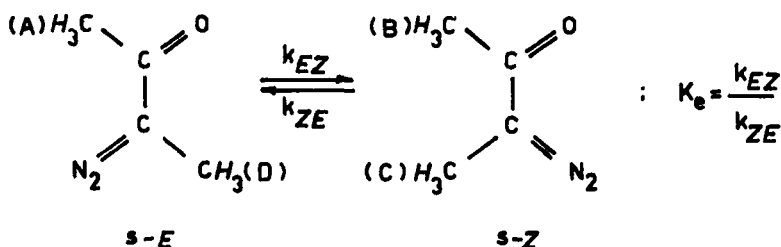
By using NMR spectroscopy, Kaplan and Meloy presented conclusive evidence that a number of α -diazoketones of the type RCO-CH=N_2 exist in solution as an equilibrium mixture of two conformational isomers having cisoid (i.e., s-Z) and transoid (s-E) configurations. For 3-diazo-2-propanone $\text{CH}_3\text{CO-CH=N}_2$ (1) in CDCl_3 solution at 25° , ΔG^\ddagger values for the E \rightarrow Z and Z \rightarrow E interconversion were estimated to be 14.1 and 15.4 kcal.mol⁻¹ respectively.² Thus, the s-Z form appears to be thermodynamically more stable than the s-E form by ca. 1.3 kcal.mol⁻¹

The observed dipole moment of 1 in benzene at 25° was found to be 3.37 D;³ on basis of calculated dipole moments of 1.76 and 3.93 D for the s-E and s-Z form respectively, a $[\text{s-Z}]_0/[\text{s-E}]_0$ ratio of 4.5 was estimated for 1 in this solvent.³ For this compound the prevalence of the s-Z form at equilibrium was rationalized invoking the unfavorable steric interaction between the methyl and the diazo-group arising in the s-E form; this must be such as to overcome the unpropitious opposition of dipoles presented by conformer s-Z.

A dipole moment of 2.45 has been found for 3-diazo-2-butanone $\text{CH}_3\text{CO-C(CH}_3\text{)=N}_2$ (2) in benzene at 25° .⁴ On comparison with the calculated dipole moments of the E and Z configurations, 1.7 and

3.9 D respectively, the hypothesis was advanced that this compound exists either as a single highly distorted structure (fixed or with restricted internal rotation) or as mixture of distorted E and Z forms.⁴

Consistent with early reports,⁵ we find that the ¹H-NMR spectra of 2 show temperature dependence both in CDCl₃ and CCl₄. At +40° the methyl protons resonances appear as two rate-broadened singlets; the singlet at lower field must be attributed to the O=C-CH₃ resonance.⁵ As the temperature is lowered, each of these singlets broadens further and then separates into two distinct, unequally intense singlets (see Figure 1 and Table 1). This clearly shows that 2 exists as an equilibrium mixture of two interconverting conformers:



In order to decide which form is prevalent,⁵ we have measured the spectra of 2 in the presence of Eu(fod)₃, a lanthanide shift reagent,⁶ at temperatures below coalescence. As expected,^{6,7} with lanthanide to substrate molar ratio > 0.1 the intensity of signals corresponding to the minor component increases with respect to that of signals of the major component with increasing [Eu(fod)₃]₀/[2]₀ ratio. However, the two conformers display a different dependence of induced shifts on Eu(fod)₃ concentration.^{7,8} For example, at -13° and [Eu(fod)₃]₀/[2]₀ ≈ 0.6 the N₂=C-CH₃ resonances of the major component show a larger induced shift (5.60 ppm) than do those of the minor component (3.23 ppm) (Table 1 and Figure 1). On basis of this evidence, assuming that bonding of the shift reagent to the α-diazoketone occurs largely at the carbonyl oxygen,^{7,8} one should conclude that in 2 the prevalent conformer has the s-E and not^{5,9} the s-Z configuration.

Thus, it appears that for 2 the situation has been reversed with respect to α-diazoketone 1. It is likely that both unfavorable steric

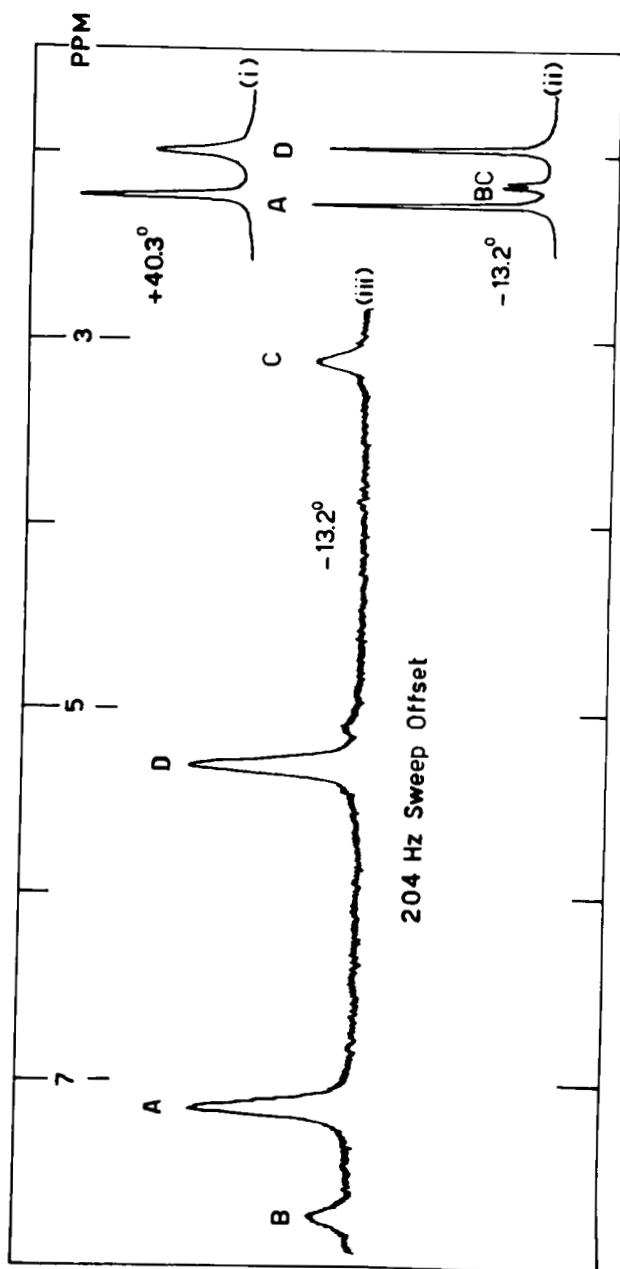


FIG. 1 - Proton Resonance Spectra (90 MHz) of 3-Diazo-2-butanone : (i) and (ii) 0.4 M in CDCl_3 ; (iii) 0.25 M in CDCl_3 , in the presence of 0.25 M Eu(fod)_3 .

TABLE 1

Chemical Shifts (δ)^a of Methyl Protons Resonances of the s-E and s-Z Conformers of 3-Diazo-2-butanone.^b

| Solvent | t, °C | δ_A | δ_{av} | δ_B | δ_C | δ_{av} | δ_D | T _c , °C ^c |
|--|-------|------------|---------------|------------|------------|---------------|------------|----------------------------------|
| CDCl ₃ | -30 | 2.28 | | 2.18 | 2.16 | | 1.96 | + 21 |
| | +46 | | 2.20 | | | 1.97 | | |
| | -13 | 2.27 | | 2.18 | 2.15 | | 1.96 | |
| CDCl ₃ + Eu(fod) ₃ ^d | -13 | 9.41 | | 9.99 | 5.38 | | 7.56 | |
| CCl ₄ | -30 | 2.19 | | 2.16 | 2.07 | | 1.92 | + 13 |
| | +46 | | 2.14 | | | 1.93 | | |

^a In ppm (TMS internal standard). ^b In all experiments the concentration of 2 was ≈ 0.4 M. ^c Estimated coalescence temperature (90 MHz). ^d [Eu(fod)₃]₀/[2]₀ ≈ 0.6 .

interaction between the methyl groups and opposition of C=O and C=N₂ dipoles arising in the s-Z form contribute to render conformer s-E prevalent in 2.

To obtain the relative energies of the two conformers and energy barrier to internal rotation, we performed a detailed line-shape analysis of the temperature-dependent methyl resonances of 2, corresponding to two unequally populated AB(DC) exchange cases with common reaction rates.¹⁰ The dependence of chemical shifts with temperature was also taken into account. High-resolution spectra were recorded at several temperatures on a Bruker HFX-10 spectrometer and calibrated to ± 0.1 Hz with a frequency counter. Sample temperatures were measured to $\pm 0.2^\circ$ using methanol standard¹¹ and corrected by the method of Van Geet.¹² Spectra were digitized point by point and the digits used for input to a DNMR program.^{10,11} Visual fitting of the computer-plotted to experimental spectra gave relative populations, lifetimes τ and hence the individual interconversion rates (to $\pm 5\%$) at each temperature. Typical fits are shown in Figure 2.

TABLE 2

Temperature Dependence of Fractional Populations, Equilibrium Constants and Rates of Interconversion of the s-E and s-Z Forms of 2.^a

| Solvent | t, °C | p _E | p _Z | 1/K _e | k _{ZE} | k _{EZ} |
|-------------------|-------|--------------------|--------------------|------------------|-----------------|-----------------|
| CDCl ₃ | -34.9 | 0.862 ^b | 0.138 ^b | 6.25 | - | - |
| | -29.8 | 0.848 ^b | 0.152 ^b | 5.58 | - | - |
| | -25.2 | 0.842 ^b | 0.158 ^b | 5.33 | - | - |
| | -15.2 | 0.836 ^b | 0.164 ^b | 5.10 | - | - |
| | -5.1 | 0.821 | 0.179 | 4.58 | 2.38 | 0.520 |
| | 0.7 | 0.814 | 0.186 | 4.38 | 4.07 | 0.930 |
| | 5.4 | 0.803 | 0.197 | 4.08 | 9.64 | 2.36 |
| | 10.9 | 0.794 | 0.206 | 3.85 | 13.1 | 3.40 |
| | 15.2 | 0.789 | 0.214 | 3.69 | 17.7 | 4.80 |
| | 20.8 | 0.774 | 0.227 | 3.41 | 27.6 | 8.10 |
| | 30.5 | 0.762 | 0.239 | 3.19 | 63.2 | 19.8 |
| | 40.3 | 0.746 | 0.251 | 2.97 | 131. | 44.0 |
| | 46.4 | 0.737 | 0.260 | 2.80 | 229. | 81.0 |
| CCl ₄ | -20.1 | 0.903 | 0.097 | 9.31 | 0.144 | 0.016 |
| | -15.5 | 0.897 | 0.103 | 8.71 | 0.359 | 0.041 |
| | -10.1 | 0.871 | 0.129 | 6.75 | 0.871 | 0.129 |
| | 0.4 | 0.856 | 0.144 | 5.94 | 5.14 | 0.865 |
| | 10.4 | 0.821 | 0.179 | 4.59 | 22.2 | 4.84 |
| | 30.0 | 0.750 | 0.250 | 3.00 | 120. | 40. |
| | 35.4 | 0.742 | 0.258 | 2.88 | 271. | 94.1 |
| | 40.9 | 0.692 | 0.308 | 2.25 | 287. | 127. |

^a Concentration of 2 was ≈ 0.4 M; k values are in sec⁻¹.

^b Estimated by integration of resonance peaks.

Assuming a transmission coefficient of unity, statistical least-squares treatment of Eyring plots¹⁰ provided approximate ΔH^\ddagger and ΔS^\ddagger values, hence ΔG^\ddagger values at 298°K. Similarly, plots of $\ln(1/K_e)$ vs. $1/T$ gave ΔH_{EZ}^0 values, whereas ΔG_{EZ}^0 was calculated as $-RT \ln K_e$. Thermodynamic and activation parameters are collected in Table 3 together with their uncertainties. Systematic errors, however, could result in errors larger than these estimates.

Noteworthy, significant increases in ΔH^\ddagger values on passing from CDCl₃ to CCl₄ solvent are not accompanied by corresponding increases in ΔG^\ddagger .

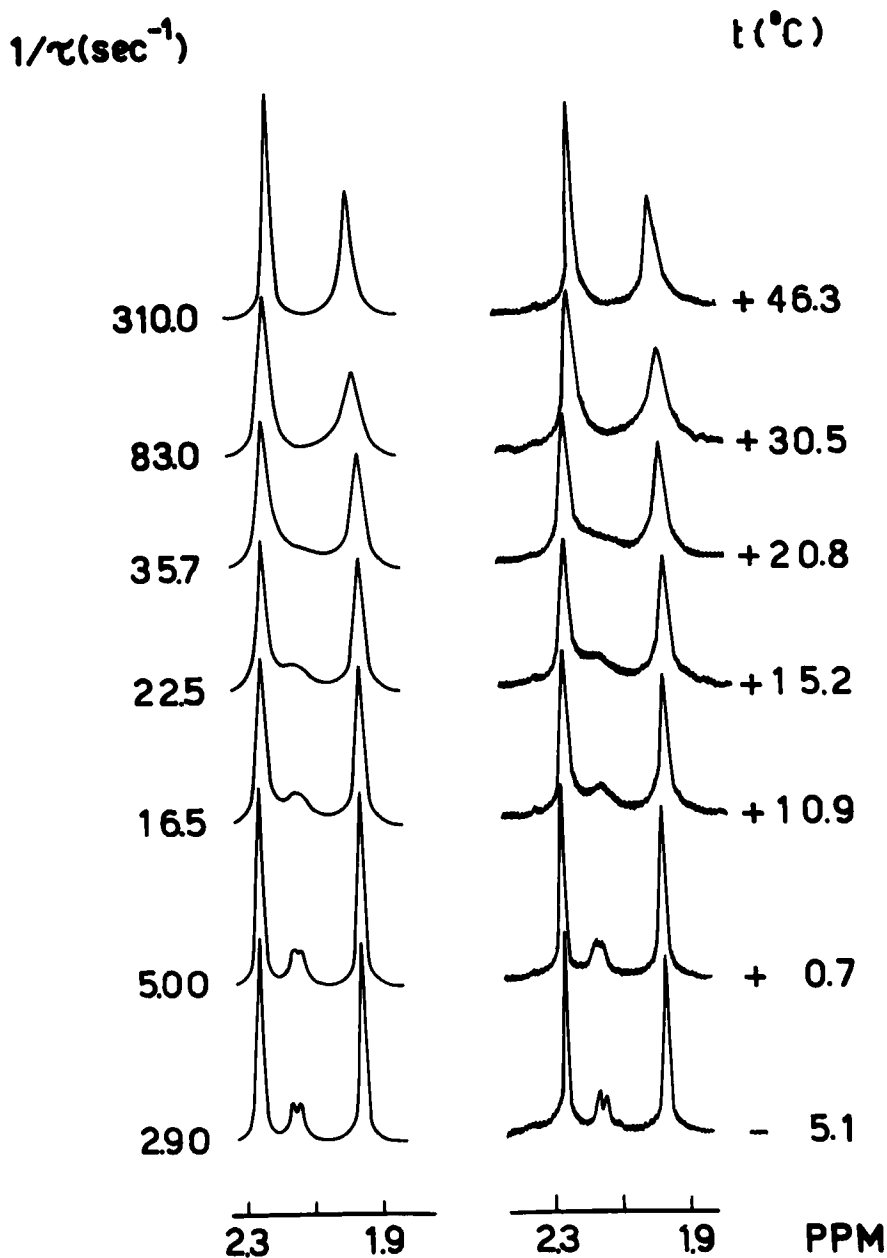


FIG. 2 - Experimental (right) and Computer-plotted (left) proton resonance spectra of ca. 0.4 M 3-Diazo-2-butanone in CDCl_3 at various temperatures.

TABLE 3

Differences in Conformational Energy and Activation Parameters of Interconversion for the s-E and s-Z Forms of 2.^a

| Solvent : | CCl ₄ | CDCl ₃ |
|--|------------------|-------------------|
| ΔH_{EZ}^0 | 3.50 ± 0.15 | 1.45 ± 0.15 |
| $\Delta G_{EZ}^0 (298^\circ K)$ | 0.71 ± 0.22 | 0.72 ± 0.15 |
| ΔH_{EZ}^\ddagger | 22.9 ± 0.7 | 15.6 ± 0.5 |
| ΔH_{ZE}^\ddagger | 19.3 ± 0.8 | 14.0 ± 0.5 |
| ΔS_{EZ}^\ddagger | 24.5 ± 3 | -1 ± 2 |
| ΔS_{ZE}^\ddagger | $15. \pm 3$ | -4 ± 2 |
| $\Delta G_{EZ}^\ddagger (298^\circ K)$ | $15.6 \pm 1.$ | 15.9 ± 0.6 |
| $\Delta G_{ZE}^\ddagger (298^\circ K)$ | $14.9 \pm 1.$ | 15.2 ± 0.6 |

^a Free-energy and enthalpy changes are in kcal mol⁻¹; entropy changes are in cal mol⁻¹deg⁻¹.

Inspection of data in Table 3 reveals that this occurs largely at expenses of activation entropies. Thus, while at 0° the interconversion rates are nearly equal in the two solvents, the ratio of rate in CCl₄ to rate in CDCl₃ would be ca. 4 at +50° and ca. 0.1 at -50°.

Clearly, reordering of solvent molecules around the C=O and C=N₂ groups on going from ground to transition state is considerably more costly in terms of entropy in CDCl₃ than in CCl₄. This is not surprising in view of the capability of chloroform (a weakly acidic solvent)¹³ to give specific solvation interactions (via hydrogen-bonding) with several organic substrates.

The magnitude of the barriers to internal rotation in 2 compares favorably with that found for α -diazoketones RCO-CH=N₂,² for aromatic α -diazoketones ArCO-CR=N₂,⁷ as well as with theoretical calculations.¹⁴ It is unlikely, therefore, that dramatic distortions of planar arrangement of O=C-C=N₂ moiety occur in each of the two conformers of 2.

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