Ionization of Tropylium Azide in Liquid Sulfur Dioxide and Selective Migration of the Azide Ligand in Less Polar Solvents[1]

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Abstract: The equilibrium between the covalent azidocycloheptatriene and ionic tropylium azide has been directly observed in the low-temperature ^1H and ^{13}C NMR spectra in solvents containing SO_2. The kinetic parameters of the ionization ($\Delta H^{\ddagger}{}_i$ = 28.8 ± 6.3 kJ, $\Delta S^{\ddagger}{}_i = -77 \pm 25$ J/grad·mol, $\Delta G^{\ddagger}{}_{i232} = 46.5 \pm 0.5$ kJ/mol) have been determined by ^{13}C NMR line shape analysis. Nonrandom migration of the azide ligand occurs in less polar media as was shown by (a) saturation transfer in the ^{13}C NMR spectrum at carefully selected temperatures; (b) ^{13}C NMR line shape analysis; (c) ^1H NMR line shape analysis of hexadeuterioazidocycloheptatriene. 1,3-Shift ([3,3] sigmatropic migration) dominates but also nonnegligible participation of 1,2-shift ([1,7] sigmatropic migration) is observed (e.g., in CD_3CN: $\Delta G^{\ddagger}{}_{298}{}^{1,3} = 59.85 \pm 0.13$ kJ/mol, $\Delta G^{\ddagger}{}_{298}{}^{1,2} = 61.4 \pm 0.2$ kJ/mol). It has been shown that the rate of the selective migration increases with increasing solvent polarity. Thus tropylium azide represents a borderline example between sigmatropic and ionic migration.

We have recently demonstrated the feasibility of studying by NMR methods barriers for the interconversion of covalent molecules and their ion pairs.[1-7] A precondition for such studies is a measurable population (>5%) of the covalent *and* the ionic forms in the equilibrium mixture. So far we have studied the tropylium,[1-3,6,7] cyclopropenylium,[8] and (substituted) trityl cations.[4,5,7] We now report a detailed investigation of tropylium azide in different solvents. Ionization of the covalent azidocycloheptatriene is observable in liquid SO_2 and the kinetics of this process could be studied in mixtures of SO_2 and $CDCl_3$. In less polar solvents, only the covalent azidocycloheptatriene is observable but migration of the azide ligand occurs at rates comparable with the NMR time scale. We have therefore been able, through the study of NMR time-dependent phenomena, to delineate the existence of preferred rearrangement pathways. This, in turn, permits us to discuss rearrangements which, mechanistically, lie in the interesting region where the distinction between concerted and dissociative processes is ill defined.

Experimental Section

NMR Spectra. The ^1H FT NMR spectra for line-shape studies were obtained with a Bruker WH 270 instrument (270 MHz) equipped with the BNC 28 computer. All other ^1H FT NMR spectra were measured with a HX 90/4-15″ instrument (Bruker, 90 MHz) and the same instrument was used for ^{13}C FT NMR measurements (22.63 MHz). With this latter spectrometer, data accumulations and transformations were performed with the NIC 1083 computer (Nicolet). A Schomandel ND 100 M frequency synthesizer was used for the $^{13}C\{^{13}C, ^1H\}$ triple resonance experiments.

The temperature of the ^1H NMR probe was determined by the frequency difference between the hydroxyl and the methyl resonance of methanol[12] while for the ^{13}C experiments an alcohol thermometer was inserted directly into the NMR tube.

Materials. SO_2 (Messer Griesheim, 99.995%) was dried over P_2O_5, $CaCl_2$, and molecular sieves and finally distilled in a sealed system under nitrogen directly into the NMR tube. 7-Azidocycloheptatriene was prepared as previously described by Wulfman et al.[9] Hexadeuteriotropylium fluoroborate was synthesized from hexadeuteriobenzene via hexadeuteriocycloheptatriene.[1]

Calculations. The NMR line shapes of the multisite exchange of uncoupled spins were simulated by a modified version of the program EXCH 10 (G. M. Whitesides) based on the Bloch equations. The *k* matrix for the exchange between sites with any given populations was defined in a manner similar to the procedure described by Reeves.[13] It is explained in detail in the supplementary material.

The activation parameters were calculated using the program ACTPAR by G. Binsch[14] which takes into account both the individual variances in *k* and *T*. The experimental spectrum at each temperature was visually compared with computed spectra of different rate constants *k*. The maximal and minimal ifk values which can fit the experimental line shapes are taken as error limits. The errors in temperature were assumed to be ±1 °C.

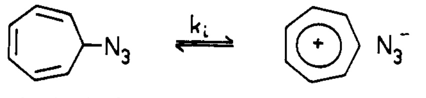
Results

Solvent Effects. The room temperature ^1H NMR spectra of tropylium azide exhibit broad lines in all common organic solvents.[2,6,9] At lower temperatures, the spectra are clearly resolved and correspond to the structure of a 7-substituted cycloheptatriene. No indication of ionization into tropylium ions and azide anions could be detected by observation of either a downfield shift or by a discrete tropylium peak in the region around 10 ppm. The very complex exchange of a coupled seven-spin system requires special treatment for its direct kinetic analysis (see below). Hence, solvent effects on the barrier were roughly estimated by comparison of the temperature which causes "coalescence" (comparable line broadening). The results (Table I) show that in less polar solvents higher temperatures are necessary to give the same topomerization rate as in acetonitrile or methanol. Normally, such a behavior is taken as an indication of an ionic transition state or intermediate. We will show that, in spite of the influence of solvent polarity, selective migration mechanisms strongly dominate.

Liquid SO_2, however, induces ionization. The NMR singlet of the ring protons caused by rapid azide migration is shifted from 6.23 ppm at 293 K to 9.43 ppm at 203 K (Figure 1). The position of the singlet at low temperatures is near that of the free tropylium ion (~10 ppm).[10] Furthermore, at intermediate temperatures, considerable line broadening occurs.

The shift of the signal to lower field on cooling is caused by an increasing population of the ions and/or ion pairs at lower temperatures. Such a behavior is typical of ionization and dissociation processes in solution.[11] The observed line broadening in the intermediate temperature range indicates slow exchange between the ions and the covalent form.

Ionization in Liquid SO_2. Since the low-temperature spectrum of tropylium azide (**1**) in liquid SO_2 consists only of one peak for the ionic form (Figure 1), a kinetic analysis of the ionization process, which requires comparable populations of both interconverting forms, could not be performed. Suitable conditions for a kinetic analysis were, however, achieved by the addition of $CDCl_3$. To avoid the problems in calculating



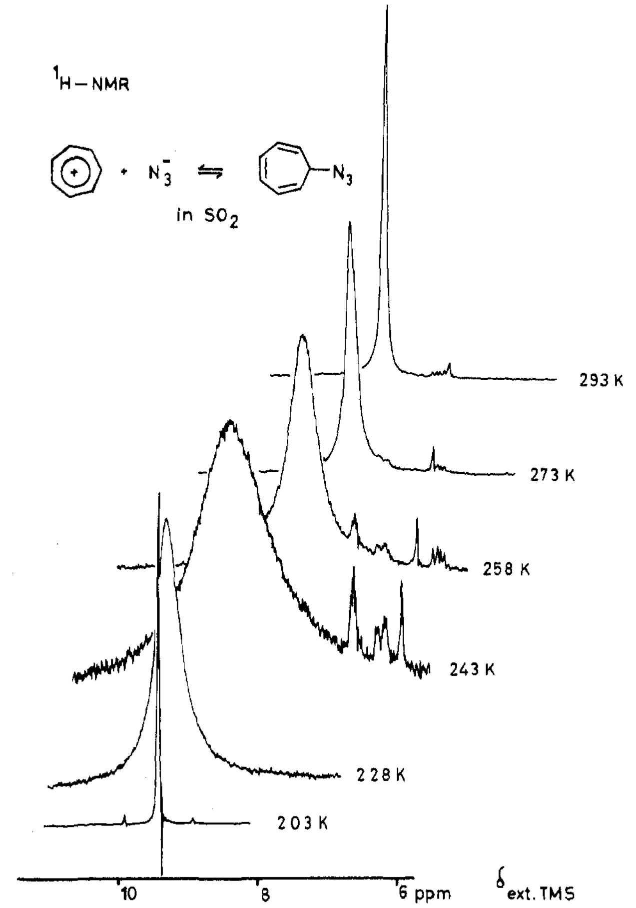


Figure 1. FT ^{1}H NMR spectrum of azidocycloheptatriene (**1**) at different temperatures in SO_2 (90 MHz, Bruker HX 90).

Table I. Temperature for Comparable Line Broadening ($\sim T_c$, K) in the ^{1}H NMR Spectrum of Azidocycloheptatriene in Different Solvents

solvent	E_T[a]	$\sim T_c$
CS_2	32.6	$\gg 340$
THF	37.4	>343
$CDCl_3$	39.1	315
CD_2Cl_2	41.1	310
$(CD_3)_2CO$	42.2	313
CD_3CN	46.0	300
CD_3OD	55.5	295
SO_2		~ 250

[a] Solvent polarity parameter as defined by C. Reichardt, "Lösungsmitteleffekte in der Organischen Chemie", Verlag Chemie, Weinheim/Bergstr., Germany, 1969. C. Reichard, *Angew. Chem.*, **91**, 119 (1979).

the multisite exchange of a coupled seven-spin system we studied the $^{13}C\{^1H\}$ (Figure 2) rather than the ^{1}H NMR spectra.

Comparison of the simulated line shapes with the experimental ones yielded the rates of ionization k_i, the Eyring plot of which gave the following activation parameters: $\Delta G^{\ddagger}{}_i$ = 46.5 ± 0.5 kJ/mol at 232 K, $\Delta H^{\ddagger}{}_i$ = 28.8 ± 6.3 kJ/mol, $\Delta S^{\ddagger}{}_i$ = −76.6 ± 25 J/K·mol. In SO_2, the tropylium ions are more stable on the enthalpy scale than the azidocycloheptatriene. The evaluation of the equilibrium constants at different temperatures from the center of gravity in the ^{1}H spectra in SO_2 containing 0–40% $CDCl_3$ gave enthalpy values $\Delta H°$ between −23 (±5) and −32 (±5) kJ/mol (see supplementary material). Strong negative *entropy* differences were also observed ($\Delta S°$ = −105 to −126 (±15) J/K·mol).

Selective Migration of the Azide Ligand in Azidocycloheptatriene. A. Saturation Transfer in ^{13}C NMR Spectroscopy. Temperature-dependent ^{1}H and ^{13}C NMR spectra indicate an azide migration even in rather nonpolar solvents. Since ionization occurs in $SO_2/CDCl_3$, migration under these conditions is necessarily random. This conclusion should not, however, be extended to less polar solvents. Indeed ^{13}C NMR saturation transfer experiments[15] gave the first indication of the operation of selective shift mechanisms. In these experiments, the signal of one carbon in the ^{1}H noise decoupled spectrum was irradiated at a third frequency. The choice of the temperature was critical. At too *low* a temperature, the relaxation rate is faster than the migration rate and no transfer of magnetization is observed, while at *high* temperatures, the fast sequence of azide migrations transfers spin saturation to all transitions (total nulling of all signals is observed). The spectra of tropylium azide at 238 K in THF are presented in Figure 3. Similar results were obtained in $CDCl_3$ at 210 K. Clearly the saturation transfer is a nonrandom process. For example, the irradiation of C-7 lowers the intensity of the C-2,5 signal more than the others. Thus the migration of the azide from C-7 to C-2 (or to the equivalent C-5) is a preferred pathway. The symmetry of the exchange is indicated in Figure 3. The complementary experiments (irradiation of C-3,4 and C-2,5) confirm this interpretation.

The above conclusions depend critically on the assignment of the carbon signals to the different ring positions. This was achieved through the correlation of the carbon and proton chemical shifts, by the stepwise single frequency off resonance decoupling technique. The ^{1}H NMR spectrum has been unambiguously analyzed and assigned from the observed coupling pattern.[16]

The observation of 1,3 migration in these experiments does not rule out small contributions from other selective shift mechanisms or participation of random migration.

B. Line-Shape Studies. The line shapes of the olefinic region of the ^{13}C NMR spectra and of the ^{1}H NMR spectra of 7-azidocycloheptatriene-d_6 are sensitive to the mechanistic pathway in the temperature range in which moderate line broadening occurs. This is shown for theoretical spectra of the carbons 1–6 in Figure 4. The comparison of these line shapes with those obtained experimentally (for an example see Figure 7) leads to the conclusion that more than one pathway must be involved in the rearrangement. The signals of both carbons 1(6) and 3(4) are too narrow to be explained by a contribution from a random shift. The same effect is observed in the ^{1}H NMR spectra (compare Figure 6, 271 K). The smaller broadening of the 1(6) peak indicates the participation of the 1,3 shift, whereas the same effect for 3(4) could be caused by a selective 1,2 shift or a shift via small amounts of ions. The latter case could be excluded since a systematic variation of the amount of ions and their recombination rates relative to the rates of the 1,3 shift revealed no combination of input parameters which could fit the experimental spectra. (This procedure is described in the supplementary material.)

Hence, the experimental spectra had to be fitted by a combination of 1,3 with 1,2 and (smaller amounts of) 1,4 shifts. The remaining problem is the multidimensional fit of three different rate parameters. This was possible in the temperature range in which the signals of the olefinic carbons are not yet fully collapsed.[17] At each temperature the broadening of the C-7 signal gives the overall rate k^{Σ}

$$k^{\Sigma} = k^{1,2} + k^{1,3} + k^{1,4} \qquad (1)$$

Variation of the remaining two parameters leads to all possible

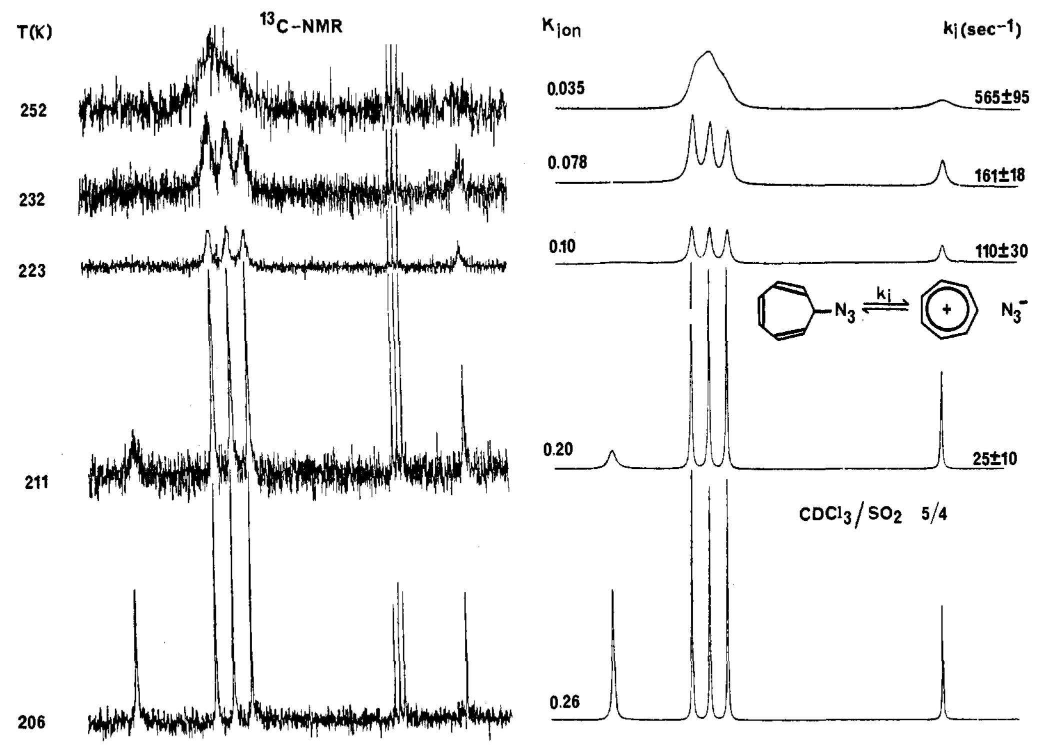


Figure 2. Experimental and calculated ^{13}C DNMR spectrum of **1** in $SO_2/CDCl_3$ (4:5) (22.63 MHz).

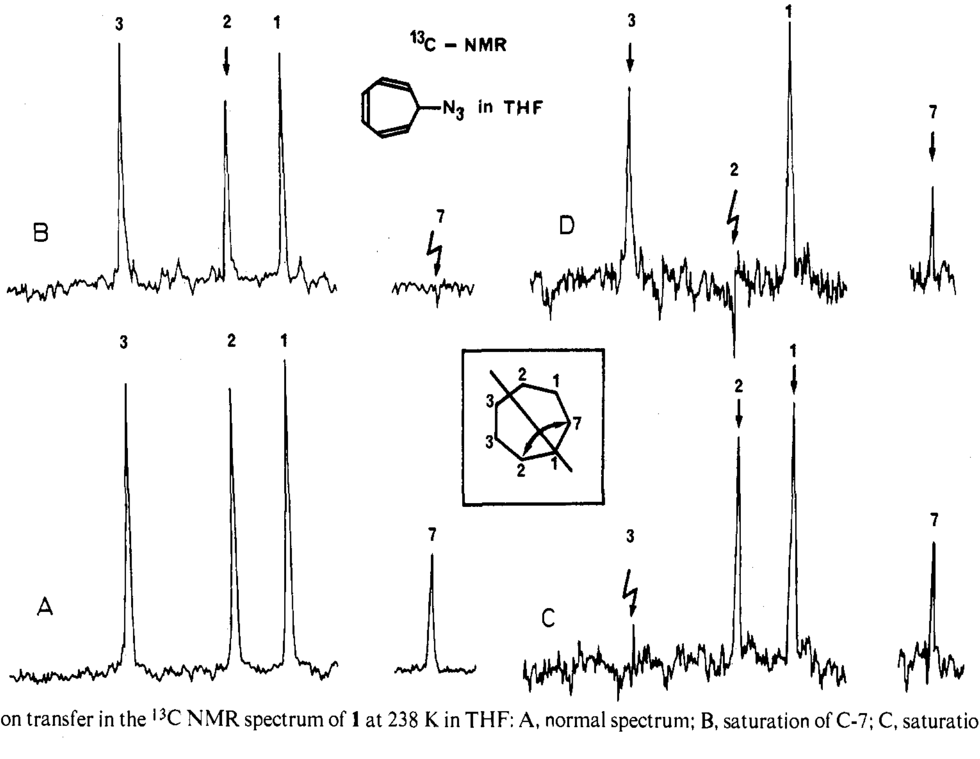


Figure 3. Saturation transfer in the ^{13}C NMR spectrum of **1** at 238 K in THF: A, normal spectrum; B, saturation of C-7; C, saturation of C-3; D, saturation of C-2.

theoretical spectra. As a first approximation the theoretical spectra were compared with the experimental ones by inspection of the relative heights of the olefinic signals. For a two-dimensional graph, the "reduced shift contributions" are defined as follows:

$$x_{23} = k^{1,2}/(k^{1,2} + k^{1,3}) \tag{2}$$

$$x_{43} = k^{1,4}/(k^{1,4} + k^{1,3}) \tag{3}$$

The values of x_{23} and x_{43} can vary between 0 and 1. The combination of eq 1-3 results in

$$k^{1,2} = k^{\Sigma}\left(\frac{1}{x_{23}} + \frac{1/x_{23} - 1}{1/x_{43} - 1}\right)^{-1} \tag{4}$$

$$k^{1,3} = k^{\Sigma}\left(1 + \frac{x_{23}}{1 - x_{23}} + \frac{x_{43}}{1 - x_{43}}\right)^{-1} \tag{5}$$

$$k^{1,4} = k^{\Sigma}\left(\frac{1}{x_{43}} + \frac{1/x_{43} - 1}{1/x_{23} - 1}\right)^{-1} \tag{6}$$

An example for a rate matrix is given in the supplementary material. The ^{13}C NMR spectra at low temperatures indicate

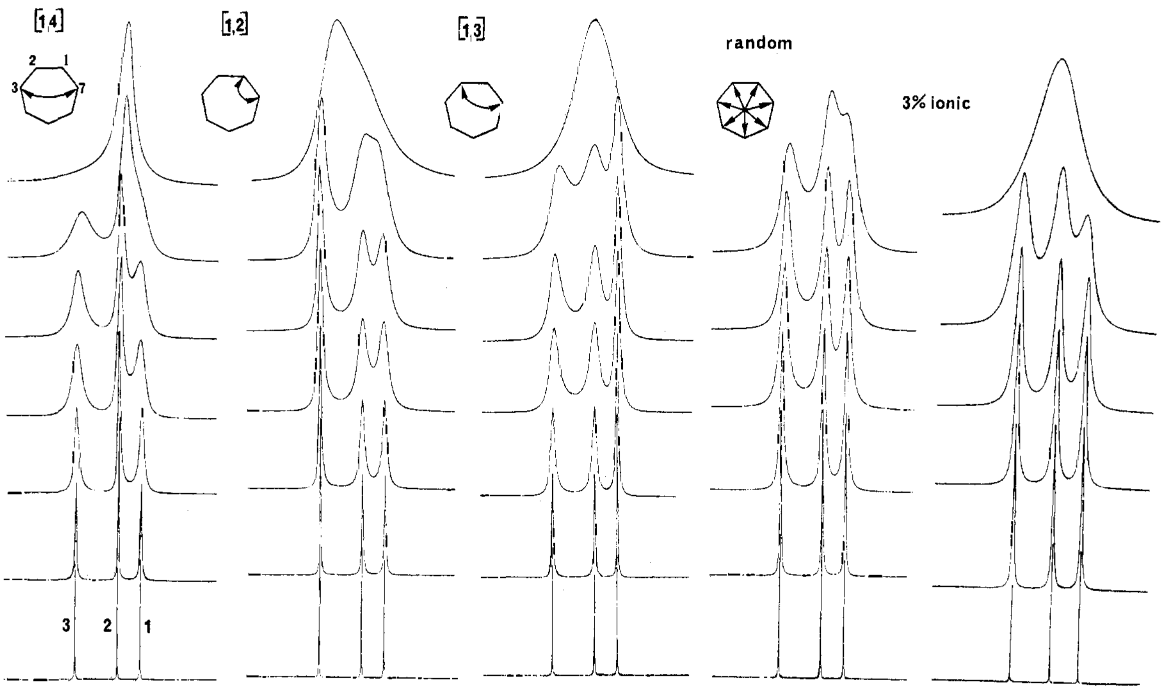


Figure 4. Theoretical ^{13}C NMR line shapes of carbons 1-6 for different shift mechanisms.

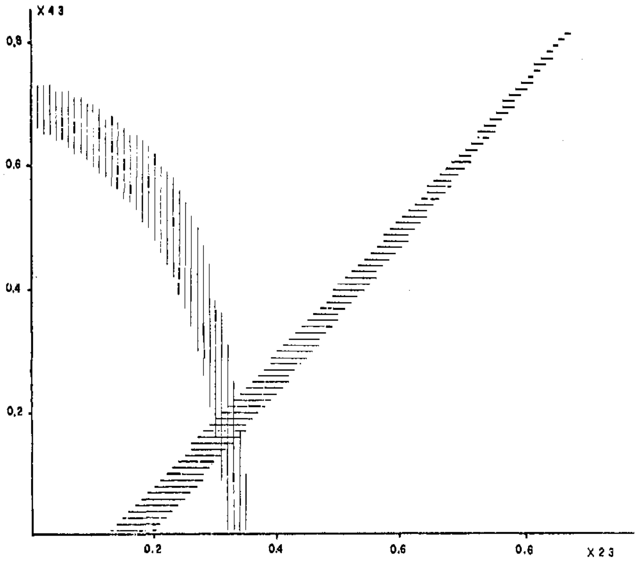


Figure 5. Example for the graphic search for optimal x_{43}/x_{23} combinations (see text) for the simulation of the relative heights of peaks of H-1,6 and H-2,5 in the ^1H NMR spectrum of **1** in CD_3CN at 276 K ($k^\Sigma = 87\ s^{-1}$). Vertical lines correspond to an error of ±2% in the relative heights of the signals H-1,6 and H-3,4; horizontal lines result from the same deviation in the heights of the H-2,5 and H-3,4 signals.

signal intensities which correspond to the number of carbon atoms. Therefore no additional correction must be applied.

The proton spectra of the hexadeuterated compound, on the other hand, exhibit a remarkable isotope effect[18] (p_n = population of signal n):

$$p_{1,6} = 1.0; p_{2,5} = 1.0; p_{3,4} = 1.0; p_7 = 0.8 \qquad (7)$$

Analysis of the kinetic isotope effect was not performed directly from the line shapes but rather by modifying the rate constant matrix from the following consideration.

$$\Delta G^{\ddagger} = 0.5(\Delta G^{\ddagger}_{ij} + \Delta G^{\ddagger}_{ji}) \qquad (8)$$

$\Delta G^{\ddagger}$ represents the barrier between isomers of equal population; $\Delta G^{\ddagger}_{ij}$ and $\Delta G^{\ddagger}_{ji}$ are related to the forward and backward reaction barriers for isomers of different population. The elements of the new matrix (k_{ij} and k_{ji}) result from the elements of the general k matrix $(0.5k^{1,x})$[19] by the equation

$$0.5k^{1,x} = (k_{ij}k_{ji})^{1/2} \qquad (9)$$

Consideration of the principle of microscopic reversibility ($k_{ij}p_i = k_{ji}p_j$) then leads to the equation

$$k_{ij} = 0.5k^{1,x}\left(\frac{p_j}{p_i}\right)^{1/2} \qquad (10)$$

The two-dimensional graph of the parameters x_{43} and x_{23} which can fit the relative peak heights in the olefinic part (the errors are given by the length of the lines) is represented in Figure 5. The area of intersection gives the best combination of x_{43} and x_{23}. The individual rate constants $k^{1,2}$, $k^{1,3}$, and $k^{1,4}$ are available via eq 4-6. These values were used for the reproduction of the total line shapes and k^Σ was varied to improve the agreement with experiment. The whole procedure was then repeated several times to optimize the fit. The relative participations of the different shift mechanisms in CD_3CN solutions are indicated in Figures 6 and 7 and are reported as $\Delta G^{\ddagger}_{298}$ values, together with the corresponding data for $CDCl_3$ and THF solutions, in Table II. The disparities between the ^1H and ^{13}C data doubtless arise from the differences in concentrations (0.2 and 1.5 M, respectively) employed in the two sets of measurements. The higher concentration of the azide results in a lower polarity of the solution (higher barriers). Eyring plots of the rates for CD_3CN solutions are presented in Figure 8 and the corresponding parameters are listed in Table III.

Discussion

Ionization of Azidocycloheptatriene. For most organic ionogenic compounds the ions are much less thermodynamically stable than the covalent species. There are several parameters which increase the ionization equilibrium constant. These include increasing stability of cations and/or anions, increasing solvent polarity, and decreasing temperature. We have studied

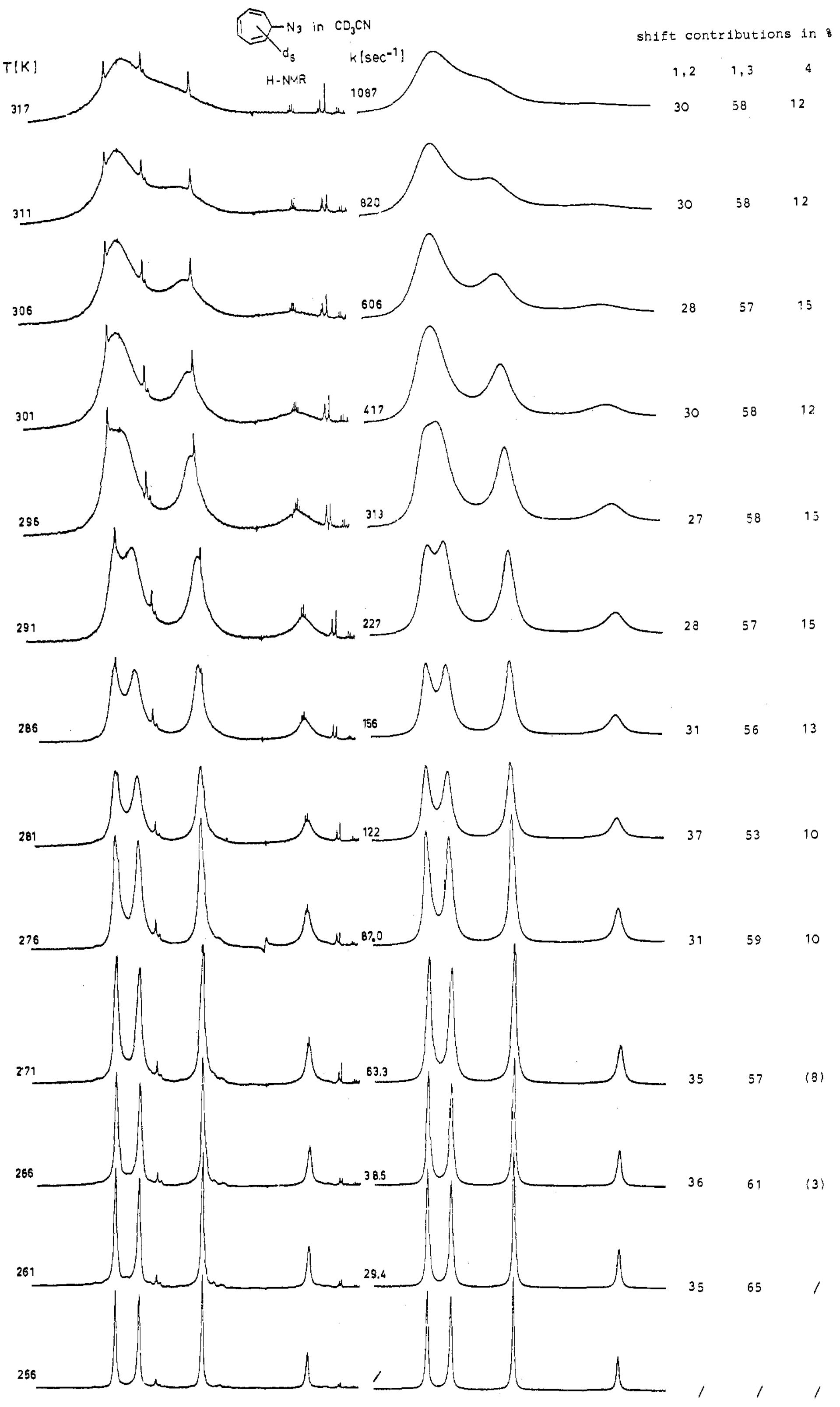


Figure 6. Experimental and calculated line shapes of the ^{1}H NMR spectrum of **1**-d_6 in CD_3CN (270 MHz).

a number of systems, in which the stability of both ions and covalent molecules are comparable, by careful adjustments of these variables. The limits of such systems are conveniently presented as a graph in which the stabilities of the cations and anions (to a first approximation the latter parallels the acidity of corresponding acids) are correlated (Figure 9). This correlation facilitates the search for suitable systems for studying the kinetics of ionization by NMR spectroscopy.[1-8,20] It is obvious from Figure 9 that there are compounds for which coexistence of comparable concentration of covalent and ionic species cannot be achieved. For example, for trityl azide the covalent form is much more stable than the ionic form but the reverse is true for tropylium halides even in the least polar medium used in our studies (CD_2Cl_2).

The free enthalpy of activation for the ionization of azidocycloheptatriene is about half enthalpic and half entropic. The

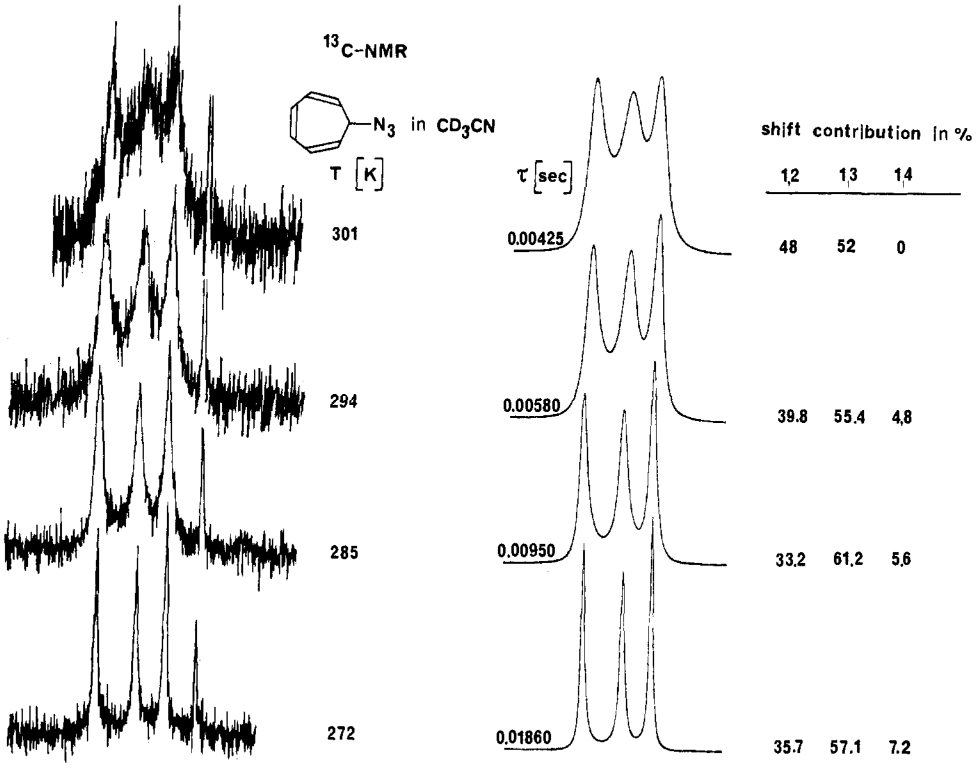


Figure 7. Experimental and calculated ^{13}C NMR line shapes of **1** in CD_3CN (22.63 MHz).

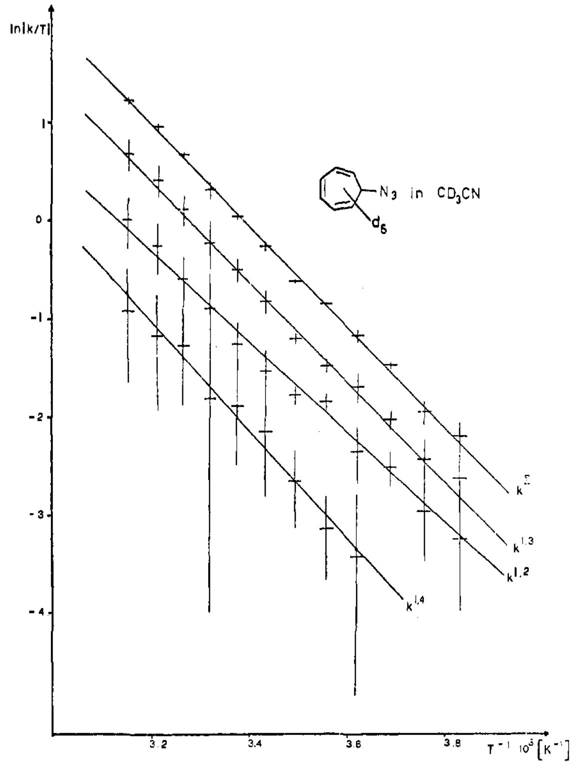


Figure 8. Eyring plot for the migration of azide in **1** (solvent CD_3CN, values from Figure 6).

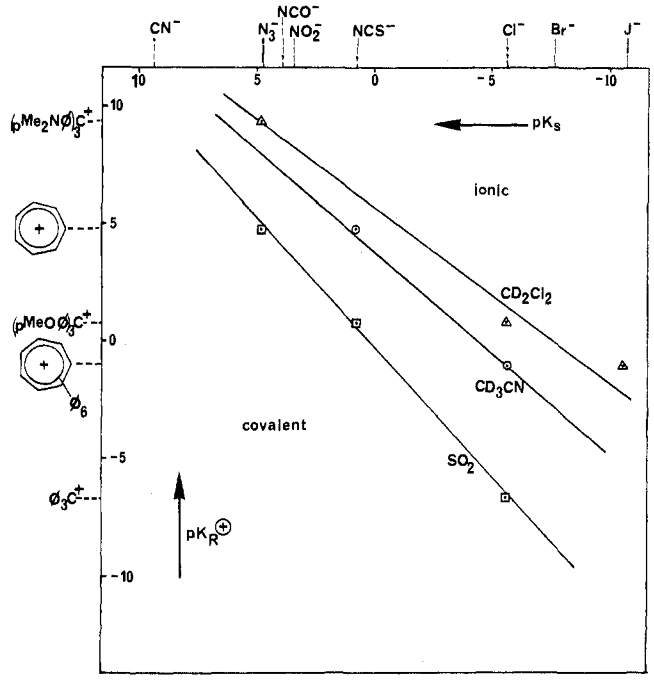


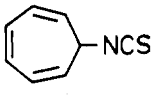
Figure 9. Graphic search for systems in which K_{ion} approximates the value 1. The values of $pK_R{}^+$ were taken from ref 32; those of pK_S from ref 33.

relatively large negative entropy term ($\Delta S^{\ddagger}{}_i = -77$ J/K·mol) is comparable to the entropic destabilization of the ionic molecules ($\Delta S° \sim -115$ J/K·mol).

Such large entropy effects are mainly determined by the change in solvation. Thus, increasing charge separation causes increasing solvation or, in other words, the charged species cause ordering of solvent molecules (negative entropy). The strong negative activation entropy thus indicates a high degree of charge separation in the transition state, which corresponds more to the ions than to the covalent species. This behavior is typical for all ionization processes which we have studied to date.[1,4,5] Our results are in agreement with measurements of the activation volumes $\Delta V^{\ddagger}$ of E1 and S_N1 reactions,[21,22] which have demonstrated that the charge separation of the transition state corresponds almost to those of the ions. This result was not necessarily expected, because our systems represent examples with higher stabilities (ΔH) of the ions, whereas for S_N1 and E1 processes of typical organic derivatives the large endothermic ionization allows the use of the Hammond postulate[23] (Figure 10). The origin of the ionization barrier of azidocycloheptatriene results from coulomb energy of charge separation with insufficient stabilization by solvation caused by a nonoptimal geometric distance.

Selective Shift Mechanisms. The olefinic ring system of cycloheptatriene, together with the azide ligand, allows a number of different migrational processes (Scheme I), which can be rationalized either by different sigmatropic shifts or by the reversible ionization process discussed above.

Rearrangements involving the cycloheptatriene ring have been studied for various migrating groups. The random migration of the isothiocyanate group in **2** has been interpreted as involving an ionization process.[1] On the other hand, the rearrangement of 7,7-dimethoxycycloheptatriene (**3**) to the 1,7 isomer **4** is believed to involve a 1,7-sigmatropic suprafacial



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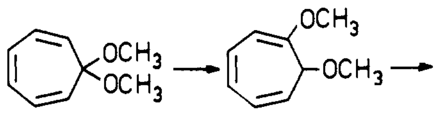

3 **4**

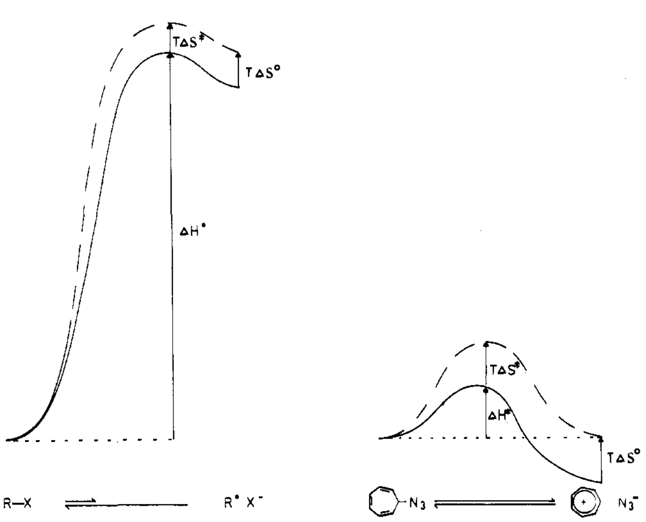

Figure 10. Reaction profiles for ionization processes. The left drawing corresponds to a typical organic substrate (S_N1 or E1 mechanism). The barriers for the ion recombination in such processes are unknown, because the stability of the ion pairs is unknown. The right drawing represents the behavior of **1** in $SO_2/CDCl_3$.

Scheme I. Possible Mechanisms of Azide Shift

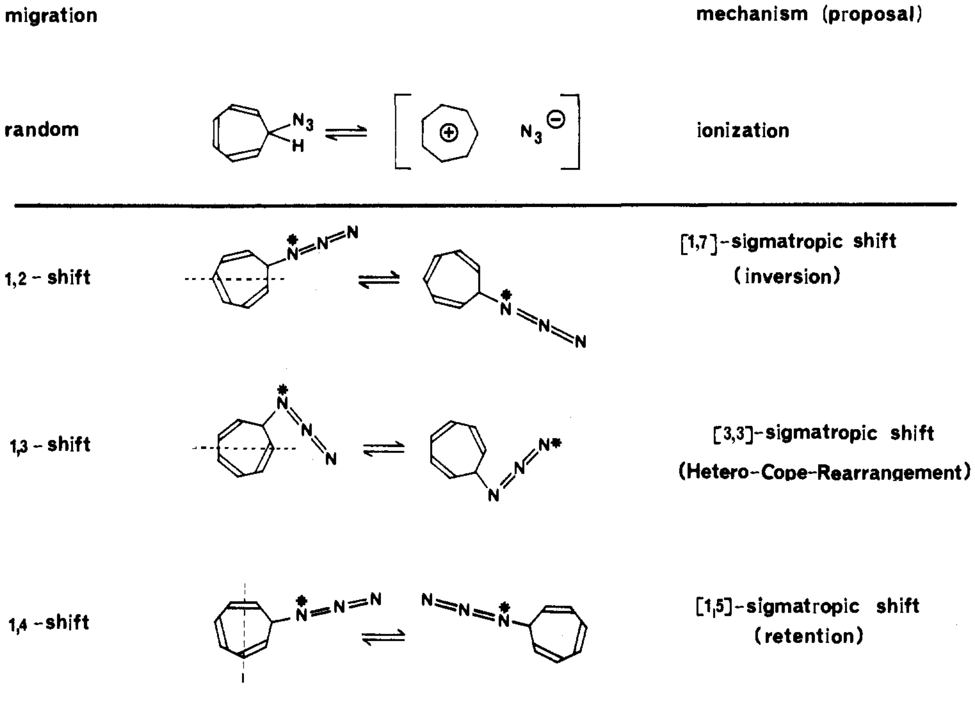

Table II. Solvent Dependence of the Free Activation Enthalpy $\Delta G^{\ddagger}_{298}$ (kJ/mol) for the Migration of the Azide Group in **1**

		migration			
solvent	nucleus	Σ	1,2	1,3	1,4
CD_3CN	^1H	58.40 ± 0.06	61.4 ± 0.2	59.85 ± 0.15	63.5 ± 0.3
	^{13}C	59.8 ± 0.4	62.0 ± 0.8	61.2 ± 0.8	67.1 ± 2.1
$CDCl_3$	^1H	61.1 ± (1)	63.4 ± 2	62.3 ± 2.6	70.9
THF	^{13}C	65.5 ± 0.6	69.0 ± 1.5	66.6 ± 1.5	71.0 ± 3

Table III. Activation Parameters for the Different Shift Processes for **1** (from ^1H NMR Spectra in CD_3CN)

	k	$k^{1,2}$	$k^{1,3}$	$k^{1,4}$
$\Delta G^{\ddagger}_{298}$[a]	58.40 ± 0.06	61.4 ± 0.21	59.85 ± 0.15	63.5 ± 0.3
$\Delta H^{\ddagger}$[a]	42.86 ± 0.63	38.5 ± 1.9	42.6 ± 1.1	46.3 ± 2.6
$\Delta S^{\ddagger}$[b]	−52.1 ± 2.1	−76.9 ± 6.7	−58.0 ± 4.0	−57.9 ± 9.2

[a] In kJ/mol. [b] In J/K·mol.

shift.[24] 1,5-Sigmatropic hydrogen shifts are well known,[25] and analogous rearrangements involving metalloorganic ligands have also been observed.[26] There is also some information on the participation of the azide ligand in sigmatropic rearrangements. Thus, [3,3] sigmatropic shifts of allylic azide are known from the literature.[27] The migration of azide in the cyclopropenylium compound is known to be facilitated by polar solvents, a fact which was taken as an argument against sigmatropic shifts.[28] Unfortunately, NMR line shape studies for this system cannot discriminate between selective and random migration. Since preferred 1,3 shifts are not usually observed in the rearrangement of cycloheptatrienyl derivatives and since there is a precedent for the involvement of the azide ligand in [3,3] sigmatropic shifts, it seems likely that this latter process is involved in the selective 1,3 rearrangement of cycloheptatrienyl azide.[29]

It is interesting to compare the values for the activation parameters for the rearrangement of allyl azide ($\Delta H^{\ddagger} \sim 82$ kJ/mol, $\Delta S^{\ddagger} \sim -42$ J/K·mol) with our data (Table III). The enthalpy for rearrangement of tropylium azide is much lower whereas the activation entropy is substantially more negative, consistent with increased charge separation in the transition state. A rather polar transition state is also indicated by the effect of solvent on the rates of the 1,3 shift (Table II). It would therefore seem that the rearrangement of tropylium azide lies in the borderline region between concerted and ionic shift mechanisms which has been discussed by Epiotis.[31]

The 1,2 migration, which contributes to the molecular rearrangement, can be interpreted as a least motion process or, in analogy to the methoxy migration, mentioned above, as a 1,7-sigmatropic shift. The lone pair of electrons of the azide substituent offers a similar mechanistic pathway, including inversion of nitrogen, as the lone pairs of the methoxy group

In our opinion, a clear-cut differentiation between ionic and sigmatropic shifts is a semantic problem sometimes of no physical relevance. Orbital control always is possible if a certain amount of covalency is present. Furthermore, our example demonstrates that it is dangerous to exclude sigmatropic migrations on the basis of the solvent effects on the rates of reaction.

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Supplementary Material Available: The thermodynamic data developed from the equilibrium between ionic and covalent forms of **1** in $CDCl_3/SO_2$ mixtures (Table S1), and additional material to demonstrate the construction of the rate matrices and to exclude the combination of 1,3 shift and ionic migration as a possibility to fit the line shapes (8 pages). Ordering information is given on any current masthead page.

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