

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 100, NUMBER 11

MAY 24, 1978

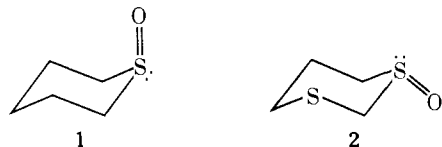
Selective Kinetic Equalization of Chemical Shifts in Protonated 1,3-Dithiane

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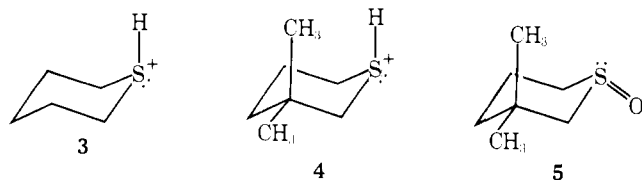
Abstract: 1,3-Dithiane is 85% monoprotinated (**6**) and 15% diprotinated (**8**) in FSO₃H or FSO₃H/SO₂. The 2-proton resonances of both the monoprotinated and the diprotinated forms are sharp singlets at 60 °C (60 MHz), indicative of fast S-H exchange and of fast ring reversal, but of slow interconversion between the two forms, **6** and **8**. At the same temperature, the 4 and 6 protons of **6** are nonequivalent. Consequently, proton exchange permits equilibration of the axial and equatorial protons at a given position, without equilibration of the two sides (the 4 and 6 positions) of the ring. Such an observation is only possible if the base that receives the S proton from the 1 position stays at that position without exchange into solution, possibly through hydrogen bonding. The invariance of the ¹³C spectrum with temperature confirms these conclusions. As the temperature is lowered, the S-H exchange is slowed ($\Delta G^\ddagger = 14.8$ kcal/mol). At 0 °C, the 2 proton gives an AB spectrum, and the 4 and 6 protons both give distinct axial and equatorial resonances. The lack of further splitting in the 2-proton AB quartet is consistent with predominant 1-equatorial protonation on sulfur. The diprotinated species (**8**), at slow S-H exchange, is a mixture of the trans (1,3-axial, equatorial) and the cis (1,3-axial-axial or 1,3-equatorial-equatorial) forms. At still lower temperatures, ring reversal is frozen out.

The dipolar effects of introducing a sulfur atom at the 3 position of thiane give rise to major alterations in the conformational preferences of substituents on the 1 sulfur. Thus in thiane 1-oxide (**1**) the oxide atom is preferentially (62%) axial,² but in 1,3-dithiane 1-oxide (**2**) it is 84% equatorial.³ Structural



studies have convincingly attributed this conformational change to the dipolar influence of the 3 sulfur on the 1 S=O bond.⁴

The monoprotinated form of 1,3-dithiane presents interesting contrasts to the monoxide. In the first place, the preference of the proton in thiane itself for the axial position (**3**)



is much stronger (>95%) than that of the oxide (**1**).⁵ Thus, 3,3-dimethyl substitution does not alter the axial preference of the proton (**4**), whereas it renders the oxide essentially all equatorial through steric interactions (**5**).⁶ The dipolar effect

of the 3 sulfur in 1,3-dithiane therefore would have to compensate for a larger axial preference in the protonated form than in the oxide. In the second place, the protonated form bears a monopole charge in addition to the ⁺S-H dipole, so that polar effects may be stronger than in the oxide. In the third place, diprotonation may be thermodynamically competitive with monoprotination. Whereas in the oxide series^{3a} the monoxide and the dioxide could be separated physically, this procedure is not possible in the acidic medium of fluorosulfonic acid. For these reasons we decided to examine the conformational preference of the S proton in protonated 1,3-dithiane. For comparison, we also briefly examined protonated 1,4-dithiane.

The proton spectrum of protonated thiane (**3**) undergoes an interesting kinetic change that proved to be critical in understanding the spectra of protonated 1,3-dithiane. We originally studied protonated thiane as its 3,3,5,5-*d*₄ derivative in order to simplify the proton spectrum.⁵ At 40 °C, the spectrum of thiane in FSO₃H/SO₂ consisted of two singlets, in the ratio 2/1, due respectively to the 2,6 and the 4 protons (see Figure 1 of ref 5). The symmetry of the spectrum was essentially that of thiane itself, when ring reversal is rapid. This result is only possible if the proton on sulfur is exchanging rapidly with the medium. In fact, cooling of the spectrum to -30 °C caused this exchange process to become slow on the NMR time scale. The 4-proton resonance became an AB quartet, the 2,6-proton resonance became the AB part of an (AB)₂X spectrum, and the S proton resonance appeared as the X part of an (AB)₂X spectrum. The vicinal coupling constants required that the S

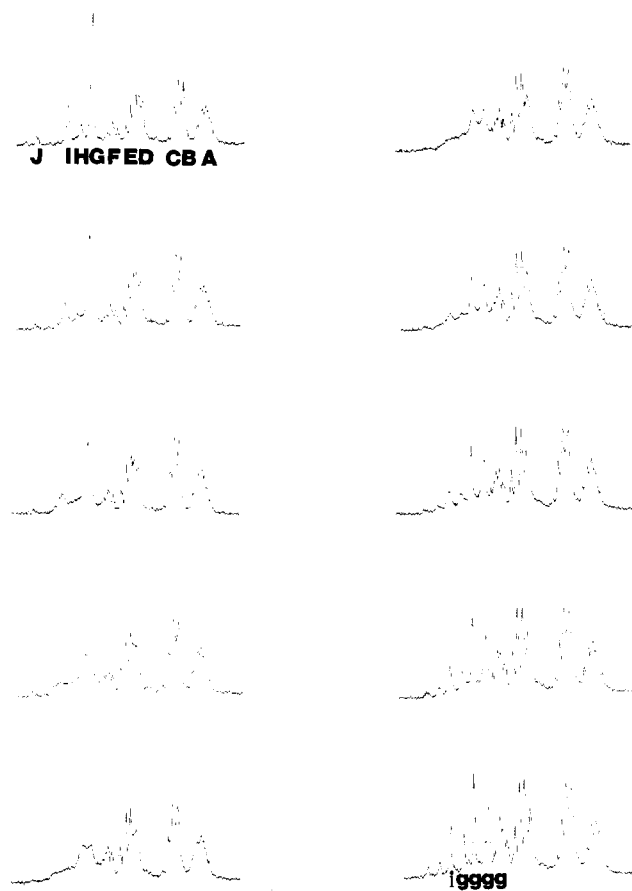


Figure 1. The 60-MHz proton spectrum of 1,3-dithiane in FSO_3H as a function of temperature (upper left to bottom left, upper right to bottom right, 60, 45, 40, 35, 30, 25, 20, 15, 10, and 0 °C). The calibration bar represents 100 Hz. At 60 °C, the following δ values apply: A (2.96), B/C (3.51), D (4.33), E (4.51), F (4.87), G (5.33), H (5.53), I (5.83).

proton be essentially all axial. Although ring reversal is probably still rapid at -30 °C, the biased nature of the equilibrium renders the spectrum equivalent to the case when ring reversal is slow. No further spectral changes were observed at lower temperatures, when ring reversal normally would be frozen out.

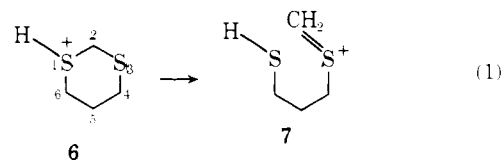
Because of proton exchange in protonated thiane, we anticipated a similar situation in the room temperature spectrum of protonated 1,3-dithiane. In fact, rapid proton exchange was observed, but with one unprecedented difference, which is the major subject of this paper.

Results and Discussion

Peak Assignments at Fast Proton Exchange. Because of the complexity of the spectrum of 1,3-dithiane in FSO_3H , it was necessary to examine it at 60, 100, and 270 MHz. Identical spectra were obtained in FSO_3H and 1/1 $\text{FSO}_3\text{H}/\text{SO}_2$, so the SO_2 component was deemed unnecessary. The 60-MHz spectrum (Figure 1) consists at 60 °C of two sharp singlets at the low-field end (G and I) and three multiplets at the high-field end (A, B, and D). At this temperature, exchange of the proton on sulfur with the medium must be rapid. As the temperature is lowered, certain reversible spectral changes take place. Several smaller multiplets remain unchanged with temperature, and these are attributed to a ring-opened species of undetermined structure. They are identified in Figure 1 by the letters C, E, F, and H. Peak C is superimposed on top of B, and peak E (a triplet) is just to the left of D. Their separations will become more obvious when we describe the 270-MHz spectrum. Peak J is formed irreversibly from the decomposition

of whatever species are formed initially. If the temperature is kept at room temperature or below, little or no decomposition occurs and the peak is quite small. When the spectrum is maintained at 70 °C for times on the order of hours, this peak begins to grow. Eventually the initially formed materials are entirely destroyed at 80 °C or higher.

Quenching of the NMR sample in water and extraction with ether gives a reasonable yield (35–50%) of recovered starting material. Products from the species giving rise to peaks C, E, F, and H were not isolated, although a material insoluble in both water and ether was also obtained but not identified. Ring opening might occur via eq 1. It is not certain what 7 might give



on reaction with water. The isolation of recovered starting material gives assurance that much of the spectrum corresponds to simple protonation products. As we will see, the temperature changes in the spectrum also require that the 1,3-dithiane ring remain intact, and there is no evidence that oxidation takes place.

Let us first sort out in a more definitive fashion the peaks of protonated 1,3-dithiane from those of apparently ring-opened materials. The latter have been identified in Figure 1 as peaks C, E, F, and H. The triplet E can be followed from 60 °C right down to 0 °C. Its quartet appearance at the low temperature is an accident of overlap with peak D. Peak F also remains essentially unchanged throughout the temperature range, although it is distorted at low temperatures because a peak derived from the splitting up of G grows up on its left shoulder. Peak H is lost among the new peaks at low temperature, and peak C is not resolved from B at 60 MHz.

Clarification of which peaks belong to which is obtained by selective proton-proton decoupling experiments, which we obtained at 100 MHz.⁷ The undecoupled spectrum at 70 °C is shown at the top of Figure 2. Peaks B and C are still not resolved, but now D and E are clearly separated. Furthermore, peak E turns out to be a doublet of triplets, which apparently were superimposed at 60 MHz. Irradiation of peak A (middle spectrum) gives rise to a clear sharpening of peaks B/C and D, but not of E or F. We therefore assign E and F to a distinct molecule. Peak A must represent a methylene group (such as the one at the 5 position in **6** of eq 1) that has methylene groups (4 and 6) on either side of it. Irradiation of B/C (bottom spectrum) causes sharpening of E and F, and to a lesser extent of A. If peak B is from the monoprotonated species **6**, it probably represents the 4 proton, irradiation of which should have no effect on the 6 position (peak D) but should sharpen peak A (the 5 protons) but only in part because coupling still exists between the 5 and 6 protons. The peak C superimposed on top of peak B must represent the central methylene group in the ring-opened product, since irradiation of this peak collapses both E and F.

In summary, the double irradiation experiments tie together peaks C, E, and F, which are temperature independent, and peaks A, B, and D, which we have assigned to the monoprotonated species **6**. We will not pay further attention to the peaks from the ring-opened species, except to note their existence now and then. The sharpness of the triplets in peak E is further evidence that they derive from a ring-opened species. Methylene groups with neighboring methylene groups tend to be broad multiplets like A in ring compounds but sharp triplets like E in open chain compounds, because of the vagaries of magnetic nonequivalence.

At 270 MHz,⁸ further spectral simplification is obtained

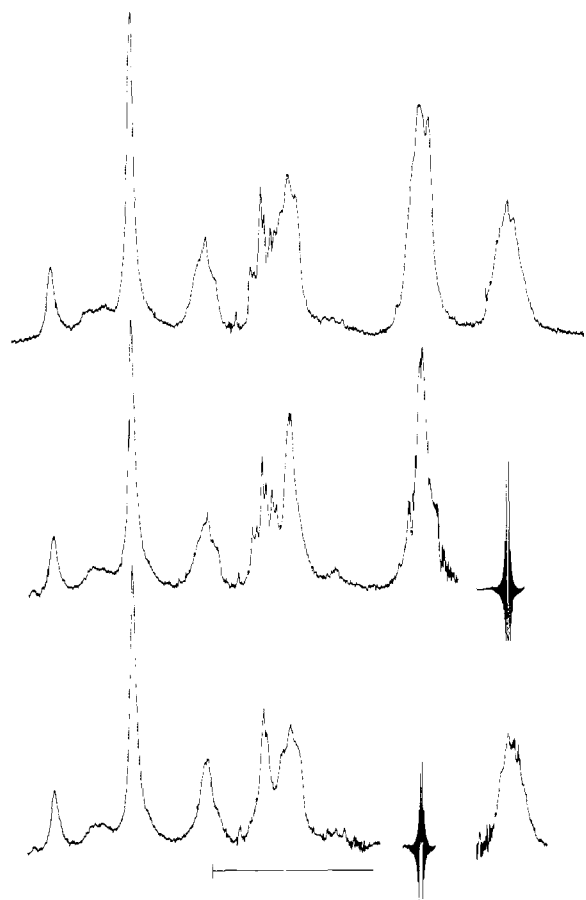


Figure 2. The 100-MHz proton spectrum of 1,3-dithiane in FSO_3H : (top) undecoupled; (middle) irradiation at peak A of Figure 1; (bottom) irradiation at peak B/C. The calibration bar represents 100 Hz.

(Figure 3). Peaks B and C surprisingly are still superimposed at 70 °C, but lowering of the temperature causes splitting of peak B (to be discussed presently) without change of C. Peaks A and D have identical integrated intensities, in agreement with the assignment to distinct methylene groups (5 and 6) in the monoprotonated species **6**. Peaks D and E are now entirely separated, and the double triplet nature of E gives a quartet by accidental overlap (compare the analogous peak in Figure 2). As is expected for nonring species, peaks C, E, and F are still independent of temperature throughout the entire range, which has now been extended to -60 °C. Peak F is somewhat more complex at 270 MHz, but its symmetrical broad doublet nature is retained at all temperatures, except when peaks derived ultimately from G become superimposed on it. Peak I is a sharp singlet in Figures 1 and 2, but appears to be rather broad in Figure 3. The higher field requires a higher temperature for the coalescence and sharpening of peaks associated with exchange of the proton on sulfur. Whereas this process was fast at 70 °C at 60 and 100 MHz, it is not fully fast exchange even at 80 °C (top spectrum) at 270 MHz. We did not want to raise the temperature higher for full sharpening of this peak because of the acceleration of the irreversible decomposition process. The dotted peak (I) in the top spectrum represents what the fast exchange peak would look like.

The assignments of the peaks for the monoprotonated form **6** are corroborated by examination of the spectrum of the methyl iodide adduct of 1,3-dithiane (**6m**). The 60-MHz ^1H

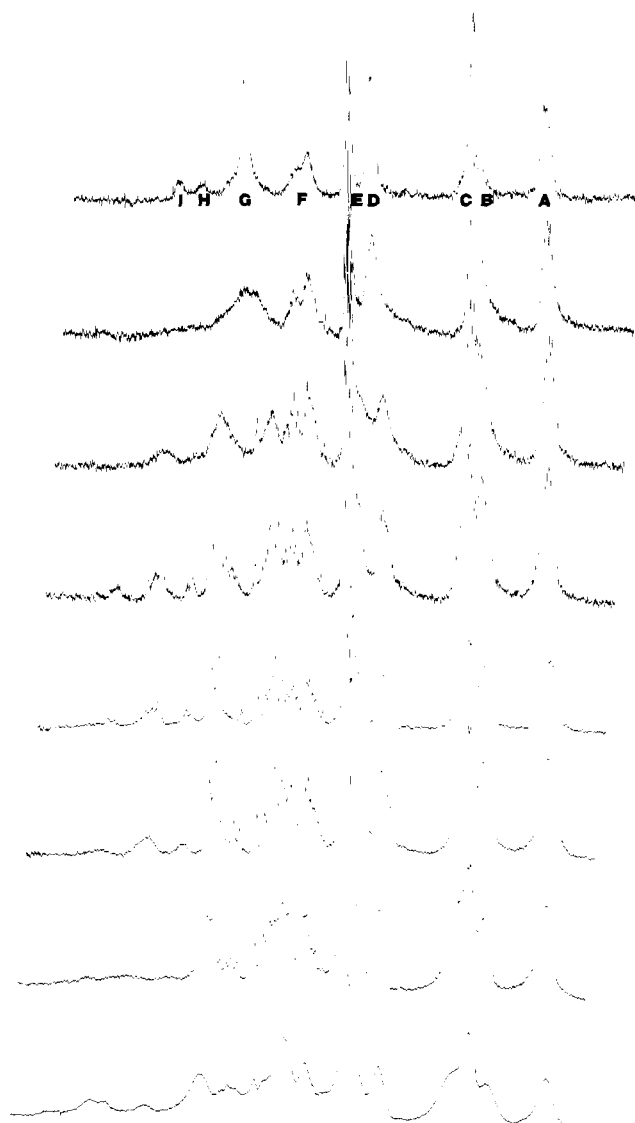
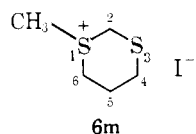
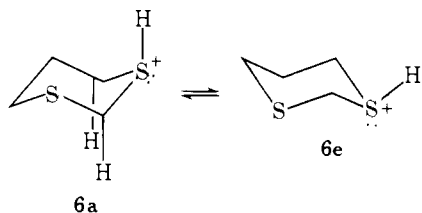


Figure 3. The 270-MHz proton spectrum of 1,3-dithiane in FSO_3H as a function of temperature (top to bottom, 80, 60, 40, 20, 0, -20, -40, and -60 °C). The full sweep width in every case is 1200 Hz.

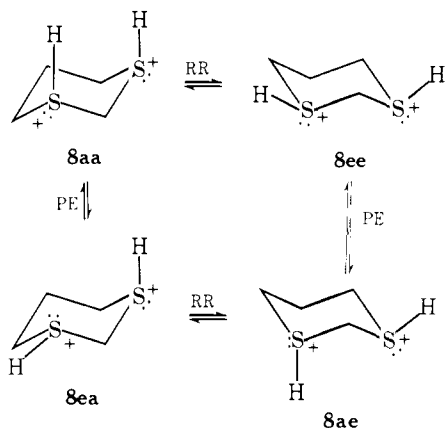
spectrum of **6m** at room temperature is almost superimposable on that of **6** at 0 °C (Figure 1). Specifically, the spectrum of **6m** in D_2O contains a multiplet at δ 2.92 (the 5 protons; cf. 2.96 for **6**), a triplet at 3.51 (4 protons; cf. 3.51 for **6**), a singlet at 3.58 (methyl), a multiplet at 4.12 (6 protons; cf. 4.33 for **6**), and an AB quartet ($\Delta\nu = 25.2$ ppm, $J = 13.8$ Hz) centered at 5.21 (2 protons; cf. 5.33 for **6**). The comparisons with **6** are taken from the 60 °C spectrum. The remarkable comparability of the spectra of **6** and **6m** supports the above assignments. The small variation for the 2 and 6 protons is caused by the difference between the S substituent (CH_3 vs. H). The methyl group of **6m** undergoes no intermolecular exchange reaction, so the 4 and 6 positions are nonequivalent. The spectrum of **6m** shows no appreciable temperature variation above 40 °C.

Were it not for the ring-opened peaks C, E, F, and probably H, the spectrum would have been much easier to analyze. Now that these peaks have been sorted out, let us examine the effect on the spectrum of the dynamic process of exchange of the proton on sulfur. We will not need to have further reference to the decoupling experiments in Figure 2, but we will discuss the spectral changes in both the 60- and 270-MHz spectra.

Dynamic Processes. There are two possible monoprotonated species, axial (**6a**) and equatorial (**6e**), which interconvert via



ring reversal. There are three diprotonated species. Two distinct cis isomers (diaxial **8aa** and diequatorial **8ee**) interconvert via ring reversal (RR), and two identical trans isomers (axial-equatorial **8ea** and **8ae**) also interconvert via ring re-



versal. The cis and the trans forms cannot interconvert with each other conformationally, although the process is possible either by sulfur inversion or by intermolecular proton exchange (PE). As there is strong evidence that sulfur inversion in sulfonium ions is slow on the NMR time scale at these temperatures,⁹ the only reasonable mechanism for cis-trans interconversion would be an intermolecular one.

The strongest signal in the fast exchange spectrum at 60 (60 MHz) or 80 °C (270 MHz) is peak G. We attribute this resonance to the 2 proton of the monoprotonated species **6**. The axial and equatorial 2 protons are equivalent at this temperature because both ring reversal and S-H exchange are fast on the NMR time scale. As the temperature is lowered, the spectrum undergoes a typical A_2 to AB transformation, with coalescence at about 35 (60 MHz) or 40 °C (270 MHz). The free energy of activation at the 40 °C coalescence is 14.8 kcal/mol. At 0 (60 MHz) or 20 °C (270 MHz), the AB quartet (labeled g in Figure 1) is fully formed ($\Delta\nu = 0.47$ ppm, $J = 14.1$ Hz). The low-field doublet is isolated and sharp; the high-field doublet is partially superimposed on top of peak F and is somewhat broad. The appearance is almost identical with that of 1,3-dithiane 1,1-dioxide under conditions of slow ring reversal (Figure 2 of ref 3a). The broader upfield peaks identify them as coming from the equatorial 2 proton, which has a W-pathway coupling to the equatorial 4 and 6 protons.^{3a} The fact that the equatorial proton is at higher field than the axial proton is in agreement with assignments in thiane, dithiane, and protonated thiane.^{3,10} These observations have been explained in terms of reversal of the C-S, C-S⁺, and C-SO₂ diamagnetic susceptibilities, in comparison with that of C-C or C-O.

Although the spectrum of the 2 protons in the monoprotonated species gives every appearance of slow ring reversal, undoubtedly this process is quite fast on the NMR time scale at 0 °C. Rather, the spectrum is characteristic of a highly biased (one-sided) equilibrium. In the axial form (**6a**), the S proton should have a large coupling to the adjacent axial 1 proton. Since the 1a-2a coupling would be comparable to the geminal 2a-2e coupling, the axial 1 proton should be a triplet (much as in the case of protonated thiane, which is nearly all axial⁵). The absence of this large coupling in the slow exchange

(with respect to S-H exchange) spectrum suggests that the predominant conformer in the monoprotonated species is the equatorial (**6e**). This change from the condition in thiane (**1**) is somewhat surprising, since we showed previously that the axial preference is not even disturbed by the introduction of a 3-axial methyl group.⁶ The ⁺S-H bond has the same polarity as the S=O bond, and in the latter case the analogous reversal of the conformational preference on introduction of a 3 sulfur atom has been attributed to the dipolar properties of the C-S bonds.⁴ It is reasonable that a similar effect would operate in the ⁺S-H case, and the larger magnitude may be due to the presence of the monopole charge in addition to the dipole. The smaller 1e-2e couplings are not resolved because of the overall relative broadness of the peaks in FSO₃H. We do not believe that the proton on sulfur is entirely equatorial, as we will mention later.

In addition to the changes in the 2-proton resonance (peak G), the 4- and 6-proton resonances (peaks B and D) also split into their axial and equatorial components as S-H exchange is slowed. At 20 °C (270 MHz only), peak B splits into two peaks (the lower field peak is under peak C), as does peak D (the lower field peak is under peak E). The 5-proton resonance (peak A) does not split into axial and equatorial components at any temperature.

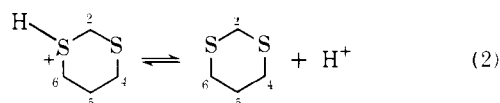
The diprotonated species (**8**) also gives a sharp singlet resonance (I) for the 2 protons at 60 (60 MHz) or >80 °C (270 MHz). The intensity of this resonance is 1/5.8 or 15% of that of the monoprotonated form. It is particularly significant that the mono- and diprotonated forms do not interconvert, even when proton exchange is rapid enough to interchange the axial and equatorial 2 protons. Thus the S-H exchange is not entirely universal in solution but occurs in a more localized fashion. As S-H exchange slows with lower temperature, the 2-proton singlet from **8** passes through a coalescence process and emerges at 0 °C as another singlet and a multiplet (possibly an AB quartet). The singlet is clearly visible at both 60 (labeled i) and 270 MHz. Possibly half the AB quartet is visible at 60 MHz, but further clarification is not obtained at 270 MHz. Because at 0 °C the process of ring reversal is rapid, the 2 protons in the trans (axial-equatorial) form (**8ae**) are still equivalent. Therefore, this form unambiguously gives rise to the singlet at 0 °C. The remaining resonances in the multiplet or quartet are from the ring reversal equilibrium between the cis forms, diaxial (**8aa**) and diequatorial (**8ee**). We have no basis on which to choose between these two cis forms. The ratio between the axial-equatorial form and the cis forms is not far from unity, but an accurate value cannot be obtained with the data available. The resonances from the 4, 5, and 6 protons in the diprotonated form are obscured by those from the monoprotonated form and the ring-opened material.

Thus from the resonances of the 2 protons, we can conclude that (1) both mono- (85%) and diprotonated (15%) forms are present; (2) interconversion between the mono- and diprotonated forms is slow on the NMR time scale at 80 °C; (3) S-H exchange is sufficiently rapid at 60 °C (60 MHz) to interconvert axial and equatorial protons; (4) the monoprotonated species is present mainly as the equatorial form; (5) the diprotonated species is present as a mixture of the trans (axial-equatorial) and cis (axial-axial and/or equatorial-equatorial) forms.

Selective Equalization of Chemical Shifts. All these conclusions have been derived without specific reference to the 4-, 5-, and 6-proton resonances, which we earlier assigned to peaks B, A, and D, respectively. Possibly the most singular aspect of the entire set of spectra is that there are distinct 4- and 6-proton resonances at the high-temperature extreme (B and D). Thus the spectrum of **6** (⁺S-H) at 60 °C closely resembles that of **6a** (⁺S-CH₃), except of course that proton exchange and ring reversal in **6** render the 2-proton resonance a singlet (methyl

exchange in **6a** is not possible, so the ring remains biased and the 2-proton resonance an AB quartet).

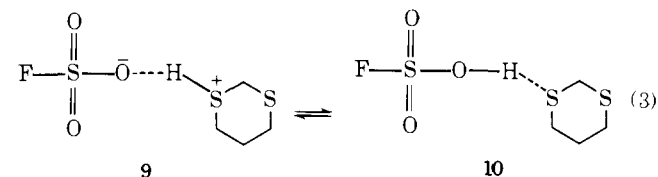
The presence of the *S*-methyl group requires that the 4 and 6 positions in **6a** be nonequivalent. If S–H exchange is indeed rapid, however, should not the 4 and 6 positions of **6** become equivalent (eq 2)? Apparently they do not. The 270-MHz



spectrum clearly shows three distinct resonances for the 4 (B), 5 (A), and 6 (D) protons, and the decoupling experiments (Figure 2) confirm their adjacency. For added confirmation, we examined the 20-MHz carbon-13 spectrum as a function of temperature. Because of the ring-opened impurities, we could not assign specific peaks to the appropriate carbons. Nonetheless, the significant aspect of the ¹³C spectrum was its complete temperature independence over the entire range of interest. This observation is consonant with the distinct 4- and 6-proton resonances at fast S–H exchange. Slowing of S–H exchange in essence is slowing of ring reversal, a process that interchanges axial and equatorial protons but in this case does not affect carbons. Thus the ¹H spectrum but not the ¹³C should be sensitive to these changes. The proton exchange process must bring about axial–equatorial proton equivalence (an average plane of symmetry through the ring atoms) since ring reversal is rapid, but it does not bring about carbon equivalence of opposite sides of the ring (plane of symmetry perpendicular to the ring and through the 2 and 5 positions, as in unprotonated 1,3-dithiane). To our knowledge, such a “halfway” or selective equivalence is unprecedented. In certain molecules examined earlier, such a process may occur but could not be detected. Protonated thiane, for example, could not exhibit selective equivalence, since a plane of symmetry passes through the site of protonation.

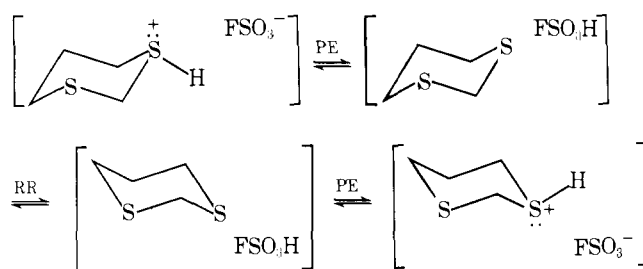
The most likely explanation for these observations is that loss of the S proton from the ring creates a dithiane–solvent complex with a long enough lifetime to permit ring reversal of the free thiane ring. Reprotonation must occur on the same sulfur but from the opposite side of the ring plane (Scheme I). Thus protonated 1,3-dithiane is capable of existing in solution both as the ionic form (⁺S–H FSO₃[–]) and as a bound complex (S⋯FSO₃H) of some sort. The solvent molecule to which the proton is transferred cannot diffuse out into solution and be lost to the substrate. It must be available for retransfer of the proton back to the same sulfur atom after the plane of the ring has been symmetrized through rapid ring reversal. This unusual process explains why the 4 and 6 protons do not equilibrate, why the ¹³C spectrum is temperature independent, and why exchange does not take place between the mono- and diprotonated forms.

The two forms in Scheme I may represent partners in a hydrogen bond equilibrium (eq 3). Species **9** is predominant



in solution, but at 60 °C (60 MHz) proton exchange over the hydrogen bond (**9** ⇌ **10**) becomes rapid on the NMR time scale. Ring reversal must be able to occur rapidly in **10**. The observed barrier ($\Delta G^\ddagger = 14.8$ kcal/mol) corresponds to the process **9** → **10**. We examined the ¹⁹F (56.4 MHz) spectrum to see if bound and unbound FSO₃H gave distinct resonances. The results were inconclusive. There were no small peaks in the vicinity of the large FSO₃H peak, but there was a very

Scheme I



small peak 270 ppm to higher field. We have not characterized this peak further.

We should emphasize that the interpretation we have given was developed ad hoc to explain the observed spectral nonequivalence of the 4 and 6 positions when proton exchange is fast. There may be other, equally tenable interpretations that have not been excluded.

Other Matters. The spectra below 0 °C in Figure 3 deserve some comment. All the peaks broaden because of the increased viscosity of the solution, but some other changes occur as well. The high-field doublet of the 2 protons (equatorial) moves upfield, and the 4a–4e splitting of peak B increases considerably. These changes of peak position without an increase in the spectral complexity may be due to a shifting of population as the minor monoprotonated conformer, presumably the axial form, is increasingly populated. Changes appear to be more drastic in the diprotonated resonances. The sharp singlet from the trans (axial–equatorial) form (**8ae**) broadens and disappears. These alterations may be due to the slowing of ring reversal, which would render the 2 protons nonequivalent in the trans form.

We have also examined 1,4-dithiane under the same conditions, but the ring protons gave an unsplit singlet at all temperatures, even at 270 MHz, probably because of chemical shift degeneracies.

Conclusions

Protonation of 1,3-dithiane in FSO₃H yields both a mono- (85%) and a diprotonated (15%) species, which do not interconvert on the NMR time scale at 60 °C (60 MHz). The monoprotonated form appears to be predominantly equatorial (**6e**), whereas the diprotonated form (**8**) is a mixture of similar amounts of the trans (axial–equatorial) and the cis (axial–axial and/or equatorial–equatorial) isomers. Exchange of the proton on sulfur is fast at 60 °C (60 MHz), since the axial and equatorial 2-proton resonances are equivalent. The base that receives the proton in this exchange process, however, must deliver it back to the same sulfur atom after rapid ring reversal averages the geminal protons. This conclusion is required by the fact that the proton exchange does not interconvert the 4 and 6 protons or the 4 and 6 carbons. Thus proton exchange interconverts the “top” and “bottom” of the molecule (axial vs. equatorial) without interconverting its “left” and “right” sides (4 vs. 6 positions). The base cannot diffuse into solution and be lost to the dithiane molecule. Some sort of complex, probably hydrogen bonded, between neutral FSO₃H and neutral 1,3-dithiane therefore is required, and this complex retains the symmetry of the monoprotonated species. That complete randomization of protons does not occur via the proton exchange process is also required by the fact that the mono- and diprotonated forms do not interconvert at the highest temperatures.

Experimental Section

The 60-MHz ¹H and 56.4-MHz ¹⁹F NMR spectra were taken on a Perkin-Elmer R20B spectrometer. The proton–proton double irradiation experiments were carried out on a Varian HA100 spec-

trometer,⁷ and the proton spectra at 270 MHz were obtained on a Bruker HX270.⁸ The ¹³C spectra were recorded on a Varian CFT20 spectrometer. For the ¹H spectra, 50 mg of 1,3-dithiane (Willow Brook) was placed in a 5-mm NMR tube, and 0.3 mL of FSO₃H (Aldrich) was added in a dropwise fashion. The tube was shaken and the spectrum recorded. For the ¹³C spectra, 300 mg of 1,3-dithiane and 1.2 mL of FSO₃H were used. After about 12 h at room temperature or 1 h at 70 °C, a precipitate formed and new peaks appeared irreversibly in the ¹H spectrum. Spectra were always recorded before this process had progressed to any significant extent. A sample prepared for the ¹³C spectrum was quenched by addition to 10 mL of H₂O. The solution was extracted three times with ether. A small precipitate developed on the first extraction, but it could not be identified because of its low solubility. The organics were dried, and the solvent was evaporated. The ¹H spectrum of the residue showed it to be uncontaminated 1,3-dithiane, which could be isolated in 35–50% yield.

1-Methyl-1,3-dithianium Iodide. To 6 g (0.05 mol) of 1,3-dithiane in 50 mL of acetone was added 21.3 g of CH₃I. The flask was stoppered and stored at room temperature for 48 h in the dark. White crystals of the product were isolated and recrystallized from CH₃OH (4 g, 0.015 mol, 30.5%): mp 126–128 °C; NMR (D₂O vs. external Me₄Si in CCl₄) δ 2.92 (m, H-5, 2 H), 3.51 (t, H-4, 2 H), 3.58 (s, CH₃, 3 H), 3.99 (m, H-6, 2 H), 5.21 (AB q, Δν = 0.35 ppm, J = 13.8 Hz,

H-2, 2 H). Anal. Calcd for C₅H₁₁S₂I: C, 22.91; H, 4.23. Found: C, 22.82; H, 3.89.

References and Notes

- (1) (a) This work was supported by the National Science Foundation, Grants CHE-75-05006 and CHE-77-08384, and by the donors of the Petroleum Research Fund, administered by the American Chemical Society; (b) Petroleum Research Fund Postdoctoral Fellow; (c) On leave from the Institute of Drug Research, Pharmaceutical Faculty of the Medical Academy, Łódź, Poland.
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- (8) We thank Mr. Robert Dykstra for recording these spectra on the Bruker 270-MHz superconducting instrument at the Department of Chemistry, the University of Chicago.
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Molecular-Beam Study of the Activation Energy Requirements for the Dioxetane Reaction

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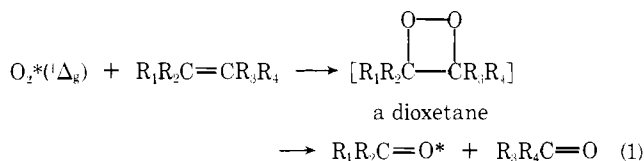
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Abstract: Using crossed, seeded nozzle beams we determined the amount and kind of activation energy required for the chemiluminescent dioxetane reaction, O₂*(¹Δ_g) + R₁R₂C=CR₃R₄ → R₁R₂C=O* + R₃R₄C=O. By varying the composition and temperature of the stagnant gas behind the nozzle we were able to study the reactive cross section as a function separately of translational energy and vibrational temperature. Three olefins were studied in detail: *N,N*-dimethylisobutenylamine, which gave no change in cross section with either variable; and methyl vinyl ether and 1,1-diethoxyethylene, whose cross sections were independent of vibrational temperature but showed a sharp rise with increasing translational energy.

Introduction

Most chemical reactions have an activation energy, which means that energy must be supplied to the reactants to make them go. Yet there is very little information on what form of energy (translation, rotation, or vibration) is needed. Brooks et al.¹ demonstrated that the slightly endoergic reaction K + HCl → KCl + H was considerably enhanced by vibrational excitation in HCl but almost unaffected by increase in translational energy. Jaffe and Anderson² found that the reaction HI + DI → HD + 2I would not proceed even if translational energy was supplied far in excess of the known activation energy. Polanyi³ has done Monte Carlo calculations for three-atom system which show that, if the crest of the barrier (transition state) is located in the entrance valley, the reaction is promoted by translational energy while vibrational energy is ineffective. Translational energy gives the reactants a velocity aimed toward the barrier while vibrational energy does not. Conversely, if the barrier is in the exit valley, the reaction is promoted by vibrational energy but not translational energy.

The reaction chosen for this study, the dioxetane reaction, is itself an intriguing reaction which has long interested organic chemists.⁴ It is chemiluminescent which vastly enhances its



detectability. The formation of the dioxetane intermediate in its ground state is symmetry forbidden as a concerted process.^{4b,5} The kinetics have been extensively studied in the gas^{6–8} and liquid phases.⁴

The experimental technique used here involves supersonic nozzle beams.⁹ When a gas is expanded through a small hole into a vacuum, it undergoes an adiabatic cooling, converting the enthalpy due to translation and rotation in the stagnant gas behind the nozzle into translational energy in the beam, while the translational and rotational temperatures in the beam drop to a few degrees Kelvin. The result is a nearly monoenergetic molecular beam with a velocity determined by the initial temperature and by the average molecular weight of the initial, stagnant gas. By using different mixtures of a heavy reactant and a light carrier gas one can both accelerate the reactant and vary its velocity. During the expansion the molecules undergo only a few dozen collisions before entering a nearly collision-