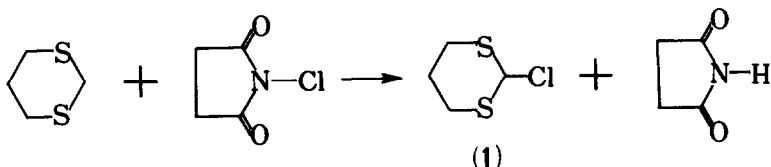


EVIDENCE FOR IONIC DISSOCIATION OF 2-CHLORO-1,3-DITHIANE
IN VARIOUS SOLVENTS

Kazutaka Arai and Michinori Ōki*
Department of Chemistry, Faculty of Science,
The University of Tokyo, Tokyo 113, Japan

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2-Benzoyloxy-1,3,5-trithiane derivatives have been found to show remarkable stereoselectivity in reactions with nucleophiles.¹⁾ In order to see the effect of leaving-group abilities on the reaction, we have prepared 2-chloro-1,3-dithiane and 2-chloro-1,3,5-trithiane and have found some unexpected interesting phenomena. This paper concerns with such findings with 2-chloro-1,3-dithiane (1) which showed the clearer and better-defined phenomena.



To a solution of 0.18 g (1.5 mmol) of 1,3-dithiane in 3 ml of sodium-dried benzene, was added 0.22 g (1.7 mmol) of powdered N-chlorosuccinimide during a 15 min period at 20°C with stirring under a nitrogen atmosphere. Stirring was continued for 15 min after completion of the addition. The reaction mixture was filtered to remove insoluble materials, contact with moisture being avoided as completely as possible. Since attempted isolation of 1 failed because of its high reactivity, the filtrate was directly submitted to some reactions. The filtrate exhibited signals at δ 5.76 (1H, s), 2.64 (4H, br. m), and 1.58 (2H, m) in its ¹H NMR spectrum and the purity of 1 was estimated to be 90-95%. Spectra of 1 in other solvents were determined by dissolving the residue in appropriate solvents after evaporation of the filtrate in vacuo.

The ¹H NMR spectra of 1 showed the remarkable solvent-dependence, as illustrated in Fig. 1. The spectra were also temperature-dependent, as shown in Fig. 2. The results suggest that an exchange process is taking place under the conditions. The process must be unimolecular, because the spectra are little concentration-dependent (0.08-0.65 M). The process is not quenched by addition of potassium carbonate to indicate that a minute amount of hydrogen

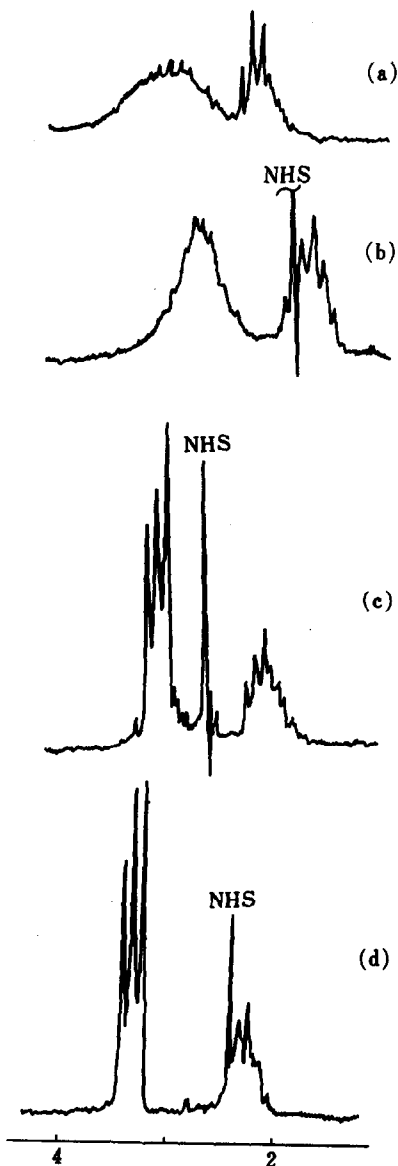


Fig. 1. Solvent-dependence of ^1H NMR spectra of 1: (a) in carbon disulfide, (b) in benzene- d_6 , (c) in chloroform- d , and (d) in sulfur dioxide. The temperature is 32°C except for (d) (-40°C). NHS is a signal of succinimide present as an impurity.

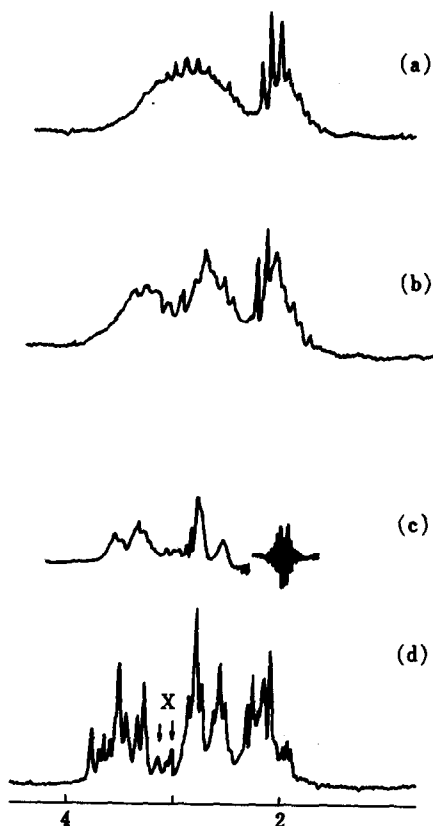
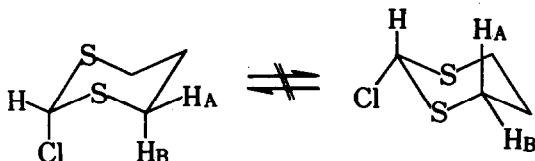


Fig. 2. Temperature-dependence of ^1H NMR spectra of 1 in carbon disulfide: (a) at 32°C , (b) at 0°C , (c) at -30°C (irradiated at δ 2.1), and (d) at -30°C . Signals marked X are due to impurities.

chloride, which is produced by hydrolysis of 1 with moisture, is not responsible to the exchange.

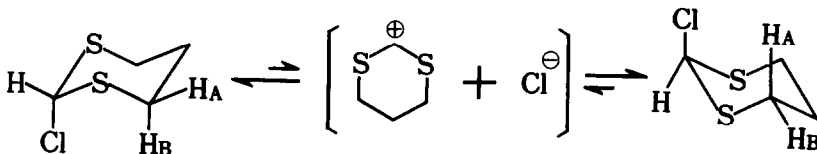
Irradiation of the 5-H resonance region (δ 2.1) of 1 in carbon disulfide solution caused the appearance of a broad AB quartet signal at -30°C to indicate that the exchange process is slow under the conditions. This phenomenon is reasonably explained by assuming that the chair conformation of 1,3-dithiane ring is now frozen on the NMR time scale and equatorial and axial protons give respective signals. Coalescence temperature is estimated to be $30\text{--}36^\circ\text{C}$ and k_c and ΔG_c^\ddagger were obtained as $1.4 \times 10^2 \text{ sec}^{-1}$ and 14 kcal/mol, respectively, with the use of the coupling constant (14 Hz) and $\Delta\nu_{AB}$ (51 Hz at 60 MHz).²⁾

Although the exchange process might be attributed to the equatorial-axial inversion, there are pieces of evidence which disfavor this process.



2-Benzoyloxy-1,3,5-trithiane exists as the benzoyloxy-axial conformer at least overwhelmingly due to the strong anomeric effect.³⁾ The chloro group, being more electronegative than the benzoyloxy group, is unlikely to assume the equatorial position to a significant extent. The appearance of a single set of AB quartet on irradiation suggests the presence of a single isomer at -30°C . If the inversion process were responsible to the coalescence of the signals, then appearance of two sets of AB quartet would be expected.⁴⁾

One of the possibilities to account for this anomaly in the ^1H NMR spectra is to assume that 1 dissociates to a limited extent to ionic species and the ring of this cation inverts easily at a high temperature to cause coalescence of the signals. Thus the chloro-axial conformation is retained in the net process but the H_A and H_B are averaged at high temperatures. The extent of



the ionic dissociation must be dependent on the solvent nature and the width of the signal for 4- and 6-H's may be taken as the reflection of the extent of the dissociation. Then it is hoped that, in a strongly ionizing solvent, 1 may dissociate into ionic species to a measurable extent. Indeed, ^1H NMR and ^{13}C NMR spectra of 1 in sulfur dioxide at -40°C gave the following data:

^1H NMR (δ), 2.27 (2H, m), 3.30 (4H, m), 10.65 (1H, s): ^{13}C NMR (δ from TMS), 16.0 (5-C), 30.5 (4- and 6-C), 184.5 (2-C). Appearance of signals of 2-H and 2-C at very low fields strongly supports the ionic dissociation. We tentatively assume that 1 dissociates completely in sulfur dioxide, because the ^1H NMR spectral features are similar with those reported for 1,3-dithian-2-yl tetrafluoroborate in nitromethane- d_3 .⁵⁾

The situation is reminiscent of the case of triphenylmethyl chloride⁶⁾ and other compounds which give stable cations on dissociation.⁷⁾ Since these and other ionizing compounds or ions are known to C-alkylate phenols and anilines,⁸⁾ if compound 1 reacts similarly when it is treated with a phenol derivative or an aniline derivative, the results may be taken as the further support for its facile ionization. Indeed, heating 1 with phenol gave 2-(p-hydroxyphenyl)-1,3-dithiane, mp 149.0-150.0°C, in 75% yield. Similarly 1 and N,N-dimethylaniline afforded 2-(p-N,N-dimethylaminophenyl)-1,3-dithiane, mp 115.5-116.5°C, in 30% yield.

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