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RATES OF DISSOCIATION OF N-(1,3-DITHIOLAN-2-YL)PYRIDINIUM PERCHLORATE IN POLAR APROTIC SOLVENTS1)

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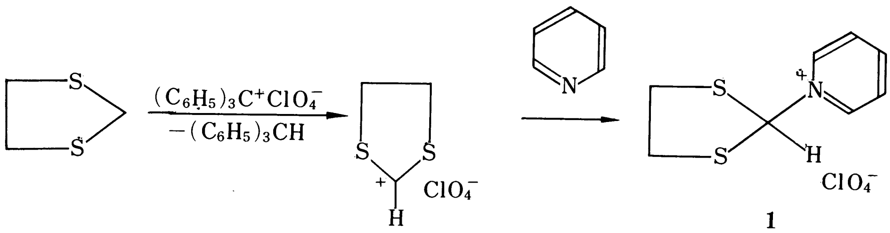
Rates of dissociation of the C-N bond in the title compound have been obtained by the dynamic NMR technique. The barriers to dissociation are 16.4 and 16.5 kcal/mol at 273 K in CD_3CN and CD_3NO_2, respectively.

The dynamic NMR technique has been proven to be useful in determination of the rates of dissociation of various molecular species, including an organic halide,2) an ammonium salt,3) an organometallic compound,4) and an ester,1) by taking advantage of the topomerization phenomena. The features of the method are that it is nondestructive and that the kinetic data can be obtained as solutions in aprotic solvents in the absence of any foreign materials.

A quaternary ammonium salt can be considered to be a molecular species in which an amine ligand coordinates to a carbocation and thus to be a derivative of an ammonium salt which is made from a tertiary amine and an acid. Because of the successful observations of dissociation of proton from a latter type ammonium salt,3) and that of an amine ligand in an organometallic compound,4) we have been naturally interested in seeking examples of quaternary ammonium salts which show appropriate rates of dissociation for the dynamic NMR technique. Since displacement reactions of quaternary ammonium salts are known,5) this study will shed light to the nature of such reactions by providing information about the earlier stages of the reaction. In search of such examples, we have found that N-(1,3-dithiolan-2-yl)pyridinium perchlorate (1) gives suitable rates of dissociation for the dynamic NMR spectroscopic study in addition to bearing appropriate pairs of diastereotopic protons in the molecule.

The compound in question was prepared by treating 1,3-dithiolane in acetonitrile with triphenylmethyl perchlorate in the same solvent and then with pyridine. After evaporation of the solvent, the residue was washed with ether and recrystallized from acetonitrile-ether to afford the pure sample.6)



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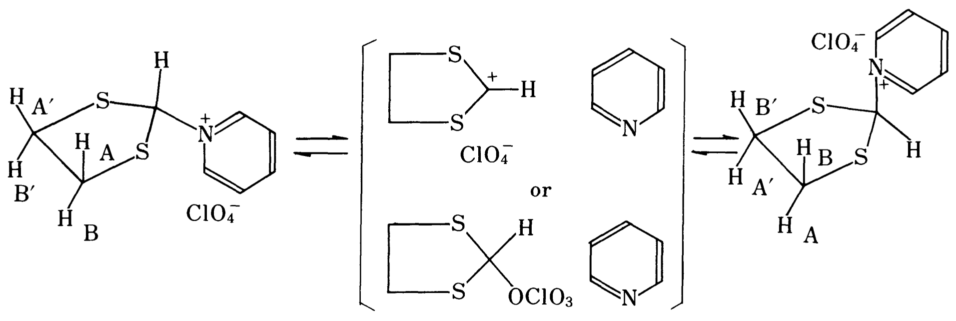
The ^1H NMR spectra of the compound were determined with the use of a JEOL GX-400 NMR spectrometer which operates at 400 MHz. The methylene protons in the 1,3-dithiolane ring exhibited broad signals at room temperature, whereas they did a very complex 20 line signal which is typical of an AA'BB' system, the theoretically expected number of lines being 24, at low temperatures.

The temperature dependence of the ^1H NMR spectra is indicative of the presence of a dynamic process in the molecular species. The most probable process is the dissociation of the C-N bond in the ammonium ion followed by topomerization. Namely, if the pyridine moiety leaves from the carbon-2 of the dithiolane and returns from the rear, this completes the topomerization. The intermediate state, either ionic or covalent species, is discussed later in this paper.



The AA'BB' spectra at low temperatures were analyzed by simulating them with the use of the LAOCN III program. The temperature dependence of the chemical shift differences and coupling constants were checked in the temperature range (-40 °C - 10 °C), where the rates of the site exchange were negligibly small. The coupling constants were constant within the error limits, whereas the chemical shift differences changed linearly with temperature. Thus the $\Delta\nu_{AB}$ values at high temperatures were obtained by extrapolation, using the correlations shown in Table 1, where T is temperature in K. The data are compiled in Table 1.

Table 1. Chemical Shift Differences and Coupling Constants of the AA'BB' System

Solvent	$\Delta\nu_{AB}$/Hz	J_{gem}/Hz	J_{cis}/Hz	J_{trans}/Hz
CD_3CN	$62.2_7 - 0.1_0\ T$	-11.9	5.4	6.8
CD_3NO_2	$87.7_6 - 0.1_5\ T$	-11.9	5.3	6.8

The rate constants of topomerization were obtained by simulation of the line shapes with the use of DNMR3 program.7) The rate constant k and the transverse relaxation time T_2 were treated as variables, while the coupling constants and the chemical shift differences were obtained as above. Thanks to the complex signal shapes, k gives a different trend in modification of the line shapes from that of T_2, thus enabling us to obtain unique solutions for k and T_2. The agreement of the calculated spectra with the observed is satisfactory, as shown in Fig. 1, where the example is taken from the CD_3NO_2 solution.

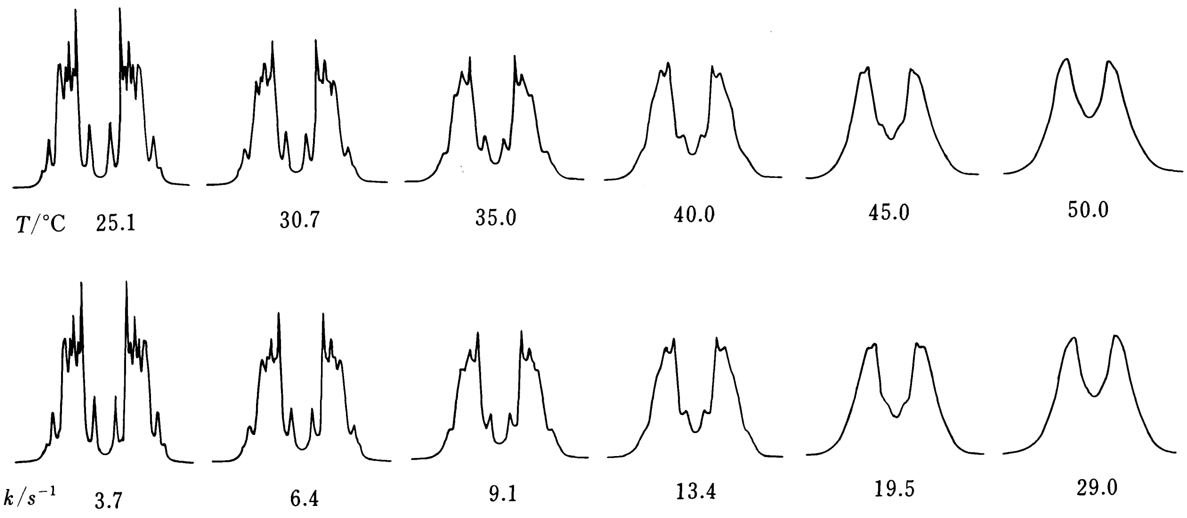


Fig. 1. Observed (top) and calculated (bottom) spectra of the AA'BB' protons of N-(1,3-dithiolan-2-yl)-pyridinium perchlorate in CD_3NO_2.

The rate constants and the temperatures were put into the Eyring equation to obtain kinetic parameters. Although the line broadening for the CD_3NO_2 solutions takes place at a little higher temperature than that for the CD_3CN solution because of the large chemical shift differences, the rate constants as well as the kinetic parameters at a given temperature are almost the same in the two solvents. This may be attributed to the very close dielectric constants of the two solvents concerned.

Table 2. Kinetic Parameters Obtained by the Eyring Plot

Solvent	CD_3CN	CD_3NO_2
Correlation Coeff.	0.9997	0.9995
$\Delta H^{\ddagger}$/kcal mol^{-1}	14.2 ± 0.5	15.0 ± 0.7
$\Delta S^{\ddagger}$ /e. u.	-8.1 ± 1.6	-5.6 ± 2.2
$\Delta G^{\ddagger}_{273}$/kcal mol^{-1}	16.4	16.5

The feature of the data is that the entropies of activation are both small negative. This makes an interesting contrast with respect to other ammonium type compounds, such as (N,N-dibenzyl)aniline hydrochloride [3] and the coordinated form of o-[(diethylamino)methyl]phenyldimethylstannyl bromide,[4] and organic halides.[2] The organic halides give large negative entropy of activation in dissociation. This is attributed to the decrease in freedom of motion of solvent molecules due to development of the electric charge.[8] By contrast, dissociation of the ammonium type compounds gives large positive entropy of activation which can be interpreted as a result of disappearance of the electric charge. Therefore, if the freedom of motion of solvent molecules is an important factor, the followings are predicted. The entropy of activation must be near zero, if the transition state is approximated by the formation of ion pairs, because the electric charge does not change from the ground state to the transition state, or it must be large positive, if the transition state is approximated by covalent species. In addition, in any of the transition states, there must be a molecule of pyridine formed. This factor should make the entropy of activation positive.

The observed entropy of activation does not conform any of the expectations. We should like to suggest that, in the transition state, the perchlorate ion forms a partial covalent bond with C-2 of the 1,3-dithiolane moiety. By doing this, the perchlorate ion loses its freedom of motion, because, in the ground state, the four oxygen atoms of the perchlorate anion are equivalent and the ion is almost freely rotating around the cationic center. Although perchlorate ester is known to be easily ionizable, it may not be inconsistent with literatures to assume the transient formation of the perchlorate ester, because there are some instances in which perchlorate esters survive for some time in aprotic solvents9) and the perchlorate ion has some nucleophilicity to afford perchlorate esters in reactions forming carbocation-like species.10) We have some pieces of evidence which supports this postulate. They may be described elsewhere.

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