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INFRARED-INDUCED CONFORMATIONAL ISOMERIZATION OF 2-CHLOROETHYLAMINE IN AN ARGON MATRIX

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The infrared spectrum of 2-chloroethylamine has been studied in an argon matrix. It has been found that the gauche to trans isomerization around the C-C bond occurs in the matrix by infrared irradiation and the spectrum of the resultant trans form changes by elevating the matrix temperature from 20 to 28 K.

One of the most interesting problems in recent matrix-isolation spectroscopy is the infrared-induced conformational isomerization. This phenomenon has been found for various molecules which have an OH group in common.[1-9] On the other hand, our recent study on allylamine and allyl alcohol[10] has shown that the conformational changes occur in amines as well as in alcohols. In the present study, we examine the infrared-induced conformational isomerization of 2-chloroethylamine in an argon matrix at various matrix temperatures.

2-Chloroethylamine was prepared from its hydrochloride (purchased from Tokyo Kasei Kogyo Co., Ltd.) by treatment with sodium hydroxide. The sample was diluted with Ar gas (purity 99.999%); the ratio of matrix/sample was about 500. The premixed gas was sprayed onto a CsI plate maintained at 20 K. Deposition was carried out in a dark room. Infrared spectra were recorded on a Hitachi 260-50 infrared spectrophotometer, and the other experimental details were described elsewhere.[6]

2-Chloroethylamine has two axes of internal rotation, namely, the C-C and C-N bonds. Figure 1 shows five possible conformers, TT, TG^+, G^+T, G^+G^+, and G^+G^-, where the first and second symbols refer to the conformations about the C-C and

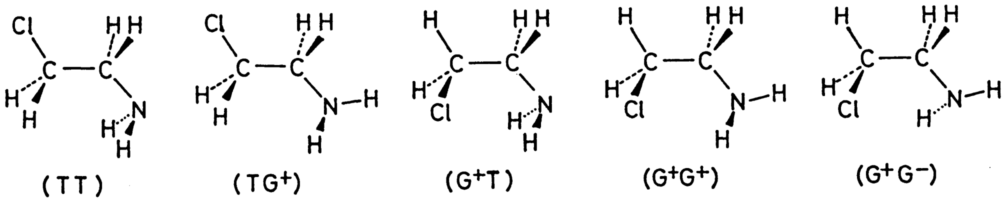

Fig. 1. Possible conformers of 2-chloroethylamine. The conformers TG^+, G^+T, G^+G^+, and G^+G^- are spectroscopically equivalent to TG^-, G^-T, G^-G^-, and G^-G^+.

C-N axes, respectively, and the signs in the superscript indicate the direction of rotation. In the three gauche forms about the C-C bond, G^+T and G^+G^+ can be expected to be more stable than G^+G^-, because G^+T and G^+G^+ have an intramolecular hydrogen bonding between the chlorine and hydrogen atoms, while the chlorine atom of G^+G^- is close to the lone pair of the nitrogen atom.

Sennitskaya et al.[11] studied the infrared spectra of this molecule in various solvents and reported the existence of the gauche and trans forms about the C-C axis. However, no consideration on the conformation about the C-N axis was given in their analysis.

Figure 2 shows the infrared spectra in the region between 810 and 630 cm^{-1} when the matrix was exposed to the infrared light from the light source of the spectrophotometer. On the lefthand side, Figs. 2a - 2d show the infrared-induced spectral changes at the matrix temperature of 28 K. The spectrum recorded immediately after deposition (Fig. 2a) mainly consists of five peaks. Comparing it with the infrared spectrum of 2-chloroethanol,[6] we assign the band at 663 cm^{-1} to the C-Cl stretching mode of the gauche forms around the C-C axis. This band is rather broad probably because of the overlapping of the four peaks arising from the ^{35}Cl and ^{37}Cl isotopic species of G^+T and G^+G^+. The intensity of this band decreased with the time of infrared irradiation, as shown in Fig. 3. The band at 758 cm^{-1} has a shoulder at the lower frequency side whose intensity is about one third of the main peak. Since the wavenumber difference between the main band and the shoulder is about 3 cm^{-1} and seems to be due to the chlorine-isotope shift, we assign this band to the C-Cl stretching mode of a trans form (TT or TG^+). The

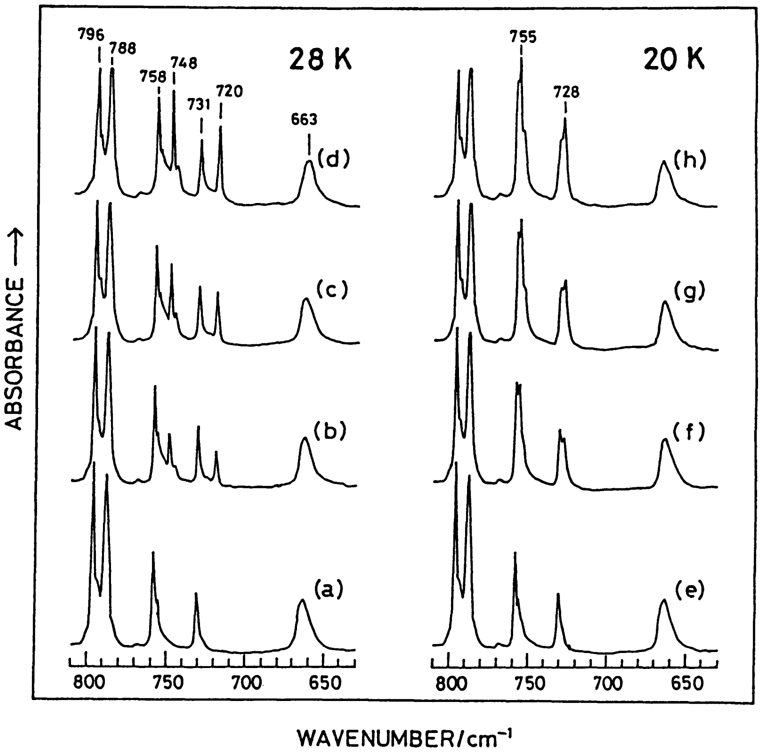

Fig. 2. Infrared spectra of 2-chloroethylamine in argon matrices at 28 and 20 K. (a) and (e), recorded immediately after deposition; (b) and (f), after 25 min in the infrared beam; (c) and (g), after 50 min in the infrared beam; (d) and (h), after 75 min in the infrared beam.

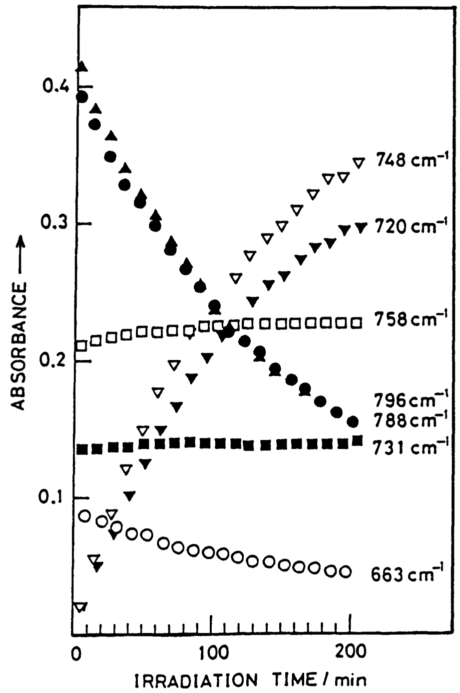

Fig. 3. Plots of absorption intensities of the NH_2 wagging and C-Cl stretching bands against the time of irradiation at 28 K.

other bands in this region are assignable to the NH_2 wagging mode. The bands at 796 and 788 cm^{-1} decreased with the time of irradiation at roughly the same rate as did the band at 663 cm^{-1}. Therefore, these bands are assignable to the gauche forms, G^+T and G^+G^+. The decreasing rates of these gauche forms were not significantly different from each other, as shown in Fig. 3. On the other hand, the intensities of the bands at 731 and 758 cm^{-1} were nearly constant against the irradiation time. Then, we can assign the 731 cm^{-1} band to the NH_2 wagging mode of a trans form (TT or TG^+). The assignment mentioned above is confirmed by the vibrational analysis of the N-deuterated species $ClCH_2CH_2ND_2$; the ND_2 wagging is greatly different from that of the normal species, whereas the C-Cl stretching bands do not shift much from 663 and 758 cm^{-1} of the normal species.

When the matrix was irradiated in the infrared beam, the intensities of the bands for the gauche forms (796, 788, and 663 cm^{-1}) decreased and the bands for the trans form (758 and 731 cm^{-1}) were constant, while new bands at 748 and 720 cm^{-1} appeared and their intensities increased rapidly with the time of irradiation. The band at 748 cm^{-1} has a shoulder like the band at 758 cm^{-1}. Then, this band can be assigned to the C-Cl stretching mode for a trans form, which was generated under infrared irradiation, though its detailed geometry is not clear at the present stage. The increasing rate of the band at 720 cm^{-1} was not significantly different from that of the band at 748 cm^{-1}. We assign the band at 720 cm^{-1} to the NH_2 wagging mode of the infrared-generated trans form.

It is interesting to examine the dependence of the spectral changes on the matrix temperature as well as the effect of infrared irradiation. Figures 2e - 2h show the infrared-induced spectral changes at the matrix temperature of 20 K. New bands at 755 cm^{-1} (with a shoulder at the lower frequency side) and at 728 cm^{-1} appeared instead of the bands at 748 and 720 cm^{-1}, respectively. The decreasing rates of G^+T and G^+G^+ were nearly equal to those at 28 K.

After recording Fig. 2h, we elevated the matrix temperature from 20 to 28 K at a rate of 2 K min^{-1} and obtained the spectrum similar to Fig. 2d. This transformation rapidly occurred in the absence of infrared irradiation. When the matrix was cooled down to 20 K once again, we found little change in the infrared spectrum. We also examined the above mentioned phenomenon in a more diluted sample (the matrix/sample ratio of about 2000) and found that the rates of the spectral change were essentially unchanged.

The rate of this transformation strongly depended on the matrix temperature. Figure 4 shows more detailed spectral changes in a matrix whose temperature was elevated to 26 K after prolonged infrared

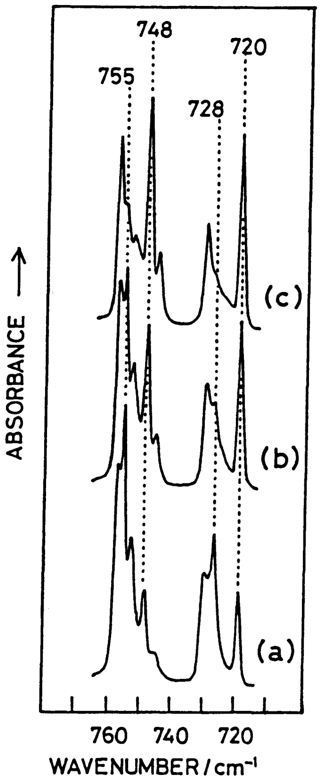

Fig. 4. Spectral changes at 26 K for the matrix irradiated for 240 min at 20 K. Measurements started at (a) 3 min, (b) 7 min, and (c) 11 min, after warming up.

irradiation (240 min) at 20 K. (At 28 K the spectral changes occurred so rapidly during the measurement that we could not obtain the spectra of intermediate stages). It was found that the bands at 755 and 728 cm^{-1} disappeared and the bands at 748 and 720 cm^{-1} appeared, whereas the intensities of the bands at 758 and 731 cm^{-1} were essentially invariant. Figure 5 shows the plots of the intensities of the C-Cl stretching bands at 755 and 748 cm^{-1} in the matrix irradiated for 240 min at 20 K against the time after warming up to various matrix temperatures. At temperatures lower than 22 K, the spectral changes could not be observed, which started slowly at 24 K and developed rapidly at temperatures higher than 26 K. The decreasing rate of the band at 755 cm^{-1} seemed to be nearly equal to the increasing rate of the band at 748 cm^{-1} at any given temperatures. The same relationship was found between the NH_2 wagging bands at 728 and 720 cm^{-1}.

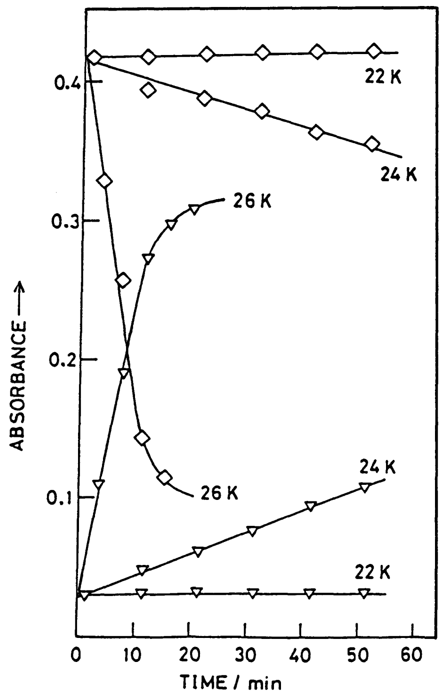

Fig. 5. Plots of absorption intensities of the C-Cl stretching bands in the matrix irradiated for 240 min at 20 K against the time after warming up to various temperatures. ◇ and ▽ represent the peaks at 755 and 748 cm^{-1}, respectively.

Räsänen et al. reported that infrared spectrum of 2-aminoethanol in a nitrogen matrix changed by elevating the matrix temperature from 13 to 16 K, but never in an argon matrix.[9)] They also reported that the spectra at 13 and 16 K changed reversibly in the infrared beam. Our present observations on the 2-chloroethylamine in argon matrices are very different from the results obtained by Räsänen et al. on 2-aminoethanol. More detailed vibrational analysis of the normal and deuterated species and discussions on the conformations of 2-chloroethylamine in Ar matrices will be published elsewhere.

References

1) A.E. Shirk and J.S. Shirk, Chem. Phys. Lett., 97,549(1983).
2) J. Murto, M. Räsänen, A. Aspiala, and L. Homanen, J. Mol. Struct., 92,45(1983).
3) W.F. Hoffman III and J.S. Shirk, Chem. Phys., 78,331(1983).
4) A.J. Barnes and R.M. Bentwood, J. Mol. Struct., 112,31(1984).
5) L. Homanen, Spectrochim. Acta, Part A, 39,77(1983).
6) H. Takeuchi and M. Tasumi, Chem. Phys., 70,275(1982).
7) M. Räsänen, A. Aspiala, and J. Murto, J. Chem. Phys., 79,107(1983).
8) H. Takeuchi and M. Tasumi, Chem. Phys., 77,21(1983).
9) M. Räsänen, A. Aspiala, L. Homanen, and J. Murto, J. Mol. Struct., 96,81(1983).
10) M. Nakata, M. Tasumi, Y. Hamada, and M. Tsuboi, Chem. Lett., 1983,467.
11) L.V. Sennitskaya, Yu.D. Timoshenkova, Yu.A. Pentin, and B.S. Kikot, Opt. Spektrosk., 37,241(1974).

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