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INFRARED-INDUCED CONFORMATIONAL ISOMERIZATIONS OF ALLYLAMINE AND ALLYL ALCOHOL IN LOW-TEMPERATURE MATRICES

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The infrared spectra of allylamine and allyl alcohol have been studied in low-temperature matrices. In argon matrices these molecules show rapid spectral changes upon exposure to the radiation from the light source of an infrared spectrophotometer. These spectral changes arise from the conformational isomerizations from a rotational isomer with the *cis* conformation about the C-C bond to those with the *skew* conformation. No such conformational isomerization has been observed in nitrogen matrices.

Matrix-isolation infrared spectroscopy is one of the most powerful techniques for studying various problems relating to molecular conformations and conformational isomerizations.1) One reason is that bands arising from different conformers can be observed separately, since the widths of absorption bands due to molecular species isolated in low-temperature matrices are generally narrow. Another reason is that this technique enables us to obtain the infrared spectra of unstable conformers which are generated by appropriate methods and trapped in low-temperature matrices.

Recently, interest in conformational isomerizations in low-temperature matrices induced by infrared or near-infrared irradiation is increasing.2-4) The infrared-induced conformational isomerizations of allylamine and allyl alcohol have some new aspects which have not been found in the other cases and will be reported in this communication.

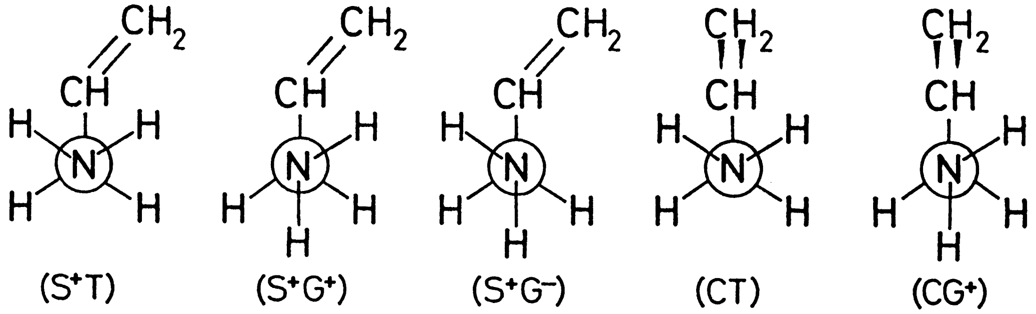

Fig. 1. Possible conformers of allylamine ($CH_2=CHCH_2NH_2$) as viewed along its C-N axis. The conformers S^+T, S^+G^+, S^+G^-, and CG^+ are spectroscopically equivalent to S^-T, S^-G^-, S^-G^+, and CG^-, respectively.

Allylamine was prepared by neutralizing its hydrochloride with sodium hydroxide and was used after vacuum distillation. Allyl alcohol was purchased from Tokyo Kasei Kogyo Co., Ltd. The Ar/sample ratios in our measurements were ~500. The premixed gas was sprayed onto a CsI plate cooled to 20 K in a deposition time of about 3 hours. During deposition the sample chamber was covered with a sheet of aluminum foil to avoid any irradiation on the matrix sample. A Hitachi 260-50 infrared spectrophotometer was used, and the details of experimental setup were described previously.[3]

The allylamine molecule has two axes of internal rotation, namely, the C-C and C-N bonds. The *cis* (C) and *skew* (S) forms are expected to be stable about the C-C bond, while the *trans* (T) and *gauche* (G) forms (with respect to the lone-pair electrons and the C atom of the -CH= group) are so expected about the C-N bond. In Fig. 1 are shown five non-equivalent conformers, S^+T, S^+G^+, S^+G^-, CT, and CG^+. (The signs in the superscript indicate the sense of rotation.) Botskor *et al.* observed and assigned the microwave spectra of the S^+T, S^+G^+, CT, and CG^+ forms.[5-8] The relative intensities of the microwave absorptions of these forms showed that the CG^+ form was less stable than the other three. On the other hand, Murty and Curl observed the microwave spectrum of allyl alcohol and assigned the absorptions due to the S^+G^- form.[9] (In the case of allyl alcohol the *trans* and *gauche* forms about the C-O bond are defined with respect to the hydroxyl H atom and the C atom of the -CH= group.)

The infrared spectrum of allylamine in an Ar matrix was found to change rapidly upon exposure to the infrared light from the light source of the spectrophotometer. The spectral changes with the time of irradiation are shown in Fig. 2. We now focus on a group of three bands at 921, 918, and 914 cm^{-1} and another group of three bands at 789, 784, and 781 cm^{-1}. The former group is assignable to the CH_2 out-of-plane wagging mode and the latter to the NH_2 wagging. Since the three bands in each group are closely located, it may seem possible that these bands result from the splitting due to matrix site effects. However, this possibility was excluded by the following observations. An analysis[10] of the spectrum of gaseous allylamine in the region around 920 cm^{-1} by a laser-microwave double

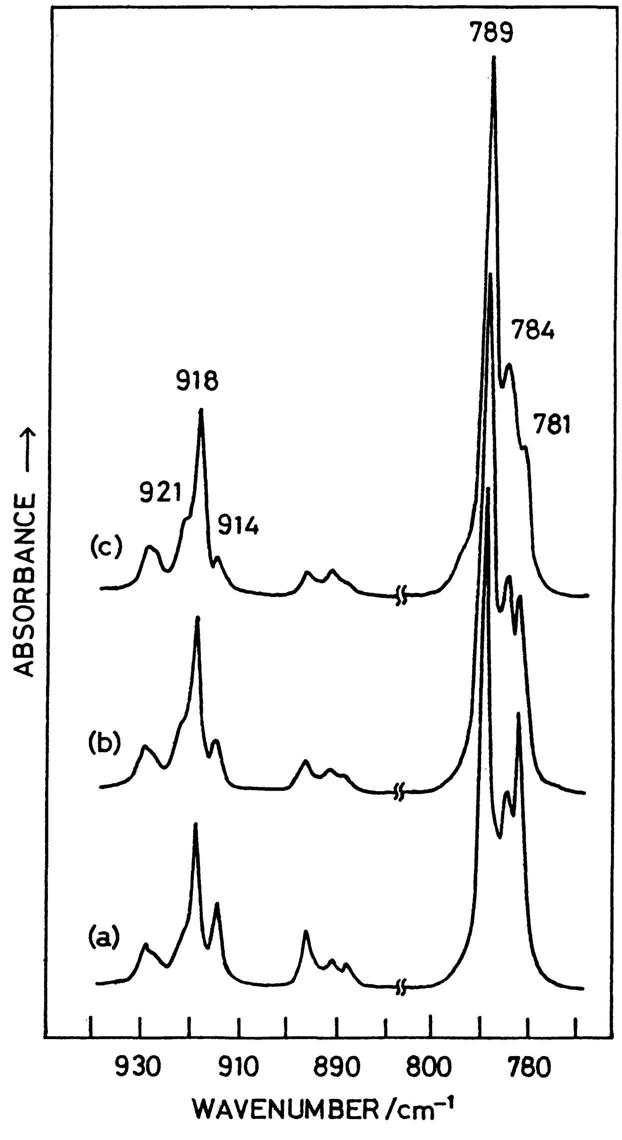

Fig. 2. Infrared spectra of allylamine (CH_2=$CHCH_2NH_2$) in Ar at 20 K:
(a) recorded immediately after deposition,
(b) after 15 min in the infrared beam,
(c) after 30 min in the infrared beam.

and triple resonance method has demonstrated the existence of two vibrational transitions (920.9 and 919.5 cm^{-1}). On the other hand, a recent study[11] of the high-resolution infrared spectrum of gaseous allylamine has shown that there are at least three vibrational transitions in both regions around 780 and 920 cm^{-1}.

It is most likely that the spectral changes with infrared irradiation reflect the conformational isomerization of allylamine. The 914 and 781 cm^{-1} bands lose their intensities with increasing time of irradiation, whereas the other four bands at 921, 918, 789, and 784 cm^{-1} show opposite behavior. Among the latter four the 918 and 789 cm^{-1} bands are much stronger than the 921 and 784 cm^{-1} bands. Therefore, there are three pairs of bands (921 and 784 cm^{-1}, 918 and 789 cm^{-1}, and 914 and 781 cm^{-1}) and each of these pairs seems to correspond to one among the three major conformers (S^+T, S^+G^+, and CT) detected by microwave spectroscopy. According to the assignments proposed by Botskor and Jones,[10] the S^+T and S^+G^+ forms in the gaseous state have their CH_2 wagging frequencies at 919.5 and 920.9 cm^{-1}, respectively. Comparing our matrix-isolation spectra with their result, we assign the bands at 918 and 921 cm^{-1} to the *skew* forms.[12] Accordingly, the bands at 789 and 784 cm^{-1} are also assigned to the *skew* forms. The bands at 914 and 781 cm^{-1} are assignable to the remaining CT form. Although Botskor and Jones associated the absorption at 916 cm^{-1} in the gaseous state with a hot band, this assignment is inconsistent with our observation which was made at 20 K, if their 916 cm^{-1} and our 914 cm^{-1} bands are of the same origin. From a recent microwave study,[10] the relative intensities of (S^+T and S^+G^+) : CT are expected to be 7 : 3. These values roughly agree with the observed relative intensities in the region around 780 or 920 cm^{-1} of our matrix-isolation spectrum measured immediately after deposition. The band assignments described above lead to the conclusion that the CT form is isomerized to either the S^+T or S^+G^+ form with infrared irradiation.

Silvi *et al.* measured the infrared spectra of allylamine and allyl alcohol in low-temperature matrices, and reported that these molecules had two conformers in a nitrogen matrix but only one in an argon matrix.[13] It is probable, however, that the disappearance of one conformer in the argon matrix might be caused by irradiation from the light source of their spectrophotometer.

The effects of infrared irradiation on the matrix-isolation infrared spectra of allyl alcohol were also observed in the same way. The spectral changes in the 950-910 cm^{-1} region are shown in Fig. 3. It is noted that the band at 916 cm^{-1} decreases in intensity with increasing time of infrared irradiation, whereas the intensities of the bands at 938, 928, 926, and 912 cm^{-1} increase. In analogy with the case of allylamine, the decreasing 916 cm^{-1} band seems to arise from a

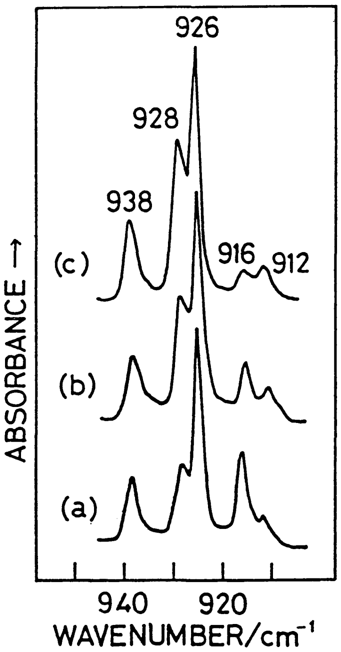

Fig. 3. Infrared spectra of allyl alcohol ($CH_2=CHCH_2OH$) in Ar at 20 K:
(a) recorded immediately after deposition,
(b) after 30 min in the infrared beam,
(c) after 60 min in the infrared beam.

conformer having the *cis* form about the C-C axis and the growing bands from the *skew* form. Little information on the conformation about the C-O axis is available. However, the 928 and 926 cm^{-1} bands are probably due to different *skew* forms, because their increasing rates are slightly different.

We measured the infrared spectra of allylamine and allyl alcohol in nitrogen matrices also, keeping the sample chamber in the dark during deposition. The results were essentially the same with those obtained by Silvi and Perchard.[13-15] Both the *cis* and *skew* forms existed in nitrogen matrices and no spectral changes with the infrared irradiation occurred.

The conformational isomerizations of allylamine and allyl alcohol with the infrared irradiation occur faster than those of 2-chloroethanol and ethylene glycol studied previously.[3,4] A common feature for the infrared-induced conformational isomerizations of the latter molecules is that the conformers having intramolecular hydrogen bonding are isomerized to the conformer without hydrogen bonding. Therefore, it was suggested that intramolecular hydrogen bonding might play an important role in the conformational isomerization in low-temperature matrices.[4] However, this is not true in the cases of allylamine and allyl alcohol, because there is no hydrogen bonding in any conformer of these molecules. The mechanism of infrared-induced conformational isomerizations in low-temperature matrices seems to be an interesting problem to be studied in future.

References

1) "Matrix Isolation Spectroscopy", ed. by A.J. Barnes, W.J. Orville-Thomas, A. Müller, and R. Gaufrès, D. Reidel Publishing Company, Boston (1981).
2) P.A. McDonald and J.S. Shirk, J. Chem. Phys., 77, 2355 (1982).
3) H. Takeuchi and M. Tasumi, Chem. Phys., 70, 275 (1982).
4) H. Takeuchi and M. Tasumi, Chem. Phys., in press.
5) G. Roussy, J. Demaison, I. Botskor, and H.D. Rudolph, J. Mol. Spectrosc., 38, 535 (1971).
6) I. Botskor, H.D. Rudolph, and G. Roussy, J. Mol. Spectrosc., 52, 457 (1974).
7) I. Botskor, H.D. Rudolph, and G. Roussy, J. Mol. Spectrosc., 53, 15 (1974).
8) I. Botskor and H.D. Rudolph, J. Mol. Spectrosc., 71, 430 (1978).
9) A.N. Murty and R.F. Curl, Jr., J. Chem. Phys., 46, 4176 (1967).
10) I. Botskor and H. Jones, J. Mol. Spectrosc., 81, 1 (1980).
11) Y. Hamada *et al.*, to be published.
12) The respective assignments of the 918 and 921 cm^{-1} bands to S^+T and S^+G^+ will be discussed in a separate paper.[11]
13) B. Silvi, F. Froment, J. Corset, and J.P. Perchard, Chem. Phys. Lett., 18, 561 (1973).
14) B. Silvi and J.P. Perchard, Spectrochim. Acta, 32A, 11 (1976).
15) B. Silvi and J.P. Perchard, Spectrochim. Acta, 32A, 23 (1976).

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