The Infrared Spectra of α-Chlorinated Acetamides

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The polarized infrared spectra of α,α,α-trichloroacetamide (TCA) and its deuterated compound (TCA-*d*) have been measured in the 400—4000 cm^{-1} region, and the infrared spectra of the series, $CCl_nH_{3-n}CONH_2$ (n= 0—3), and their deuterated compounds have been observed in the solid state. On the basis of the results, the vibrational assignments, the orientation of TCA, the intermolecular hydrogen bonds, and the inductive effect of the introduction of the chlorine atom, and the conformation of TCA have been discussed. It has been proposed that TCA in the solid state has two conformations, which are in linear-chain associations through hydrogen bonds.

The infrared spectra and vibrational analyses of acetamide[1-5] and *N*-alkylacetamides[6-8] have been extensively studied, with special interest taken in them as model molecules of polypeptides and proteins. However, the infrared spectra of α-chlorinated acetamides have been less widely studied than those of acetamide and *N*-alkylacetamides. Herman and Bièvre[9] have observed the infrared spectra of α-chlorinated acetamides in the solid state, but their spectra are in the sodium chloride region and the spectra of their *N*-deuterated compounds have not been reported. There is a spectroscopic study of chlorinated acetamides in a carbon tetrachloride solution as a part of the study of primary acid amides,[10] in which their molecular structure has been discussed by analogy with the intramolecularly-bonded structure of *N*-alkyl-α-chlorinated acetamides offered by Nyquist.[11]

As α,α,α-trichloroacetamide (TCA) grows into considerably large plate crystals by recrystallization from an ether solution, we were able to prepare the oriented crystal of TCA between potassium bromide plates.

In this paper, we will describe our findings on the polarized infrared spectra of TCA and TCA-*d* and on the infrared spectra of chlorinated acetamides and their *N*-deuterated compounds in the $CCl_nH_{3-n}CONH_2$ series (n=0—3).

Experimental

Materials. The TCA, DCA (α,α-dichloro-), MCA (α-monochloro-), and NCA (nonchloro-acetamide) were obtained from Nakarai Chemicals, Ltd., and each sample was purified by repeated recrystallization from an aqueous solution. The deuteration of MCA was done by a usual method,[12] while those of DCA and TCA were done by the method for water-insoluble compounds described in a previous paper.[13]

The oriented crystals of TCA and TCA-*d* were obtained by allowing the molten sample to crystallize between potassium bromide plates, with a temperature gradient. We observed through a microscope many long crystals arranged parallel to each other.

Infrared Spectra. The infrared absorption measurements in the 400—4000 cm^{-1} region were made by use of a Hitachi EPI-2G Infrared Grating Spectrophotometer. The spectra in the solid state were measured as potassium bromide discs and Nujol mulls. The spectra in the liquid state of TCA and TCA-*d* were obtained by the use of a cell with an electrically-heated and beam-transparent box, in which the solid sample between the window plates was heated to *ca.* 145°C, which is slightly higher than its melting point (141°C). The dichroic measurements of the oriented crystals were made with a pair of silver chloride polarizers.

Results and Discussion

Vibrational Assignment of TCA. The observed bands in the infrared spectra of TCA and TCA-*d* were assigned by observing the changes in the spectra according to the state of aggregation (Table 1) and by comparing them with the spectra of NCA, MCA, and DCA (Fig. 1).

As expected,[6,14] with the change in state from the solid to the liquid, the frequencies of a few $\nu(NH_2)$ bands in the 3μ region and the ν(C=O) band around 1700 cm^{-1} increase, but the frequencies of the other amide bands decrease more or less.

On deuteration, the two bands at 1379 and 1351 cm^{-1} are replaced by a band at 1395 cm^{-1} and a shoulder band at 1370 cm^{-1} assignable to the ν(C–N) modes, while, instead of a sharp $\delta(NH_2)$ band at 1616 cm^{-1} in TCA, a new band appears at 1159 cm^{-1} assignable to the $\delta(ND_2)$ mode. The upward frequency-shift of the ν(C–N) bands by deuteration may be due to the decoupling of the contribution of the $\delta(NH_2)$ mode, just as in NCA.[2] The bands at 1105, 922, and 437 cm^{-1} correspond to the bands at 1155, 875, and 464 cm^{-1} in NCA, which have been assigned by Suzuki[2] to the $\delta r(NH_2)$, ν(C–C′), and δ(C′–C=O) modes respectively. The strong bands near 825 cm^{-1}

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TABLE 1. INFRARED FREQUENCIES (cm^{-1}) OF TRICHLOROACETAMIDE

I CCl_3CONH_2

Solid (KBr disk)	Dichroism (Oriented crystal) ⊥	∥	Solid (103°C)	Liquid (145°C)	$CHCl_3$ soln	Assign.
					3519	$\nu as(NH_2)$, free
3393(s)	s	s	3400(s)	3480(s)	3485	ν(N–H)
					3404	$\nu s(NH_2)$, free
3338(s)	s	< s	3340(s)	3355(s)	3325	} ν(N–H)
3260(s)	s	s	3250(s)	3300(sh)	3250	
3196(s)	s	s	3200(s)	3175(sh)	3165	
2783(w)	vw	w	2800(w)			1694+1105=2799
2695(w)	w	< w	2700(vw)			1348×2=2696
1740(sh)	w	—				922+825=1747
1694(s)	w	s	1694(s)	1714(s)	1736	ν(C=O)
1616(s)	s	> s	1602(s)	1582(s)	1580	$\delta(NH_2)$
1379(s)	s	m	1374(s)	1352(s)	1358	} ν(C–N)
1351(m)	s	m	1342(sh)	1334(sh)	1335	
1270(vw)	w	m				646×2=1292
1220(vw)	—	—				615×2=1230
1105(s)	m	s	1095(s)	1093(m)	1098	$\delta r(NH_2)$
922(m)	m	m	917(m)	906(w)	908	ν(C′–C)
850(sh)					844	437×2=874
825(s)	s	s	818(s)	819(s)	822	} ν(C–Cl)
820(sh)						
746(s)	s	m	740(m)	680(m)	680	$\pi(NH_2)$, π(C=O)
646(s)	s	m	640(s)	617(m)	614	π(N–C=O)
615(s)	s	vw	592(w,sh)	490(w)	?	$\pi(NH_2)$
437(m)	s	—	426(m)	420(vw)	?	δ(C′–C–N)

II CCl_3COND_2

Solid (KBr disk)	Dichroism (Oriented crystal) ⊥	∥	Solid (100°C)	Liquid (145°C)	Assign.
3065(vw)					1683+1395=3078
2930(vw)					?
2840(vw)					1683+1159=2842
2780(vw)					1395× 2 =2790
2510(s)	s	s	2548(s)	2600(s)	$\nu as(ND_2)$
2380(s)	s	s	2396(s)	2427(s)	$\nu s(ND_2)$
2360(sh)			(sh)	(sh)	
2345(sh)					
1683(s)	w	s	1694(s)	1710(s)	ν(C=O)
1500(w)	w	m	1493(w)	1480(w)	Amide I
1395(s)	—	s	1387(s)	1361(s)	} ν(C–N)
1370(sh)	m	—	—	—	
1159(m)	m	m	1156(m)	1142(w)	$\delta(ND_2)$
940(m)	w	s	940(m)	940(m)	$\delta r(ND_2)$
884(s)	s	s	884(s)	878(s)	ν(C′–C)
821(s)	sh	s	820(s)	818(s)	} ν(C–Cl)
817(sh)	s	sh			
678(s)	s	w	676(m)	669(s)	π(C=O)
591(s)	s	s	585(s)	554(s)	δ(N–C=O)
517(m)	m	w	500(vw,sh)	—(vw,b)	$\pi(ND_2)$
460(s)	m	w	426(w,b)	—(vw,b)	$\pi(ND_2)$
406(w)					δ(C′–C–N)

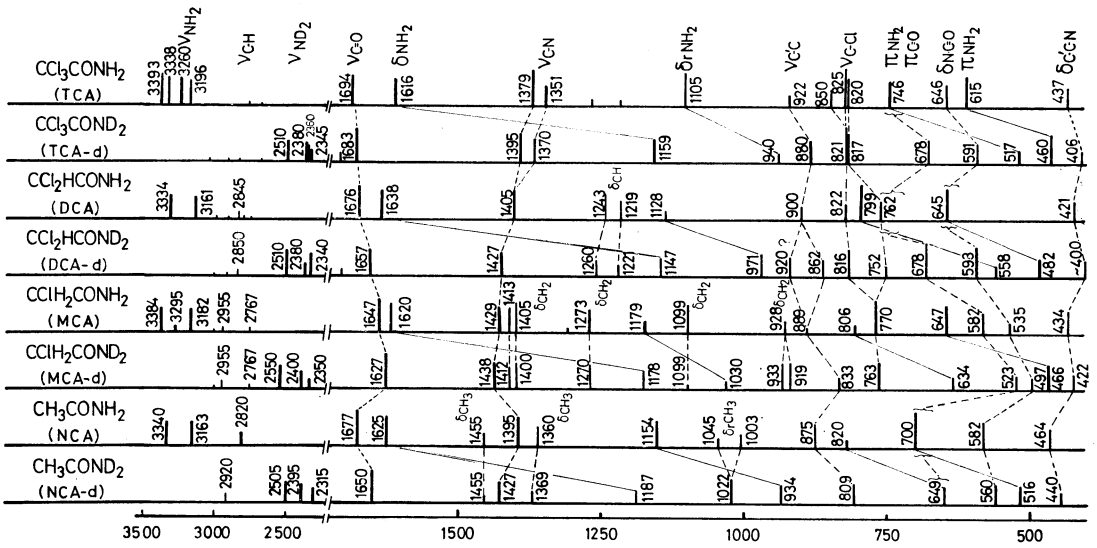

Fig. 1. Observed frequencies and relative intensities of $CCl_nH_{3-n}CONH_2$ ($n=0-3$) and these *N*-deuterated compounds. Bands combined with a solid line between an undeuterated and its deuterated compounds are related to a vibration due to NH_2 or ND_2 group, and among their compounds these bands are not combined with any lines. Data for NCA-*d* are by Suzuki (Ref. 2).

which are unshifted on deuteration and on the change in state are associated with the ν (C–Cl) vibrations.

In the 500—800 cm^{-1} region, four amide bands are predicted; a δ(N–C=O), a π(C=O), and two $\pi(NH_2)$ bands. In the observed spectra, only three bands are observed for TCA, whereas four bands are observed for TCA-*d*. The bands at 746 and 615 cm^{-1}, which disappear on deuteration, are assigned to the two $\pi(NH_2)$ modes, since these bands are very broad and the most sensitive to the change in state (see Table 1), just like the amide V band (mainly the π(N–H) vibration) of secondary amides[6] and dialkylureas.[12,13] The band at 646 cm^{-1} and an undetectable band probably covered by the higher $\pi(NH_2)$ band[12,13,15] may be associated with the δ(N–C=O) and π(C=O) modes respectively.

The observed frequencies and the vibrational assignment obtained are in agreement with those obtained by Herman and Bièvre[9] except for the assignment of the band at 746 cm^{-1}, which we assigned to the $\pi(NH_2)$ mode since this band disappears on deuteration.

Polarized Infrared Spectra of TCA and TCA-d. The polarized infrared spectra of TCA and TCA-*d* are shown in Fig. 2. The ν(C=O) band exhibits a definitely parallel dichroism in both samples. This means that the direction of the C=O bond is parallel to the long direction of the oriented crystal and that the association of TCA shown below is acceptable. The parallel ν(C=O) band is contrasted with the ν(C=O) band of benzamide[16] at 1656 cm^{-1}, having an indistinguishable dichroism. The structure of the associated molecules of benzamide[17] has a chain association of dimer units, with a center of symmetry, in which the C=O bonds are placed in an inclined position to the

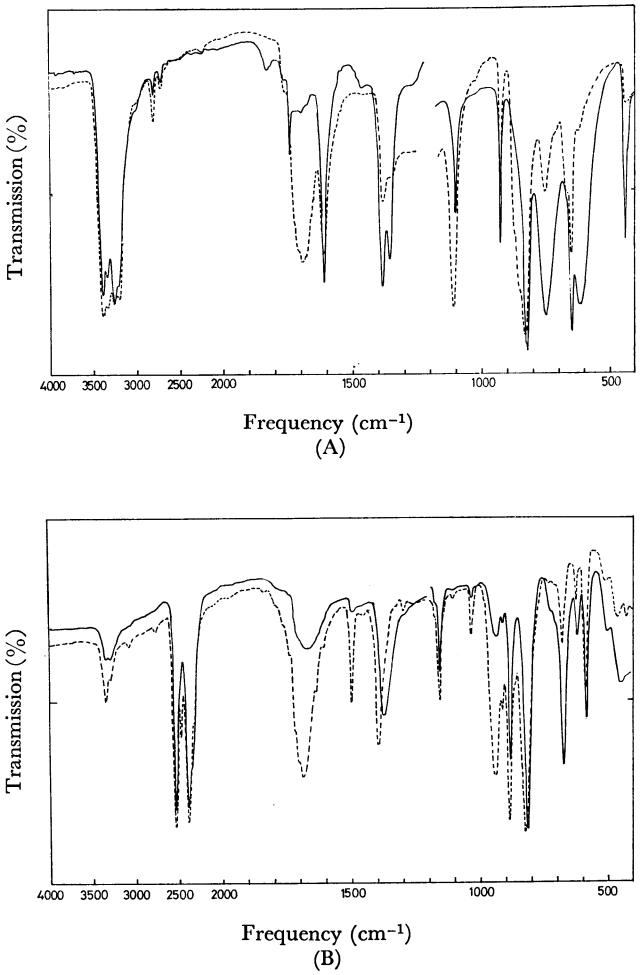

Fig. 2. The polarized infrared spectra of TCA (A) and TCA-*d* (B) with the electric vector of the incident infrared beam being parallel (broken line) or perpendicular (solid line) to the long direction of the oriented crystal.

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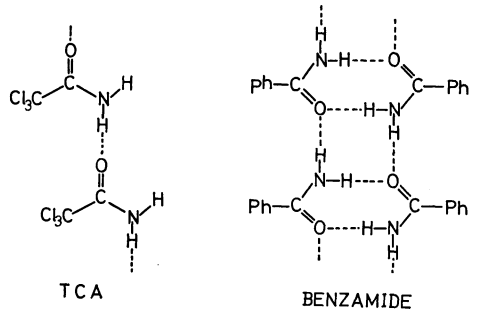
Table 2. The CO stretching frequencies (cm^{-1}) in the carbon tetrachloride solution and the solid state

	CH_3CONH_2 (NCA)	$CH_2ClCONH_2$ (MCA)	$CHCl_2CONH_2$ (DCA)	CCl_3CONH_2 (TCA)
Free (CCl_4 soln.)	1711[a)]	1724	1731	1751
Associated (Solid)	1677	1647	1676	1694
Difference	34	77	55	57

a) E. A. Cutmore and H. E. Hallam, *Spectrochim. Acta.*, **25A**, 1767 (1969).

oriented axis;



From the above figure, one can understand the indistinguishable dichroic property of ν(C=O) band of benzamide, and can see that the structure of TCA is not like that in benzamide. If such a chain association of TCA is assumed, it may be expected that $\nu a(NH_2)$ and $\delta r(NH_2)$ bands will exhibit a rather parallel dichroism, whereas $\nu s(NH_2)$, $\delta(NH_2)$, ν(C–N), and ν(C–C′) bands will exhibit a rather perpendicular dichroism. The polarized spectra of TCA almost satisfy the above expectation. This indicates that the assumed chain association model of TCA is reasonable. The dichroic properties of some bands of TCA-*d* do not satisfy the expectation. The unsatisfactory dichroism may be due to the insufficient deuteration and/or orientation. All bands related to out-of-plane vibrations exhibit a perpendicular dichroism in both samples, as expected. This indicates that the assignment of these bands is correct, and that the chain association suggested is also reasonable.

Amide Bands and Their Frequency Changes in $CCl_nH_{3-n}CONH_2$. The correlation among the observed frequencies for $CCl_nH_{3-n}CONH_2$ (n=0—3) and their *N*-deuterated compounds are graphically summarized in Fig. 1. With the successive introduction of a chlorine atom into the methyl group of NCA, the frequencies of the ν(C=O) and ν(C–N) bands sensitively and regularly move upwards and downwards respectively, and the frequencies of three NH_2 deformation bands (but not the $\delta(NH_2)$ band) also move downwards. These frequency changes may be explained as being due to the changes in the electronic state of the amide structure and the intermolecular hydrogen bonds.

The difference in the free ν(C=O) frequency (in nonpolar solvent) among the α-chlorinated acetamides may be due to the inductive effect of the α-substituent, which tends to raise its frequency.[14] The frequency-difference between the free ν(C=O) band and the associated ν(C=O) band (solid state) may be considered to be a qualitative measure of the strength of the hydrogen bonds. In Table 2, it can be understood that, with the α-successive introduction of a chlorine atom, the inductive effect regularly becomes larger; the more chlorine atoms are introduced to the methyl group, the larger the double bond character of the C=O bond becomes, at the expense of that of the C–N bond. Table 2 also indicates that α-chlorinated acetamides have stronger intermolecular hydrogen bonds than acetamide and that the frequency lowering of 37 cm^{-1} (1677—1640) from NCA to MCA in the solid state may be due mainly to the stronger hydrogen bonds of α-chlorinated acetamides.

The two $\pi(NH_2)$ bands seem to receive the inductive effect of chlorine atoms regularly. The behavior of the π(C=O) and δ(N–C=O) bands, on the other hand, is rather complicated.

Conformation of TCA. Contrary to our expectations for two ν(N–H) bands, four ν(N–H) bands appear definitely in TCA in the solid state. Also, two ν(C–N) bands are observed. These facts suggest that TCA has two different conformations in the solid state, just as

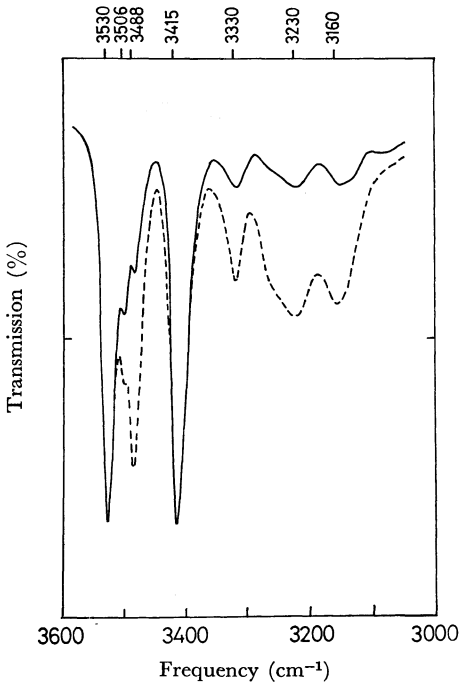


Fig. 3. The N–H stretching bands of TCA in carbon tetrachloride solution; ——: 1×10^{-3}M (10 cm cell), ------: 5×10^{-3}M (2 cm cell).

TABLE 3. THE N–H STRETCHING FREQUENCIES (cm^{-1}) OF α-CHLORINATED ACETAMIDES IN CARBON TETRACHLORIDE SOLUTION AT A CONCENTRATION OF 0.005 M

	Free $\nu as(NH_2)$	Associated ν(N–H)[a]			Free $\nu s(NH_2)$	2ν(C–O)	Typical associated ν(N–H)		
		A	B	C					
TCA	3530		3506	3488[b]	3415		3330	3230	3160
(Solid)				(3393)			(3338)	(3260)	(3196)
DCA	3528		3503	3481[b]	3413		3310	3210	3160
(Solid)							(3334)		(3161)
MCA	3529		3504	3479[b]	3413		3295	3200	3160
(Solid)				(3384)			(3295)	(3182)	
NCA	3540		3503[b]		3422	3362	3295	3228	3181
NCA[a]	3540.5	3518	3504[b]	3486	3420.5				
(Solid)							(3340)		(3170)
(Ar matrix)[c]	(3557)				(3436)				
			(3515)						(3140)
	(3554)				(3434)				

a) Bands named by Krueger and Smith in Ref. 10 and their data for NCA.
b) Concentration-dependent band.
c) The data obtained by King in Ref. 5; $\nu as(NH_2)$ and $\nu s(NH_2)$ bands alike are a doublet.

in *N*-methyl-α-monochloroacetamide.[18] This suggestion is supported by the chlorine NQR studies[19] of chlorinated acetamides from 77K to the melting point. In those studies, six lines in TCA, two lines in DCA, and one line in MCA are observed. They can be classified into two types on the basis of the different temperature coefficients of the NQR frequency (the slope); the two lines of DCA and the one line of MCA belong to the different types, while of the six lines of TCA, three lines belong to one type and remaining three lines to the other type. These NQR data indicate that TCA has two crystallographically-inequivalent CCl_3 groups.

In the infrared spectra of TCA in a dilute carbon tetrachloride solution, we observed two additional bands on the lower-frequency side of the $\nu as(NH_2)$ band at 3530 cm^{-1}, as is shown in Fig. 3. With an increase in the concentration, the intensity of the lower band at 3488 cm^{-1} increases more sensitively than the higher band at 3506 cm^{-1} and the typical associated N–H bands in the 3150—3350 cm^{-1} region. Also, the other chlorinated acetamides show similar spectral behavior, as is shown in Table 3. The lower band corresponds to the C band of three additional bands, at 3518 (named the A band), 3504 (B), and 3486 cm^{-1} (C), in the solution spectra of NCA, interpreted as being due to a cyclic dimer, a trimer, and a higher polymer of NCA with a free N–H bond and a bridged N–H bond respectively.[10]

In the solution spectra of NCA, we observed a concentration-dependent band at 3504 cm^{-1}, porbably corresponding to the B band. In the infrared spectra of NCA in the argon matrix, King[5] has observed only two bands in the 3500—3600 cm^{-1} region and assigned the lower band at 3515 cm^{-1} to the ν(N–H) mode due to a dimer species of the associated polymers. With due consideration of the frequency-differences (*ca.* 15 cm^{-1}) between the free $\nu as(NH_2)$ or $\nu s(NH_2)$ band in the matrix and in the solution, the 3515 cm^{-1} band in the matrix may be said to correspond to the B band. The lower frequency of the concentration-dependent band of chlorinated acetamides (the C band) than that of NCA (the B band) indicates that chlorinated acetamides may be in a higher polymer than in a dimer in the carbon tetrachloride solution.

With the change in state from the solution, through the liquid, to the solid state, the frequency of the corresponding C band of TCA is lowered and reaches 3393 cm^{-1} in the solid state, as is listed in Tables 1 and 3. The highest band at 3393 cm^{-1} in the solid state may be also characterized by the higher polymer of TCA with a weakly hydrogen-bonded N–H bond and a bridged N–H bond, but not by the associated polymer of dimer units, such as in benzamide. Considering the results of the previous NQR studies, two of the remaining three ν(N–H) bands of TCA in the solid state may be due to another higher polymer with two bridged N–H bonds.

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