Vibration Spectra and Rotational Isomerism of Chain Molecules. VI.[1)] 2-Chloro-, 2-Bromo-, and 2-Iodoethyl Methyl Ethers

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(Received April 13, 1977)

The Raman and infrared spectra of 2-chloro-, 2-bromo-, and 2-iodoethyl methyl ethers, $CH_3OCH_2CH_2X$ (X=Cl, Br, and I), were measured for the liquid, glassy, and crystalline states. The gaseous-state spectra of the chloride were also measured. The vibrational frequencies of these molecules were calculated by the use of the force constants transferred directly from unbranched ethers and alkyl halides. The rotational isomerism was studied and the following conclusions were obtained. (1) In the crystalline state, the molecule takes the form having the *trans* conformation about the CO–CC axis and the *gauche* conformation about the OC–CX axis. (2) In addition to this form (TG), three other forms (GG, TT, and GT) exist in the gaseous, liquid, and glassy states. (3) In the liquid state, the TG form is the most stable and the GT form is the least stable. (4) The less polar TT and GT forms are more favored and the more polar TG and GG forms are less favored in the gaseous state than in the liquid state.

In a series of previous papers, we reported the vibration spectra and rotational isomerism of chain molecules which include ethers,[1,2)] paraffins,[3)] sulfides,[1,4,5)] and alkyl halides.[6)] These studies gave us knowledge on the stable conformations of the chain molecules. For consistent elucidation of the conformational stabilities, it is important to examine rotational isomerism of molecules which contain two or more different kinds of chemical groups. Such studies are also important for confirming reliability and transferability of the force constants determined from observed vibrational frequencies.

In the present study, therefore, we deal with the rotational isomerism of 2-halogenoethyl methyl ethers, $CH_3OCH_2CH_2X$ (X=Cl, Br, and I), which contain oxygen and halogen atoms in a molecule. The study on these molecules also gives information on the effect of the two polar groups on the conformational stability. The vibrational spectra of 2-chloroethyl methyl ether have been measured by Hayashi[7)] and the rotational isomerism has been discussed.

Experimental

2-Chloroethyl methyl ether was synthesized by treating ethylene glycol monomethyl ether with thionyl chloride, and 2-bromoethyl methyl ether by treating 2-bromoethanol with dimethyl sulfoxide. 2-Iodoethyl methyl ether was prepared from 2-chloroethyl methyl ether by treating with sodium iodide in acetone. The samples were distilled prior to the measurements.

The measurements of Raman spectra were made on a JEOL JRS-400D spectrophotometer with a Coherent Radiation CR-3 argon ion laser in the region below 1600 cm^{-1}. The Raman spectra of the chloride were measured for the gaseous, liquid, glassy, and crystalline states and those of the bromide and the iodide for the liquid, glassy, and crystalline states. A multireflection accessory and a gas cell with a heater were used for the measurements of the spectra in the gaseous state. The Raman spectra of the liquid state were recorded at various temperatures to examine the temperature dependence of Raman intensities. The glassy state was obtained by putting into liquid nitrogen the sample enclosed in an ampoule and cooling it rapidly, and the crystalline state by cooling the sample slowly or annealing it repeatedly.

The measurements of infrared spectra were made on a JASCO DS-402G grating spectrometer and a Hitachi EPI-G2 grating spectrometer in the region 1600—400 cm^{-1} and a Hitachi EPI-L grating spectrometer in the region 700—200 cm^{-1}. The infrared spectra of the chloride were measured for the gaseous, liquid, glassy, and crystalline states and those of the bromide and the iodide for the liquid, glassy, and crystalline states. For the measurements in the region below 700 cm^{-1}, the spectrometer was flushed with dry air to get rid of water vapor absorptions. The glassy state was obtained by depositing the sample onto a cooled window of KBr or KRS-5, and the crystalline state by annealing it repeatedly.

Normal Coordinate Treatment

The normal coordinate treatment of 2-halogenoethyl methyl ethers was carried out with a computer program NCTB2[8)] and a HITAC 8700/8800 computing system at the Computer Center of the University of Tokyo. The force constants associated with the oxygen and halogen parts were transferred from the unbranched ethers[1,2,8)] and alkyl halides.[6,8)] The force constants for the C–C stretching and the methylene-methylene interactions were transferred from the corresponding alkyl halides. No further adjustment of the force constants was made. The transferred values were found to be accurate enough for determining the rotational isomerism of the molecules not only in the crystalline state but also in the glassy and liquid states.

Structural parameters and symmetry coordinates used in the calculation and the detailed results of the calculation are reported in a separate paper.[8)]

Results

The Raman and infrared spectra of 2-halogenoethyl methyl ethers in various states are shown in Figs. 1—10 and the vibrational assignments based on the calculated potential-energy distributions are listed in Tables 1—3. Each of the molecules has five possible rotational isomers, TT, TG, GT, GG, and GG′, as given in Table 1 of Part I of this series,[2)] where the first and second

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Table 1. Observed frequencies and vibrational assignments of 2-chloroethyl methyl ether

Observed frequency (cm^{-1})[a]								
Gas		Liquid		Glass		Crystal		Assignment[b]
R	IR	R	IR	R	IR	R	IR	
				1479 M	1479 M, sh	1486 M		(O)CH$_2$ scis, CH$_3$ ip-d-deform, CH$_3$ s-deform, CH$_3$ op-d-deform, CH$_2$(Cl) scis
	1470 M	1470 W	1474 M, sh	1472 M	1473 M		1475 M	
		1465 W, sh	1465 M, sh		1463 M, sh	1459 VW	1460 M	
1458 M		1457 W, sh	1457 M					
	1448 M, sh	1451 M		1450 M, sh	1453 M	1451 W		
		1443 M		1441 M		1443 VW	1440 M	
		1433 W	1433 M	1431 W, sh	1433 M	1437 M		
1390 VW	1390 W	1388 VW	1390 M	1388 VW	1391 M	1392 W	1395 M	(O)CH$_2$ wag
1305 VW, sh	1313 W 1303 W	1300 VW	1302 M	1299 VW	1300 M	1299 VW	1301 M	(O)CH$_2$ twist
		1270 VW, sh						CH$_2$(Cl) wag (GG)
1261 W	1260 W	1255 W	1258 W	1255 M	1256 W	1258 M	1261 M	CH$_2$(Cl) wag (TG, TT, GT)
	1230 M	1218 VW	1221 M	1219 W	1221 M	1222 W	1223 S	CH$_2$(Cl) twist
	1209 S	1207 VW, sh						CH$_3$ ip-rock (TT)
	1199 S	1197 VW, sh	1198 M		1196 VW			CH$_3$ ip-rock (GG, GT)
1176 VW, sh	1186 M, sh	1173 VW	1176 M	1174 VW	1178 M	1179 VW	1179 S	CH$_3$ ip-rock (TG)
1155 VW, sh		1154 VW	1155 W, sh	1159 VW	1159 VW	1162 W	1160 W	CH$_3$ op-rock
		1146 VW		1143 VW		1145 VW		Origin unknown
1134 W	1139 VS	1126 W	1130 VS	1124 W	1127 VS	1125 M	1130 VS	CO stretch (TG, TT)
	1115 M, sh	1104 VW	1105 S		1102 W			CO stretch (GT, GG)
1063 W	1070 W 1061 W	1058 VW	1058 M	1059 W	1060 S	1055 W	1056 S	CC stretch (TG, GG, TT)
1045 VW, sh		1043 VW						CC stretch (GT), (O)CH$_2$ rock (TT, GT)
1009 W	1011 W	1004 W	1005 M	1005 W	1006 S	1004 M	1006 S	CH$_2$(Cl) rock (TG)
970 M	967 W	963 M	964 M	963 M	962 M	964 M	962 M	(O)CH$_2$ rock (TG, GG), CO stretch (GG, TT)
935 W	941 W, sh	923 W	923 VW					CO stretch (GT)
835 VW, sh		835 VW						CH$_2$(Cl) rock (GG)
820 W	820 VW	816 S	816 M	818 M	817 M	833 VW 823 M	824 M	CO stretch (TG)
765 S	773 M 765 M	751 M	752 M	748 W	746 VW			CCl stretch (TT, GT)
684 S	691 M 680 M	666 VS	666 S	661 VS	660 S	665 S 658 VS	663 S, sh 658 S	CCl stretch (TG, GG)
508 VW		507 W	506 W	510 W	510 W	515 W 505 W	512 W 505 W	OCC deform (TG)
			493 VW, sh					OCC deform (GG)
			463 VW					COC bend (GT)
439 W		438 VW	438 VW					COC bend (TT)
412 VW		421 VW, sh	418 VW, sh					COC bend (GG)
349 S		348 M	345 VW	346 VW, sh				OCC deform (TT, GT)
328 W		329 W	330 VW	327 W	327 W	338 M	332 VW	COC bend (TG)
		282 W, sh						CCCl deform (GT)
		273 W, sh	272 W	285 W	279 W	295 W	293 W	CCCl deform (TG)
252 W		261 W	257 W	264 VW	266 VW, sh			CCCl deform (GG)
				229 VW		228 W	230 W	CH$_3$ torsion
162 W		≈180 VW, sh						CCCl deform (TT)

TABLE 1. (Continued)

Observed frequency (cm^{-1})[a]								Assignment[b]
Gas		Liquid		Glass		Crystal		
R	IR	R	IR	R	IR	R	IR	
						150 W		Torsions and lattice vibrations
				130 W, b		140 M		
						113 VW		
						89 M		
						76 S		
						66 S		
						55 W		

a) VS: very strong, S: strong, M: medium, W: weak, VW: very weak, b: broad, sh: shoulder. The broadness of the band shapes in the gaseous state does not always allow us to correlate the individual bands in the liquid state to those in the gaseous state. Only approximate correlations are made in such cases and in other cases of similar situations. b) For the notation and definition of the local symmetry coordinates, see Ref. 16.

conformation symbols in each isomer designation are those for the CO–CC and OC–CX axes, respectively.

The following spectral features are observed for the three halogenoethers studied in this work. (1) The spectra have combined features of ethers and alkyl halides. (2) The number of the bands observed in the crystalline state is the smallest among the various states and corresponds to what is expected for one molecular form. (3) In the glassy and liquid states, additional bands appear in the spectra. The relative band intensities in the two states are considerably different. (4) Systematic variations of frequencies and intensities are observed with the change of the halogen atom.

In the following subsections, the rotational isomerism of the individual molecules is described. The results are summarized in Table 4.

2-Chloroethyl Methyl Ether. The Raman and infrared spectra are shown in Figs. 1 and 2 and the com-

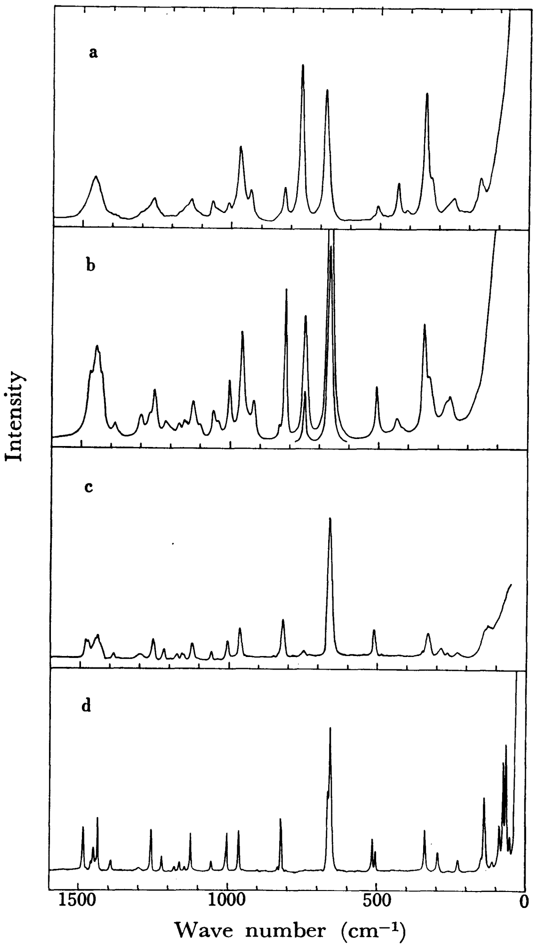

Fig. 1. Raman spectra of 2-chloroethyl methyl ether. a: Gas, b: liquid, c: glass, d: crystal.

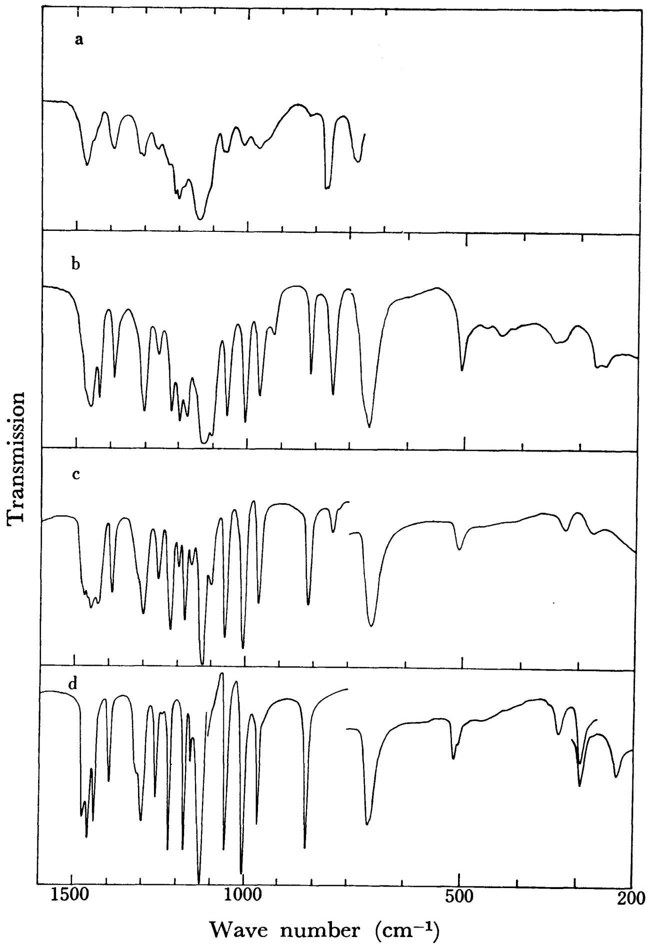

Fig. 2. Infrared spectra of 2-chloroethyl methyl ether. a: Gas, b: liquid, c: glass, d: crystal.

TABLE 2. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF 2-BROMOETHYL METHYL ETHER

Observed frequency (cm^{-1})[a]						Assignment[b]
Liquid		Glass		Crystal		
R	IR	R	IR	R	IR	
				1479 M	1480 M	(O)CH$_2$ scis, CH$_3$ ip-d-deform, CH$_3$ s-deform, CH$_3$ op-d-deform, CH$_2$(Br) scis
		1471 M	1472 M	1477 M		
1467 W	1468 M, sh		1464 M	1464 VW	1468 W	
1457 W, sh	1458 M		1456 M		1456 M	
1449 M	1450 M, sh		1447 M	1448 W	1451 M	
1442 M	1442 M, sh	1439 M	1435 W	1438 W		
			1428 M	1431 M		
1424 W	1423 M	1424 W	1423 M	1427 M	1428 M	
1382 VW	1385 M	1382 W	1386 M	1387 W	1389 M	(O)CH$_2$ wag (TG, GG)
1372 VW, sh						(O)CH$_2$ wag (TT, GT)
			1348 VW			Impurity
1298 VW	1299 M	1301 VW	1301 VW			(O)CH$_2$ twist (GG, GT)
1276 W	1279 S	1276 M	1279 S	1276 M	1278 S	(O)CH$_2$ twist (TG, TT)
1235 W	1236 M	1236 W	1237 W	1240 M	1243 M	CH$_2$(Br) wag (TG, GG)
1224 W						CH$_2$(Br) wag (TT, GT), CH$_2$(Br) twist (GT)
1218 W, sh						CH$_2$(Br) twist (GG)
1212 VW, sh	1212 M	1211 W	1212 M	1214 VW 1208 VW	1214 M	CH$_3$ ip-rock (TG), CH$_2$(Br) twist (TT)
1189 VW	1190 S		1189 W			CH$_3$ ip-rock (TT, GT)
	1174 M					CH$_3$ ip-rock (GG)
1163 VW	1164 M	1165 VW	1166 M	1166 VW	1169 M	CH$_2$(Br) twist (TG), CH$_3$ op-rock (GG, GT)
1154 VW	1154 W	1153 VW	1154 W	1153 VW 1150 VW	1154 W	CH$_3$ op-rock (TG, TT)
1127 VW	1128 VS	1121 W	1124 VS	1117 W	1122 VS	CO stretch (TG)
1095 VW	1096 S	1092 VW	1095 W			CO stretch (TT)
1056 VW	1056 W	1059 VW				CO stretch (GG, GT)
1045 VW, sh	1044 S	1044 W	1046 S	1045 W	1046 S	CC stretch (TG, GG, TT)
1037 VW	1036 W, sh					CC stretch (GT)
1002 VW	1003 VW	1015 VW			1004 VW	Overtone of OCC deform (TG)
987 W	988 S	988 M	990 S	983 M	987 S	(O)CH$_2$ rock (TG, TT, GT)
952 M	951 M	948 M	948 M	948 M 942 M	949 M 945 M	CO stretch (TG, GG, TT), (O)CH$_2$ rock (GG)
918 W	917 W	914 VW	915 VW			CO stretch (GT)
					905 VW	Impurity
	889 VW		889 VW			Impurity
	875 VW		873 VW		870 VW	Impurity
836 VW		833 VW				Origin unknown
802 M	801 W	803 M	803 W	803 M	806 M, sh 802 M	CH$_2$(Br) rock (TG, GG)
	778 VW					CH$_2$(Br) rock (TT, GT)
668 S	668 M	669 W				CBr stretch (GT)
		658 W	661 W			CBr stretch (TT)
			608 VW			Impurity
571 VS	570 M	566 VS	565 M	567 VS	565 M	CBr stretch (TG, GG)
500 W	499 W	500 M	499 W	500 M	499 W	OCC deform (TG)
482 VW, sh	483 VW, sh	482 VW, sh				OCC deform (GG)
	445 VW					COC bend (GT)
433 VW	434 VW	427 VW	423 VW			COC bend (TT)
315 W, sh	316 VW					OCC deform (GT)
307 W, sh	307 VW, sh	310 M	308 W	306 M	305 W	COC bend (TG)
295 M		292 W				OCC deform (TT)
262 W	260 VW	275 M	271 W	287 M	284 W	CCBr deform (TG)

Table 2. (Continued)

Observed frequency (cm^{-1})$^{a)}$						Assignment$^{b)}$
Liquid		Glass		Crystal		
R	IR	R	IR	R	IR	
223 W	218 VW	226 W		220 VW		CCBr deform (GG), CH_3 torsion
189 VW		189 VW				CH_3 torsion
≈160 VW, sh						CCBr deform (TT)
				135 S		Torsions and lattice vibrations
		112 M		104 M		
				82 W		
				72 M		
				62 M		
				45 M		
				34 W		

a), b) See a) and b), respectively, of Table 1.

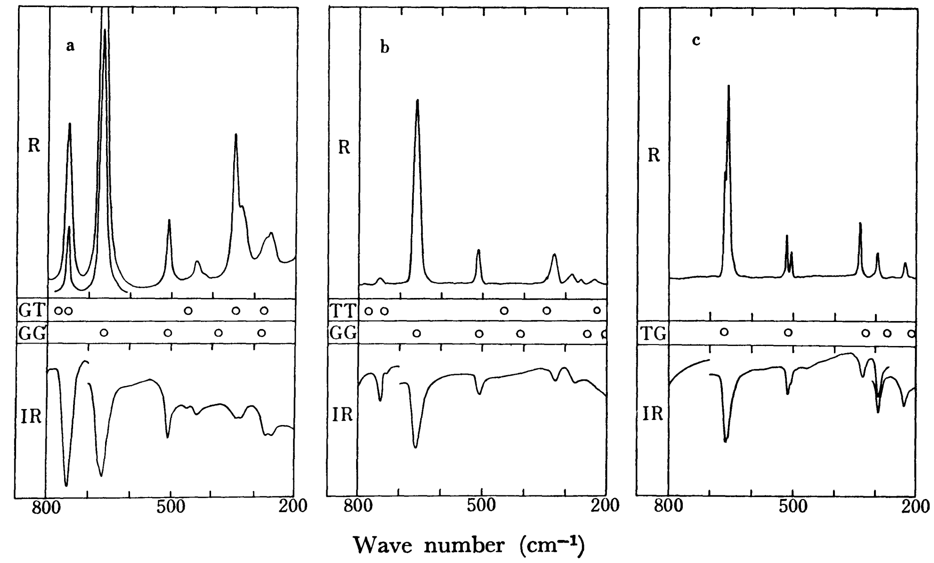

Fig. 3. Comparison of the observed and calculated frequencies of 2-chloroethyl methyl ether. a: Liquid, b: glass, c: crystal.

parison of the observed and calculated frequencies are shown in Fig. 3.

In the crystalline state, the bands due to the CCl stretching vibration are observed at 658 and 665 cm^{-1} in the Raman spectrum and at 658 and 663 cm^{-1} in the infrared spectrum, the doublet being ascribed to the crystal field splitting. These frequencies indicate clearly that the OC–CCl axis is in the *gauche* conformation.[9] Figure 3 shows that the observed frequencies in the skeletal deformation region are explained only by the TG form. This conclusion agrees with the result of the previous study by Hayashi.[7]

In the glassy state, the bands due to the CCl stretching vibration of the *trans* OC–CCl axis appear at 748 cm^{-1} in the Raman spectrum and at 746 cm^{-1} in the infrared spectrum. The Raman band observed as a shoulder at 346 cm^{-1} is assigned to either one or both of the TT and GT forms. However, the bands assignable only to the TT or GT form are not observed definitely in the spectra. The Raman band at 264 cm^{-1} and the infrared band at 266 cm^{-1} are assigned only to the GG form. Thus, in the glassy state, the TG and GG forms and either one or both of the TT and GT forms exist. The TG form is dominant as seen from the relative band intensities.

The liquid-state spectra exhibit more bands than the glassy-state spectra. In the region below 550 cm^{-1}, the skeletal deformation bands of the individual rotational isomers are clearly observed; the bands at 507, 329, and 273 cm^{-1} are assigned to the TG form,** those at 493, 421, and 261 cm^{-1} to the GG form, those at 463, 348, and 282 cm^{-1} to the GT form, and those at 438 and 348 cm^{-1} to the TT form.

** The band at 273 cm^{-1} shifts to 285 cm^{-1} in the glassy state and to 295 cm^{-1} in the crystalline state. The result of the normal coordinate treatment indicates that the CH_2–CH_2 torsion contributes to this vibration to some extent, making the frequency shift upward on solidification. Similar frequency shifts are observed for the bromide (262 cm^{-1} in the liquid state and 287 cm^{-1} in the crystalline state) and the iodide (248 cm^{-1} in the liquid state and 276 cm^{-1} in the crystalline state).

TABLE 3. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF 2-IODOETHYL METHYL ETHER

Observed frequency (cm^{-1})[a]						Assignment[b]
Liquid		Glass		Crystal		
R	IR	R	IR	R	IR	
				1482 W		(O)CH$_2$ scis, CH$_3$ ip-d-deform, CH$_3$ s-deform, CH$_3$ op-d-deform, CH$_2$(I) scis
1468 W	1468 M	1472 W	1471 M	1476 M	1477 M	
1457 W	1458 M		1464 M		1463 M	
1450 W	1450 M	1455 VW	1455 M	1447 VW, sh	1455 M	
1441 W	1432 W	1440 W	1446 M	1437 VW	1444 M	
		1422 VW	1423 M, sh	1425 W		
1415 W	1416 M	1414 VW	1415 M		1417 M	
1377 VW	1381 M	1378 W	1381 M	1382 VW	1384 M	(O)CH$_2$ wag (TG, GG)
1365 VW	1365 W, sh					(O)CH$_2$ wag (TT, GT)
1291 VW	1293 W		1293 W			(O)CH$_2$ twist (GG, GT)
1263 W	1265 M	1262 W	1263 S	1263 M	1264 S	(O)CH$_2$ twist (TG, TT)
					1239 VW	Impurity
1216 W	1220 M	1219 W	1220 S	1221 W	1222 W	CH$_3$ ip-rock (TG), CH$_2$(I) wag (GG)
1200 W, sh		1202 VW, sh				CH$_3$ ip-rock (GG, TT, GT)
1189 M	1188 M	1191 M	1189 M	1192 M	1194 M	CH$_2$(I) wag (TG, TT, GT)
1162 M	1161 M	1162 W	1159 M	1160 VW	1159 M	CH$_3$ op-rock (TG, GG, GT), CH$_2$(I) twist (TT, GT)
	1148 M, sh	1150 VW	1148 M	1146 VW	1148 W	CH$_2$(I) twist (GG), CH$_3$ op-rock (TT), origin unknown (crystal)
1123 VW	1124 S	1120 W	1119 VS	1113 W	1115 S	CO stretch (TG), CH$_2$(I) twist (TG)
1112 VW	1108 S	1105 VW	1107 S			CO stretch (TT)
1089 VW	1088 S		1083 M			CO stretch (GT)
1052 VW		1057 VW	1056 VW			CC stretch (GG)
1038 VW, sh	1037 M	1040 W	1039 S	1042 VW	1040 M	CC stretch (TG)
1030 VW	1030 M, sh	1030 VW, sh	1030 W, sh	1029 VW	1027 W	CO stretch (GG), CC stretch (TT), overtone of CI stretch (TG)
1017 VW	1019 W, sh					CC stretch (GT)
			1005 VW		1003 VW	Combination tone of CI stretch and COC bend (TG)
966 W	967 M	968 M	968 S	966 M	966 S	(O)CH$_2$ rock (TG, TT, GT)
949 M	950 M	950 W	949 W			CO stretch (TT)
933 W	933 M	933 M	932 M	935 M 932 M	932 M	CO stretch (TG, GG), (O)CH$_2$ rock (GG)
909 W	909 M	907 VW	906 VW			CO stretch (GT)
		896 VW	895 VW			Impurity
			871 VW			Impurity
			815 VW			Impurity
775 W	777 VW	777 W	777 W	779 W	778 M	CH$_2$(I) rock (TG, GG)
753 VW	752 VW		757 VW			CH$_2$(I) rock (TT, GT)
	723 VW		712 VW		714 VW	Impurity
619 S	615 S	620 M	618 W			CI stretch (TT, GT)
516 VS	514 W	517 VS	515 M	518 VS 506 VW	518 W	CI stretch (TG, GG)
489 M	486 W	488 S	487 M	490 S	489 W	COC bend (TG)
468 M	463 VW	469 W	468 VW			OCC deform (GG)
	440 VW		441 VW			COC bend (GT)
427 W	425 VW	420 VW	420 VW			COC bend (TT)
≈390 VW, sh	393 VW		397 VW			COC bend (GG)
304 M	304 W	304 M	303 M	302 M	301 W	OCC deform (TG, GT)
266 M	260 VW					OCC deform (TT)
248 W, sh	250 VW	266 M	264 W	276 S	273 W	CCI deform (TG)
		223 VW	223 W			CCI deform (GT)
200 M		212 VW	210 W	200 W		CCI deform (GG), CH$_3$ torsion
≈140 W, sh						CCI deform (TT)
				123 M		Torsions and lattice vibrations
				114 M		
				95 M		
				72 M		
				60 M		
				46 S		

a), b) See a) and b), respectively, of Table 1.

Table 4. Rotational isomers of 2-halogenoethyl methyl ethers

	$CH_3OCH_2CH_2Cl$	$CH_3OCH_2CH_2Br$	$CH_3OCH_2CH_2I$
Gas	TG GG TT GT	—	—
Liquid	TG GG TT GT	TG GG TT GT	TG GG TT GT
Glass	TG GG TT[a)] GT[a)]	TG GG TT GT	TG GG TT GT
Crystal	TG	TG	TG

a) Either one or both of the TT and GT forms exist.

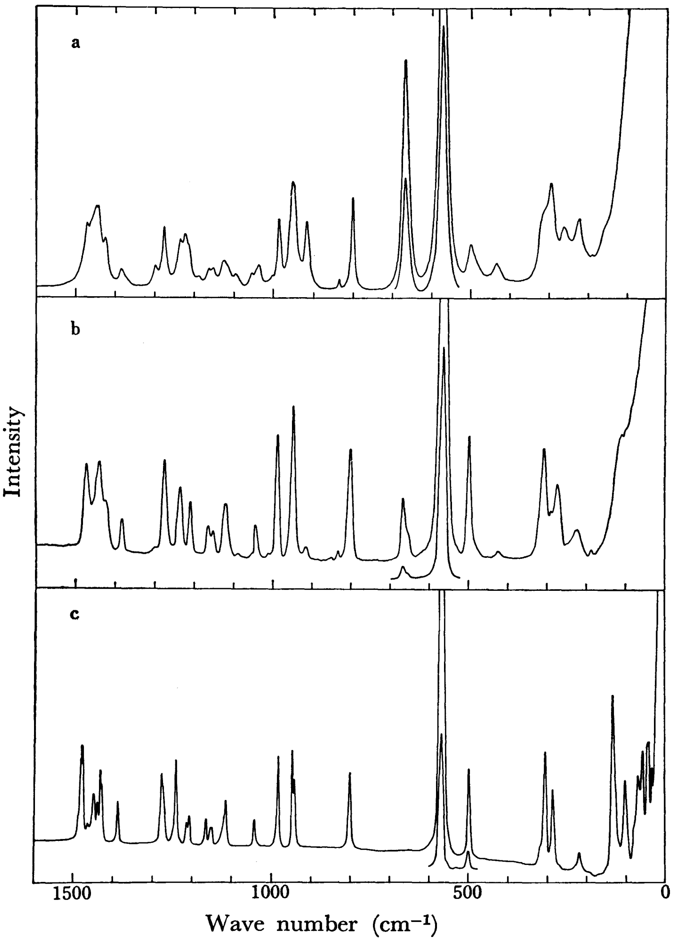

Fig. 4. Raman spectra of 2-bromoethyl methyl ether. a: Liquid, b: glass, c: crystal.

In the gaseous state, the number of the observed bands is essentially the same as that in the liquid state, indicating the coexistence of the four forms of TG, GG, TT, and GT. However, the relative intensities of several bands are remarkably different between the two states. It is evident from Figs. 1 and 2 that the bands of the TT and GT forms become relatively stronger than those of the TG and GG forms in going from the liquid to the gas. This intensity alteration will be discussed later.

The existence of the GG′ form is unlikely. The result of the normal coordinate treatment for the GG′ form shows that a band due to the vibration of 385 cm^{-1} would be detectable in the Raman spectrum, if this form existed, since the mode of this vibration is a quasi-totally symmetrical deformation of the molecular skeleton. However, no Raman band is actually observed in the region 360—400 cm^{-1} in the liquid or gaseous state.

2-Bromoethyl Methyl Ether. The Raman and infrared spectra are shown in Figs. 4—6. A comparison of the observed and calculated frequencies shows that the spectra in the crystalline state can be explained only by the TG form. In the glassy-state spectra, there appear the bands which are assigned only to the GT form (914 and 669 cm^{-1}), TT form (658, 427, and 292 cm^{-1}), and GG form (482 cm^{-1}). The liquid-state spectra exhibit a similar spectral pattern but considerably different relative intensities. Thus, the four forms of TG, GG, TT, and GT are found to coexist in the glassy and liquid states.

2-Iodoethyl Methyl Ether. The Raman and infrared spectra are shown in Figs. 7—9. A comparison of the observed and calculated frequencies shows that the spectra in the crystalline state are explained only by the TG form, similarly to the cases of the chloride and the bromide. In the glassy- and liquid-state spectra, additional bands appear which are assigned only to the GT form (907 and 441 cm^{-1}), TT form (420 cm^{-1}) and GG form (469 and 397 cm^{-1}). Accordingly, the four forms of TG, GG, TT, and GT are found to coexist in the glassy and liquid states.

Temperature Dependence of the Raman Spectra in the Liquid State. The liquid-state Raman spectra measured at high and low temperatures are shown in Fig. 10. For the chloride, the relative intensities of the bands at 507, 329, and 273 cm^{-1} which are assigned to the TG form are strikingly stronger at the lower temperature. On the other hand, the band at 923 cm^{-1} assigned to the GT form loses its intensity as temperature is lowered. Similar spectral changes are observed for the bromide and the iodide; the bands assigned to the TG form of the bromide at 500, 307, and 262 cm^{-1} and that of the iodide at 489 cm^{-1} become stronger and the band assigned to the GT form of the bromide at 918 cm^{-1} and that of the iodide at 909 cm^{-1} become weaker as temperature is lowered. These spectral observations indicate that for the three molecules in common the TG form is the most stable and the GT form is the least stable in the liquid state.

In the glassy state, the bands of the TG form is dominant and those of the GT form are further weaker than in the cooled-liquid state. This spectral feature is consistent with the conformational stability obtained for the liquid state.

Discussion

The following results were obtained for the three halogenoethers studied in this work. (1) Only the TG form exists in the crystalline state. (2) In the glassy

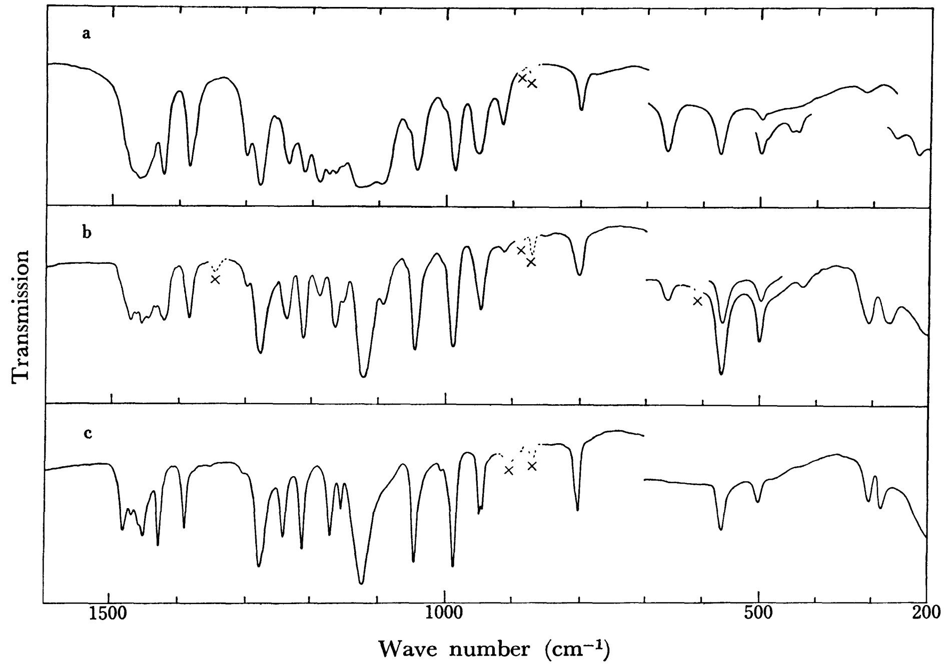

Fig. 5. Infrared spectra of 2-bromoethyl methyl ether.
a: Liquid, b: glass, c: crystal. ×: Bands due to impurities.

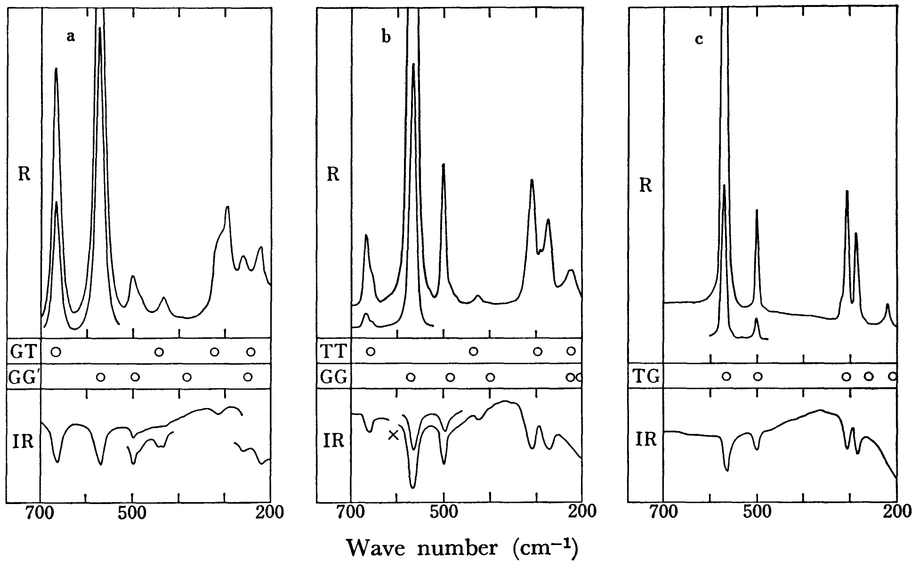

Fig. 6. Comparison of the observed and calculated frequencies of 2-bromoethyl methyl ether.
a: Liquid, b: glass, c: crystal. ×: Band due to impurity.

and liquid states, the GG, TT, and GT forms coexist in addition to the TG form. (3) The TG form is the most stable and the GT form is the least stable in the liquid state.

The stability of the *trans* conformation about the CO–CC axis over the *gauche* conformation is consistent with the results obtained for ethyl methyl ether,[10—12] diethyl ether,[13,14] and longer ethers.[1,2] The enthalpy difference between the *trans* and *gauche* conformations has been obtained as 1.1—1.5 kcal/mol for the former two ethers.

The OC–CX axis was found to be in the *gauche* conformation in the most stable isomer in the liquid state. This result may be compared with the previous findings that the *gauche* conformation about the CC–CX axis in butyl halides is more stable than the *trans* conformation in the liquid state[6] and that the *gauche* conformation about the OC–CC axis in longer chain ethers is as stable as the *trans* conformation in the liquid state.[2]

A comparison of the liquid-state Raman spectra of the three halogenoethers (Figs. 1, 4, and 7) indicates the systematic variation of the intensity ratio of the CX stretching band assigned to the *trans* OC–CX conformation to that assigned to the *gauche* OC–CX conformation. Namely, the intensity ratio, *I(trans)/I(gauche)*, is the smallest for the chloride and is the largest for the iodide. This observation suggests that the stability of the *trans* OC–CX conformation relative to that of the

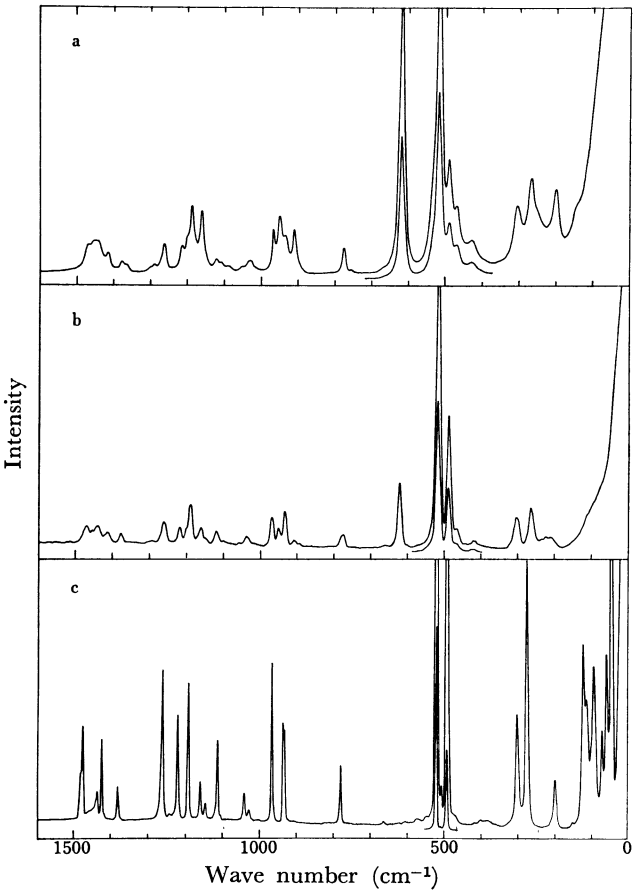

Fig. 7. Raman spectra of 2-iodoethyl methyl ether.
a: Liquid, b: glass, c: crystal.

gauche OC–CX conformation is larger in a molecule with a heavier halogen atom. The steric hindrance between the methylene group and the halogen atom accounts, at least in part, for the difference in conformational stability.

Each of the three halogenoethers contains two polar groups, the oxygen and halogen atoms, in a molecule. The five possible molecular forms are classified into two types on the basis of the polarity of the molecule. By assuming a simple vector summation, the dipole moment μ of the molecule is given by

$$\mu^2 = \mu_{\mathrm{CX}}^2 + \mu_{\mathrm{COC}}^2 - (2/\sqrt{3})\mu_{\mathrm{CX}}\mu_{\mathrm{COC}}$$

for the TT, GT, and GG′ forms and

$$\mu^2 = \mu_{\mathrm{CX}}^2 + \mu_{\mathrm{COC}}^2 + (2/\sqrt{3})\mu_{\mathrm{CX}}\mu_{\mathrm{COC}}$$

for the TG and GG forms, where μ_{CX} and μ_{COC} are the dipole moments of the CX and COC groups, respectively, and the all bond angles are assumed to be tetrahedral. Accordingly, the TT, GT, and GG′ forms are less polar and the TG and GG forms are more polar. For the chloride, as seen from Figs. 1 and 2, the bands assigned to the TT and GT forms (less polar) become relatively stronger than those of the TG and GG forms (more polar) in going from the liquid to the gas. The intensity ratio of the 751 cm^{-1} band to the 666 cm^{-1} band is reversed between the two states. These observations are consistent with the theoretical expectation that less polar conformations are better stabilized in less polar solvents or gas and that more polar conformations are better stabilized in more polar media.[15] It is thus clear that the *trans* OC–CX conformation of the halogenoethers is more favored in the gaseous state than in the liquid state. Similar intensity variations are observed in the spectra of the cyclohexane solution and the acetone solution.

In conclusion, the rotational isomerism of 2-halogenoethyl methyl ethers was determined from the vibrational spectra. The satisfactory transferability of the force

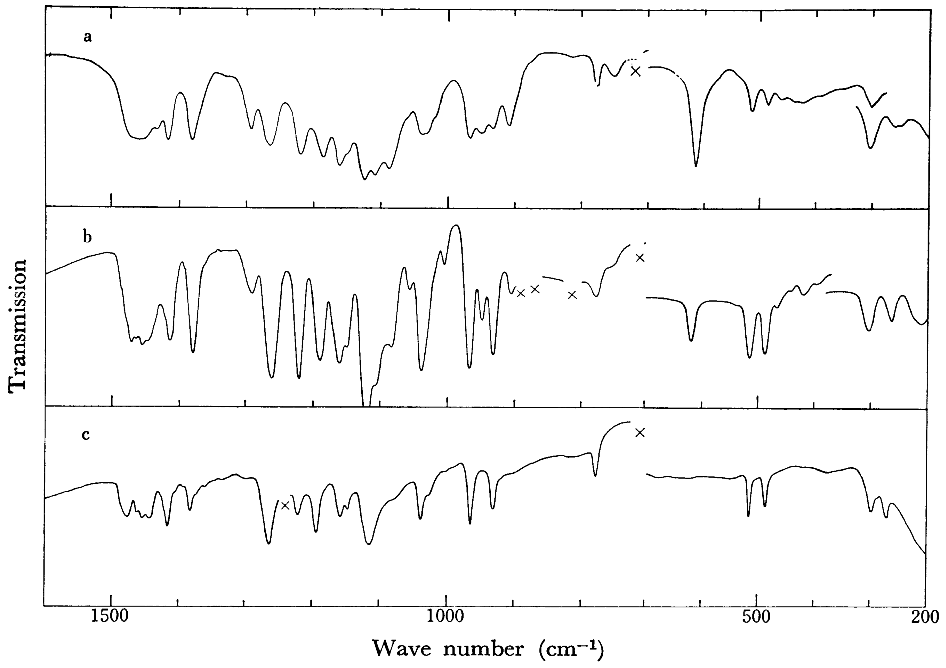

Fig. 8. Infrared spectra of 2-iodoethyl methyl ether.
a: Liquid, b: glass, c: crystal. ×: Bands due to impurities.

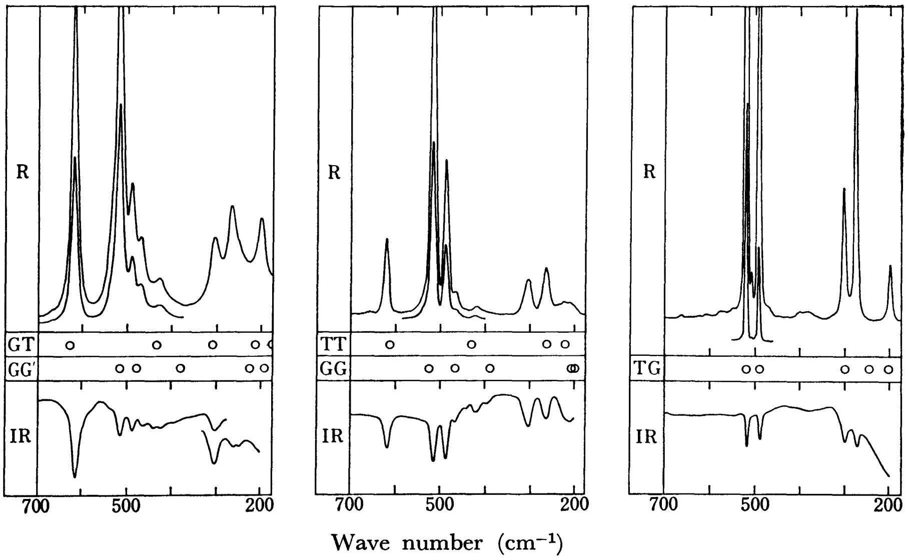

Fig. 9. Comparison of the observed and calculated frequencies of 2-iodoethyl methyl ether.
a: Liquid, b: glass, c: crystal.

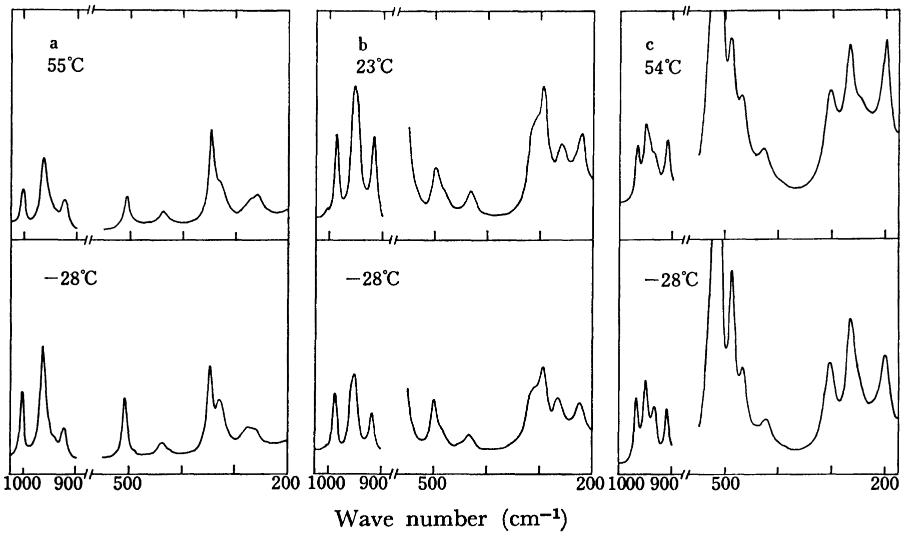

Fig. 10. Raman spectra in the liquid state at high and low temperatures.
a: 2-Chloroethyl methyl ether, b: 2-bromoethyl methyl ether, c: 2-iodoethyl methyl ether.

constants from the ethers and the alkyl halides to the halogenoethers was also shown. These conclusions confirm that the combination of the systematic measurements of vibrational spectra and the systematic calculations of normal vibrations is a reliable method for studying the rotational isomerism of chain molecules. Theoretical studies on the stabilities of rotational isomers should be made on the basis of accumulated experimental data, by taking account of intramolecular and intermolecular interactions.

Erratum

Erratum in Table 2 of Part V.[1] For 764 M,sh listed in the column of R of Crystal read 764 M.

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