Infrared and Raman Spectra of Dialkoxymethanes in Various Phases and the Assignment of Spectra of Methoxyethoxymethane

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The study of internal rotation around the C–C bond has been carried out in great detail by several authors[1], but detailed discussion of that arround the C–O bond has not been carried out so far.

In this paper, the rotational isomerism of compounds containing two C–O bonds such as dialkoxymethanes ($R_1OCH_2OR_2$) is discussed from the spectroscopical point of view. Infrared spectra of vapor, liquid and solid phases and Raman spectra of liquid phase were obtained, and the possible interpretation of these results was given by referring to other available data such as dipole moment.

With the conclusion thus obtained, the assignments of vibrational frequencies of dimethoxymethane and diethoxymethane are reported in the other papers[2,3], and that of methoxyethoxymethane is presented in this paper.

Experimental

The samples used were dimethoxymethane (DMM, $CH_3OCH_2OCH_3$), methoxyethoxymethane

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[1] S. Mizushima, "Structure of Molecules and Internal Rotation", Academic Press, New York (1954).

[2] K. Nukada, *Spectrochim. Acta*, to be published.

[3] K. Nukada, This Bulletin, to be published.

(MEM, $CH_3OCH_2OC_2H_5$), diethoxymethane (DEM, $C_2H_5OCH_2OC_2H_5$) and diisopropoxymethane (DPM, $(CH_3)_2CHOCH_2OCH(CH_3)_2$). All the compounds were synthesized in our laboratory and their purity was checked by gas chromatography[4,5].

Infrared spectra of vapor and liquid phases were obtained by means of Perkin Elmer 21 spectrophotometer and those of solid phase were obtained by means of Perkin Elmer 12C spectrophotometer, both equipped with a sodium chloride prism. Infrared spectra at an elevated temperature were obtained with a gas celll designed and constructed by Mr. H. Tomita of our laboratory[6]. Because dialkoxymethanes are rapidly decomposed at high temperature by oxygen in air, care should be taken to remove oxygen as completely as possible from a gas cell in a high temperature experiment. Solid infrared spectra were obtained with a low temperature cell designed by us[7].

Raman spectra were taken by means of Cary 81 spectrophotometer. The degree of depolarization was measured by wrapping two types of polaroids around a Raman tube.

Results and Discussion

Infrared Spectra of Dimethoxymethane in Various Phases. — The spectra of vapor and liquid phases are shown in Fig. 1a.

The intensity of vapor bands at 1235 and 1110 cm^{-1} shows an appreciable decrease as compared with that of liquid bands. Of these, the liquid band at 1110 cm^{-1} is known as a branch of "methylal's doublet", and it is a remarkable fact that in vapor phase a branch of the doublet turns to be a shoulder. As will be described in the following section and in the other paper[8], in other dialkoxymethanes and in ethylidene dialkyl ethers ($R_1OCH(CH_3)OR$) the smae behavior of spectra were also observed.

The low temperature infrared spectra are shown in Fig. 1b. It was found that two types of spectra are obtained at low temperature below melting point. It is dependent upon

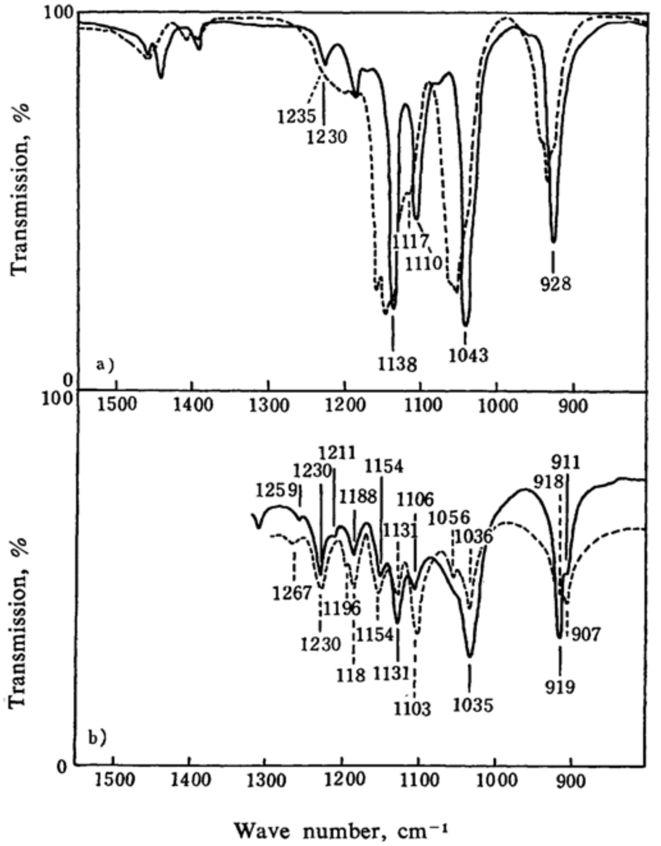

Fig. 1. Infrared spectra of dimethoxymethane ($CH_3OCH_2OCH_3$).

a) Solid line, CCl_4 solution, cell thickness: 0.15 mm., 1.5%. Dashed line, vapor
b) Solid line, Type A spectrum of solid phase. Dashed line, Type B spectrum of solid phase

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[4] K. Nukada, *Reports Govn. Chem. Ind. Research Inst. Tokyo*, **55**, 92 (1960).

[5] K. Nukada, ibid., to be published.

[6] H. Tomita, unpublished.

[7] K. Nukada, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 218 (1959).

[8] K. Nukada, This Bulletin, to be published.

the critical condition of freezing the material. An example of freezing procedure is as follows: After cooling gradually, spectrum A (solid line in Fig. 1b) was obtained at −150°C, then after once melting and cooling again, spectrum B (dashed line in Fig. 1b) was obtained at −134°C. The last procedure was repeated and spectrum B was obtained again. After once melting and cooling again, spectrum A was obtained at −135°C. Lastly, on raising the temperature, spectrum B was obtained at −110°C. It is not clear at present that the difference of these spectra is due either to the difference of crystallized states between two types of solid phase, or is due to the fact that one of them is in a super-cooled state. Spectrum A is more similar to that of the solution except for the band at 1230 cm^{-1}, the relative intensity of which is greater than that of liquid phase spectrum, and for new bands at 1259, 1211, 1051 and 911 cm^{-1}, appearing as shoulders. Spectrum B is, on the other hand, quite different from that of the solution, that is, the intensity ratio of the band at 1131 cm^{-1} to one at 1103 cm^{-1} changes appreciably.

From these results the following assumption seems to be possible. In DMM, two rotational isomers exist, namely α and β forms. The bands at 1138, 1043 and 928 cm^{-1} are due to vibrations belonging to the α form, and the bands at 1230 and 1110 cm^{-1} are due to vibrations belonging to the β form. If this assumption is true, both forms are mixed moderately in liquid phase and the α form exists predominatingly in vapor phase. In solid phase, both forms are still mixed but the abundance ratio of the two forms changes as compared with that in the case of the liquid phase, that is, the β form is more predominant. The possible forms may be gauche-gauche form (or less polar form), two methyl groups of which rotate about 120° from the central OCO plane in an anticlockwise sence, and trans-trans form (or more polar form), the COCOC skeleton of which is planar.

If this assumption is ture,

1) The dipole moment of vapor and liquid phase should be considerably different at room temperature,

2) Some solvent effect is expected since the dipole moments of two isomers are considerably different, and

3) The appearance of the vapor spectrum should change to some extent with increasing temperature.

In the following description, the above-mentioned assumption is examined by checking these three items in detail.

1) In his prewar paper, Kubo illustrated the diagram showing the correlation between dipole moment and azimuthal angles of rotation of methyl groups in DMM[9]. From this diagram together with the observed value of dipole moment, Kubo has concluded that in the vapor phase DMM has one stable configuration, in which two methyl groups rotate to the opposite sides of central OCO plane (gauche-gauche form). Recently, Uchida et al. measured the dipole moment of DMM in liquid phase at 25°C (0.67D) and found that it is in good agreement with the value of vapor extrapolated to 25°C (0.69D)[10]. Uchida et al. has concluded that DMM is a mixture of rotational isomers, most of which is helical or almost helical in structure (gauche-gauche form). These results lead to a definite conclusion that at least at room temperature, the abundance ratio of isomers are, if they exist, almost equal in vapor and liquid phases.

Therefore, the cause of appreciable change between infrared spectra of vapor and condensed phases is not due to the change of abundance ratio of isomers between two phases, but due to some other kind of effect such as the change of intermolecular interaction between two phases.

2) In Fig. 2, the infrared spectrum of acetonitrile solution of DMM is shown. As acetonitrile is a very polar solvent (dielectric constant of which is 38), there must be some systematic change of spectra between acetonitrile solution and non-polar solvent solution, if the rotational isomerism actually exists in solution. From Fig. 2, the ratio of absorbance of the band at 1140 cm^{-1} to that of the band at 1111 cm^{-1} (K_{1140}/K_{1111}) is calculated to be 0.374.

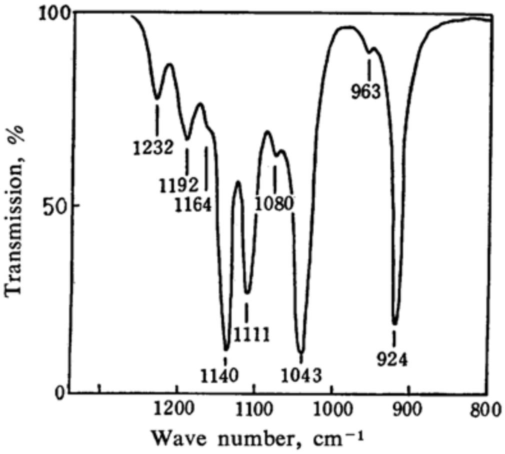

Fig. 2. Infrared spectrum of dimethoxymethane ($CH_3OCH_2OCH_3$). Acetonitrile solution, cell thickness: 0.015 mm., 20%.

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[9] M. Kubo, *Sci. Papers Inst. Phys. Chem. Research*, **29**, 179 (1936).

[10] J. Uchida, Y. Kurita and M. Kubo, *J. Polymer Sci.*, **19**, 365 (1956).

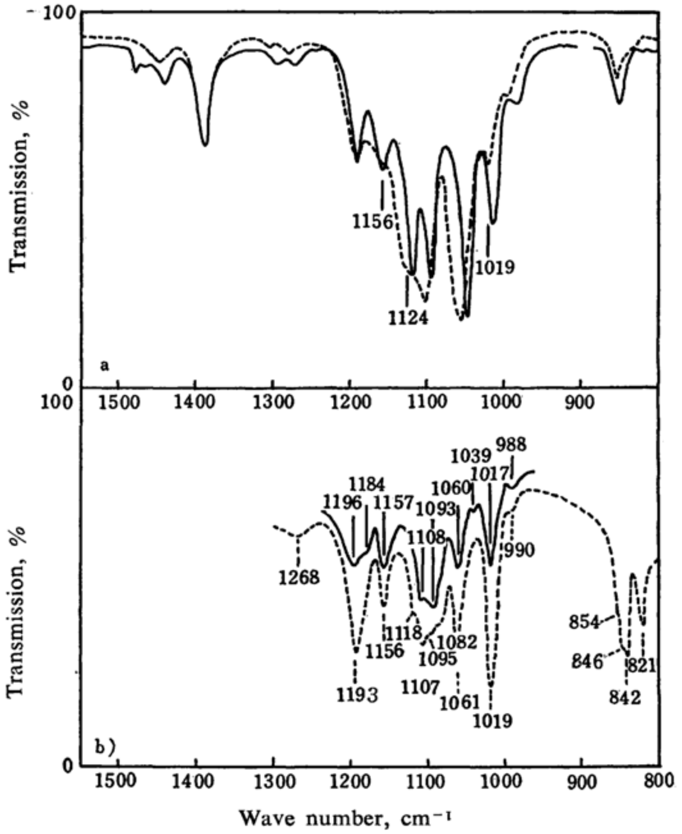

Fig. 3. Infrared spectra of diethoxymethane ($C_2H_5OCH_2OC_2H_5$).

a) Solid line, CCl_4 and CS_2 solutions, cell thickness: 0.15 mm., 2%. Dashed line, vapor.

b) Solid phase spectra, solid line, cell thickness: 0.015 mm. Dashed line, cell thickness: 0.05 mm.

The ratio is also calculated to be 0.331 in the case of carbon tetrachloride solution. Though it is impossible to obtain such a ratio in the case of vapor (Fig. 1a), it is clear that is has a very high value. Hence if these two bands belong to another type of rotational isomers, a more polar form must be predominant in the vapor phase, but this is inconsistent with the measurement of dipole moment[9]. From these considerations, it is reasonable to assume that these two bands belong to the same type of isomers.

3) Vapor spectra of DMM were taken at the temperature range between 24 and 100°C. No change in the appearance of the spectra was observed. The dipole moment of the vapor varies with the temperature as mentioned by Uchida et al., and they have explained this as the change of abundance ratio between isomers with temperature variation[10]. The present observation seems to be inconsistent with the conclusion of them. The most reasonable interpretation to make a compromise between the results of infrared spectra and those of dipole moment is as follows. This molecule has one form (gauche-gauche form) below 100°C, both in the vapor and liquid phases. The variation of dipole moment with temperature is due to the increase of amplitude of torsional oscillation, while the change of appearance of spectra among three phases is due to the change of intermolecular interaction.

As will be described in detail in the other papers[2,3], the change of band intensity among different phases is sometimes a useful measure in assigning spectra. One example is as follows. If an infrared band is strong in the liquid phase but weak in the vapor phase and the corresponding Raman band is strong and polarized, this band is safely assigned to a totally symmetrical vibration. The change of band intensity between vapor and liquid phases is also observed in the case of DMM-d_2 ($CH_3 \cdot OCD_2OCH_3$), DMM-d_6 ($CD_3OCH_2OCD_3$), DMM-d_8 ($CD_3OCD_2OCD_3$), DEM and DEM-d_2 ($C_2H_5OCD_2OC_2H_5$). The author has found that in all cases the above-mentioned rule can be used in the assignment of spectra.

Infrared and Raman Spectra of Diethoxymethane in Various Phases. — Since DEM has four internal rotational axes, a possible number of rotational isomers may be larger than that of DMM. But from the spectroscopical point of view, isomers concerning C–ethoxy axes are important and those concerning C–C axes are less important.

In Fig. 3a, infrared spectra of vapor and liquid phases of DEM are shown. As in the case of DMM, the appearance of spectra is rather different between two phases, that is, the intensity of vapor bands at 1156, 1124 and 1019 $\mathrm{cm^{-1}}$ shows an appreciable decrease as compared with those of liquid phase spectra.

Solid infrared spectra of DEM are shown in Fig. 3b. Just as in the case of DMM, two types of spectra, namely A and B, are observed according to the slight change of the critical condition of freezing the material. In the type A spectrum, the intensity of the bands at 1193, 1019, 842 and 821 $\mathrm{cm^{-1}}$ shows an appreciable increase and that of the band at 1095 $\mathrm{cm^{-1}}$ shows a decrease as compared with those of carbon tetrachloride solution. The appearance of the type B spectrum is similar to that of the carbon tetrachloride solution, except for the doublet at 1100 $\mathrm{cm^{-1}}$.

In Fig. 4, the infrared spectrum of acetonitrile solution is shown. There exists no difference between the spectra of carbon tetrachloride and of acetonitrile solutions.

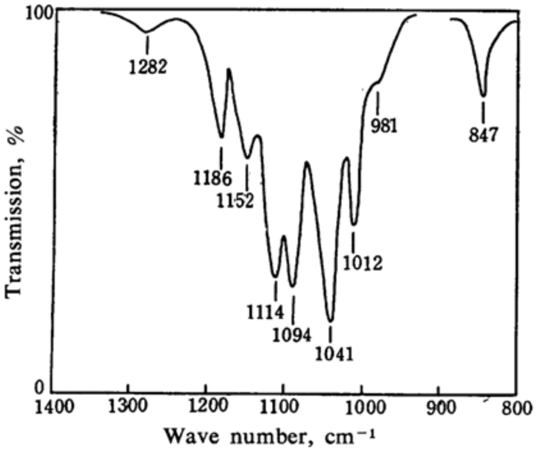

Fig. 4. Infrared spectrum of diethoxymethane ($C_2H_5OCH_2OC_2H_5$). Acetonitrile solution.

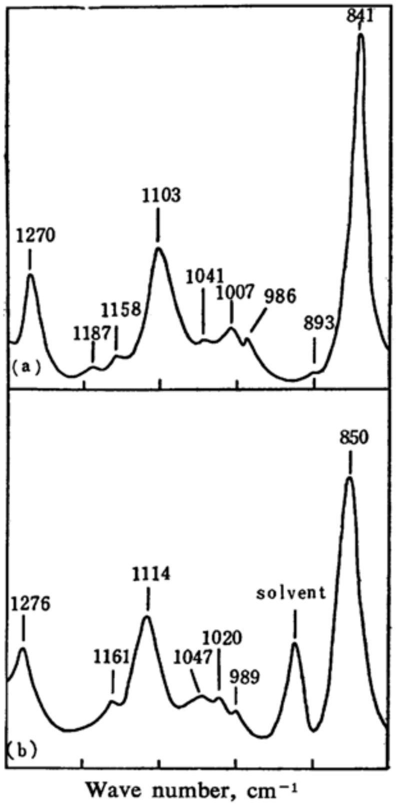

Fig. 5. Raman spectra of diethoxymethane ($C_2H_5OCH_2OC_2H_5$).

a) Pure liquid.
b) Acetonitrile solution (60%).

In Fig. 5, Raman spectra of carbon tetrachloride and acetonitrile solutions of DEM are shown. The intensity of the band at 1047 $\mathrm{cm^{-1}}$ increases and that at 1187 $\mathrm{cm^{-1}}$ decreases in acetonitrile solution. There is, however, no other experimental evidence that the former band belongs to the more polar form and the latter to the less polar form, hence the intensity change is probably due to simple solvent effect, that is, is due to the difference of intermolecular interaction between two kinds of solutions.

Vapor spectra of DEM were taken at the temperature range between 24 and 100°C. As no change was observed in the appearance of spectra within the temperature range, DEM has almost one and the same form in vapor phase below 100°C.

According to the measurement of Kubo, dipole moment of DEM is, in vapor phase, 1.22D at 56°C and slightly increases with rising temperature (1.26D at 203°C). Kubo has concluded that this molecule has one stationary form in vapor and that the difference of dipole moment between DMM and DEM (0.5D) is due to the difference of azimuthal angles of alkyl groups from the central OCO plane(11). Since there is no dipole measurement on liquid phase the molecular structure of DEM of liquid phase is not clear, but from the analogy

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11) M. Kubo, *Sci. Papers Inst. Phys. Chem. Research*, **30**, 169 (1936).

with DMM one could assume that the molecular form is the same both in vapor and liquid phases (nearly gauche-gauche form, but that the azimuthal angles of ethyl groups from central OCO plane are smaller than those of methyl groups in DMM), and that the change of appearance of spectra among different phases is dependent on the difference of intermolecular interaction. The detail of assignment will be reported elsewhere[3].

Infrared Spectra of Methoxyethoxymethane in Various Phases.—In Figs. 6 and 7, infrared spectra of vapor, liquid and solid phases of MEM are shown.

The vapor bands at 1131 and 926 cm^{-1} become weaker as compared with the liquid bands, and the doublet at 1112 cm^{-1} (and 1096 cm^{-1}) in the liquid phase is distorted in the vapor phase,that is, it becomes singlet in the vapor phase. The solid bands at 1218 cm^{-1} and 1013 cm^{-1} become much stronger and one at 1135 cm^{-1} becomes weaker as compared with the liquid bands.

It is quite hard, as in the case of DMM and DEM, to interpret such a complicated change of spectra among various phases as the change of abundance ratio of the rotational isomers. It is better to assume that from the analogy of

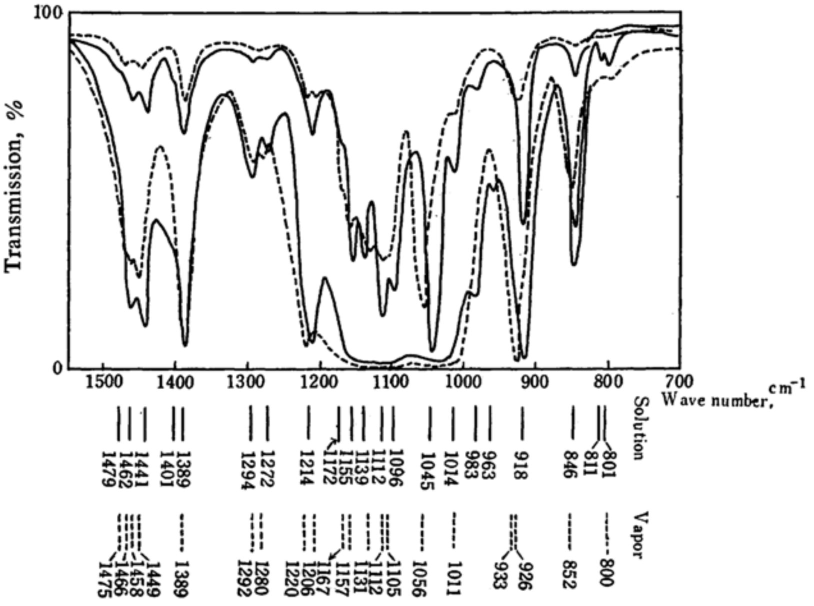

Fig. 6. Infrared spectra of methoxyethoxymethane ($CH_3OCH_2OC_2H_5$).
Solid line, CCl_4 and CS_2 solutions, cell thickness: 0.15 mm., 20% and 2%. Dashed line, vapor.

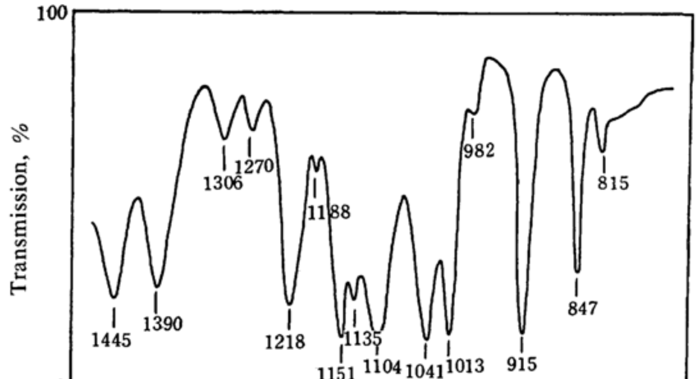

Fig. 7. Infrared spectrum of methoxyethoxymethane ($CH_3OCH_2OC_2H_5$).
Solid, cell thickness: 0.015 mm.

DMM, MEM has also one form in the liquid and vapor phases at least near room temperature. If the dipole moment of the vapor and liquid phases are observed, one can establish the validity of the above-mentioned assumtion.

Assignment of Infrared and Raman Spectra of Methoxyethoxymethane. — In this section the assignment of the infrared and Raman spectra (Fig. 8) of MEM is given by assuming that this molecule has only one form in its vapor and liquid phases.

The assignment of bands at 3000 cm^{-1} has

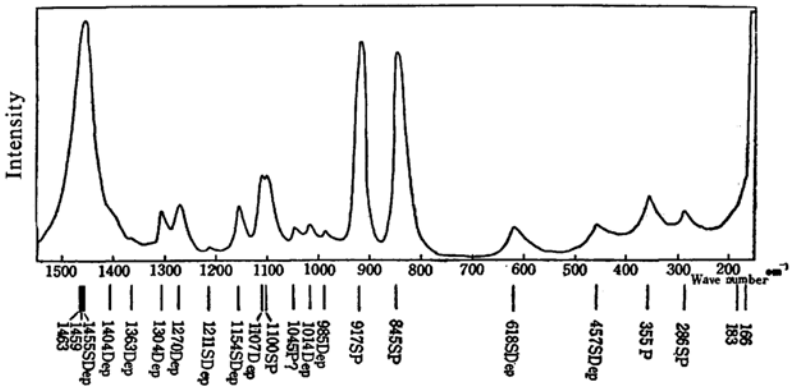

Fig. 8. Raman spectrum of methoxy ethoxy methane ($CH_3OCH_2OC_2H_5$).

TABLE I. VIBRATIONAL FREQUENCIES OF METHOXYETHOXYMETHANE

Infrared		Raman	Assignment
Vapor	Liq.		
1475 (vw)	1479 (w)		CH_2 scissoring (MeO and EtO)
1466 1458 (m)	1462 (m)	1463 (m, sh)	sym. CH_3 deformation (MeO)
		1459 (m, sh)	
1449 (m)	1441 (m)	1455 (s) S. Dep.	asym. CH_3 deformation (MeO and and EtO)
	1401 (w)		
1389 (m)	1389 (m)	1404 (w) Dep.	sym. CH_3 deformation (EtO)
		1363 (w) Dep.	CH_2 wagging (OCH_2O) ?
1292 (vw)	1294 (w)	1304 (m) S. Dep.	CH_2 rocking (EtO)
1280 (w)	1272 (w)	1270 (m) S. Dep.	CH_2 twisting (OCH_2O and EtO)
1220 1206 (w)	1214 (m)	1211 (w) S. Dep.	CH_3 rocking (MeO)
1167 (w)	1172 (w)		
1157 (m)	1155 (s)	1154 (m) S. Dep.	asym. COCOC stretching CC stretching CH_2 rocking (EtO) CH_3 rocking (EtO)
1131 (sb)	1139 (s)		
1112 1105 (s)	1112 (s)	1107 (s) Dep. ?	
1011 (w)	1014 (m)	1014 (w) Dep.	
	983 (w)	985 (w) Dep.	
	963 (vw)		
	1096 (s)	1100 (s) S. P.	sym. COCOC stretching
1056 (s)	1045 (s)	1045 (w) P. ?	asym. COCOC stretching
933 926 (m)	918 (s)	917 (s) S. P.	CH_3 rocking (MeO)
852 (w)	846 (m)	845 (s) S. P.	sym. COCOC stretching
	811 (w)		
800 (vw)	801 (w)		
		618 (m) S. Dep.	asym. COCOC deformation
		457 (m) S. Dep.	sym. COCOC deformation
		355 (m) P.	sym. COCOC deformation
		286 (m) S. P.	CCO deformation
		183 (sh) 166 (sh)	torsional vibration ?

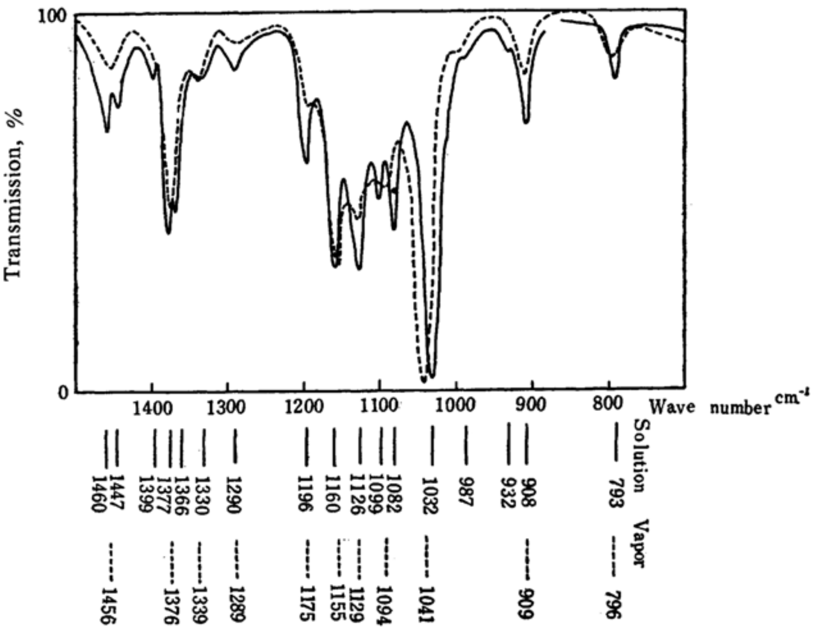

Fig. 9. Infrared spectra of diisopropoxymethane ($(CH_3)_2CHOCH_2OCH(CH_3)_2$). Solid line, CCl_4 and CS_2 solutions, cell thickness: 0.15 mm., 2%. Dashed line, vapor.

already been given by the same author⑫.

The appearance of infrared spectra between 1500 and 1250 cm^{-1} is quite similar to that of DEM and DEM-d_2, except for the lack of a very weak band a 1360 cm^{-1}. It means that the absorbance of bands in the ethoxyl group is greater than that of the methoxyl group. The appearance of Raman bands is, on the other hand, slightly different from that of DEM and DEM-d_2, that is, the intensity of the band at 1404 cm^{-1} decreases and that at 1304 cm^{-1} increases.

As the interaction between methoxyl and ethoxyl groups may be weak, the spectra of MEM within this region may be reasonably explained by assuming the simple superimposition of spectra, of methoxyl and ethoxyl compounds as shown in Table I.

A medium infrared band at 1214 cm^{-1} (having a corresponding weak Raman band) is assigned to the methyl rocking of methoxyl group. This is consistent with the fact that at this frequency many compounds containing methoxyl group have a medium infrared band and that the homologues of these compounds having no methoxyl group have no infrared band(2,3,13,14).

Spectra between 1150 and 800 cm^{-1} are very complicated not only in this molecule but in many other molecules containing oxygen atoms such as ethers, other dialkoxymethanes, ethyldene alkyl ethers, 2,2-dialkoxypropane and orthoaliphatic acid esters. The skeletal COCOC stretching should clearly exist within this region. As shown in the discussion of DMM and its deuterated compounds②, DEM and DEM-$d_2$③ and dimethyl ether and dimethyl ether-d_6(15,16), skeletal stretchings are mixed with CH deformation vibrations to some extent, and from inspection without exact calculation it is quite hard to give a rigorous assignment. Nevertheless, some bands could be assigned reasonably from the strong similarity of spectra among homologues.

The strong liquid infrared band at 1096 cm^{-1} (having no vapor infrared band and a strong and strongly polarized Raman band) is assigned to the symmetrical COCOC stretching. In DMM and DEM, liquid infrared bands around 1100 cm^{-1} have a corresponding very weak vapor infrared band and a medium or strong and strongly polarized Raman band. They have been assigned to the symmetrical COCOC stretching in good agreement with the present assignment.

The strongest infrared band at 1045 cm^{-1} (having a corresponding weak Raman band) is assigned to the asymmetrical COCOC stretching by the analogy with DMM.

Two very strong and strongly polarized

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12) K. Nukada, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 976 (1959).

13) K. Nukada, ibid., **80**, 1112 (1959).

14) K. Nukada, ibid., **81**, 1028 (1960).

15) Y. Kanazawa and K. Nukada, This Bulletin, to be published.

16) Y. Kanazawa and S. Saeki, ibid., to be published.

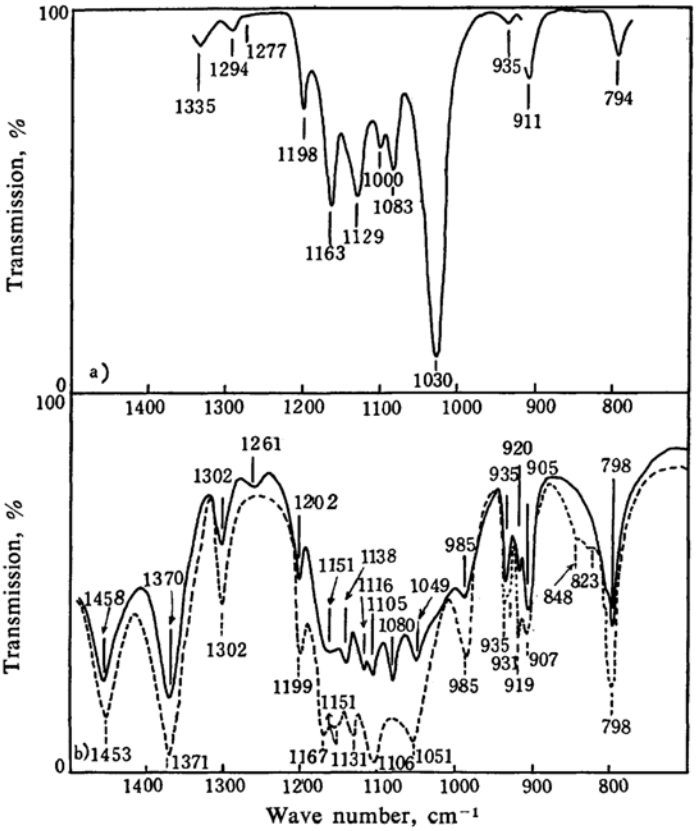

Fig. 10. Infrared spectra of diisopropoxymethane $(CH_3)_2CHOCH_2OCH(CH_3)_2$.

a) Acetonitrile solution, cell thickness: 0.015 mm., 20%

b) Solid, solid line, cell thickness: 0.015 mm. Dashed line, cell thickness: 0.05 mm.

Raman bands at 917 and 845 cm^{-1} (having corresponding strong and weak infrared bands, respectively) are assigned to the methyl rocking of the methoxy group and the symmetrical COCOC stretching, respectively. The basis of the assignment will be described in other papers[2,3].

The assignment of the remaining bands between 1150 and 800 cm^{-1} is very difficult only from the comparison of the spectra of homologues. They may be mixtures of asymmetrical COCOC stretchings, CC stretching, methylene rocking of ethoxyl group, and methyl rocking of methoxyl and ethoxyl groups.

The bands below 700 cm^{-1} are due to the skeletal deformation and torsional vibrations.

In DMM, DMM-d_2, DMM-d_6, DMM-d_8[2], DEM and DEM-d_2[3], three medium Raman bands appear at 640~560 cm^{-1} (depolarized), 450~370 cm^{-1} (depolarized) and at 325~295 cm^{-1} (polarized). The present data of MEM are completely consistent with these results. Therefore, they could be assigned to the asymmetrical, symmetrical (central angle OCO and two terminal angles COC vibrate in the opposite phases) and symmetrical (all angles vibrate in the same phase) COCOC skeletal deformations, respectively, from the analogy with the case above mentioned. In DEM and DEM-d_2, an additional strongly polarized Raman band appears at 240 cm^{-1}. In MEM, the band at 286 cm^{-1} is strongly polarized and the origin of this band is probably like that of the band at 240 cm^{-1} in DEM and DEM-d_2, hence this band is assigned to OCC deformation as in the case of DEM and DEM-d_2.

Torsional vibrations are expected to exist below 250 cm^{-1}, and Raman bands at 183 and 166 cm^{-1} may be assigned to these vibrations, although the assignment is somewhat doubtful as these bands are very weak and appear as a shoulder of very strong exciting line.

Infrared Spectra of Diisopropoxymethane in Various Phases.—Infrared spectra of DPM in vapor and liquid phases are shown in Fig. 9. As in the case of other dialkoxymethanes, the intensity of some bands (1175, 1129 and 1094 cm^{-1}) become smaller in the vapor phase.

No appreciable difference is found between the spectra of carbon tetrachloride and acetonitrile solutions (Fig. 10a).

Solid infrared bands have at least two different shapes, which are dependent on the critical condition of freezing the material, as shown in Fig. 10b.

The vapor spectra were taken at the temperature range between 24 and 106°C, but no change was observed.

The results are thus very similar to those in the case of DMM, DEM and MEM. Therefore, the same assumption as the above-mentioned one may also be held in this case. Because DPM has great bulk at the terminals (isopropyl groups) and the steric repulsion between isopropyl groups and the central methylene group is expected to be very large, this molecule may take a nearly planar zig-zag form.

Summary

The rotational isomerism of dialkoxymethanes ($CH_3OCH_2OCH_3$, $CH_3OCH_2OC_2H_5$, $C_2H_5OCH_2OC_2H_5$ and $(CH_3)_2CHOCH_2OCH\cdot(CH_3)_2$) is discussed from the spectroscopical point of view. The experimental results are as follows.

1) The appearance of infrared spectra is appreciably different among the vapor, liquid and solid phases. Of these, the solid spectrum gives the most complicated figure.

2) No solvent effect is obtained in acetonitrile solution.

3) No change is observed in the vapor infrared spectrum between room temperature and 100°C.

It is concluded from these results and data of dipole moment that dimethoxymethane exists as one configuration in the liquid and vapor phases, the terminal methyl groups of which are rotating about 120° anticlockwise sense from the central OCO plane.

The configuration of other dialkoxymethanes are assumed to be of one form by the analogy of experimental results.

Finally, the assignment of vibrational spectra of methoxyethoxymethane is presented.

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