Infrared and Raman Spectra of Ethylidene Dialkyl Ethers

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The author has investigated the infrared and Raman spectra of dialkoxymethanes such as $CH_3OCH_2OCH_3$, $CH_3OCH_2OC_2H_5$, $C_2H_5OCH_2 \cdot OC_2H_5$ and $(CH_3)_2CHOCH_2OCH(CH_3)_2$ in various phases. He has concluded that dimethoxy methane ($CH_3OCH_2OCH_3$) takes one forms in both its vapor and liquid phases, at least near room temperature, and that the different figures of the vapor and liquid spectra are not due to the existence of rotational isomerism but to different intermolecular forces in the two phases. It was not clear whether or not in the other dialkoxy methanes such a conclusion is also reasonable, but from the similarity of behavior of spectra in various conditions he assumed that in the other dialkoxy methanes the molecule exists as one form in both the vapor and liquid phases[1]. With this assumption, the assignment of spectra of these compounds has been undertaken[1-3].

It is now interesting to study the rotational isomerism in ethylidene dialkyl ethers ($R_1OCH(CH_3)OR_2$), in which one hydrogen atom of the central OCH_2O group of dialkoxy methanes is replaced by a methyl group. In this paper, he presents the infrared spectra of ethylidene dimethyl ether ($CH_3OCH(CH_3)OCH_3$), ethlidene methyl ethyl ether ($CH_3OCH(CH_3)OC_2H_5$), and ethylidene diethyl ether ($C_2H_5OCH(CH_3)OC_2H_5$) in vapor at various temperatures, and in carbon tetrachloride and acetonitrile solutions. They are abbreviated as EDM, EME and EDE, respectively.

From a comparison of the spectra obtained, he has found that ethylidene dialkyl ethers

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[1] K. Nukada, This Bulletin, 34, 1615 (1961).

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

[3] K. Nukada, This Bulletin, 34, 1624 (1961).

have a possibility of having two or more rotational isomers in their vapor and liquid phases.

Raman spectra of these compounds were also obtained, and the assignment of spectra is presented with the observation that rotational isomerism could exist in these molecules.

Experimental

EDM and EDE were prepared from methanol and acetoaldehyde, and from ethanol and acetoaldehyde, respectively. EME was prepared from a mixture of methanol and ethanol and acetoaldehyde[4]. A detailed description of the preparation of EME will be given elsewhere. The purity of samples was checked by a gas-chromatograph.

Infrared spectra of vapor and liquid phases were taken by using a Perkin Elmer 21 spectrophotometer equipped with a sodium chloride prism. Vapor spectra at elevated temperatures were obtained by means of a high temperature gas cell designed and constructed by Tomita of the author's laboratory[5]. It must be noticed that ethylidene dialkyl ethers are decomposed very quickly at the vapor phase in the presence of oxygen at elevated temperatures, so the high temperature cell should be completely deoxygenized before using.

Raman spectra of pure liquid were taken by using a Cary 81 spectrophotometer. The degree of depolarization was obtained by wrapping two types of silver chloride polarizers around a Raman tube alternately.

Results and Discussion

Infrared Spectra of Ethylidene Dialkyl Ethers. — *Ethylidene Dimethyl Ether.* — The relative intensity of the bands at 1121 and 1052 cm^{-1} decreases in the vapor phase, and that of the band at 1087 cm^{-1} in acetonitrile solution decreases slightly, as compared with that of the corresponding band in carbon tetrachloride solution (Figs. 1 and 2). The vapor spectra at elevated temperatures, however, show no appreciable change. Therefore, in EDE, there is no definite evidence that this molecule has two or more rotational isomers in its vapor and liquid phases.

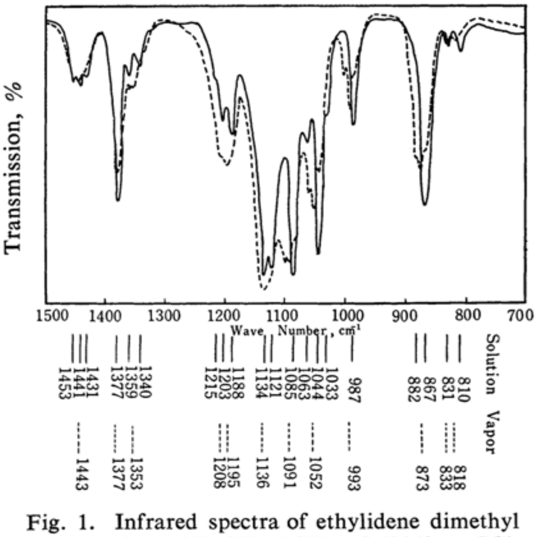

Fig. 1. Infrared spectra of ethylidene dimethyl ether ($CH_3OCH(CH_3)OCH_3$). Solid line, CCl_4 and CS_2 solutions, cell thickness: 0.15 mm., 2%. Dashed line, vapor.

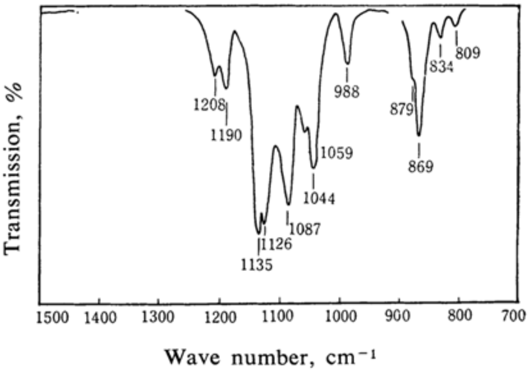

Fig. 2. Infrared spectrum of ethylidene dimethyl ether ($CH_3OCH(CH_3)OCH_3$). Acetonitrile solution, cell thickness: 0.015 mm., 20%.

Ethylidene Methyl Ethyl Ether.—The relative intensity of the bands at 1083, 1050 and 942 cm^{-1} decreases in the vapor phase, and that of the corresponding bands in acetonitrile solution definitely increases, as compared with that of the carbon tetrachloride solution bands (Figs. 4 and 5). In vapor spectra at elevated temperatures, the positions of maximum absorption are shifted from 1111 to 1098 cm^{-1} and from 935 cm^{-1} to a higher frequcncy, respectively (Fig. 6).

To interpret these results, the following theory is reasonable.

In this molecule, there are two rotational isomers, one with a less and the other with a more polar configuration both in the vapor and liquid phases. The bands at 1083, 1050 and at 942 cm^{-1} are due to the more polar form, while the band at 1105 cm^{-1} is due to the less polar form. From Figs. 4 and 5, it is clear that the abundance ratio of the more polar form to the less in acetonitrile solution is greater than that in carbon tetrachloride solution. In the vapor phase at low temperatures, the less polar form is predominant, but at higher temperature the number of molecules having the more polar form increases. In carbon tetrachloride solution, both forms exist almost equally.

Ethylidene Diethyl Ether.—The relative intensity of the band at 1095 cm^{-1} decreases in the

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[4] K. Nukada, *Reports Gov. Chem. Ind. Research Inst. Tokyo*, **55**, 99 (1960).

[5] H. Tomita, unpublished.

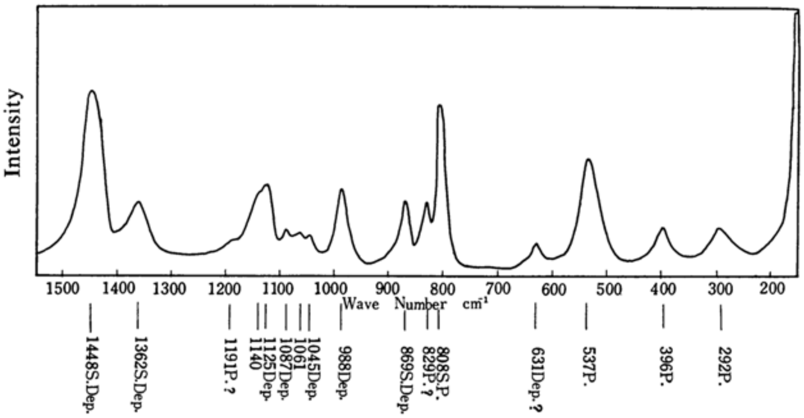


Fig. 3. Raman spectrum of ethylidene dimethyl ether ($CH_3OCH(CH_3)OCH_3$).

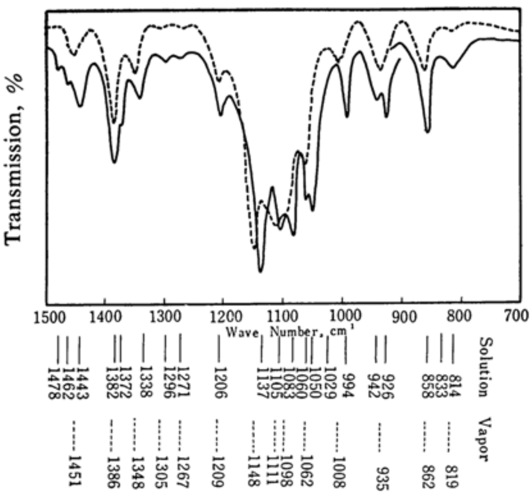
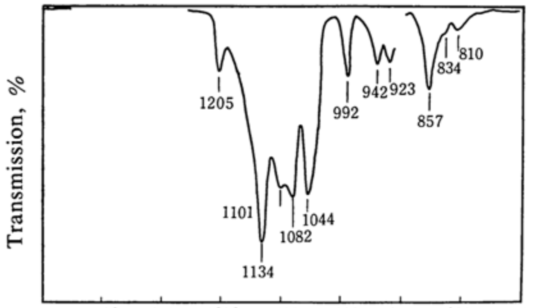
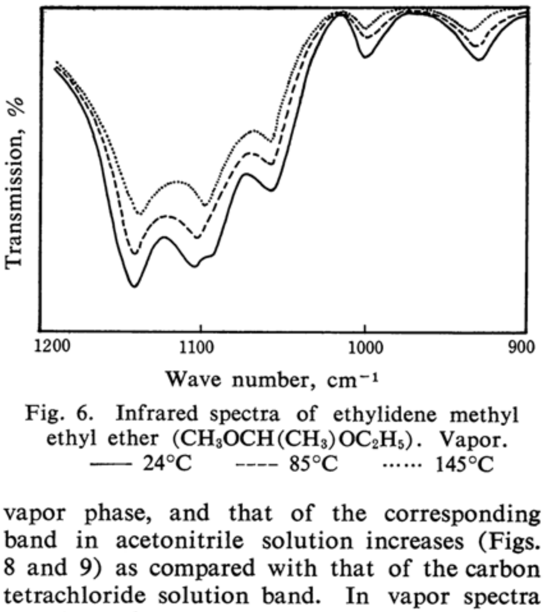


Fig. 4. Infrared spectra of ethylidene methyl ethyl ether ($CH_3OCH(CH_3)OC_2H_5$). Solid line: CCl_4 and CS_2 solutions, cell thickness: 0.15 mm., 2%. Dashed line: vapor.



Wave number, cm⁻¹

Fig. 5. Infrared spectrum of ethylidene methyl ethyl ether ($CH_3OCH(CH_3)OC_2H_5$). Acetonitrile solution, cell thickness: 0.015 mm., 20%.



Wave number, cm⁻¹

Fig. 6. Infrared spectra of ethylidene methyl ethyl ether ($CH_3OCH(CH_3)OC_2H_5$). Vapor.
—— 24°C ---- 85°C …… 145°C

vapor phase, and that of the corresponding band in acetonitrile solution increases (Figs. 8 and 9) as compared with that of the carbon tetrachloride solution band. In vapor spectra at elevated temperatures, the position of maximum absorption is shifted from 1109 to 1095 cm⁻¹ (Fig. 10).

Hence, as in the case of EME, it is reasonable to assume that in EDE there also exists rotational isomerism. The bands at 1080 and 1060 cm⁻¹ are due to a more polar form, and the band at 1099 cm⁻¹ is due to a less polar form. The more polar form is predominant in acetonitrile solution and in vapor at higher temperatures. In carbon tetrachloride solution, both forms are mixed almost equally.

Next the author will consider the molecular configuration of these compounds by assuming the existence of rotational isomerism. As one can easily understand from the actual molecular model, a planar zigzag form and a gauche-gauche form, in which terminal alkoxy groups rotate counterclockwise about 120° from the

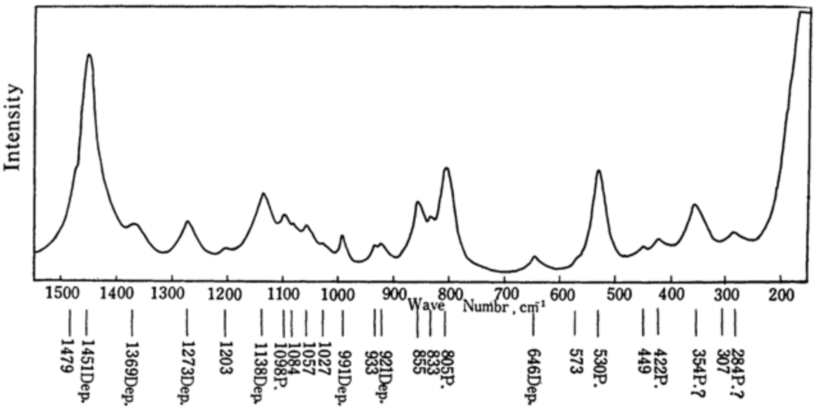


Fig. 7. Raman spectrum of ethylidene methyl ethyl ether ($CH_3OCH(CH_3)OC_2H_5$).

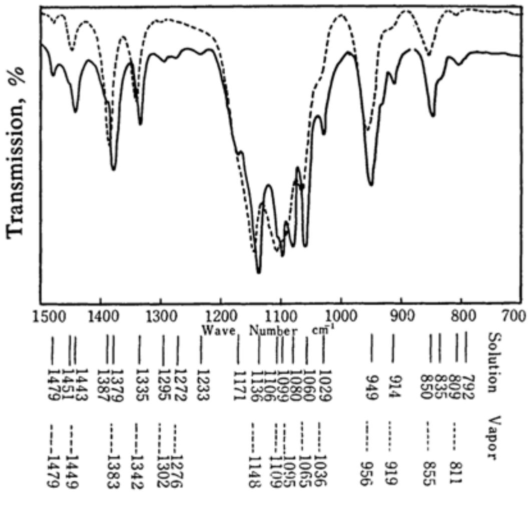


Fig. 8. Infrared spectra of ethylidene diethyl ether ($C_2H_5OCH(CH_3)OC_2H_5$). Solid line: CCl_4 and CS_2 solutions, cell thickness: 0.15 mm., 2%. Dashed line: vapor.

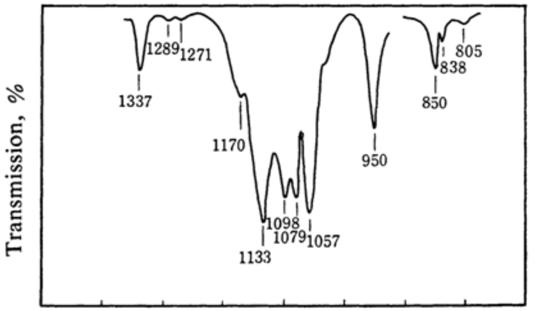


Fig. 9. Infrared spectrum of ethylidene diethyl ether ($C_2H_5OCH(CH_3)OC_2H_5$). Acetonitrile solution, cell thickness: 0.015 mm., 20%.

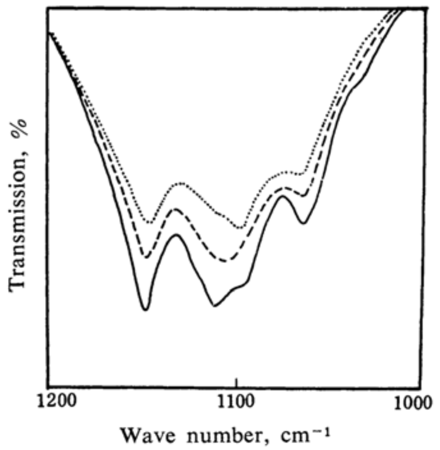


Fig. 10. Infrared spectra of ethylidene diethyl ether ($C_2H_5OCH(CH_3)OC_2H_5$). Vapor.
—— 24°C ---- 78°C ······ 155°C

central OCO plane, could not exist, since the repulsion between central methyl ($OCH(CH_3)O$) and terminal alkyl groups is fairly large. Kubo has produced a diagram showing the relation between the dipole moment of a R_1–O–C–O–R_2 type molecule and the azimuthal angles φ and ϕ of terminal alkoxy groups from the central OCO plane. From the observed value of the dipole moment of EDE in the vapor phase, Kubo has suggested that the molecule has a configuration in which $\varphi=120°$ and $\phi=240°$ (A form), or one in which $\varphi=180°$ and $\phi=240°$ (B form)[6]. From the diagram given by Kubo, it is concluded that the more polar form is the A form and the less polar one is the B form, if rotational isomerism exists in EME and EDE.

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

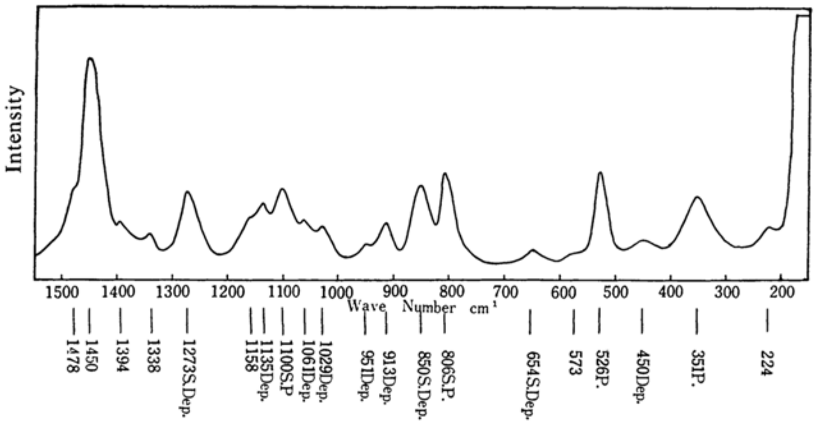

Fig. 11. Raman spectrum of ethylidene diethyl ether ($C_2H_5OCH(CH_3)OC_2H_5$).

As in the case of dialkoxy methanes, however, the difference in intermolecular interaction could produce some changes in the appearance of spectra in various phases[1]. Hence, a rigorous conclusion regarding the existence of rotational isomerism in EME and EDE in not obtained only from the present observation. To examine the reliability of the present interpretation of infrared spectra, the accurate measurement of the dipole moment in both the vapor and liquid phases at various temperatures is necessary, as in the case of dimethoxy methanes[1].

Assignment of Spectra of Ethylidene Dialkyl Ethers.—In this section, the assignment of the spectra of EDM, EME and EDE will be described by referring to that of dialkoxy methanes and related compounds. As discussed in detail in the preceding section, there is a possibility of the existence of rotational isomerism in EME and EDE. But in the assignment of these two compounds it is very difficult to decide one by one which band is due to which configuration, except for the few bands mentioned in the preceding section. So in the following description, an assignment to a definite molecular configuration is not presented except for a few cases. Raman spectra are shown in Figs. 3, 7 and 11.

A very weak infrared and medium Raman band appears at 1478∼11479 cm^{-1} in EME and EDE, but no band appears at this frequency in EDM. As was discussed in detail in another paper[3], this band is assigned to the methylene scissoring of the ethoxy group.

From the study of the spectra of diethoxy methane[3] and dimethoxy methane[2], an asymmetrical methyl deformation of the ethoxy and methoxy groups is expected to appear at 1460 and 1455 cm^{-1} respectively. A symmetrical methyl deformation of methoxy group should exist at 1460 cm^{-1}, according to Nakagawa[7], Sheppard[8] and Nukada[3]. The position of the asymmetrical methyl deformation of central $OCH(CH_3)O$ group is not clear, but presumably it exists near 1460 cm^{-1}. Therefore, at least four kinds of vibrations could exist around 1460 cm^{-1}, and it is not possible to assign the spectra of EDM, EME and EDE in this region definitely. If spectra of deuterated compounds were obtained, one could assign the bands in this region clearly.

The strong infrared band at 1377 cm^{-1} (having no corresponding Raman band) in EDM completely disappears in dimethoxy methane[3]. Therefore, this band is due to the $OCH(CH_3)O$ group. Since the CH deformation is expected to appear at a much lower frequency, this band is assigned to the symmetrical methyl deformation of $OCH(CH_3)O$ group. In EME and EDE, strong infrared bands are observed also at 1382 and 1379 cm^{-1} respectively which have no corresponding Raman bands. The medium Raman bands appear at 1362, 1369 and 1394 cm^{-1} in EDM, EME and EDE respectively; they have corresponding very weak infrared bands. As there is no other appropriate mode at this frequency, these bands are also assigned to the symmetrical methyl deformation of $OCH(CH_3)O$ group. To interpret these results reasonably, it is better to conclude that these two types of bands correspond to two different types of rotational isomers. Since the more polar form (A form as defined in the preceding section) and the less polar form (B form) belong to the Cs and C_1 point groups (ignoring the species of terminal alkyl groups), the former band (strong in infrared and no Raman) is assigned to the

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[7] I. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 68 (1956).

[8] N. Sheppard, *Trans. Faraday Soc.*, **51**, 1465 (1955).

TABLE I. VIBRATIONAL FREQUENCIES

EDM			EME		
IR		Raman	IR		Raman
Vapor	Liq.		Vapor	Liq.	
				1478(w)	1479(m)
	1453(m)	1448(s) Dep.		1462(w)	
1443(m)	1441(m)		1451(m)	1443(m)	1451(m) Dep.
	1431(m)				
1377(s)	1377(s)		1386(s)	1382(s)	
1353(w)	1359(w)	1362(m) Dep.		1372(w)	1369(mb) Dep.
	1340(w)		1348(m)	1338(m)	
			1305(w)	1296(w)	
			1267(w)	1271(w)	1273(s) Dep.
1208(m)	1215(sh)				
1195(s)	1203(m) 1188(m)	1191(w) P. ?	1209(w)	1206(m)	1203(w)
1136(s)	1134(s)	1140(m, sh)	1148(s)	1137(s)	1138(s) Dep.
	1121(s)	1125(s) Dep.	1111(s)	1105(s)	1098(m) P.
			1098(w)	1083(s)	1084(w)
1091(s)	1085(s)	1087(s)	1062(m)	1060(s) 1050(s)	1057(m)
	1063(w)	Dep.			
1052(s)	1044(s)	1061(w)			
	1033(sh)	1045(w) Dep.		1029(sh)	1027(w)
993(m)	987(m)	988(s) Dep.	1008(m)	994(m)	991(m) Dep.
				942(m)	933(m)
			935(m)	926(m)	921(m) Dep.
873(s)	882(sh) 867(s)	869(s) S. Dep.	862(m)	858(s)	855(s) S. Dep.
833(w)	831(w)	829(m) P. ?		833(vw)	833(w)
818(w)	810(w)	808(s) S. P.	819(w)	814(m)	805(s) S. P.
		631(m) Dep. ?			646(m) Dep.
		537(s) P.			530(s) P.
		396(s) P. 292(s) P.			354(m) P.? 284(w) P.?
					573(vw) 449(w) 422(w) P. 307(vw)

* s, m, mb, w and vw mean the qualitative intensities, strong, medium, medium and broad, weak and very weak. P., S. P., Dep. and S. Dep. mean the qualitative degree of depolarization,

more polar form and the latter one (strong in Raman and very weak in infrared) to the less polar form.

The medium infrared band at 1338～1335 cm^{-1} in EME and EDE is assigned to the methylene wagging of ethoxy group by analogy with diethoxy methane⁴⁾. The origin of the very weak band at 1340 cm^{-1} in EDM is not clear at present.

The very weak infrared bands at 1295～1296 (with no corresponding Raman band) and 1271～1272 cm^{-1} (the corresponding Raman band being strong and depolarized) both in EME and EDE are assigned to the methylene rocking and twisting of the ethoxy group respectively, because no band appears in this region in EDM and the appearance of the spectra is similar to that of diethoxy methane and diethoxy methane-$d_2$⁴⁾.

The bands at 1215 and 1203 cm^{-1} and one at 1206 cm^{-1} in EDM and EME are assigned to the methyl rocking of the methoxy group, as will be explained in detail in another paper²⁾.

OF ETHYLIDENE DIALKYL ETHERS*

EDE			
IR		Raman	Assignment
Vapor	Liq.		
1479(w)	1479(w)	1478(m)	CH_2 scissoring (EtO)
	1451(w)	1450(s)	Asym. CH_3 deformation ($OCH(CH_3)O$, MeO, EtO)
1449(s)	1443(m)		Sym. CH_3 deformation (MeO)
1383(s)	1379(s)		Sym. CH_3 deformation ($OCH(CH_3)O$, EtO) L-form
	1387(w)	1394(mb)	Sym. CH_3 deformation ($OCH(CH_3)O$, EtO) M-form
1342(m)	1335(m)	1338(w)	CH_2 wagging (EtO)
1302(w)	1295(w)		CH_2 rocking (EtO)
1276(w)	1272(w)	1273(s) S. Dep.	CH_2 twisting (EtO)
	1233(w)		
			CH_3 rocking (MeO)
	1171(w)		
		1158(sh)	
1148(s)	1136(s)	1135(m) Dep.	Asym. COCOC stretching
1109(s)	1106(sh) 1099(s)	1100(s) S. P.	L-form sym. COCOC stretching
1095(w)	1080(s)		M-form sym. COCOC stretching
1065(m)	1060(s)	1061(m) Dep.	Asym. COCOC stretching M-form
1036(w)	1029(m)	1029(m) Dep.	CC stretching ($OCH(CH_3)O$)
			CH_3 rocking (MeO)
956(m)	949(s)	951(w) Dep. ?	CC stretching, CH_3 rocking (EtO)
	935(sh)		
919(w)	914(m)	913(m) Dep.	
855(m)	850(m)	850(s) S. Dep.	Asym. COCOC stretching
	835(sh) 792(w)		
811(w)	809(m)	806(s) S. P.	Sym. COCOC stretching
		654(m) S. Dep.	Asym. COCOC deformation
		526(s) P.	Sym. COCOC deformation
		351(s) P.	Sym. COCOC deformation
		573(vw) 450(w)	Combination or overtone of torsional vibrations, skeletal deformations
		224(sh)	Torsional vibration

polarized, strongly polarized, depolarized and strongly depolarized.

Skeletal stretchings are expected to appear between 1150 and 700 cm^{-1} as in the case of dialkoxy methanes[1,2].

The strong infrared band (with a corresponding medium or strong and depolarized Raman band) around 1135 cm^{-1} in EDM, EME and EDE is assigned to an asymmetrical COCOC skeletal stretching. Since the intensity of this band does not change in vapor, and in carbon tetrachloride and acetonitrile solutions, it is not clear to which molecular configuration this band belongs.

The bands at 1105 cm^{-1} in EDM and one at 1099 cm^{-1} in EDE (strong in infrared and medium or strong and polarized in Raman) are due to the less polar configuration, as described in the last section. Since the Raman band is strongly polarized, these bands are assigned to a symmetrical COCOC skeletal stretching.

The band at 1083 cm^{-1} in EME and that at 1080 cm^{-1} in EDE (strong in infrared and very weak in Raman) are due to the more polar configuration, as described in the last section. Since the Raman band is depolarized (in EDE), these bands are assigned to an asymmetrical COCOC skeletal stretching.

Within the above-mentioned frequency region, the observed infrared and Raman bands of EDM do not correlate with those of EME and EDE. The band at 1121 cm^{-1} (strong both in liquid infrared and Raman and depolarized in Raman) in EDM is assigned to a symmetrical COCOC skeletal stretching, since the intensity of the vapor infrared band is very weak and that of the Raman band is strong. Although the definite assignment of the bands at 1085 and 1052 cm^{-1} in EDM is difficult, they have been assigned to asymmetrical stretchings since the intensity of the vapor and liquid infrared bands is very strong and that of the Raman bands is weak. It is not clear either that these bands are branches of doublet being caused by Fermi resonance, or that they are due to different molecular forms.

The weak or medium infrared bands around 1030 cm^{-1} (with depolarized Raman bands) in EDM, EME and EDE are assigned to a CC stretching of the OCH(CH_3)O group.

The medium infrared bands around 990 cm^{-1} (with corresponding medium or strong and depolarized Raman bands) in EDM and EME are assigned to the methyl rocking of the methoxyl group.

There are three infrared bands between 960 and 910 cm^{-1} in EME and EDE. As no band appears in EDM and a few bands appear in diethoxy methane and diethoxy methane-d$_2$ in this region$^{3)}$, they are assigned to vibrations due to the ethoxy group. More detailed assignment is quite hard, but they are presumably CC stretching or methyl rocking.

Between 870 and 850 cm^{-1}, strong and strongly depolarized Raman bands appear in EDM, EME and EDE. These bands have corresponding strong or medium infrared bands. As Raman bands are strongly depolarized. they are assigned to an asymmetrical COCOC skeletal stretching.

The Raman bands around 815 cm^{-1} are the strongest ones below 1300 cm^{-1} in EDM, EME and EDE. They are strongly polarized and have cerresponding medium or weak infrared bands. These bands are therefore definitely assigned to a symmetrical COCOC skeletal stretching.

In EDM, the number of bands assigned to the asymmetrical skeletal stretching exceeds two, so 1) at least two of them are the branches of doublet being caused by Fermi resonance, or 2) they are due to two rotational isomers.

The appearance of Raman spectra below 700 cm^{-1} is quite similar among EDM, EME and EDE; that is, the strongest and polarized bands appear around 530 cm^{-1}, while two medium or strong bands appear around 640 cm^{-1} (depolarized) and at 400$\sim$290 cm^{-1} (polarized). The position and the degree of depolarization of the bands are similar to those of dimethoxy methane, diethoxy methane and the deuterated compounds$^{2,3)}$. In accordance with the assignment of the spectra of dialkoxy methanes and the degree of depolarization observed, the following assignment has been obtained.

The bands around 640 cm^{-1} are assigned to the asymmetrical COCOC skeletal deformation because they are strongly depolarized. The strongest bands around 530 cm^{-1} and the next strongest bands between 400 and 280 cm^{-1} are assigned to the symmetrical COCOC deformations. In EDM, two bands having almost equal intensities appear, and it is not possible to give a more definite assignment for them at present.

Many weak bands appear below 600 cm^{-1} in EME and EDE; they should be 1) CH_3-C skeletal deformation, 2) overtone and/or combination of torsional vibrations, and 3) the skeletal deformations of the rotational isomers which are less predominant in the liquid phase.

Torsional vibrations are expected to exist below 250 cm^{-1}, but only one band was observed at this region in EDE.

The assignments thus obtained are tabulated in Table I.

Summary

Infrared spectra of three kinds of ethylidene dialkyl ethers ($CH_3OCH(CH_3)OCH_3$; EDM, $CH_3OCH(CH_3)OC_2H_5$; EME and $C_2H_5OCH\cdot(CH_3)OC_2H_5$; EDE), of vapor at various temperatures, and of carbon tetrachloride and acetonitrile solutions are presented.

From a comparison of the spectra obtained, it has been concluded that rotational isomerism could at least exist in EME and EDE.

Raman spectra of pure liquid have been obtained, together with the degree of depolarization.

The assignment of these spectra is given by referring to those of the homologues, such as dialkoxy methanes.

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