Summary

For pharmacological evaluation, 1-(3,4-ethylenedioxybenzyl)-2-methyl-1,2,3,4,5,6,7,8-octahydroisoquinoline was resolved into optical antipodes, using *d*-tartaric acid or dibenzoyl-*d*-tartaric acid.

When these compounds were cyclized according to the method of Grewe, there were produced two pairs of optically active position-isomers, *d*-1-(3,4-ethylenedioxybenzyl)-2-methyl-1,2,3,4,5,6,7,8-octahydroisoquinoline gave *d*-2,3- and *d*-3,4-ethylenedioxy-N-methylmorphinan and *l*-1-(3,4-ethylenedioxybenzyl)-2-methyl-1,2,3,4,5,6,7,8-octahydroisoquinoline yielded *l*-2,3- and *l*-3,4-ethylenedioxybenzyl derivatives.

d-2,3- and *l*-2,3-Ethylenedioxy-N-methylmorphinans were submitted to the Hofmann degradations and their structures were confirmed from their degradation product, 2,3-ethylenedioxyphenanthrene. *d*-3,4- and *l*-3,4-Ethylenedioxy-N-methylmophinans were found to be identical with authentic samples obtained by optical resolution of 3,4-ethylenedioxy-N-methylmorphinan.

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164. Goro Chihara : Medical and Biochemical Application of Infrared Spectroscopy. V.[1] Infrared Absorption Spectra of Organic Sulfate Esters. (1).

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It has been found in recent years that many important sulfate esters of organic compounds are present in medical and biological fields. Heparin and chondroitinsulfuric acid, sulfate conjugates in detoxication, and cerebroside sulfate are all organic sulfate esters. More recently, active sulfate has been found by Lipmann and others,[2,3] and the presence of energy-rich sulfate, corresponding to energy-rich phosphate, is being discussed. In order to know directly the nature of such a bond and to obtain fundamental data for qualitative and quantitative analyses, studies based on infrared absorption spectra seemed to be required. The present series of work was instigated for such a purpose.

Systematic studies on the infrared absorption spectra of organic sulfate esters are rare. Siebert[4] made assignments of chiefly Raman spectra of potassium methylsulfate, and a few other works are found in the works of Klotz,[5] La Lau,[6] and Hadži[7] on some organic sulfates, and those of Orr[8] and Nakanishi[9] on the sulfate of polysaccharide, in

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2) P. W. Robbins, F. Lipmann : J. Am. Chem. Soc., **78**, 6409(1956).
3) J. D. Gregory, F. Lipmann : J. Biol. Chem., **229**, 1081(1957).
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5) I. M. Klotz, D. M. Gruen : J. Phys. & Colloid Chem., **52**, 961(1948).
6) C. la Lau, E. A. M. F. Dahmen : "Colloquim Spectroscopicum International. VI." (Spectrochim. Acta Suppl.), 594(1957).
7) S. Detoni, D. Hadži : *Ibid.*, 601(1957).
8) S. F. D. Orr : Biochim. et Biophys. Acta, **14**, 173(1954).
9) K. Nakanishi, N. Takahashi, F. Egami : Bull. Chem. Soc. Japan, **29**, 434(1956).

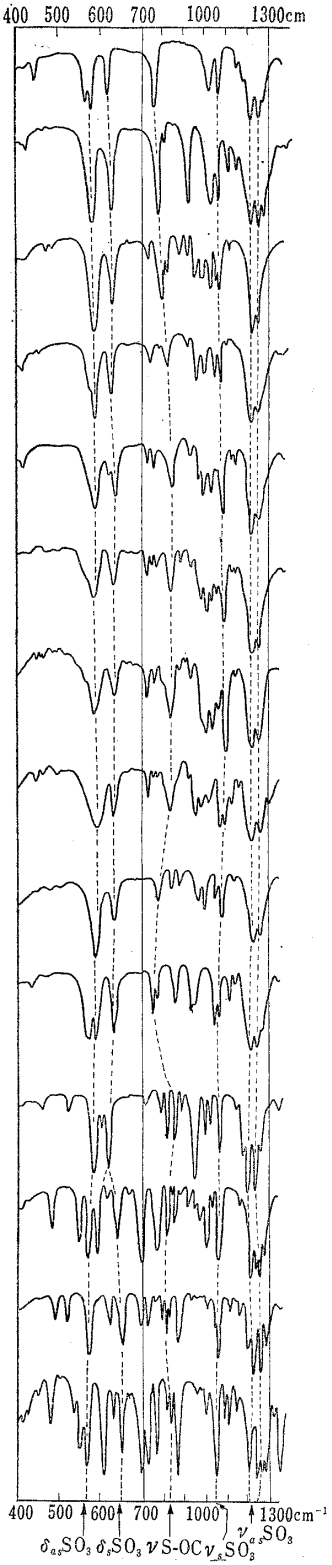

Fig. 1. Infrared Absorption Spectra of Organic Sulfate Esters

which the absorptions at around 1240 and around 800 cm^{-1} were assigned to those of the sulfate.

The present author made systematic studies on the infrared absorption spectra of organic sulfate esters, clarified some of their characteristic absorption bands, and a part of this work was briefly reported.[10]

In the present series of work, detailed assignments were made on the absorption bands of potassium methyl sulfate and infrared spectra were measured of 14 kinds of aliphatic and aromatic sulfates. From the comparison of these spectra with those of corresponding alcohols and phenols, position and variation of their characteristic absorption bands were clarified. The present work forms a basis for studies on energy-rich bond and infrared spectral examination of synovial fluid from this department.[11]

Experimental

Material—The samples used for infrared measurements were prepared by the method of Burckhardt and others[12] in 1926. The products were recrystallized several times from H_2O-EtOH mixture. K and Na salts of organic sulfate esters undergo decomposition on being heated and do not show the melting point. Purity of the samples was checked by determinations of K, Na, and acid-labile sulfate. When the found values agreed with those calculated within 0.5%, the sample was considered to be pure and submitted to measurement.

These substances were negative to the halogen test with AgCl and negative to inorganic sulfate test with $BaCl_2$.

The samples submitted to infrared measurement were the 14 kinds of organic sulfate listed in Table I, and their corresponding alcohols and phenols.

Infrared Spectra—Alkali salts of sulfate esters are all solid and are practically insoluble in various solvents. The samples were therefore measured as a KBr pellet and the spectra thereby obtained showed no appreciable shift from the spectra taken in Nujol mull.

Measurement of the corresponding alcohols and phenols was made as such when they were liquids and as KBr pellets if solid. Infrared measurement was taken in the range of 4000 to 350 cm^{-1}, using the Hilger Model H-800 Infrared Spectrophotometer. LiF prism was used for the region of 4000~2000 cm^{-1}, NaCl prism for 2000~700 cm^{-1}, and KBr prism for the region of 700~350 cm^{-1}.

10) G. Chihara: This Bulletin, **6**, 114(1958).
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12) G. N. Burckhardt, A. Lapworth: J. Chem. Soc., **1926**, 684.

Table I. Purity of Organic Sulfate Esters used for Measurement

Sulfate ester	K or Na (%)		SO_4 (%)	
	Calcd.	Found	Calcd.	Found
CH_3OSO_3K	26.01	26.1	63.95	63.2
$C_2H_5OSO_3K$	23.80	23.9	58.49	58.0
n-$C_3H_7OSO_3K$	21.93	21.9	53.89	53.2
n-$C_4H_9OSO_3K$	20.33	20.5	50.48	50.1
n-$C_8H_{17}OSO_3Na$	9.90	8.9	41.36	40.8
n-$C_{10}H_{21}OSO_3Na$	8.83	8.9	36.90	36.2
n-$C_{12}H_{25}OSO_3Na$	7.97	8.0	33.31	32.9
n-$C_{14}H_{29}OSO_3Na$	7.29	7.3	30.36	29.9
$(CH_3)_2$-$CHCH_2CH_2OSO_3K$	18.95	18.5	46.56	45.9
$(CH_3)_2$-$CHOSO_3K$	21.93	22.1	53.89	53.2
	17.91	18.5	44.00	43.5
$C_6H_5CH_2$-OSO_3K	17.28	17.3	42.45	42.2
$(p)CH_3$-C_6H_4-OSO_3K	17.28	17.4	42.45	41.9
$(p)NO_2$-C_6H_4-OSO_3K	15.19	15.0	37.34	37.0

Results and Discussion

The infrared absorption spectra of organic sulfate esters so obtained are indicated in Fig. 1.

1. Assignment of Infrared Spectrum of Potassium Methylsulfate

$CH_3OSO_3^-$ has 9 atoms so that it has 21 fundamental modes of vibration.[13] If CH_3 were to be considered as one group, then the vibrations due to the characteristic organic sulfate would be 12, i.e. 2 for ν_{as} SO_3, 1 for ν_s SO_3, 2 for δ_{deg} SO_3, 1 for δ_s SO_3, 2 for ρ SO_3, 1 for ν S–(O–CH_3), 1 for ν CH_3–O, 1 for δ C–O–S, and 1 for torsion. These were assigned respectively as indicated in Table II, which also contains the result of assignment of Raman spectrum of aqueous solution of CH_3OSO_3K by Siebert,[4] assignment of the Raman spectrum of aqueous solution of CH_3SO_3K by Simon,[14] and normal vibration of $CH_3SO_3^-$ by Fujimori.[15]

Table II. Assignment of Infrared Absorption Spectrum of Potassium Methylsulfate

	Absorptions (in cm^{-1})		
CH_3OSO_3K (Infrared)	CH_3OSO_3K (Raman)	$CH_3SO_3^-$ (Infrared)	CH_3SO_3K (Raman)
1252, 1215 $\nu_{as}SO_3$	1257, 1221 $\nu_{as}SO_3$	1182 $\nu_{as}SO_3$	1225, 1184 $\nu_{as}SO_3$
1063 ν_sSO_3	1063 ν_sSO_3	1055 ν_sSO_3	1054 ν_sSO_3
1022 νCO	1006 νCO		
		789 νCS	789 νCS
757 νS–O–C	781 νS–O–C		
617 δ_sSO_3	615 $\delta_{as}SO_3$	560 $\delta_{deg}SO_3$	557 δSO_3
576, 562 $\delta_{deg}SO_3$	559 δ_sSO_3	536 δ_sSO_3	533 δSO_3
440 ρSO_3	4438, 413 ρSO_3	349 ρSO_3	348 $\delta_{skeletal}$

The stretching and deformation vibrations of SO_3 in $CH_3OSO_3^-$ show somewhat higher values than those in $CH_3SO_3^-$ and this is a natural result arising from the difference in

13) G. Herzberg: 'Infrared and Raman Spectra of Polyatomic Molecules,' (1954). Van Nostrand Company, Inc., New York.
14) A. Simon, H. Kriegsmann: Chem. Ber., **89**, 1718(1956).
15) K. Fujimori: Bull. Chem. Soc. Japan, **32**, 621(1959).

nature of CH_3 and CH_3O.

The greatest difference in the present assignment and those made by other workers is the reversal of totally symmetric and degenerated vibrations of S–O bending vibration in SO_3. As will be seen in Fig. 1, the band at 617 cm^{-1} is a single sharp absorption, while the absorptions at 576 and 562 cm^{-1} are stronger than that of 617 cm^{-1} and split into two. The same can be said of other organic sulfate esters indicated in Fig. 1, in which the absorption at around 580 cm^{-1} is invariably split into two or is in the point of splitting. The absorption at around 620 cm^{-1} is always sharp and never shows the tendency to split into two. In the case of a solid crytal, the three S–O bonds in SO_3 are not necessarily of the same order. For example, from the result of X-ray analysis,[16] atomic distances of three S–O bonds in $C_2H_5OSO_3K$ crystal are 1.49, 1.44, and 1.45 Å, and their angles $\angle$O–S–O are 110°, 116°, and 112°. In such a case, doubly degenerate vibration is more liable to split into two.

The positions of the absorption of δ_{sym} SO_3 and δ_{deg} SO_3 may be attributed to the size of the force constants of deformation vibration H_{O-S-O} and repulsion F_{O-O}. In the case of $CH_3SO_3^-$, δ_{sym} SO_3 is more sensitive to changes of H_{O-S-O} and F_{O-O} than δ_{deg} SO_3.[17] Changes in δ_{sym} SO_3 to the change of force constant of H_{O-S-O} is about 6 times greater than that of δ_{deg} SO_3 and about 9 times greater against changes in force constant of F_{O-O}.

$$\frac{\partial(\delta_{sym}\ SO_3)}{\partial(H_{O-S-O})} \approx 6\ \frac{\partial(\delta_{deg}\ SO_3)}{\partial(H_{O-S-O})} \qquad \frac{\partial(\delta_{sym}\ SO_3)}{\partial(F_{O-O})} \approx 9\ \frac{\partial(\delta_{deg}\ SO_3)}{\partial(F_{O-O})}$$

It is therefore possible that δ_{sym} would become greater than δ_{deg} in some compounds. For the foregoing reasons, the absorption at 617 cm^{-1} was assigned to δ_s SO_3 and the two absorptions at 576 and 562 cm^{-1} to δ_{deg} SO_3.

Similarly, X-ray structural analysis by Jarvis has shown the atomic distance of S–O atoms in C–O–S bond of $C_2H_5OSO_3K$ to be 1.60 Å and this is far longer than that of other S–O bonds. Consequently, its absorption band should appear in a lower frequency and the extremely strong absorption at 757 cm^{-1} was assigned to this stretching vibration. Methanol and ethanol do not show any absorption in this region.

2. SO_3 Asymmetric Stretching Vibration

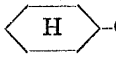
The organic sulfate esters measured all showed two very strong absorptions at around 1250 and 1210 cm^{-1}. These are asymmetric stretching vibration of SO_3 and its exact position is indicated in Table III, together with other characteristic absorptions.

Absorptions of ν_{as} SO_3 of sulfonate indicated by Fujimori[18] are at 1230~1200 and 1192~1175 cm^{-1} for aliphatic sulfonates and by Bellamy[19] at 1200~1160 cm^{-1} for aromatic sulfonates. Values for organic sulfate esters are somewhat higher.

This absorption is very stable and is hardly affected by the substituent present. As will be seen from Table III, the absorptions appear in the very narrow ranges of 1256~1244 and 1220~1210 cm^{-1} in aliphatic sulfate esters. There are not many compounds which show strong absorptions in this region so that this region is useful for identification of sulfate esters, together with other characteristic absorptions. Exception to this rule is cyclohexyl sulfate which has absorption in a lower region. Aromatic sulfates also have absorptions in approximately this region.

16) J. A. J. Jarvis : Acta Cryst., **6**, 327(1953).
17) K. Fujimori : Private communication.
18) K. Fujimori : Bull. Chem. Soc. Japan, **32**, 850(1959).
19) L. J. Bellamy : 'The Infra-red Spectra of Complex Molecules,' 301(1954). Methuen & Co., Ltd., London.

TABLE III. Position of Characteristic Absorptions in Organic Sulfate Esters

Sulfate ester	Absorptions (in cm^{-1})					
	ν_{as} SO_3	ν_s SO_3	δ_{deg} SO_3	δ_s SO_3	ρ SO_3	ν S-O-C
CH_3OSO_3K	1252, 1215	1063	562, 576	617	440	757
$C_2H_5OSO_3K$	1256, 1218	1062	576	625	425	773
n-$C_3H_7OSO_3K$	1247, 1220	1067	584	626	426	777
n-$C_4H_9OSO_3K$	1247, 1219	1069	586	625	426	819
n-$C_8H_{17}OSO_3Na$	1245, 1215	1079	590	632	417	830
n-$C_{10}H_{21}OSO_3Na$	1244, 1220	1078	591	631	411	834
n-$C_{12}H_{25}OSO_3Na$	1246, 1219	1081	590	632	419	836
n-$C_{14}H_{29}OSO_3Na$	1252, 1211	1078	597	631	418	838
$(CH_3)_2CHCH_2CH_2OSO_3K$	1244, 1214	1070	587	628		789
$(CH_3)CHOSO_3K$	1246, 1216	1041	570, 584	630	438	761
	1241, 1204 (1245)	1075	588	620		822
$C_6H_5CH_2OSO_3K$	1258, 1219	1067	(593), 573	642		788
$(p)CH_3C_6H_4OSO_3K$	1268, 1233	1060	571	650		799
$(p)NO_2$-$C_6H_4OSO_3K$	1244, 1214 (1265) (1278)	1052	551, 566	650		838

As will be seen in Fig. 1, absorption of ν_{as} SO_3 is split into small absorptions or is accompanied with a soulder. The degree of this splitting is far stronger in aromatic than in aliphatic sulfates. This is thought to be due to the difference in the three S-O bonds of SO_3, as stated above.

From the foregoing facts and as far as the present series of work is concerned, absorption of ν_{as} SO_3 appears as two strong bands in the region of 1260~1240 and 1220~1210 cm^{-1}.

3. SO_3 Symmetric Stretching Vibration

With regard to the absorption of ν_s SO_3, Fujimori[18] assigned that at 1063~1053 cm^{-1} for alkane 1-sulfonate, and Bellamy[19] reported that at 1060~1030 cm^{-1} for aromatic sulfonates.

In the case of organic sulfate esters, the absorption appears in somewhat lower frequency than that of sulfonates. The straight-chain alkyl sulfates show strong absorption in the region of 1081~1062 cm^{-1} and the position of the absorption tends to shift to a higher wave number with lengthening of the chain. The absorption appears in somewhat lower wave numbers in aromatic sulfates with the exception of isobutyl sulfate which absorbs at 1041 cm^{-1}. The few exceptions are due to the absorption of νCO at around 1000 cm^{-1}.

Consequently, this absorption appears in a fairly wide region and is at 1081~1040 cm^{-1} according to the present measurements.

4. SO_3 Bending Vibration

Organic sulfate esters generally show two strong absorptions in the KBr region. As stated above, absorption at around 580 cm^{-1} was assigned to doubly degenerate SO_3 bending vibration and that at a higher wave number of 630 cm^{-1} to SO_3 symmetrical bending vibration. As shown in Fig. 1, the absorption at around 630 cm^{-1} is a single sharp band while the absorption at around 580 cm^{-1} is split into two or becomes broad, mostly carrying a shoulder.

As indicated in Table III, straight-chain alkyl sulfates have absorption for δ_{sym} SO_3 in the region of 631~617 cm^{-1} and that of δ_{deg} SO_3 in the region of 597~576 (562) cm^{-1}. These absorptions shift to a higher wave number as the length of straight chain increases. This is also true in the case of branched-chain alkyl sulfates such as isopropyl and iso-

amyl sulfates, and in cyclohexyl sulfate. There is entirely no absorption in this region in the corresponding alcohols so that this band could also be adopted as the characteristic absorption of organic sulfates, together with other characteristic absorption bands.

In aromatic sulfates, absorptions other than that of a sulfate sometimes appear in this region and the spectrum becomes somewhat complicated. Of the corresponding alcohols and phenols measured in the present work, benzyl alcohol showed an absorption at 594 cm^{-1} and *p*-nitrophenol, at 627 cm^{-1}. The strong absorption at 593 cm^{-1} in benzyl sulfate and that at 617 cm^{-1} in *p*-nitrophenyl sulfate were considered to be absorptions other than those due to sulfate. Consequently, aromatic sulfate shows absorption for δ_{deg} SO_3 at 550~570 cm^{-1} and that for δ_s SO_3 at around 650 cm^{-1}. Because the number of aromatic sulfates submitted to measurement is rather small, these cannot be taken as the region of characteristic absorption bands but it may be said that the absorption band of δ_{deg} SO_3 appears in a lower and that of δ_s SO_3 in a higher wave-number region than those in characteristic absorption of alkyl sulfates. The difference between δ_s SO_3 and δ_{deg} SO_3 is also greater than that in the case of aliphatic sulfates. The region of δ_{sym} SO_3 and δ_{deg} SO_3 in organic sulfate esters may therefore be indicated as 617~650 cm^{-1} for δ_{sym} SO_3 and 550~590 cm^{-1} for δ_{deg} SO_3.

5. SO_3 Rocking Vibration

In Table III, the weak absorption appearing at around 410~440 cm^{-1} has been assigned to ρSO_3. The corresponding alcohols and phenols show weak absorption in a slightly higher wave-number region so that these absorptions in the organic sulfate esters cannot all be assigned to ρSO_3. It can be said, however, that the absorption of ρSO_3 does not appear in any definite position.

6. S-O-C Stretching Vibration

The atomic distance of S–O bond in $C_2H_5OSO_3K$ is 1.60 Å, according to X-ray analysis, and this is far longer than that of S–O bond in SO_3, thought to have a strong single-bond property. Its absorption should appear in lower wave number than that of ν SO_3.

Simon and others[20] assigned the absorption at 694~737 cm^{-1} to ν S–O–C or ν C–S in Raman spectra of $CH_3SO_2OCH_3$, $CH_3SO_2OC_2H_5$, $C_2H_5SO_2OCH_3$, and $C_2H_5SO_2OC_2H_5$, and the absorption at around 700 cm^{-1} to that of ν S–O–C in CH_3OSO_3Li, CH_3OSO_3Na, and CH_3OSO_3K.[21] La Lau[6] also assigned the absorption at around 800 cm^{-1} in the cyclohexylammonium salts of several detergents to ν S–O–C. As has already been stated, the absorption at 757 cm^{-1} in CH_3OSO_3K can definitely be assigned to that of ν S–O–C. Based on this, the absorption of ν S–O–C was assigned as indicated in Table III. In the case of aliphatic sulfates, skeletal vibration of C–C appears in this region and the absorptions are complicated.

Carrington and others[22] studied infrared spectra of cyclohexylammonium salts of several detergents and revealed that absorption of medium strength appears at 790 cm^{-1} when a substituent is attached to the even-numbered position in the hydrocarbon chain and at 810~837 cm^{-1} when attached to the odd-numbered positions. Assignment of this absorption to –S–O stretching was denied.[23] The absorption at 757 cm^{-1} in CH_3OSO_3K is very strong, the intensity being only slightly less than those of ν SO_3 and δ SO_3 absorptions. Marked changes in this coupling ratio cannot be considered in the case of aliphatic sulfates, excluding the instances of coupling. In the case of methyl, propyl, and butyl sulfates, the absorptions at 773, 777, and 819 cm^{-1} were respectively assigned to the sulfate

20) A. Simon, H. Kriegsmann, H. Dutz: Chem. Ber., **89**, 2378(1956).
21) *Idem*: *Ibid.*, **89**, 2390(1956).
22) R. A. G. Carrigton, H. C. Evans: J. Chem. Soc., **1959**, 1701.
23) K. W. F. Kohlrausch: "Ramanspektren, Hand- und Jahrbuch der Chemischen Physik," Vol. **9**, 411(1943). Becker und Erler, Leipzig.

because the corresponding alcohols do not show any strong absorptions in this region. In the case of $C_4H_9OSO_3K$, the absorption at 819 cm^{-1} is not especially strong but the absorption at 744 cm^{-1} is clearly due to C–C skeletal vibration, so that the absorption at 819 cm^{-1} must be assigned to that of ν S–O–C.

As will be clear from the foregoing, the absorption of ν S–O–C shifts to a higher wave-number region. The absorptions of ν S–O–C in alkyl sulfates were assigned as shown in Table III from the foregoing tendency and the absence of apparent absorptions in this region in the corresponding alcohols.

Sulfate esters with an aromatic group have strong out-of-plane absorption in this region but these absorptions should not show any great shift and they could be eliminated approximately with the aromatic out-of-plane vibrations appearing in the corresponding alcohols and phenols. Consequently, the absorptions at 788 cm^{-1} in benzyl sulfate, at 799 cm^{-1} in *p*-cresyl sulfate, and at 838 cm^{-1} in *p*-nitrophenyl sulfate were assigned to that of ν S–O–C.

The foregoing results have shown that, as far as the present measurement is concerned, the absorption of ν S–O–C in aliphatic sulfates appears in the region of 757~838 cm^{-1} and the absorption appears in a higher wave-number region with the lengthening of the hydrocarbon chain. There is no great difference of this tendency in secondary sulfates like isopropyl and cyclohexyl sulfates. The same assignment can also be made in the case of aromatic sulfate, within the limit of the present measurements.

This S–O–C bond is generally energy-poor in aliphatic sulfates, becomes slightly energy-rich with increasing size of the alkyl group, and *p*-cresyl and *p*-nitrophenyl sulfates are energy-rich compounds. The work is still in progress regarding this point but examinations made to date failed to show any marked difference in νS–O–C stretching absorptions between the energy-rich and energy-poor compounds.

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Summary

Systematic studies were made on the infrared absorption spectra of organic sulfate esters. Based on the detailed examination of potassium methylsulfate, measurement of infrared spectra was made of 14 kinds of organic sulfates and the following facts were revealed :

1) The absorption of ν_{as} SO_3 appears as two strong bands in the regions of 1260~1240 and 1220~1210 cm^{-1}, and the absorption is stable.

2) The absorption of ν_{sym} SO_3 appears at 1081~1040 cm^{-1}, the absorption being very strong.

3) The absorption of δ_{deg} SO_3 appears as a broad and strong band at 590~550 cm^{-1} and is sometimes split into two.

4) The absorption of δ_{sym} SO_3 is at 650~617 cm^{-1} and is somewhat weaker than that of δ_{deg} SO_3. This absorption shifts to a higher wave number within this range as the length of the chain increases.

5) The absorption of νS–O–C is also in the region of 838~757 cm^{-1} and the absorption shifts to a higher wave number as the chain becomes longer in aliphatic sulfates.

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