through which Maxted's fundamental researches will be remembered as well in the practical field of catalysis. A view worked in this manner will be opened elsewhere.

The authors wish to thank the Scientific Research Grant of the Ministry of Education for having defrayed part of the expense for this research and Dr. H. Fujii, the director of the Research Institute of Nippon Suisan Co., for use of his facilities for carrying out the experimental work.

Summary

Substrates containing electronegative groups have a strong trend to reduce hydrogenation activity of catalysts owing to self-poisoning, and fat hydrogenation is not exceptional. Paid due cautions on self-poisoning, zero order with respect to substrates is readily confirmed. Discussions, putting aside the problem of poisoning, are concentrated on the behaviors of reactants on catalysts in connection with ethylene hydrogenation.

Fat hydrogenation is considered as a specific instance of ethylene hydrogenation, where partial pressure of ethylene is enormously excess. A theory of local mobilization respecting reactants is advanced to meet the ethylene hydrogenation kinetics of independency on partial pressure of major species at low temperatures and of dependency on partial pressures of both species at high temperatures. Only for the latter case the Langmuir-Hinshelwood theory is applicable. Discrimination between active and inactive sites is thereby necessary.

Interpretation for the preferential hydrogenation of linoleic acid to oleic acid on nickel catalyst is made in terms of equilibrium shift between two assumed quasi-complex compounds involving all the components concerned, one with linoleic acid and the other with oleic acid as a component, which also accounts for the failure of selectivity under high hydrogen pressures.

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111. Yukiko Tanaka and Yoshimasa Tanaka : Infrared Absorption Spectra of Organic Sulfur Compounds. II.*1 Studies on S–N Stretching Bands of Methanesulfonamide Derivatives.

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In the previous paper of this series, it was reported that the S–N stretching vibration always appeared near 900 cm^{-1} region in a variety of aromatic sulfonamide derivatives, and one more characteristic band appeared at the 1090 cm^{-1} region. Moreover, the S–N band shifted to the lower wave number region by deuteration work, but the band near 1090 cm^{-1} did not shifted as S–N band.[1)]

In this work, the infrared spectra of 15 kinds of methanesulfonamide derivatives were measured and the S–N stretching vibrations were examined in comparison with the aromatic sulfonamide derivatives.

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*1 Part I : This Bulletin, **13**, 399 (1965).

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1) Y. Tanaka, Y. Tanaka : This Bulletin, **13**, 399 (1965).

Experimental

The methanesulfonamide derivatives were prepared by the reaction of methanesulfonyl chloride and amine with standard procedures.[2] All compounds were recrystallized or redistilled immediately before measurment.

Measurements : The Koken DS-301 IR spectrophotometer was used with NaCl or KBr prisms (3600~650 cm^{-1}) (900~400 cm^{-1}). The measurement of IR spectra were carried out for KBr tablets as solid substance or liquid film as liquid sample.

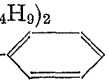
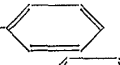
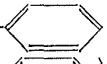
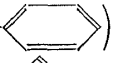
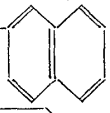
Results and Discussion

As shown in Fig. 1, in methanesulfonyl chloride no band was found near 900 cm^{-1} region, but in methanesulfonamide, a band was found at 882 cm^{-1} as has been indicated previously. In 14 kinds of other derivatives, the bands near 900 cm^{-1} region were observed as shown in Table I.

From the above observation, the band near 900 cm^{-1} region can be attributed to the S-N stretching vibration.

However, no appreciable band was detected near 1090 cm^{-1} region in most of the measured compounds. In some of them a band of weaker intensity appeared in a comparatively lower wave number region, but no characteristic band as seen in benzenesulfonamide derivatives was found. But only in two samples abnormally strong absorption bands were found, namely in $CH_3SO_2NHCH_3$ at 1073 cm^{-1}, and in $CH_3SO_2NH(CH_2)_3CH_3$ at 1083 cm^{-1}. The S-N bands of N,N-disubstituted derivatives located at higher wave number region than those of N-monosubstituted derivatives as shown in Table I and Fig. 2.

Table I. Infrared Spectra of Methanesulfonamide Derivatives

	near 1090 cm^{-1}	ν_{S-N} (cm^{-1})	ρ_{CH_3}? (cm^{-1})	ν_{C-S}? (cm^{-1})	state
CH_3SO_2Cl	—	—	968	751	liq. film
$CH_3SO_2NH_2$	—	882	988	774	KBr
$CH_3SO_2NHCH_3$	1073 (s)	836	973	763	liq. film
$CH_3SO_2N(CH_3)_2$	—	947	988	780	KBr
$(CH_3SO_2)_2NCH_3$	1080 (m)	836	966	766	〃
$CH_3SO_2NHC_2H_5$	—	875	979	785	liq. film
$CH_3SO_2N(C_2H_5)_2$	—	928	965	770	KBr
$CH_3SO_2NHC_4H_9$	1083 (s)	855	978	760	〃
$CH_3SO_2N(C_4H_9)_2$	—	921	960	780	〃
CH_3SO_2NH- 	—	895	978	776	〃
$CH_3SO_2N(C_6H_5)_2$	—	906	973	764	〃
$(CH_3SO_2)_2N$- 	—	885	942	780	〃
$CH_3SO_2NHCH_2$- 	—	877	977	768	〃
$CH_3SO_2N(CH_2$-  $)_2$	—	935	960	790	〃
CH_3SO_2NH- 	—	940	994	768	〃
CH_3SO_2N 	—	930	987	775	〃

2) B. Helferich, H. Grünert : Chem. Ber., **73**, 1131 (1940); A. Simon, H. Kriegsmann : *Ibid.*, **89**, 1718 (1956); C. S. Marvel, M. D. Helfrick, J. P. Belsley : J. Am. Chem. Soc., **51**, 1273 (1929).

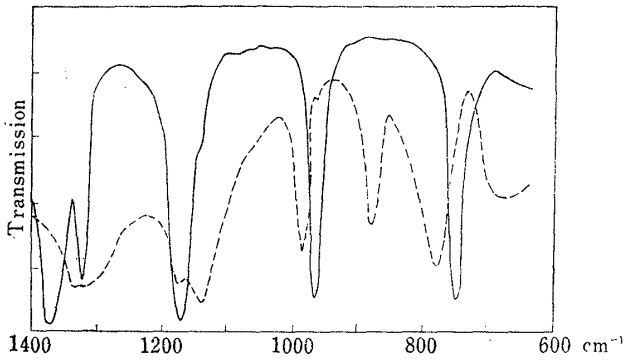


Fig. 1. Infrared Spectra of CH_3SO_2Cl (solid line) and $CH_3SO_2NH_2$ (broken line)

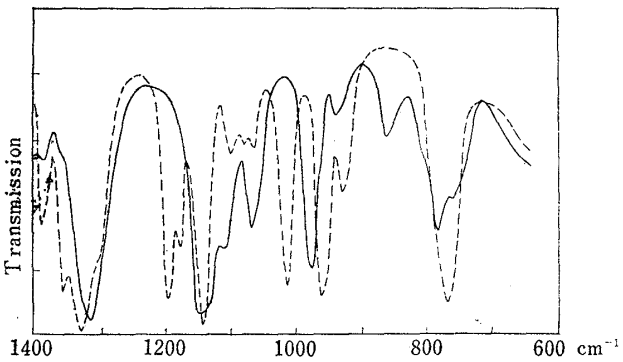


Fig. 2. Infrared Spectra of $CH_3SO_2NHC_2H_5$ (solid line) and $CH_3SO_2N(C_2H_5)_2$ (broken line)

In this research two interesting bands were observed at 942~994 cm^{-1} and 763~790 cm^{-1} region, which, according to Momose, *et al.*[3] can be attributed to CH_3 rocking frequencies of SO_2CH_3 group in dimethyl sulfone, methanesulfonamide, N-methylmethanesulfonamide and N,N-dimethylmethanesulfonamide. Assuming the Momose's proposal was correct, one more absorption as C-S stretching vibration should appear between about 800 cm^{-1} to 600 cm^{-1} region. However any characteristic band was found at 800 ~500 cm^{-1} region, and it has been reported[4] that the C-S stretching vibration normally appears in the infrared as a weak absorption in the range 700~600 cm^{-1}. This correlation applies to all types of sulfur compounds containing this linkage and a band in this region is found in mercaptans, sulfides, sulfoxides, sulfones etc. Katrizky and Jones[5] reported that in $ArNHSO_2Me$, $ArNMeSO_2Me$, Me_2NSO_2Me, $MeNHSO_2Me$, and NH_2SO_2Me, the position of that of higher frequency is tentatively assigned to the C-S mode and lower one is probably to S-N mode, at the region between 974~899 cm^{-1}. Moreover, Simon, *et al.*[6] reported that in the study of a series of methanesulfonic acid derivatives, the band at 763~790 cm^{-1} region is stretching vibration of C-S mode and the band at 942~994 cm^{-1} region is CH_3 rocking frequency. Though extensive study to assign to CH_3 rocking frequency of SO_2CH_3 group and to C-S stretching vibration is to be done, it will be most reasonable to assign that the higher one is CH_3

Table II. The Spectral Shift on N-deuteration

	H (cm^{-1})	D (cm^{-1})
$CH_3SO_2NH_2$	882	837
$CH_3SO_2NHCH_3$	836	816
$CH_3SO_2NHC_2H_5$	875	835
$CH_3SO_2NH-C_6H_5$	895	823
$CH_3SO_2NHCH_2-C_6H_5$	877	848
$CH_3SO_2NH-C_{10}H_7$	940	898

3) T. Momose, Y. Ueda, T. Shoji : This Bulletin, **7**, 734 (1959).
4) L. J. Bellamy : " The Infrared Spectra of Complex Molecules," 2nd Ed., 353 (1958). Metheun and Co., Ltd., London.
5) A. R. Katritzky, R. A. Jones : J. Chem. Soc., **1960**, 4497.
6) A. Simon, H. Kriegsmann : Chem. Ber., **89**, 1718, 2384 (1956); A. Simon, H. Kriegsmann, H. Dntz : *Ibid.*, **89**, 1883, 1990, 2378, 2390 (1956).

rocking vibration and lower is C-S stretching vibration in CH_3-S group.

The S-N band near 900 cm^{-1} region of methanesulfonamide and N-monosubstituted compounds shifted to lower wave number about 72~20 cm^{-1} on N-deuteration, as shown in Table II and Fig. 3. The definitely position of S-N stretching vibration can be decided by to examine the spectral shift on N-deuteration of sample.

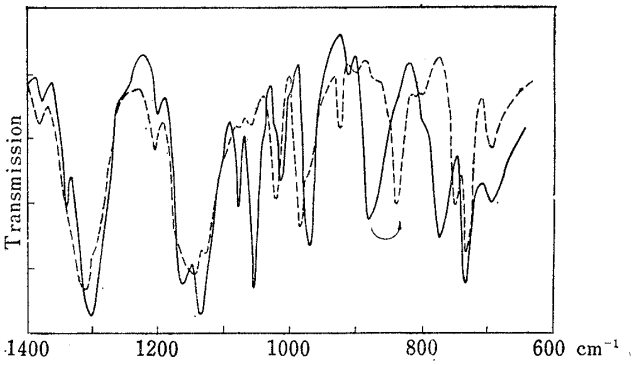


Fig. 3. Infrared Spectra of $CH_3SO_2NHCH_2C_6H_5$ (solid line) and $CH_3SO_2NDCH_2C_6H_5$ (broken line)

The authors wish to thank Prof. T. Uno of Kyoto University for many helpful discussions and suggestions during this work.

Summary

The infrared spectra of methanesulfonamide derivatives and their N-deuterated compounds were measured. The S-N stretching vibrations were recognized between 947~836 cm^{-1} as in benzenesulfonamide derivatives. The spectral shift of N-deuterated compounds were recognized lower wave number region about 72~20 cm^{-1} than ordinary compounds. In addition the S-N bands of N-monosubstituted compounds is located in the lower wave number region than N,N-disubstituted compounds.

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112. Kiichiro Kakemi, Takaichi Arita, and Shozo Muranishi : Absorption and Excretion of Drugs. XXV.*1 On the Mechanism of Rectal Absorption of Sulfonamides.

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It is well known that a number of drugs are readily absorbed through the rectum, and the elucidation of the mechanism of rectal absorption is important for a view-point of dosage schedule. Concerning the rectal absorptions, the reports have been used to evaluate the level of drug in blood[1,2] or urine[3,4] following the rectal administration in rabbit, and the other[5] measured the residual amount in the rectum of rat by an isotope technique. Because most of studies have involved different techniques and various

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