generous supply of digoxin. The author is indebted to Mr. K. Achiwa for optical rotatory dispersion mesurement and to all the staff of the central analysis laboratory of this Faculty for elemental analyses, infrared and ultraviolet spectral measurement.

Summary

Some 12-oxosteroids related to 12-dehydrodigoxigenin were synthesized and their optical rotatory dispersion was examined. On the basis of the optical data obtained conformation of ring C of these 12-oxo-14β-steroids was discussed.

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110. Ryoichi Miyake, Yoshizo Shimamura, and Hisa Yajima : Kinetics of Fat Hydrogenation.*[1]

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Preliminary remarks: In the previous paper[1] it is concluded that the reaction is of zero order with respect to the concentration of substrate in the hydrogenation of whale oil on copper catalyst, whereas its rate is retarded by self-poisoning. An effort was made to formulate the poisoning effect, however, it was noticed that this condition was not restricted to any special material. This article follows the previous paper wherein examples are presented with the most familiar materials, oleic acid ester and nickel catalyst.

Discussion, however, is centered on the independency of concentration of substrate in greater detail with the advancing of the hypothesis of local mobility of reactants on catalyst surface, and in connection with this the conditions are criticized, under which the most acceptable Langumuir-Hinshelwood theory is applicable.

Under these considerations, it is hoped that liquid hydrogenation may be proved to be providing a potent basis to the development of the theory heterogeneous catalytic reaction keeping pace with ethylene hydrogenation.

Fat hydrogenation, having a tremendous literature, is most pertinent for advancing a general theory of liquid hydrogenation. Nevertheless, it has not played a significant roll in the relevant field of kinetic or the chemical engineering as its studies had been confined chiefly for practical purposes. In other words, it has not established its own theory, from which imaginative endeavors can be evolved.

The principal reason for this retrogression lies without a doubt in the complexities in determining the reaction order with respect to the concentration of substrate, which is at least one of the important starting points to reach a overall self-consistent comprehension.

There have appeared many references concerning the reaction order, reporting zero, first, and a combination of both, since the establishment of fat hydrogenation industry. If reviewing the recent literatures appearing in J. Am. Oil Chemists' Soc.,

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*[1] Presented at the Annual Meeting of Chem. Soc. Japan, April 6, 1951.

*[2] Chiba, Japan (三宅良一, 島村芳三, 矢島 尚).

[1] R. Miyake, Y. Shimamura : Bull. Chem. Soc. Japan, **29**, 611 (1956).

a tendency to follow the consideration of the first order kinetics.[2~4] However, readers must not overlook the fact that even authors of these references do not content themselves with these results. Bailey in his book[5] expresses his firm opinion in relating the complicated fashions of kinetic order in substrate with reaction conditions.

Attention must also be given to the process of determining the reaction order. A straightforward application of an empirical formula $-dc/dt=kc^n$ has been made. In accordance with the conventional mathematical procedure, the cited examples in the present paper give approximately a unity as the value of the order (Fig. 4). Other examples having zero and various numerical orders exceeding unity will be presented in succeeding papers under the thesis of poisoning features of catalysts.

The adoption of mathematical method is a hypothetical extention of the mass law to heterogeneous reaction, due to the lack of the knowledge about the definite specificity of this system. In addition, there is an inevitable characteristic involved in heterogeneous reaction, namely, the deactivation of catalyst. The mathematical treatment, neglecting the deactivation of catalyst, might well be compared with a behavior of organic chemist who attempts to deduce a chemical structure of a substance containing impurities.

One of the simplest method as to examine whether deactivation of catalyst is accompanied, when the reaction is found to be decreasing in rate, is to measure the reaction rate by changing the initial concentration of substrate with its product. This method is, of course, the one which gives a kinetic order with respect to the concentration of substrate based on the original definition.

Unfortunately, this orthodox method in the determination of reaction order has long been ignored, because of too frequent encounters with apparent first order in substrate, which conforms with the researcher's subconscious reasonings.

The same state of affairs is seen in almost all of the liquid hydrogenation of other compounds. The present tendency in this field is to consider zero order manner in substrates as rather an extraordinary case governed by hydrogen diffusion.[6,7]

On the contrary, reviewing precisely all the references available,[*3] the reverse of the current tendency is probably valid, and if allowed to run to the extreme, only a discovery of the real unimolecular reaction with respect to the concentration of substrate will deserve a particular notice in the low temperature hydrogenation where no appreciable dehydrogenation will take place. The most doubtfulness is the acceptance of the formulation $-dc/dt=k\,P/V$,[8] as far as the volume of liquid phase (V) is concerned.

Detailed discussion on deactivation by poison will not be given until further examples are presented, but the readers will be able to predict the outline by referring to the previous paper.[1] Also, the hydrogen pressure effect will be likewise laid aside, as confusions will surely arise from it, unless self-poisoning features have been better comprehended.

[*3] As will be stated in the later section, re-examinations will suffice for the substrates involving electronegative groups, others being mostly of zero order, and short critics for crotonic acid and *p*-nitrophenol are given there.

2) L. J. Swicklik, C. A. Hollingsworth, B. F. Daubert: J. Am. Oil Chemists' Soc., **32**, 69 (1955).

3) F. A. Vandenheuvel: *Ibid.*, **33**, 347 (1956).

4) K. Nielsen, H. J. M. Hansen, V. R. Nielsen: *Ibid.*, **37**, 271 (1960).

5) A. E. Bailey: "Industrial Oil and Fat Products," 2nd Ed., 683 (1951). Interscience Publishers, Inc. New York.

6) A. A. Zinov'ev: Zhur. Priklad. Khim. (J. Applied Chem.), **23**, 99 (1950); C.A., **44**, 4320 (1950).

7) H. C. Yao, P. H. Emmett: J. Am. Chem. Soc., **81**, 4125 (1959).

8) "Advances in Catalysis" (IX), 727 (1957). Academic Press Inc., Publishers, New York.

Many formulations of rate for specific entities, however, should not be merely discarded as worthless, even if, in all the cases self-poisonings are really confirmed, because they are regarded as poisoning features demonstrated in terms of concentration of substrates, which are certainly affording some characteristic informations on poison formation and state of catalyst surface.

There is another facet of problems arising in the experiments presented here. The rate does not increase in proportion to the amount of catalyst; we intentionally avoided dealing with this problem as much as possible, since it is separable in reason from the facet of the kinetic order determination, although it is difficult to make a complete detour of this matter phenomenally. Miyake and Yajima[9] interpreted this phenomenon by introducing the idea of gas-liquid interface. According to this theory, reaction occurs exclusively in this hydrogen rich zone, to which catalysts are readily attracted. Other complicated effects on the rate such as temperature, agitation, and hydrogen pressure beside the amount of catalyst, are expected to be understood better on this theory. And also it is true that they were not able to realize the importance of the roll of this specific zone, until having confirmed the kinetic order with respect to the concentration of substrate and accumulated enough informations on the poisoning behavior of catalyst.

Experimental Results

Hydrogenations were carried out on Tsubaki oil and Finback whale oil with nickel barium sulfate catalyst at 180° under normal hydrogen pressure. Measurement of the absorbed hydrogen in the catalyst reduction and the hydrogenation reaction was conducted in the same apparatus and with the same precautions as reported in the previous papers.[1,10]

No effect of the amounts of oil on reaction rate was confirmed up to about ten grams, under 200 r.p.m. horizontal circular agitation, which were applied throughout these experiments.

The Tsubaki oil, which was obtained from Tsubaki seeds, *Thea japonica* Nois, is very similar to olive oil in all respects, having a saponification value of 193, an iodine value of 80 and contained 9.3% saturated acids (by Twitchell's lead salt alcohol method). The oil with the above characteristics should contain 87% oleic acid and 3% linoleic acid by weight. The content of linoleic acid in one gram of the oil, an amount used in the experiments, is too small to give any detectable variance in the hydrogenation rates for oleic acid, although its rate is twice as rapid as that of oleic acid.

The saturated oil used as a diluent, having iodine value below 0.1, was prepared from Tsubaki oil by hydrogenation, and was refined carefully by alkali neutralization and bleached by active clay just as in the case of Tsubaki oil, since it involves some injurious substance which was not present before hydrogenation.

The purified Finback whale oil having iodine value of 110 and saponification value of 193, was selectively hydrogenated on nickel catalyst.

The higher unsaturated acids vanish after consuming 37 ml. of hydrogen gas per gram of oil, left most of the oleic acid series acids as unsaturated acids.[1,11]

The catalyst, developed by Okada in our laboratory, was prepared by mixing a nickel sulfate solution with a barium hydroxide solution, washing the precipitate, and drying and reducing in hydrogen at 350° for 3 hours. An average of 6 ml. of hydrogen was consumed per 0.1 g. of this catalyst, which has substantially similar activity

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9) R. Miyake, H. Yajima: Actes du Deuxième Congrès International de Catalyse. Paris. 2359 (1960).
10) R. Miyake: Yakugaku Zasshi, **68**, 8 (1948).
11) *Idem*: *Ibid.*, **68**, 1 (1948).

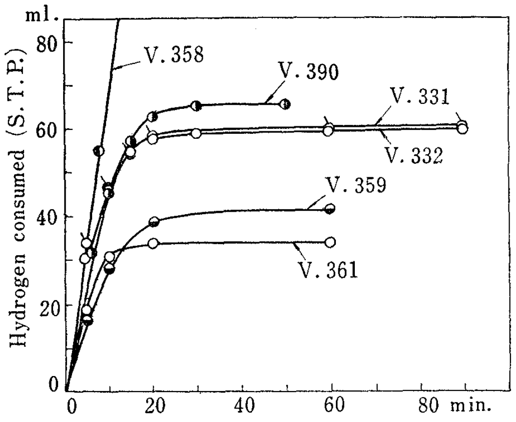

Fig. 1.

Hydrogenation rate of oleic acid in Tsubaki oil is independent of dilutions with its hydrogenated product. Initial rates remain constant when amounts of nickel barium sulfate catalyst exceed 0.1 g.

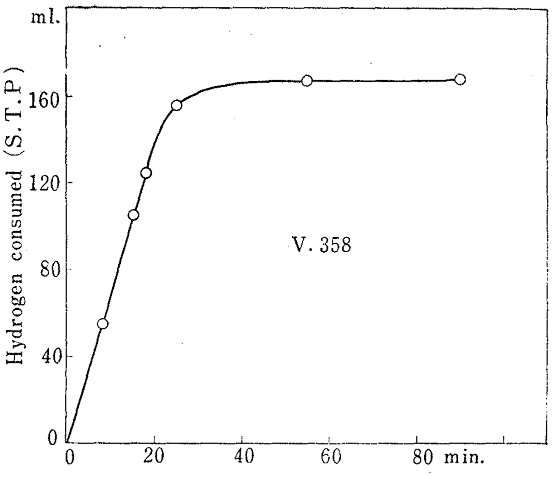

Fig. 3.

Feature of self-poisoning varies frequently with a portion of the catalyst taken even from the same stock. The rate of V. 358 was linear nearly to the end of reaction, an exemplification of prolongation of the (a-b) stage shown in Fig. 4 for V. 332.

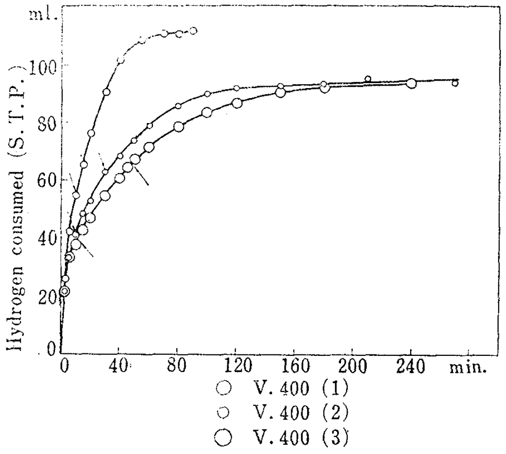

Fig. 2.

With repeated use of the catalyst in the hydrogenations of whale oil, a successive self-poisoning occurred over the whole course in the lower unsaturated acids of each run, but no appreciable degradation in the higher unsaturated acids. Heatings in a vacuum for three hours, marked by arrows, produced little effect on the subsequent rates.

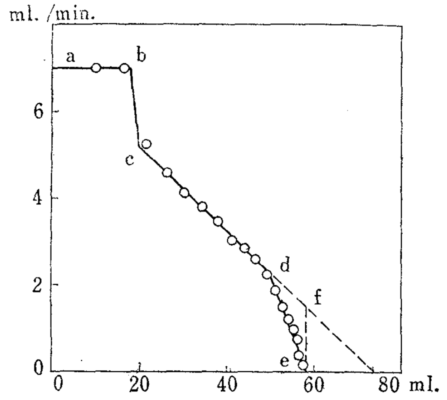

Fig. 4.

dx/dt-x relation for run V. 332. An expression of self-poisoning of catalyst.[1] a-b: a linear portion. c-d: a portion which can be expressed by the typical poisoning equation $dx/dt = k_1(N_0 - k_2x)$, where k_1N_0 and k_1k_2 are estimated to be 7.068 ml./min. and 0.09594 min^{-1} respectively. Formally the whole course may be expressed by the first order formulation; $2.303 \log(60.20 - x) = -0.1448t + 4.1086$.

TABLE I.

Run No.	Catalyst (g.) (before reduction)	Tsubaki oil (g.)	Completely hydrogenated Tsubaki oil (g.)
V. 331	0.1222	0.8567	1.069
V. 332	0.1125	0.8193	1.910
V. 359	0.0556	0.6026	1.020[a]
V. 361	0.0548	0.4942	
V. 390	0.1082	0.9443	
V. 358	0.2668	2.5400	

a) used without purification after separation of catalyst.

TABLE II.

Run No.	Catalyst (g.) (before reduction)	Finback whale oil (g.)
V. 400 (1)	0. 0701	1. 1440
V. 400 (2)		0. 9733
V. 400 (3)		0. 9870

and function as the usual nickel kieselguhr catalyst in this reaction. The reduced catalyst was used without exposing to air.

Hydrogenation was made with 10 per cent of catalyst at 180° under atmospheric pressure. Tsubaki oil was diluted down to one third with its completely hydrogenated product and hyrogenation rates were compared in two series, using 0.1 g. and 0.05 g. of catalyst respectively (Fig. 1). Similar experiments were done with Finback whale oil, but the catalyst was used in succession for the three times by suppiying new oil after completion of each run (Fig. 2, Table I).

Oil and catalyst were subjected to heat treatment for three hours several times, by evacuating the whole assembly during hydrogenation of whale oil, other conditions being unchanged (Fig. 2).

Dilutions evidently did not substantially affect the rate throughout the reaction course with the Tsubaki oil, and also with the portion of higher unsaturated acids of whale oil for the first 36 ml. of hydrogen consumption.

Reaction rates, however, decreased to a considerable degree especially toward the end of each run in Tsubaki oil series, and similarily in the lower unsaturated acids of whale oil which corresponds practically to Tsubaki oil so far as the hydrogenation manner is concerned. The rate, however, became slower than the preceding one as a whole, as would be expected from the repeated use of the catalyst. This is one of the typical form of deactivation of catalyst on repeated use. Comparable experiments with Tsubaki oil and others were omitted though.

V. 358 is introduced as an example following a linearity almost over the entire range (Fig. 1 and 3). A rare case for 10 per cent of this catalyst, in which oil was weighted 2.5 g. greater than other instances, but this linearity could not be attributed to the difference of oil quantity, because the other cases under the identical conditions gave ordinary curved results.

Features of decreasing rate could not be insured to reproduce even with a portion taken from the same stock of catalyst, while the initial rate is rather easily kept uniform for a fixed amount of catalyst.

General attitude of decreasing rate is a slight curvature at the beginning, becoming greater as it approaches the end, that is, in most cases, a straight line reveals itself at the very start of each run (Fig. 4). The range of linearity tends to prolong as the percentage of catalyst is increased.

To summarize, hydrogenation proceeds mostly in a curved, with a straight line appearing in the initial stage and extending longer or shorter according to the nature of catalyst. The catalyst is difficult to be controlled and the rate cannot be connected directly to the concentration of the unsaturated acids.

No deterioration of the oil or the catalyst was incurred by simple agitating and heating to 180°.

Rate of hydrogenation increased with increase in the amount of catalyst between 0.05 to 0.1 g., but no changes occurred between 0.1 to 0.25 g. The upper limit was observed with the oleic acid ester. The total volnme of liquid did not affect the rate between 0.5 to 3 g., as had been shown in a test utilizing up to about 10 g. of oil.

Discussion

1. Kinetic Order with Respect to Substrates and Establishment of Adsorption Equilibrium

Discussion will be made principally on oleic acid hydrogenation in order to tackle the problem of independency of rate on the concentration of substrate and only minor comments to the associated problems obtained in the expeiments. This conventional restriction on oleic acid will vanish when all the other factors are fully discussed in the subsequent notes.

The experimental results with Tsubaki oil diluted with its hydrogenated product imply that this is a zero order with respect to the hydrogen acceptors accoording to classical kinetics, in spite of the fact that reaction rates are not linear.

General expressions for diffusion of liquid species are directly induced from zero order dependence of liquid reactants : any steps described as mass transfer are not controlling the reaction, for all these steps evidently depend on bulk concentration, here diffusions in liquid phase, through solid-liquid interface and on the surface of solid being implied.

It is in accord with a kinetic criterion on the occurrence of selective hydrogenation with Finback whale oil, in which the higher unsaturated acids are preferentially hydrogenated in the presence of the lower unsaturated acids irrespective of the quantities of the latter.

As for hydrogen diffusion, the same conclusion should be arrived at, in view of its mass of the lightest. When the hydrogen absorption rate reaches a limiting rate by the increase in the amount of catalyst, as encountered in the experiments with oleic acid, one is apt to consider it as the arrival of the limitation of dissolution velocity of hydrogen on the liquid surface, and no one seem to doubt this concept. But this in itself is hardly acceptable, since the dissolution rate of hydrogen will control the overall process only when the reaction on the catalyst is considerably faster than any diffusional steps. On the contrary, the hydrogenation is the slowest step compared with diffusion processes even in a non-agitational condition.[12] Furthermore, there is no theoretical foundation that the rate of hydrogen dissolution on the surface of the oil is slower than the diffusion rates of gas and liquid molecules in the bulk.

An added remark is that the upper limiting rate is specific for a certain combination of oil and catalyst with other factors being constant, otherwise, the comparison of readiness to hydrogenation of many organic substances and the test of the activity of catalysts described in the past references would not be succeeded first of all and become unreliable, as most of the studies were performed with sufficient amounts of catalyst.

For the present, convincing experimental evidences will be given to advance this discussion : A larger consumption of hydrogen than that of the upper limiting rate for oleic acid ester is observable, by merely replacing the nickel catalyst with the more active catalysts such as platinum. The limiting rate is about 1 ml./min. for Cu-Cr-O catalyst in whale oil,[1] while under the comparable conditions V. 400 gave 10 ml./min. of rate with nickel catalyst.

At any rate under the conditions used in this work, the controlling step is the catalysis, thus, an equilibrium concerning adsorption of reactants and resultants on catalyst was conclusively established.

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[12] R. Miyake, H. Yajima : Yakugaku Zasshi, 85, 618 (1965). Outline was presented at the 17th Annual Meeting of Chem. Soc. Japan, Apr. 2 (1964).

2. Poisoning as a Main Factor Influencing Change in Reaction Rate

The above conclusion is in accord with the general view that catalyst should be put in the slowest step of reaction. The activity of catalyst is a key on which reaction rate sensibly depends, therefore, the reduction in catalytic activity is only the considerable factor decreasing the reaction rate.

At the same time, as a cause of dropping rate, it is natural to be sought also in the change in the constitution of the substrate. because the isomerized oleic acids (iso-oleic acids) are known to be produced invariably during hydrogenation. Its production is not small, but its proportion to oleic acid is ordinarily maintained almost constant throughout the reaction.

It can be demonstrated that the rate of isomerization is very rapid when compared to hydrogenation rate, and the hydrogenation rates of iso- and normal-oleic acids do not differ to a great degree. Coincidence with this conclusion in many references[13] is supported also by the linear rate of V. 358 (Fig. 3).

A catalyst gradually loses its activity by the unavoidable sintering and self-poisoning in the long run.

Sintering is largely promoted by heating, a part of which being evolved in the exothermic reaction. In the runs of short duration, however, such a permanent deterioration seems not to be so predominately extensive, for which an evidence are being given by the hydrogenation of whale oil (V. 400) : rates fell off to a great extent and successively in repeated runs, to be true, in lowered unsaturated acids, but they recovered their activities almost completely on the next addition of higher unsaturated acids.

This is predictable from two standpoints, namely, the nickel catalyst has already been exposed to a temperature higher than 350° in the reduction of nikel oxide, and even the copper catalyst, whose melting point being lower than that of nickel, proved to be eliminated from sintering effect, regardless of its low temperature reduction at 180°.[1]

Before entering upon the problem of self-poisoning, some remarks should be made of impurities occurring in the original oils. Those probably are phosphatides, oxidation products and other degradation products of oil. Free fatty acid is sometimes mentioned as being a hazard, which was found true in the case of the Cu-Cr-O catalyst, nevertheless an addition of stearic acid in quite a large amount gave no appreciable problem to our nickel catalyst. Purification with an active bleaching clay after alkali refining is insured to remove any of those common oil-bearing impurities.

Of the above impurities, oxidation product generally designated as peroxide, is of a decisive character to halt hydrogenation. Peroxide is not only drastic in its effect but is difficult to be desorbed from the catalyst, that it is proper to designate it as a permanent poison for the procedure used in this study. Peroxide is yielded even in the carefully conducted ordinary refining process, due to the inevitable exposure to air, and its formation is accelerated in highly unsaturated oil like whale oil. However, oils tested were clean enough to satisfying our purpose. If the purification of oil were insufficient, to the contrary of the fact, successive additions of oil would have caused a damaging influence upon the following hydrogenation rate in V. 400.

Gradual lowering of rate, therefore, has to seek its source in production of some material possessing a moderate adsorbing affinity toward catalyst, such as to be removable from catalysing point either by washing with ether[1] or with addition of unsaturated oil as seen in the whale oil hydrogenation (V. 400). It is obviously adsorbed

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[13] A. E. Bailey : "Industrial Oil and Fat Products", 2nd Ed., 691 (1951). Interscience Publishers, Inc., New York.

in competetion with unsaturated compounds for the catalyst, accordingly it may be termed as temporary and reversible poison. It should be remembered that there has been a thought of recovering the used catalysts by washing with unsaturated oils.[4,14]

The poison in question must be a saturated substance, formed during hydrogenation, present in a minor quantity, as reaction proceeds almost quantitatively, and it is assumed to possess a larger molecular weight than the original fat judging from its relatively strong affinity to catalyst.

As for the removal of this reversible poisonous substances, it is effectively conducted in the preparation of the diluent in our study by alkali refining when in combination of active clay treatment. A mere application of the latter process does not ensure its accomplishment, effective is supposingly an occlusion of poison in soap. In conclusion, this should be some products arising from polymerization reaction.

Unsaturated fats, when subjected to heat treatment, undergo somewhat polymerization, which may incidentally developed by the presence of catalyst. At 180°, however, this unfavorable conversion is too small, it is confirmed by the experiment of heating oil and catalyst in a vacuum causing no drop of the subsequent rate after 3 hours heating, which is long enough to render hydrogenation rate to drop, if hydrogen were admitted. Neither were there any observed improvements of rate, thus an evidence for the absence of volatile poison is furnished at the same time (Fig. 2).

There is, however, formation of some volatile poisonous substance, which is found especially in the early stage of hydrogenation, reaction rate is frequently improved at the very first of evacuation, this is operated several times during reaction in need of supplying hydrogen. The source of volatile poison may be a pre-oxidized state of original fat, which will readily be decomposed at the start of hydrogenation operation.

The above result of simple heat treatments is the correspondence to the negligence of a term of hydrogenation duration in the poisoning equation.[1]

In any event the formation of the poison necessitates the existence of three components, hydrogen, olefinic compound and catalyst, it is concluded eventually one of the side reactions in hydrogenation.

Concerning the self-poisoning in the hydrogenation, it has been mentioned in no rare cases even with gaseous olefines, such as ethylene,[15] propylene,[16] isobutylene,[17] and 1-butene.[18] And at the same time, polymerization products were isolated in the hydrogenation of ethylene.[19],[20] These two side reactions are presumably in a close relation.

Turning aside from the catalytic functions of metal, the action of hydrogen atoms produced thermally, photochemically, or from an electric discharge, there occurs a polymerization of ethylene and its homologues[21] and unsaturated compounds including acids to a great extent simultaneously with occurring hydrogenation.[22]

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14) K. Omiya : Japan. Pat. No. 39805 (1921).
15) G. Matsuzaki : Shokubai, **1**, 22 (1959).
16) O. Toyama : The Review of Phys. Chem. Japan, **14**, 88 (1940).
17) R. Kiyama : *Ibid.*, **15**, 137 (1941).
18) R. Amemiya : Shokubai, **2**, 1 (1960).
19) K. Morikawa : N.R. Trenner, H.S. Taylor : J. Am. Chem. Soc., **59**, 1103 (1937).
20) O. Beeck : Discussions Faraday Society, 8, 121 (1950).
21) A.R. Olson, C.H. Meyers : J. Am. Chem. Soc., **49**, 3131 (1927); R. Klein, M.D. Scheer, R. Kelley : J. Phys. Chem., **68**, 598 (1964).
22) C. Ellis: "Hydrogenation of Organic substances." 3rd Ed., 22, 184, 866 (1930). D. Van Nostrand Co., Inc., New York; H.I. Waterman, C. Boelhouwer, L. J. Revallier : "Hydrogenation of fatty oils," 241 (1951). Elsevier Publishing Co., New York.

This series of events suggest the dissociation of hydrogen molecules occurring on the catalyst surface, but the resulting hydrogen atoms seem rather unfavorable to the hydrogenation.

Although questionable, the existence of perfectly dissociated atomic hydrogen must be presumed, at least a production of the half dissociated state of hydrogen molecule during hydrogenation, in view of the occurring transformation as follows, exchange reactions of ethylene and butylene with deuterium,[23] isomerization from *cis*-double bond to *trans*-double bond involving migration of double bond,[13] and in deuterogenation on platinum methyl oleate was converted to light methyl elaidate.[24]

This hydrogen molecule featured as radical-like state will promote most probably a formation of a radical olefine,from which polymerization supposedly will be further induced in addition to the above mentioned transformations.

The extension of polymerization in this way will possibly be enhanced by the stabilization of this radically featured or radical olefine, and negative function of carboxlic group linked with the olefines are expected to stabilize its radical state, in the similar way as nitro- or carbonyl compounds.

It is interesting to indicate that the grave problem in determining the kinetic order with respect to the substrates are always confronted with those having electronegative groups in their constitutions.

Actually a deep red polymeric oil was produced in the reduction of 2-nitro-1-butene in glacial acid over Adams' platinum catalyst besides saturated amine,[25] and this polymer is seemingly inhibitory, as reduction stopped at only about 10 per cent of theoretical saturation.

While in simple olefines, cyclic or non-cyclic, and aromatic compounds, zero order kinetics are immediately established by a linear manner of hydrogenation.[8,26~29]

This is only a rough trend, and linearities with those having negative groups have also been reported at the same time.[30,31] For instance, with *p*-nitrophenol it was reported[7] as behaving miscellaneous kinetics completely similar to fat hydrogenation, but the independency of rate was confirmed on dilution with its hydrogenated product, as was done in fat hydrogenation[32].

One will recognize from the references that hydrogenation using much catalyst unexceptionally follows a linear process, even with electronegative groups involving compounds in which the excess catalyst should be regarded as an adsorbent of poison. Indeed, charcoal, and active clay were found on their addition recovering the lowered rate to some degree.[32]

The intermediate type are frequently reported, linearites in the first half being followed by declining rate in the second half.[26~31] On closely tracing the hydrogenation, Tsubaki oil (Fig. 4) shows itself of this type, detailed formulation of which will be opened in a serial paper.

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23) J.N. Wilson, J.W. Otvos, D.P. Stevenson, A.D. Wagner: Ind. Eng. Chem., **45**, 1480 (1953).
24) J.H. Baxendale, E. Warhurst: Trans. Faraday Soc., **36**, 1186 (1940).
25) H.A. Smith, W.C. Bedoit Jr.: J. Phys. Colloid Chem., **55**, 1089 (1951).
26) R.H. Price, D.B. Schiewetz: Ind. Eng. Chem., **49**, 807 (1957).
27) S.V. Lebedev, G.G. Koblianskii, A.C. Yakubchik: J. Chem. Soc., **1925**, 418.
28) G. Gilman, G. Cohn: "Advances in Catalysis" (K). loc. cit., 733.
29) H.A. Smith, H.T. Meriwether: J. Am. Chem. Soc., **71**, 413 (1949).
30) S.S. Scholnik, J.R. Reasenberg, E. Lieber, G.B.L. Smith: *Ibid.*, **63**, 1192 (1941).
31) H.A. Smith: "Catalysis" Vol. 3 edited by P.H. Emmett, 149 (1955), Reinhold Publishing Corporation, New York.
32) R. Miyake, H. Yajima: Yakugaku Zasshi, 85, 618 (1965).

To the end of this paragrph, all the liquid hydrogenations are to be reexamined from the view of self-poisoning of catalyst as previously reasoned from the standpoint of kinetics.

3. Consideration on the Independency of Rate in Regards to Substrate Concentration

Rate determining in fat hydrogenation is in consequence the pursuit of poisoning of catalytic surface and the adsorption ot referring substances in the broad sense.

To exclude the poisoning, zero order behavior with respect to substrate is one of the characteristics of liquid hydrogenation. The final section will be devoted to general consideration on this problem. The authors try to approach the subject from a number of different angles and works reported in the literature, the selection of materials being somewhat arbitrary.

To those concerned with subject pertaining to liquid hydrogenation, this independency of rate on substrate can be considered more or less a complex problem.

3a. Distribution of Reaction Species on Catalyst

Experiments on ethylene hydrogenation give zero order on ethylene under its excess pressure compared with hydrogen pressure and it is ensured especially at low temperature.[33] The situation of liquid hydrogenation with olefines and benzene homologue may be accepted with easiness by analogy, if regarded as that of ethylene in extreme state of high pressures and low temperatures. The reduction of nitro-compounds and aldehydes is to be lined in the same scope for their identical behavior.

Classical kinetic consideration will immediately indicate an overwhelmingly strong adsorption characteristic of oleic acid, after establishing its zero order kinetics. But it is not unconditionally realizable in general. It is more natural to postulate the adsorption equilibrium on catalyst with every species in liquid bulk. In view of the formation of iso-oleic acids, adsorption of hydrogen is of significance. Adsorption of stearic acid ester cannot be ignored in an admittance of hydrogen adsorption, considering its molecular weight and concentrations is liquid phase.

A concept of likeness must be advanced in the case of selective hydrogenation of whale oil, adsorption of the lower unsaturated acid should be occurring even in the preferential hydrogenation of the higher unsaturated acids. In this case, the concurrent adsorptions of the higher and lower unsaturated acids are evident, as the application of high pressure of hydrogen causes failure of seleectivity.[34]

With copper catalyst, the above situation will be more clearly demonstrated. Under atmospheric pressure and temperature below 180°, it hydrogenates exclusively higher unsaturated acids with the lower unsaturated acids remaining unaltered, but it does not guarantee delation of adsorption of the lower unsaturated acids, because the latter is subjected to saturation above 200°.[35] Furthermore, if applied high temperatures and pressures, saturation of double bonds and reduction of carboxylic radical occur simultaneously to produce corresponding saturated alcohol, where preferential reduction of carboxylic sadical to corresponding olefinic alcohol has been achieved with no success. With nickel catalyst, the reaction is more drastic to result in producing hydrocarbons.[36] It seems to provide the information that all the species in liquid bulk should be adsorbed on copper and nickel catalyst.

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33) H. Eyring, C.B. Colburn, B.J. Zwolinski: Discussions Faraday Society, 8, 43 (1950).

34) A.E. Bailey: "Industrial Oil and Fat Products," 2nd Ed., 704 (1951). Interscience Publishers, Inc., New York.

35) Y. Shimamura, R. Miyake: Yakugaku Zasshi, 84, 516 (1964).

36) A.E. Bailey: "Industrial Oli and Fat Products," 2nd Ed., 762 (1951). Interscience Publishers, Inc., New York.

3b. Limiting Use of the Langmuir-Hinshelwood Hypothesis

In the present instances, therefore, concurrent adsorption of all the species is naturally to be considered for the whole surface of nickel. The following adsorption, taking the Langmuir isotherm for convenience of illustration, can be formulated, provided its surface is uniform.

$$\theta_E = \frac{k_E(E)}{1+k_E(E)+k_S(S)+k_H(H)} \qquad (1)$$

where species placed in brackets refer to their concentrations in liquid phase: E, S, and H, are ethylenic compound, saturated compound, and hydrogen molecule respectively.

According to the Langmuir-Hinshelwood hypothesis, accountable for many of the data for catalytic reaction of gas phase, rate (V) is proportional to the product of the fractions (θ) for hydrogen and ethylenic compound.

$$V \propto \theta_H \theta_E \qquad (2)$$

The idea is nothing but a suitable modification of the mass product law in homogeneous reaction. Correspondingly, the traditional explanation of decreasing rate in term of the change in bulk concentration of oleic acid ester is not necessarily itself unreasonable.

An important clue, however, to approach the catalysis is to be sought in this apparent discontinuity between the natural course of thinking and the experimental results.

Equation (1) is derived from the assumption that nickel catalyst consists of uniform surface. On the contrary, surface of nickel catayst used practically is by not means considered uniform, apart here from barium sulfate, a carrier, which reasonably can be put out of consideration because of its intrinsically inert character.

H. S. Taylor assigned some sensitive area for reaction to an active center, differing from other inactive part with many experimental evidences by using gaseous materials.

Positive evidences for active center theory can also be presented in liquid phase hydrogenation. It is considered that active area is confined in extremely small portion in common catalysts.

Acetic acid has been recommended for a long time as one of the best solvents, in which benzene is well hydrogenated on platinum[29] and rhodium,[28] following zero order, thus benzene may be taken adsorbed strongly in classical consideration. While carrying out the adsorption experiment on metal catalyst, materials to be adsorbed at this time are fatty acids, and benzene as solvent, since the latter is adsorbed in negligibly small amount.[37] To compute the surface of nickel is best done by means of higher fatty acids in benzene.[37] Okada, recently in our laboratory, confirmed acetic acid is adsorbed as much as other fatty acids on Raney nickel, and he also gave comparable hydrogenation rates as zero order with crotonic acid and its ester on Raney nickl in alcoholic solution, while finding the expected results of adsorption in alcohol for acid and ester.

In connection with Okada's data, it is interesting to mention that the rate of consumption of hydrogen was of zero order up to 90 per cent of oleic acid in acetic acid and acetic anhydride with platinum-barium sulfate-catalyst.[38]

Active area might as well have a specific adsorption favoring double bond. As a whole, each species, giving their respective distribution pattern throughout the nickel surface, will establish a statistical distribution in term of adsorption potential.

Hence, a modification must be made for adsorption pattern in active portion, where adsorption coefficient k_E for olefinic compound is supposed to be exceedingly greater than that for other species, namely, $k_E \gg k_S + k_H$.

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[37] H. A. Smith, J. F. Fuzek: J. Am. Chem. Soc., **68**, 229 (1946).

[38] V. I. Gol'danskii, S. Yu. Elovich: J. Phys. Chem. (U. S. S. R.), **20**, 1085 (1946), C. A., **41**, 2973 (1947).

Equation (1), corresponding to the active portion, reduces to

$$\theta_E = \frac{k_E(E)}{1+k_E(E)} \tag{3}$$

For other patch in the active portion most favoring hydrogen, in the similar way,

$$\theta_H = \frac{k_H(H)}{1+k_H(H)} \tag{4}$$

And the rate may be expressed by the product of fractions, provided reaction occurs on a overlapping of distribution portions regarding the two species.

$$V \propto \frac{k_E(E)}{1+k_E(E)} \times \frac{k_H(H)}{1+k_H(H)} \tag{5}$$

Since the surface is in contact with liquid phase, a further modification is allowed to exercise such that $k_E(E) \gg 1$ in the equation (5), then the velocity becomes independent of the concentration of unsaturated acid, It apparently illustrates the present result, and the kinetic concept of strong adsorption concerning oleic acid ester will be approved, if the account is limited within active portions. Equation (5) is given in ethylene hydrogenation,[39] but a differential consideration between the active and inactive portions are not taken in.

An additional criterion will be made here about active portion. It is restricted not only to a small area, but its capacity for functioning of hydrogenation seems to be under some restriction. Rates of hydrogenation were identical, whether glyceride or ethylester of oleic acid was used, the bulky glyceride rest does not interfere an approach of double bond to active point. It is a specific place best disposed to hydrogenation of double bond and is not connected with ester structures.

According to the present theory of distribution patterns, adsorption distribution for poison should be located different from the active portions, and an actual poisoning will reveal only after the saturation of this specific area by poison. The linear portion may be proportional to the capacity for accomodating poison, and the large range of linear portion in the catalyst used in V. 358 will be attributed to its large capacity of poison adsorption. There is a trend that a rather low active catalyst possesses the large capacity to be proof against poisoning. We have not suceeded in controlling the proportion of distribution patterns.

3c. Local Mobility of Molecules Adsorbed

Hitherto, discussion, dealing solely with the line of rearrangement of molecules between two phases of liquid and solid, leaves the mobility of molecules untouched after the occurrence of their adsorption, however, suggestions for which have been seemingly provided from liquid and gas hydrogenations.

Selective hydrogenation achieved fairly well under low pressure of hydrogen on nickel catalyst, as shown in whale oil experiment, is injured by an application of high pressure.[34] The simultaneous hydrogenation of higher and lower unsaturated acids observed under high pressures indicates that all the unsaturated acids are being co-adsorbed on the active portion of nickel catalyst irrespective of hydrogen pressures.

An adsorption pattern in the active portion will be described in a similar way of equation (3) and (4).

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39) D. D. Eley: "Catalysis" Vol. 3 edited by P. H. Emmett, 50 (1955), Reinhold Publishing Corporation, New York.

$$\theta_L = \frac{k_L(L)}{1 + k_L(L) + k_O(O)}$$

$$\theta_O = \frac{k_O(O)}{1 + k_L(L) + k_O(O)}$$

where linoleic acid (L) is assigned as the representative of higher unsaturated acids, and oleic acid as one of lower unsaturated acids. An appropriate mathematical treatment will permit these relations to accomplish a velocity expression after the fashion of deriving equation (5), so as to be compatible with the experimental result for a certain condition.

At any rate, it must be madé in this treatment an assumption involving a preferential attraction of hydrogen to linoleic acid, and this assumption appears to illustrate various experimental results under varied conditions.

In the active portion, where a finite number of hydrogen adsorbed, will all hydrogen be attracted to linoleic acid to give a hypothetical couple of them on active nickel atoms, so that the selective hyd rogenation will be retained until concentration of linoleic acid becomes less than that of hydrogen, and a comparable relation will be realized in the application of high hydrogen pressure.

After completion of partial hydrogenation of linoleic acid to oleic acid, the hydrogen will be coupled in the same way with oleic acid preferentially than with stearic acid to establish zero order kinetics, even if the concentration of oleic acid decreases on the increase of stearic acid in the active portion.

There is a misunderstanding about selective hydrogenation, this is not a matter of difference in rate of individual species. A rate of linoleic acid was about twice as rapid as that of oleic acid on nickel catalyst at 180° under atmospheric pressure,[32] but the reverse is true in the selective hydrogenation of acetylene, in which its rate is slower than that of ethylene on nickel at some reaction conditions.[20]

An acceptance of the hypothesis of mobility explains in the same manner the kinetics of ethylene at low temperatures. Here it must be recalled of the actual occurrence in the usual experiments undertaken in a constant volume, that is, pressure lowerings of ethylene and hydrogen follow simultaneously.

Rate will be controlled only by a decreasing velocity of the lower concentration species, when assumed it is used up on catalyst after pairing with the excess species, whatever the amount of the latter may be varied. In case the hydrogen is small in amount, for instance, then the rate must remain independent of decreasing ethylene pressure in accordance with experimental results.

3d. Restriction on Mobility

It seems, however, necessary to lay down some restriction on the extent of mobility on catalyst, in excercising this hypothesis of mobility further to the case of hydrogenation with ethylene at high temperatures.

Rate becomes influenced by partial pressures of hydrogen and ethylene on risng reaction temperatures or decreasing each partial pressure to a great degree. Under these circumstances, adsorptions decrease and the distance between adsorbed molecules will increase accordingly.

In this instance, allowed to make an additional postulation of localized mobility, the result is that a coupling of two species may be given by an opportunity to encounter both reactants. At the same time, the extent of mobility is certainly increased at high temperatures, but this effect seems unable to overcome the opposing trend of increasing separation. Thus the chance for hydrogen and ethylene to pair may be in proportion to the product of their concentrations, one of this expression being equation (5).

Therefore, liquid hydrogenation is theoretically predicted to also appear itself as first order with respect to substrate, when its concentration decreases lower than that of hydrogen, however, under atmospheric pressure it will not be realized in a practical sense.

The restricted mobility might as well be considered alternatively as a lateral extension of influence of one species adsorbed to the neighboring species on catalyst. Whatever the real character of localized mobility may be, a solid concept of non-mobility must be modified considering general case.

The weakness involved in the non-mobility will also be pointed out from the following contemplations. In this case, assuming the strong tendency toward pairing, hydrogen and ethylene are brought together only through repeatedly quick hitting from gas phase and bouncing off the surface, which will always cause independent rate on the species of lower partial pressure, irrespective of their concentrations on surface. And if completely ignored the existence of tendency to bring about pairing, a primary controlling factor will be the chance of collision on the surface between both reactants from gas phase, then it is difficult to interprete the occurrence of zero order in either species at low temperatures, because of ensuing steady decrease in partial pressures of the two in the mean time.

Same with the liquid phase hydrogenation, and moreover the selective hydrogenation could not be interpreted.

3e. Intermediate Complex Compound Formation

The final subject is to give any possible suggestion on reasoning for the tendency of hydrogen to approach the high unsaturated acid than to low unsaturated acid on the catalyst surface, to outcome ultimately the selective hydrogenation. Namely, it is on the threshold to realize the occurrence of catalytic reaction.

Nickel atoms constituting the active portion must have a special affinity to double bond, accordingly if any resultant arises from this affinity, it will be a kind of simulated chemical linkage between nickel and double bond. Hydrogen may also have the similar relation with nickel atom.

To give riso to hydrogenation these two quasi compounds must be brought into a close connection, namely it is to construct a pertinent transtional state. As a start of reaction, a concept of complex for the transitional state will be postulated, consisted of three components in a way that hydrogen and double bond being centered on a nickel atom. The central nickel atom is surrounded on the other hand by neighboring nickel atoms, thus, this transitional complex is consequently made up with two ligands of hydrogen and ethylenic compound and several atoms of nickel neighboring the central nickel atom.

The active portion is supposingly such a place where a certain number of nickel atom could participate in the formation of this kind of complex, which, if followed by an intramolecular rearrangement so as to bring hydrogen close to double bond, will finally give rise to addition of hydrogen to double bond.

A complex is generally stabilized by replacing one of the ligands by another ligand which more firmly coordinates the central metal atom,[40] probably due to a resonance, in term of quantum mechanics, working to reduce all the coordination energies to uniformity as much as possible.

In these premises, let us consider two complexes, oleic acid-nickel-hydrogen and linoleic acid-nickel-hydrogen, then the hydrogen linkage of the latter should be stronger

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[40] R. Tsuchida : "Colours and Structures of the Metallic Compounds." 142 (1944). Zoshindo, Osaka, Japan. H. J. Taufen, M. J. Murray, F. F. Cleveland : J. Am. Chem. Soc., 63, 3500 (1941).

of the two, as the doubly unsaturated linoleic acid will be coordinated more firmly with nickel atom in active areas.

Correspondingly there arises a trend of hydrogen shifiting to the more stable complex of linoleic acid-nickel-hydrogen in an equilibrium between the two complexes. The equilibrium will govern the selectivity in conformity with the variation of linoleic acid content.

To summarize the above relationships, inasmuch as the ratio of the specific reaction rates for linoleic and olcic acids is valued as approxinately two, the degree of selective hydrogenation shown by Bailey as 38,[41] which though modified here as 38/2 by taking the hydrogenation rate ratio into consideration, will correspond to so-called an equilibrium constant for the above imaginary complexes.

A formation of quasi-complex may evidently be the prerequisite for the interaction between hydrogen and unsaturated compound, but if the constitution of it is too stable to pass into the succeeding transformation, the hydrogenation rate will be rather retarded. The acetylene hydrogenation may be considered such a case, although the formation of the quasi-complex is preferred, its hydrogenation velocity becomes slower than that of ethylene.

Some additional notices concerning the quasi-complex assumption will be given, rather to invoke some interesting connection with catalytic reactions.

It is interesting to refer that transition elements capable of constituting a great deal typical coordinated compounds are also catalyzing a great diversity of reaction, platinum group, iron group, and copper show themselves specific in both fields.

Carriers at the same time may take a part of ligand as well as surrounding metal atoms, the following may be taken as adequate examples, polyvinyl alcohol and related polymers developed by Nord,[42] these are applied as carriers for noble metals.

Even inorganic materials appear to function as ligands for the central metal atom: kieselguhr seems to enter a molecular arrangement with nickel oxide, because in hydrogen the most difficultly reduced was the mixture of equal weight ratio, although no specificity in hydrogenation rate of fat was found among mixtures of other ratios,[43] the roll of carriers is decisive for copper catalyst in the hydrogenation of higher unsaturated fat; copper alone showed no hydrogenation ability under atmospheric pressure, strikingly differing from nickel catalyst, accordingly such an idea is induced that the active portion for this reaction may be located along the boundary between copper and carriers.

Acknowledgement of the self-poisoning and the independency of rate on the bulk concentration of substrate will surely render liquid hydrogenation progress in a newly systematic and steady way of thinking, with a hope to give stimulations to the studies on various domain of science concerned.

One of these is the analysis of the feature of self-poisoning. If one makes an intentional inspection of the countless past reports on hydrogenation of liquid substances, they will be found as one of the way, through which the real matters of catalyst and catalysis will be approached.

To follow this work, it is understandable that a serial study of Maxted and his collaborators on poisoning of catalyst with addition of artificial injurious materials is indispensable for the study of the basic state of affairs. It is felt necessary, however, to modify the expressions made by the original authors in a general fashion into a more practical form, before referring their results to the self-poisoning in hydrogenations,

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[41] A. E. Bailey: J. Am. Oil Chem. Soc., **26**, 644 (1949).

[42] K. E. Kavanagh, F. F. Nord: J. Am. Chem. Soc., **65**, 2121 (1943).

[43] H. Yajima: unpublished.

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.

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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.

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

[*2] Oe-machi, Kumamoto (田中由紀子, 田中善正).

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