BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 4—8 (1973)

The Isomerization of Propylene Oxide on Metal Oxides and Silica-Magnesia Catalysts

Yasuaki OKAMOTO, Toshinobu IMANAKA, and Shiichiro TERANISHI
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka

(Received December 6, 1971)

The isomerization of propylene oxide was carried out over silica-magnesia catalysts and metal oxides at 260—270°C using a pulse reactor. The main products of the reaction were propionaldehyde, acetone, allyl alcohol, 1-propanol, and acrolein. Propionaldehyde and acetone are produced on acidic and basic sites respectively. Allyl alcohol is formed over acid-base bifunctional catalysts. 1-Propanol and acrolein are mainly produced through hydrogen-transfer reactions between allyl alcohol and propionaldehyde and propylene oxide. As regards these reactions, acid-base bifunctional catalysts are favorable and the reaction rate depends on the electron-donating power of the hydrogen acceptor and the basic strength of the catalyst. The acid sites on silica-magnesia catalysts are attributed to the forsterite produced by the reaction of magnesium oxide and silica gel, and the basic sites, to the magnesium oxide remaining. The metal oxides, such as magnesium and calcium oxides, are considered to have very weak acid sites.

The activities and selectivities of a reaction on solid acids and bases are determined by studying their acidic and basic properties. It is important to clarify the relations between them. In our preceding papers,[1,2] it was found that the activities and selectivities of propylene oxide isomerization on zeolite catalysts and metal phosphates could be elucidated by the acidic and basic properties of catalysts.

According to Niiyama and his co-workers,[3] silica-magnesia catalysts prepared from magnesium hydroxide and silica gel by calcination at 600°C have acid and basic sites. In the present investigation, propylene oxide isomerization was carried out on silica-magnesia and metal oxide catalysts in order to confirm the proposed mechanisms of the reaction and the relationships between the selectivities and acidic and basic characters of the solid acids and bases. In the cases of zeolites[1] and metal phosphates,[2] the main products were acetone, propionaldehyde, and allyl alcohol. However, it was found that silica-magnesia and metal oxides produce considerable 1-propanol, the hydrogenated compounds of allyl alcohol, propionaldehyde, and propylene oxide. The reaction steps of 1-propanol formation are discussed. Moreover, the production mechanism of the acidic and basic properties of silica-magnesia catalysts was deduced from the results of X-ray diffraction.

Experimental

Materials. Silica-magnesia catalysts with different compositions were prepared as follows. Silica gel (Nakarai Chemicals, Ltd.; Silica gel No. III 200 mesh) and magnesium hydroxide (Wako Pure Chemical Industries, Ltd.) were mixed in water at 90°C for 12 hr, filtered, and calcined at 600°C for 6 hr in air. The compositions of the silica-magnesia catalysts used in our experiments were 0, 34, 51, 67, 76, and

---

[1] T. Imanaka, Y. Okamoto, and S. Teranishi, This Bulletin, **45**, 3215 (1972).

[2] T. Imanaka, Y. Okamoto, and S. Teranishi, *ibid.*, **45**, 1353 (1972).

[3] H. Niiyama, S. Morii, and E. Echigoya, *Shokubai*, **13**, 57 (1971).

100 mol% of the magnesium oxide content. The surface areas of these catalysts were 405, 142, 307, 158, 145, and 68 m^2/g respectively. The metal oxides used were MgO, CaO, MnO, BaO, SrO, and ZnO. They were all commercial-grade except for MnO. MnO was prepared by the decomposition of $MnCO_3$ at 500°C under a vacuum for 48 hr. The reactants were commercial-grade.

Procedures. The isomerization of propylene oxide was carried out using a conventional pulse reactor in a helium carrier. The catalysts (20 mg) were treated at the reaction temperature in streaming helium for about 2 hr before reactions. The amount of reactant injected into the catalyst was 2 μl.

The acidic and basic properties of the catalysts, which were heated at 300°C for 2 hr in air, were measured by the conventional titrating method in benzene with a benzene solution of *n*-butylamine, and benzoic acid, using Hammett indicators.[4]

The structures of the calcined silica–magnesia catalysts were determined by X-ray analysis.

Results and Discussion

The surface areas, acidities, and basicities of the metal oxides are shown in Table 1. Figure 1 shows the dependencies of the acidity (measured at $H_0=+6.8$) and the basicity ($H_0=+7.2$) of the silica-magnesia catalyst on the magnesium-oxide content. Niiyama *et al.*[3] have reported almost the same behavior of the acidic and basic properties of these catalysts. According to Fig. 1, the acidities of silica–magnesia catalysts increase and then decrease with an increase in the magnesium oxide content. An equimolar mixture of silica gel and magnesium oxide has the maximum acidity. The maximum acid strength of the silica–magnesia catalyst (measured for the 51% MgO-catalyst) is stronger than that of silica gel only; their H_0 values are $+1.5$ and $+2.0$ respectively. These facts indicate that new compound produced by a reaction of silica gel and magnesium oxide possesses stronger acid sites than does silica gel. According to Brewer and Steinberg,[5] silica–magnesia catalysts tempered at 400—700°C, and which have been prepared from an equimolar mixture of silica tetraethoxide and magnesium ethoxide, have a forsterite structure (Mg_2SiO_4) and strong Lewis acid sites. In the case of magnesia–boria catalysts, Tanaka and his co-workers[6] have reported that the unknown product formed is an active center for the aldol condensation of acetone. The X-ray analysis of our silica–magnesia catalysts indicates that silica gel has a structure of α-cristobalite, magnesium hydroxide disappears, magnesium oxide is formed, and forsterite is produced. According to Jander and Wuhrer,[7] the main product of the solid-state reaction of silica gel and magnesium oxide is forsterite and the amount of enstatite ($MgSiO_3$) is very small. Our results coincide with theirs. Figure 2 shows the dependence of the amounts of magnesium oxide, silica gel, and forsterite, as measured by X-ray analysis, on the magnesium oxide content. A comparison of Figs. 1 and 2 shows that the acidity correlates to the amount of forsterite and that the basicity correlates to that of the magnesium oxide remaining. Consequently, the strong acid sites on the silica–magnesia catalysts are

Table 1. Properties of metal oxide catalysts

Catalyst	Surface area (m^2/g)	Acidity[a] (mmol/g)	Basicity[b] (mmol/g)
MgO	55.6	—	0.288
CaO	13.3	—	0.014
SrO	5.3	—	0.005
MnO	4.7	?[c]	?[c]
BaO	1.9	—	0.005
ZnO	7.4	0.046	—

a) measured at $H_0=+6.8$
b) measured at $H_0=+7.2$
c) cannot be measured due to its dark color

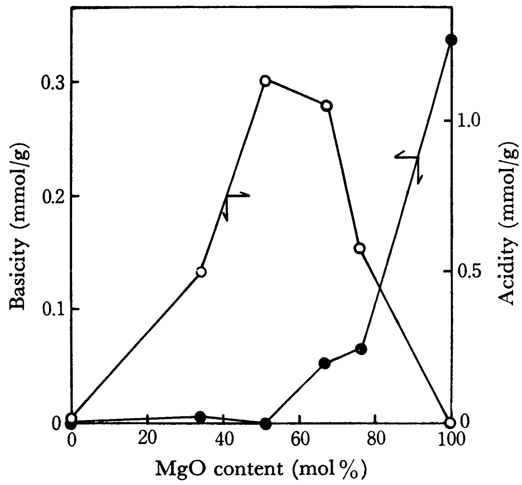


Fig. 1. Dependence of acidity and basicity of silica-magnesia catalysts on magnesium oxide content.
○: acidity, ●: basicity

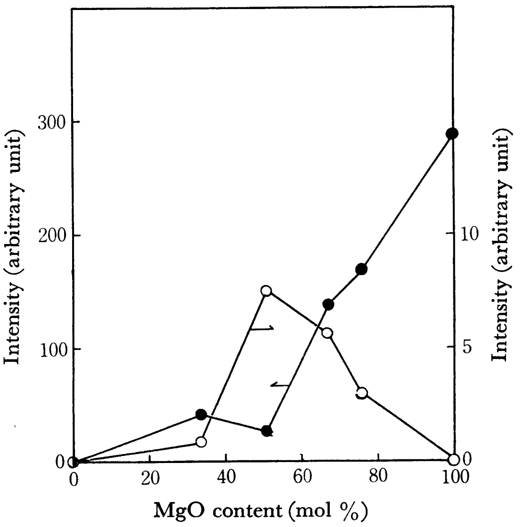


Fig. 2. Dependence of the amounts of magnesium oxide, and forsterite on the magnesium oxide content in silica-magnesia.
●: magnesium oxide, ○: forsterite

---

[4] K. Tanabe "Solid Acids and Bases" Kodansha, Tokyo, Academic Press, New York, London (1970) pp. 6, 36.

[5] H. Bremer and K. H. Steinberg, 4th Int. Congr. Cat. Moscow, Preprint of the paper No. 76 (1968).

[6] A. Tanaka, I. Nozawa, and T. Shirasaki, *Shokubai*, **11**, 87 (1969).

[7] W. Jander and J. Wuhrer, *Z. Anorg. Allg. Chem.*, **226**, 225 (1936).

Table 2. Product distributions of propylene oxide isomerization over silica–magnesia catalysts

Catalyst	R.T. (°C)	Conv[a] (%)	G.P. (%)	A (%)	PA (%)	AC (%)	ACR (%)	1-PrOH (%)	AA (%)	O.P. (%)
SM(0)	267	7.3	0.9	0.5	79.5	—	—	—	13.2	5.9
SM(34)	270	37.0	1.1	1.6	55.7	4.5	0.9	12.6	22.3	1.3
SM(51)	266	56.2	10.3	2.6	64.6	1.5	1.2	10.0	10.2	0
SM(67)	270	42.7	4.0	3.1	56.1	1.8	1.7	20.8	12.8	0
SM(76)	272	49.1	4.0	2.4	61.1	4.6	1.9	12.3	11.7	2.0
SM(100)	267	11.9	1.3	4.8	3.8	31.4	3.3	24.9	30.5	0

a) Conversion (%)/10 mg-Cat.

b) SM denotes silica-magnesia and the number in parenthesis indicates magnesium oxide content (mol %).

G.P.: Gaseous products, A: Acetaldehyde, PA: Propionaldehyde, AC: Acetone, ACR: Acrolein, 1-PrOH: 1-Propanol, AA: Allyl alcohol, O.P.: Other products.

Table 3. Product distributions of propylene oxide isomerization over metal oxide catalysts

Catalyst	R.T. (°C)	Conv[a] (%)	G.P.[a] (%)	A[a] (%)	PA[a] (%)	AC[a] (%)	ACR[a] (%)	1-PrOH[a] (%)	AA[a] (%)	O.P.[a] (%)
MgO	260	9.7	3.4	8.1	—	26.9	21.2	31.9	8.0	0.5
CaO	260	2.8	3.0	10.3	—	31.6	19.3	28.4	7.4	0
SrO	260	0.49	40.6	—	—	28.4	—	8.0	5.7	17.3
MnO	260	1.48	42.7	3.8	29.3	8.1	—	0.8	11.9	3.4

a) See Table 2.

deduced to be caused by the forsterite produced by the reaction of magnesium oxide and silica gel, and the basic sites, by the magnesium oxide. It is considered that the production of strong acid sites can be ascribed to the difference in electronegativity between silicon and magnesium, and that magnesium forms strong Lewis acid sites.

The isomerization of propylene oxide was carried out on silica–magnesia and metal oxide catalysts at 260°C. Tables 2 and 3 show the product distributions of this reaction on these catalysts. Barium oxide and zinc oxide have only a very low activity. The "other products" in these Tables contain condensed products. The gaseous products and acetaldehyde are decomposed products. Here, we will discuss the formation of propionaldehyde, acetone, allyl alcohol, *n*-propanol, and acrolein. In them, propionaldehyde, acetone, and allyl alcohol are the products of the propylene oxide isomerization. Figure 3 shows the dependence of the formations of propionaldehyde and acetone on the magnesium-oxide content of the silica–magnesia catalysts. When we compare Figs. 1 and 3, it is clear that propionaldehyde is formed on acid sites, and acetone on basic sites, as has been reported earlier.[2] Figure 4 shows the dependence of allyl alcohol and 1-propanol on the magnesium-oxide content. In the cases of zeolite catalysts and metal phosphates (except for calcium phosphate), the production of 1-propanol is very small, but silica–magnesia and metal oxide catalysts form very large amounts of 1-propanol. Taking into account the effects of pyridine and dichloroacetic acid on reactions over metal phosphates, 1-propanol has been assumed to be produced from hydrogen-transfer reactions of allyl alcohol.[2] In this paper, 1-propanol formation will be studied in detail.

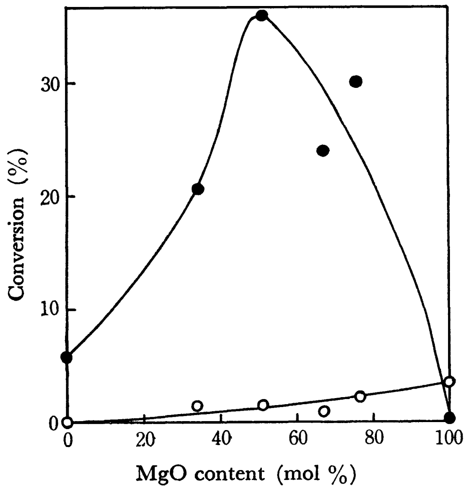


Fig. 3. Dependence of the conversion to propionaldehyde and acetone on the magnesium oxide content.
●: propionaldehyde, ○: acetone

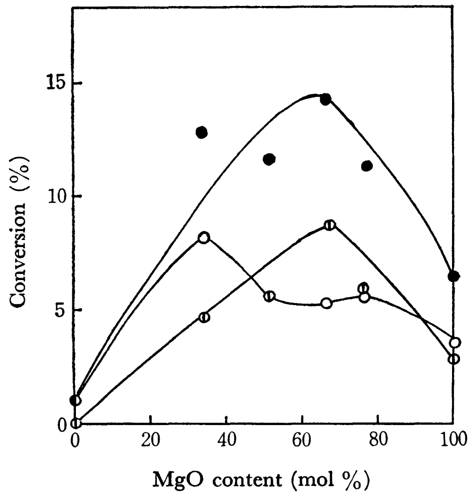
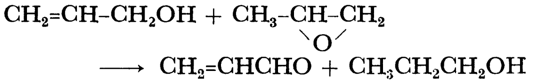


Fig. 4. Dependence of the conversion to allyl alcohol, 1-propanol, and original allyl alcohol on magnesium oxide content.
○: allyl alcohol, ⦶: 1-propanol
●: original allyl alcohol

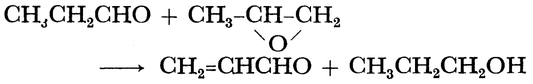
1-Propanol is considered to be a hydrogenated compound of allyl alcohol, propionaldehyde, and propylene oxide and to be formed by the following reaction processes (1)—(4):

$$CH_2{=}CH\text{-}CH_2OH + CH_2{=}CH\text{-}CH_2OH \longrightarrow CH_2{=}CHCHO + CH_3CH_2CH_2OH \qquad (1)$$



$$CH_2{=}CH\text{-}CH_2OH + CH_3\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} \longrightarrow CH_2{=}CHCHO + CH_3CH_2CH_2OH \qquad (2)$$

$$CH_2{=}CH\text{-}CH_2OH + CH_3CH_2CHO \longrightarrow CH_2{=}CHCHO + CH_3CH_2CH_2OH \qquad (3)$$



$$CH_3CH_2CHO + CH_3\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} \longrightarrow CH_2{=}CHCHO + CH_3CH_2CH_2OH \qquad (4)$$

TABLE 4. HYDROGEN-TRANSFER REACTIONS OVER SM(67) AT 260°C

Hydrogen donor	Hydrogen acceptor	Reactivity/g[a)] (arbitrary unit)	$\Delta\nu_D$ (cm^{-1}) of hydrogen acceptor
AA	AA	1.3	~0[b)]
AA	PO	30	59
AA	PA	61	85
PO or PA	PO or PA	0	59 or 85

a) calculated from the formation of 1-propanol.
b) estimated value.
AA: Allyl alcohol
PO: Propylene oxide
PA: Propionaldehyde

In Table 4, the reactivities for each reaction are given; here, in the case of propylene oxide, the formation of 1-propanol from Process (3) caused by the isomerization of propylene oxide is corrected. As is shown in Tables 2 and 3, considerable acrolein is produced over a series of catalysts. Though the amount of acrolein is smaller than that of 1-propanol, this fact is due to the high reactivity of the polymerization of acrolein; there is an approximate correlation between the amount of acrolein and that of 1-propanol. Therefore, Reactions (2) and (3) are found to be the main processes of 1-propanol formation. As alcohol is more easily dehydrogenated on basic sites than other reactants, it is deduced that allyl alcohol is the hydrogen donor and propionaldehyde and propylene oxide are acceptors. When one mole of 1-propanol is formed, one mole of allyl alcohol is consumed. Therefore, the sum of the formations of allyl alcohol and 1-propanol is considered to be the original amount of allyl alcohol formed. In Fig. 4, their sum is plotted against the magnesium-oxide content. The original formation of allyl alcohol has a maximum; this fact indicates that allyl alcohol is formed by an acid-base bifunctional catalyst, as was reported earlier.[2)]

As regards the metal oxides, magnesium and calcium oxides have a high activity of allyl-alcohol formation. Malinowski *et al.*[8)] deduced from ammonia adsorption studies that magnesium oxide has a very weak acid site. Taking into account the products of propylene-oxide isomerization, the other metal oxides can also be considered to have very weak acid sites, though the presence of acid sites cannot be detected by the indicator method. For allyl-alcohol production, even very weak acid sites are deduced to be favorable.

The acidic and basic properties of manganese monoxide cannot be measured because of its dark color. It is considered, on the basis of the product distribution of the propylene-oxide isomerization, that it has both acidic and basic properties.

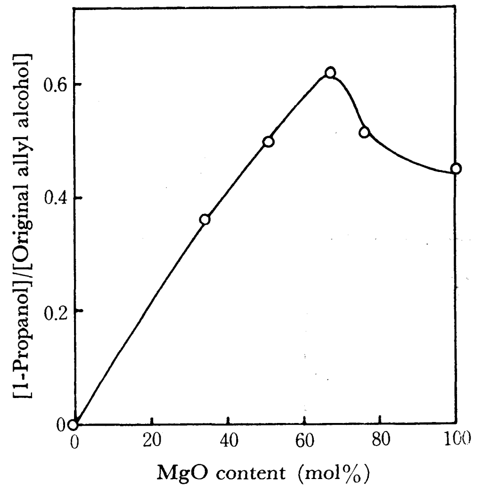


Fig. 5. Dependence of the ratio of 1-propanol to original allyl alcohol on magnesium oxide content.

Niiyama *et al.*[9)] have reported that hydrogen-transfer reactions between alcohol and ketone are catalyzed by acid-base bifunctional catalysts. Figure 5 shows the relation between the ratio of the formation of 1-propanol and the original formation of allyl alcohol and magnesium oxide contents. The ratio has a maximum; this fact suggests the same conclusion. According to Table 4, magnesium and calcium oxides produce a very large amount of 1-propanol among all the metal oxides used. Magnesium oxide prepared from magnesium hydroxide gives a product distribution different from that of magnesium oxide supplied in the production of 1-propanol; that is, the selectivities for 1-propanol are 24.9 and 31.9% for prepared and supplied MgO respectively. According to the basic-strength measurements, the supplied MgO($H_0 = +17.2$) has stronger basic sites than the prepared MgO($H_0 = +15.0$). Therefore, as regards the basic properties favorable to the reaction, strong basic sites are effective.

The order of the activity of the hydrogen-transfer reaction between allyl alcohol and hydrogen acceptor is: propionaldehyde>propylene oxide>allyl alcohol; this order is that of the electron-donating power, $\Delta\nu_D$, of the hydrogen acceptor, which is given in Table 4. According to Kagiya,[10)] the electron-donating power of a compound is defined as the relative difference (counted as wave numbers) of the OD adsorption band of methanol-*d* observed in the compound from

---

[8)] ST. Malinowski, S. Szczepanska, A. Bielanski, and J. Sloczynski, *J. Catal.*, **4**, 324 (1965).

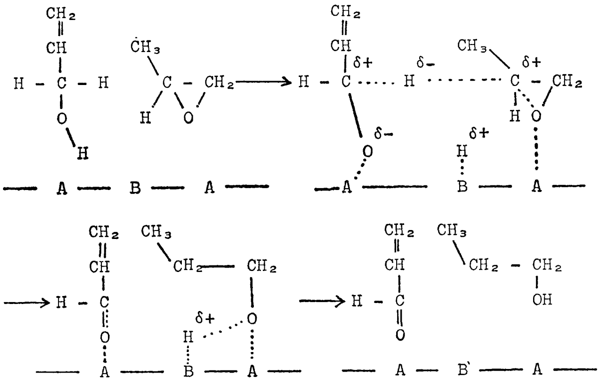
[9)] H. Niiyama and E. Echigoya, 23rd Annual Meeting of the Chemical Society of Japan, No. 1 p. 51 (1970).

[10)] T. Kagiya, Y. Sumida, and T. Inoue, This Bulletin, **41**, 767 (1968).

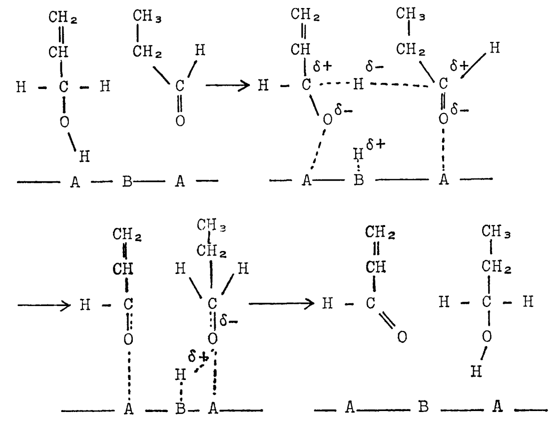
that observed in benzene. The $\Delta\nu_D$ of allyl alcohol is estimated by taking into account the values of the electron-donating power of the C–C double bond in benzene ($\Delta\nu_D$; 0 cm^{-1}), styrene ($\Delta\nu_D$; 4 cm^{-1}), and so forth.

As regards the mechanism of the hydrogen-transfer reaction Niiyama *et al.*[9] have proposed a mechanism similar to that of Meerwein-Ponndorf reduction. Our results support their mechanism in the case of silica-magnesia catalysts. The following mechanism is plausible.

For process (2)



For process (3)



A: acid site B: basic site

That is, propionaldehyde or propylene oxide adsorbs on the acid site at the oxygen atom in them, and the electron density of the carbon atom adjacent to the oxygen atom becomes more positive. The larger the electron-donating power of the hydrogen acceptor, the more positive the carbon atom becomes. Allyl alcohol adsorbs on the basic site, dissociating the hydroxyl group, the electron density of the hydrogen atom at α-carbon becomes negative, and the hydride ion transfers to the positively-charged carbon atom of aldehyde or oxide. Therefore, a strong base is favorable. In the case of propylene oxide adsorbed on a weak acid site, 1-propanol is formed preferentially, as the electron density of α-carbon is smaller than that of β-carbon.[11]

However, in the cases of metal oxides which have only very weak acid sites, it may be considered that the interaction between the acid site and the oxygen atom of the hydrogen acceptor is negligible.

Conclusion

Propylene-oxide isomerization was carried out over silica-magnesia catalysts and metal oxides at 260—270°C using a pulse reactor. It has been concluded that propionaldehyde and acetone are produced on acidic and basic sites respectively. Considerable amounts of 1-propanol are formed on these catalysts, whereas it is not produced on metal phosphates and zeolites. Allyl alcohol is formed by acid-base bifunctional catalysts. It has been found that 1-propanol is mainly produced through the hydrogen-transfer reactions between allyl alcohol and propionaldehyde and propylene oxide. It has also been made clear that acid-base bifunctional catalysts are favorable for the hydrogen-transfer reactions and that the reaction rate depends on the electron-donating power of the hydrogen acceptor and also on the basic strength of the catalyst.

The production mechanisms of the acidic and basic properties of silica–magnesia catalysts were studied by X-ray analysis. The acid site is due to forsterite, while the basic site is due to the magnesium oxide remaining. In view of their reaction products, the metal oxides, such as magnesium and calcium oxides, are considered to have very weak acid sites.

---

[11] K. Shimizu, K. Kato, and T. Yonezawa, 20th Annual Meeting of the Chemical Society of Japan (1967).