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Competition of the Two Reaction Mechanisms of Maleic Anhydride Formation in Vapor-Phase Oxidation of Butadiene over Supported Molybdena Catalysts

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Vapor-phase oxidation of butadiene, 2,5-dihydrofuran and furan over supported molybdena catalysts has been investigated with reference to the reaction mechanism and the rate-determining step of maleic anhydride formation from butadiene. Formation of maleic anhydride during the oxidation of butadiene was found to follow two reaction mechanisms, (a) *via* 2,5-dihydrofuran and furan, and (b) *via* 2,5-dihydrofuran but not *via* furan. The energy barrier for the addition of oxygen species to adsorbed butadiene or furan is very high, *i.e.*, 28.9 or 21.9 kcal/g-mol, respectively, as compared to that for the oxidative dehydrogenation of the intermediate compounds such as 2,5-dihydrofuran. Formation of 2,5-dihydrofuran is rate-determining in these mechanisms during the oxidation of butadiene to maleic anhydride. The second mechanism plays a more important role in maleic anhydride formation at low temperatures, the role of the first mechanism increasing with a rise in the reaction temperature.

The increasing technical importance of maleic anhydride has strongly stimulated interest in its production by the direct oxidation of C_4-fraction obtained from petroleum. Many attempts to oxidize butane, butenes, and butadiene with gaseous oxygen, forming maleic anhydride, have been made, but most of them have been mainly devoted to the development of new catalysts.[1] In contrast, there are only a few studies on the mechanism and the rate-determining step for anhydride formation.[2] Ai, Harada, and Suzuki[3] studied extensively the vapor-phase oxidation of *n*-butenes to maleic anhydride over P_2O_5–V_2O_5 catalyst and concluded that the anhydride is formed *via* butadiene and furan. However, the exact mechanism and the rate-determining step have not yet been clarified.

In previous studies on the vapor-phase oxidation of butadiene over supported molybdena catalysts, it was shown that the selectivity for maleic anhydride formation is strongly affected not only by the kind of oxygen species formed on molybdenum ion but also by the nature of adsorbed butadiene species and that 2,5-dihydrofuran is the first intermediate compound for the anhydride formation from butadiene.[4,5] Thus, it is meaningful to study the oxidation of butadiene, 2,5-dihydrofuran, and furan over supported molybdena catalyst with reference to the reaction path for maleic anhydride formation in the oxidation of butadiene. Detailed investigation of these oxidation reactions has been made over various molybdena catalysts followed by the prediction of the reaction mechanism for anhydride formation. The reaction step for maleic anhydride formation at which the energy barrier is highest was also determined.

Experimental

The apparatus and procedure used for the oxidations were the same as those reported,[5] except that 2,5-dihydrofuran and furan were evaporated by bubbling air through the liquids cooled with ice-water followed by dilution with a large amount of air and then by introduction of the mixtures into the reactor. As reactants, very pure butadiene, reagent grade 2,5-dihydrofuran and furan were used.

Various supported molybdena catalysts and molybdena-titania modified with 5B group element were prepared by the method reported.[5,6]

The gaseous effluent from the reactor was analyzed by gas chromatography. PEG 20 M 20 wt% on Neopak 1 A (80 °C, 2,5-dihydrofuran, furan, acrolein), propylene carbonate 40 wt% on Celite 545 (room temp, butadiene, carbon dioxide) and molecular sieve 13X (room temp, carbon monoxide, nitrogen, oxygen) were used as separating columns. Since maleic anhydride was the only acid obtained, the product was absorbed into water followed by titration with an aqueous solution of sodium hydroxide using a pH meter, after boiling off carbon dioxide.

Results and Discussion

Reaction Mechanism for Maleic Anhydride Formation. Anatase-type titania is a very good carrier for molybdena catalyst in vapor-phase oxidation of butadiene to maleic anhydride, in contrast with alumina and magnesia and a maximum activity and selectivity is obtained at a molybdena content of 25 mole%.[4] In order to predict the intermediate compound for anhydride formation, the effects of the contact time on the selectivity to maleic anhydride formation and on the distribution of the reaction products were

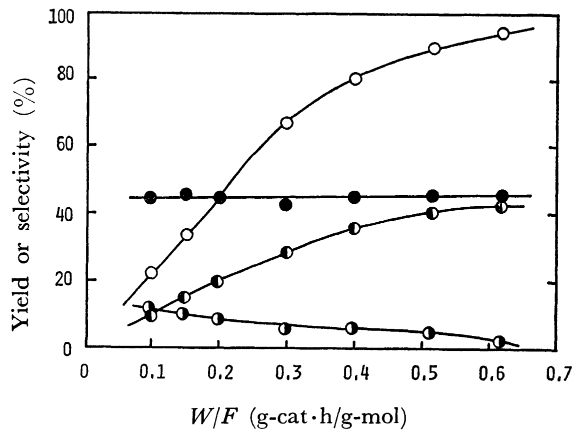


Fig. 1. Effect of the contact time on the distribution of the products in the oxidation of butadiene. Cat.: MoO_3-TiO_2-Sb_2O_3 [$MoO_3/TiO_2=1/3$, Sb/Mo= 15 atom%], reaction temp: 380 °C, butadiene: 1.50 vol% in air, ○: conversion of butadiene, ◐: yield of (CO_2+CO), ●: selectivity to maleic anhydride, ◑: selectivity to furan

Table 1. Oxidation of furan over MoO_3-TiO_2 (1 : 3) catalyst[a)]

Temp (°C)	Conversion (%)	Yield (%)		Selectivity (%)
		CO_2+CO	Maleic anhydride	Maleic anhydride
284	negligible	0.40	0.34	—
295	6.00	1.06	1.26	21.0
313	20.9	3.42	2.93	14.0
326	32.0	9.74	5.56	17.4
338	41.2	12.1	10.4	25.3
353	54.1	15.1	16.2	29.9
369	72.0	21.1	24.2	33.6
393	89.3	25.4	31.2	35.0

a) Furan: 1.54 vol% in air, contact time: $W/F=0.376$ (g-cat·h/g-mol).

investigated with MoO_3–TiO_2 (1 : 3 mole ratio) catalyst modified with a small amount of antimony oxide at 380 °C and butadiene 1.50 vol% in air. The result obtained is graphically represented in Fig. 1. 2,5-Dihydrofuran is hardly obtained in the oxidation. Formation of a small amount of furan is observed in the reaction product. Increase in the contact time results in a decrease of selectivity for furan formation in contrast with conversion of butadiene and yield of (CO_2+CO), but the selectivity for maleic anhydride remains almost unchanged. For the sake of comparison, the oxidation of furan over MoO_3–TiO_2 (1 : 3) catalyst was carried out. The results obtained are summarized in Table 1. It seems that furan is easily converted into the anhydride at 380 °C. Thus, furan formed is possibly oxidized consecutively to the anhydride during the course of oxidation of butadiene at this temperature. However, if furan is an intermediate compound for the anhydride formation, it is expected that the selectivity for maleic anhydride is enhanced with decrease in the slectivity for furan formation. This is not in line with the results shown in Fig. 1. They suggest that furan is an intermediate compound for maleic anhydride formation from butadiene (denoted by mechanism A) in accordance with the result of earlier workers[3)] and also the presence of a reaction path through which the anhydride is formed not *via* furan (denoted by mechanism B).

As 2,5-dihydrofuran was already assumed to be the first intermediate for the anhydride formation from butadiene, it is very likely that furan is formed as a result of oxidative dehydrogenation of 2,5-dihydrofuran produced during the course of oxidation of butadiene over the molybdena catalyst. For the purpose of confirming this assumption, oxidation of 2,5-dihydrofuran was carried out over unsupported Bi_2O_3–MoO_3 (1 : 2) catalyst, *i.e.*, a typical catalyst for oxidative dehydrogenation of butenes to butadiene, and MoO_3–TiO_2 (1 : 3) catalyst with reference to the formation of furan (Table 2). The selectivity for furan formation over the Bi_2O_3–MoO_3 catalyst is very high, in contrast with that over the MoO_3–TiO_2. This can be attributed to the different nature of the catalysts, *viz.*, the latter catalyst has the ability of oxidizing 2,5-dihydrofuran to maleic anhydride in addition to oxidative dehydrogenation even at low temperatures. The results show definitely the formation of furan by oxidative dehydrogenation of 2,5-dihydrofuran produced during the oxidation of butadiene.

For the sake of clarifying the difference between mechanisms A and B, vapor-phase oxidation of 2,5-dihydrofuran was studied in detail using MoO_3–TiO_2 (1 : 3) catalyst. Figures 2 and 3 show the effect of the contact time and that of the reaction temperature on the distribution of the reaction products in the oxidation of 2,5-dihydrofuran. The selectivity for maleic anhydride formation at 320 °C is found to be

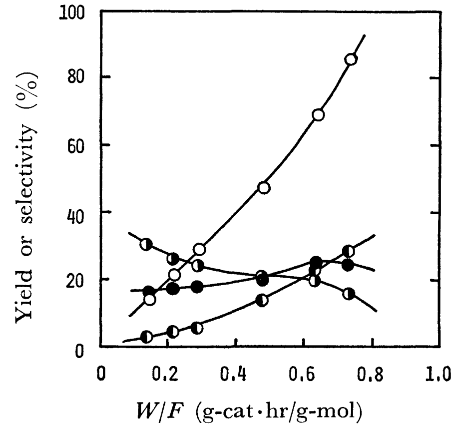


Fig. 2. Effect of the contact time in the oxidation of 2,5-dihydrofuran.
Cat.: MoO_3-TiO_2 (1 : 3), reaction temp.: 320 °C, 2,5-dihydrofuran: 1.50 vol% in air, ○: conversion of 2,5-dihydrofuran, ◐: yield of (CO_2+CO), ●: selectivity to maleic anhydride, ◑: selectivity to furan

Table 2. Oxidative dehydrogenation of 2,5-dihydrofuran

Catalyst	Temp (°C)	Conversion (%)	Yield of furan (%)	rate × 10^3 (furan g-mol/g-cat·h)	E_{all} (kcal/g-mol)
Bi_2O_3-MoO_3 (1 : 2)[a)]	256	8.9	8.21	1.683	
unsupported	273	11.4	11.2	2.285	9.5
	288	13.6	13.8	2.821	
MoO_3-TiO_2 (1 : 3)[b)]	258	8.4	2.36	0.929	
	270	10.0	2.65	1.044	6.0
	284	12.1	3.07	1.209	

a) 2,5-Dihydrofuran: 1.52 vol% in air, contact time: $W/F=0.724$ (g-cat·h/g-mol). b) 2,5-Dihydrofuran: 1.48 vol% in air, contact time: $W/F=0.377$ (g-cat·h/g-mol).

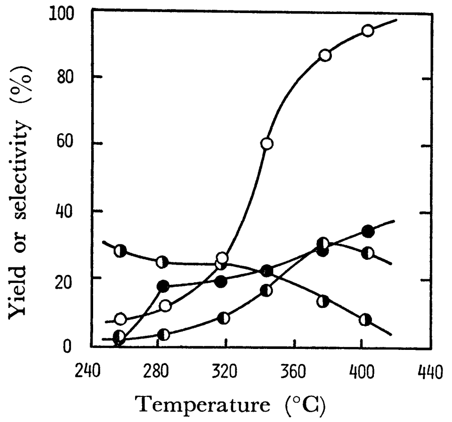
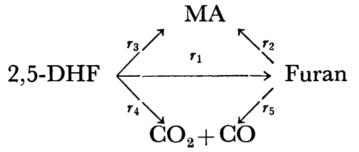


Fig. 3. Effect of the reaction temperature in the oxidation of 2,5-dihydrofuran.
Cat.: MoO_3-TiO_2 (1 : 3), 2,5-dihydrofuran: 1.49 vol% in air, contact time: $W/F=0.377$ [g-cat·h/g-mol], ○: conversion of 2,5-dihydrofuran, ◐: yield of (CO_2+CO), ●: selectivity to maleic anhydride, ◑: selectivity to furan

gradually enhanced with increase in the contact time in contrast with that to furan, which together with the results given in Table 1 give good evidence for the formation of maleic anhydride from 2,5-dihydrofuran *via* furan. A sudden enhancement of selectivity for maleic anhydride formation is observable without a large decrease in the selectivity for furan when the reaction temperature varies from 258 °C to 284 °C, though formation of maleic anhydride in the oxidation of furan is thought to be negligible at these temperatures (Table 1). Mechanism B seems to play an important role in maleic anhydride formation especially at these low temperatures, where furan is not an intermediate compound for the anhydride, being formed immediately from 2,5-dihydrofuran. Selectivity for both maleic anhydride- and furan-formations is almost unchanged at 284—320 °C though an increase in anhydride formation from furan with the rise in temperature is remarkable. This suggests formation of maleic anhydride *via* furan and at the same time not *via* furan as discussed below.



r: rate

In the reaction path, the selectivities are defined by the following equations.

$$\text{select. to MA}=\frac{r_2+r_3}{r_1+r_3+r_4},\quad \text{select. to furan}=\frac{r_1-r_2-r_5}{r_1+r_3+r_4}$$

Assuming that these rates are independent of the concentration of 2,5-dihydrofuran and furan, if $r_2 \fallingdotseq 0$, the overall activation energies in r_1, r_3, r_4, and r_5 are expected to be equal in order to obtain these constant selectivities. However, this condition can not be satisfied. In the case where $r_3 \fallingdotseq 0$, the constant selectivities can be obtained so long as the activation energies in r_1, r_2, r_4, and r_5 are equal. The latter condition seems also not to be attained. Thus, it is impossible to deny that maleic anhydride is formed through mechanisms A and B at these temperatures. Therefore, the anhydride appears to be formed *via* furan (mechanism A) above 284 °C in addition to the mechanism B, and the role of mechanism A seems to become important with rise in the reaction temperature.

Table 3. Kinetic parameters for maleic anhydride formation[a)]

Reactant	Temp range (°C)	α	β	E_{all} (kcal/g-mol)
Butadiene	340—390	−0.17	0.65	28.9
Furan	340—370	0.00	0.49	21.9
2,5-Dihydrofuran	258—320	—	—	17.2

a) Cat.: MoO_3-TiO_2 (1 : 3), α,β: reaction order with respect to the reactant or oxygen, reactant: 1—2.5 vol%, oxygen: 7—20 vol%.

Rate-Determining Step for Maleic Anhydride Formation For the purpose of determining the reaction step for maleic anhydride formation from butadiene at which the energy barrier is the highest, butadiene, furan and 2,5-dihydrofuran were oxidized over the MoO_3–TiO_2 catalyst by means of a differential method. The kinetic parameters obtained are summarized in Table 3. Yield of furan is larger than that of maleic anhydride in the oxidation of 2,5-dihydrofuran (Fig. 3). It is likely because of the low reaction temperatures that the anhydride is formed mainly from 2,5-dihydrofuran and not *via* furan. Unlike the reaction orders of maleic anhydride formation, a striking difference appears between the overall activation energies for the anhydride formation from butadiene, furan, and 2,5-dihydrofuran. This suggests that the real activation energy for maleic anhydride formation from butadiene is also larger than that from furan and 2,5-dihydrofuran, the energy barrier from 2,5-dihydrofuran being the lowest.

The rates of furan formation in the oxidative dehydrogenation of 2,5-dihydrofuran over the Bi_2O_3–MoO_3 and the MoO_3–TiO_2 catalyst are included with the overall activation energy required for this reaction step in Table 2. The energy barrier for the oxidative dehydrogenation step is very low, *i.e.*, only 6.0—9.5 kcal/g-mol, as compared to that for maleic anhydride formation in the oxidation of butadiene and furan. This is presumably attributed to the larger delocalization of π-electrons even over oxygen atom in the intermediate compound formed by the abstraction of α-hydrogen from 2,5-dihydrofuran. Thus, the energy barrier for hydrogen abstraction from various oxygenated intermediate compounds is expected to be very low. The activation energy 28.9 or 21.9 kcal/g-mol is possibly required for the addition of the selective oxygen species to adsorbed butadiene or furan forming 2,5-dihydrofuran or maybe 5,6-dioxabicyclo[2.1.1]-hex-2-ene, respectively. Hence, it can be said that oxidative dehydrogenation of 2,5-dihydrofuran to furan is not rate-determining because of the very low energy barrier. This is also valid in oxidative dehydrogenation of the bicyclo-compound and other intermediate compounds. This is strongly supported by the absence of 2,5-dihydrofuran and the bicyclo-compound in the reaction product in contrast with furan during the oxidation of butadiene. Therefore, it can be concluded that the reaction step for maleic anhydride formation from butadiene, at which the energy barrier is the highest, is an addition of the selective oxygen species to adsorbed butadiene followed by 2,5-dihydrofuran formation.

Double bond type lattice oxygen $Mo^{6+}=O$ is selective for maleic anhydride formation and its reactivity as a radical oxygen decreases with the electronegativity of molybdenum ion on which the lattice oxygen is bonded.[4,6] When the molybdena catalyst is modified with a relatively small amount of oxide of 5B group element, the reactivity of the double bond oxygen can be expected to be $Bi_2O_3 > Sb_2O_3 > As_2O_3 > P_2O_5$ as a sequence of modifiers. The oxidation of butadiene was thus studied over MoO_3–TiO_2 (1 : 3) catalysts modified with various 5B group elements by a differential method, and the rate of maleic anhydride formation per unit surface area was carefully measured (Fig. 4). We see that the order of the activities of the catalysts for the anhydride formation is $Bi_2O_3 > Sb_2O_3 > P_2O_5 > As_2O_3$, in line with that of the reactivities of the double bond oxygen in these modified catalysts. This provides further evidence for the above conclusion. Butadiene, furan, and 2,5-dihydrofuran were oxidized over the MoO_3–TiO_2 catalyst by means of a differential method with respect to the reaction temperature at which formation of the anhydride becomes remarkable (Fig. 5). The order in the rate of maleic anhydride formation is 2,5-dihydrofuran > furan > butadiene at 250—320 °C, in line with the sequence of the rate as judged from the height of the energy barrier. A relatively large rate of the anhydride formation is observed even at 258 °C in the oxidation of 2,5-dihydrofuran as compared to furan and butadiene oxidations. Thus, the results strongly suggest the presence of mechanism B through which maleic anhydride is produced not *via* furan.

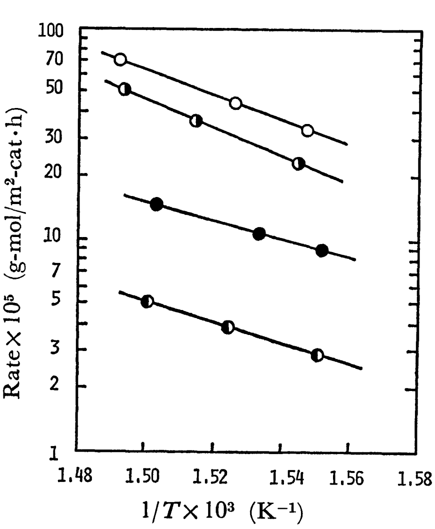


Fig. 4. Rate of maleic anhydride formation in the oxidation of butadiene over modified MoO_3-TiO_2 catalysts.
Cat.: X_mO_n-MoO_3-TiO_2 [$MoO_3/TiO_2 = 1/3$, X/Mo = 30 atom%, X = Bi, Sb, As, or P], butadiene: 1.50 vol% in air, ○: Bi, ◑: Sb, ◐: As, ●: P

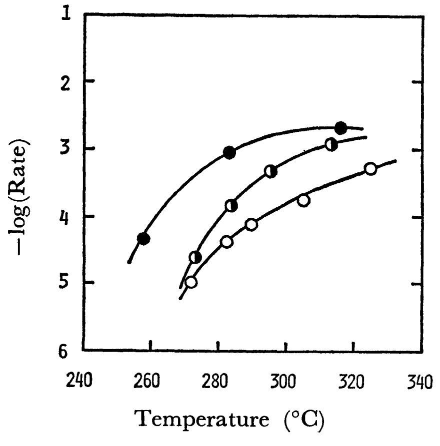
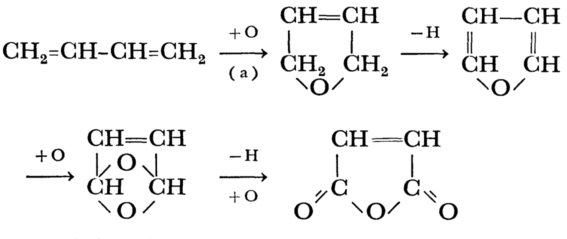


Fig. 5. Oxidation of butadiene, furan, and 2,5-dihydrofuran over MoO_3-TiO_2 catalyst.
Cat.: MoO_3-TiO_2 (1 : 3), feed: 1.50 vol% in air, rate: [g-mol MA/g-cat·h], ●: 2,5-dihydrofuran, ◑: furan, ○: butadiene

In general, the rate of catalytic reaction is proportional to the rate constant of surface reaction and the concentration of adsorbed reactant species. Determination of the surface concentration of the intermediate compounds such as 2,5-dihydrofuran, furan, and 5,6-dioxabicyclo[2.1.1]hex-2-ene during the oxidation of butadiene was not carried out. However, it is apparent that addition of the selective oxygen species to adsorbed butadiene or furan species forming 2,5-dihydrofuran or 5,6-dioxabicyclo[2.1.1]hex-2-ene is the rate-determining step for maleic anhydride formation from butadiene. Conversion of butadiene and the selectivity to furan formation are 44% and 8.5%, respectively, at $W/F = 0.200$ g-cat·h/g-mol and 380 °C (Fig. 1). From this, the average concentrations of butadiene and furan in the vapor-phase along the catalyst bed are calculated to be 1.17 vol% and 0.028 vol%, respectively. The concentration of butadiene is very high relative to that of furan, but rate (butadiene→2,5-dihydrofuran), rate (2,5-dihydrofuran→furan), and rate (furan→maleic anhydride) through mechanism A are the same. This suggests the lowest reactivity of butadiene for anhydride formation. Formation of 2,5-dihydrofuran seems to be rate-determining, as previously presumed, as regards the activation energy. The reaction mechanisms are assumed as follows.

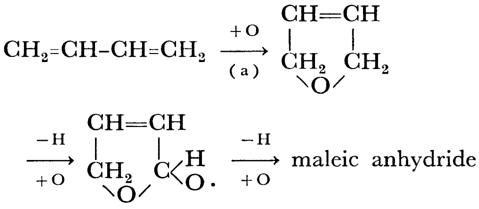
Mechanism A



5,6-dioxabicyclo-[2.1.1]hex-2-ene

where step (a) is rate-determining.

Mechanism B



where step (a) is rate-determining.

In the case of mechanism B, since the intermediate compound formed from 2,5-dihydrofuran by the hydrogen abstraction is a radical, addition of the double bond oxygen to this compound seems to proceed more easily than that to adsorbed furan species. Thus, this path is energetically advantageous, as is evident from the oxidation of 2,5-dihydrofuran to maleic anhydride (Table 3). Consequently, it is natural that mechanism B plays the main role in anhydride formation especially at low temperatures. However, with a rise in temperature, rate of furan formation from 2,5-dihydrofuran becomes very large and thus the role of mechanism A seems to increase. It is, therefore, not unlikely that the selectivity for maleic anhydride formation is almost independent of that for furan formation (Fig. 1).

There is no direct evidence for the formation of 5,6-dioxabicyclo[2.1.1]hex-2-ene. As formation of an intermediate such as the bicyclo-compound was proposed in the vapor-phase oxidation of furfral to maleic anhydride,⁷⁾ it is probable that the anhydride is formed from butadiene *via* the bicyclo-compound in mechanism A. With the exception of 2,5-dihydrofuran and furan, formation of 5,6-dioxabicyclo[2.1.1]hex-2-ene is not really confirmed.

In conclusion, two mechanisms A and B have been found to participate in the selective oxidation of butadiene to maleic anhydride over supported molybdena catalyst. Mechanism B seems to play the main role of anhydride formation at low temperatures. Addition of the double bond oxygen to adsorbed butadiene species leading to 2,5-dihydrofuran formation is rate-determining in these mechanisms.

References

1) R. H. Bretton, S. W. Wan, and B. F. Dodge, *Ind. Eng. Chem.*, **44**, 594 (1952); N. Nagasako, M. Matsumoto, T. Ikawa, and S. Sakamoto, *Coal Tar*, **11**, 121 (1959); M. Matsumoto, T. Ikawa, and N. Nagasako, *Kogyo Kagaku Zasshi*, **63**, 734 (1960); M. Matsumoto, T. Ikawa, M. Kozai, N. Nagasako, and Y. Tsuchiya, *J. Japan. Petr. Inst.*, **3**, 394 (1960); B. L. Moldavskii and Y. D. Kernos, *Kinet. Katal.*, **1**, 267 (1960); W. A. Skinner and D. Tieszer, *Ind. Eng. Chem.*, **53**, 557 (1961); T. C. Bissot and K. A. Benson, *Ind. Eng. Chem. Prod. Res. Develop.*, **2**, 57 (1963); M. Ai, T. Niikuni, and S. Suzuki, *Kogyo Kagaku Zasshi*, **73**, 165 (1970); M. Ai, *ibid.*, **73**, 950 (1970).

2) Y. D. Kernos and B. L. Moldavskii, *Neftekhimiya*, **2**, 519 (1962); C. F. H. Tipper, "Oxidation and Combustion Reviews," vol. 1, Elsevier, Amsterdam (1965) p. 271; I. Komuro, *Shokubai*, **10**, 252 (1968).

3) M. Ai, K. Harada, and S. Suzuki, *Kogyo Kagaku Zasshi*, **73**, 524 (1970).

4) M. Akimoto and E. Echigoya, *J. Catal.*, **29**, 191 (1973).

5) M. Akimoto and E. Echigoya, *ibid.*, **31**, 278 (1973).

6) M. Akimoto and E. Echigoya, *ibid.*, **35**, 278 (1974).

7) N. A. Milas and W. L. Walsh, *J. Amer. Chem. Soc.*, **57**, 1389 (1935).