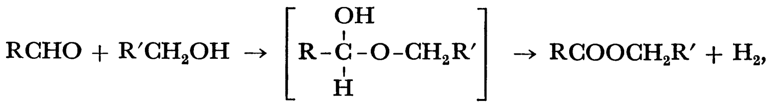
BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (9), 2622—2627 (1978)

Reduced Copper Catalyzed Conversion of Primary Alcohols into Esters and Ketones

Kenji Takeshita,* Shigeaki Nakamura,** and Kazuaki Kawamoto
Institute of Commodities, Faculty of Economics, Kagawa University,
Saiwaimachi, Takamatsu, Kagawa 760

(Received November 17, 1977)

Vapor phase reactions of a mixture of two types of primary alcohols to esters and ketones over a reduced copper catalyst have been investigated. The reactions between primary alcohols and propionaldehyde have also been investigated. The effects of the molar ratio of the reactants and the reaction temperature on the yields of esters, ketones, and aldehydes have been examined. A mixture of ethyl alcohol and propyl alcohol when passed over the catalyst, the main products have been found to be propyl acetate, ethyl acetate, propyl propionate, ethyl propionate, ethyl methyl ketone, diethyl ketone, acetone, acetaldehyde, and propionaldehyde. The formation of the ester and the ketone may be presented as follows:



$$RCHO + R'CH_2OH \rightarrow \left[R\text{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\text{-}O\text{-}CH_2R' \right] \rightarrow RCOOCH_2R' + H_2,$$

$$RCHO + R'CH_2OH \rightarrow RCOR' + CO + 2H_2.$$

Many investigators[1] have shown that the esters and the ketones were obtained, upon passing primary alcohols, aldehydes, and mixtures of them over catalysts such as copper chromite, zinc oxide, copper, metallic palladium, magnesia, and alkalized zinc chromium oxide. These papers have shown that primary alcohols with n carbon atoms are readily converted to symmetrical ketones with $2n-1$ carbon atoms and esters with $2n$ carbon atoms. The mechanism has been described in these papers for ester formation as the Tischenko Reaction mechanism. Recently, another mechanism for ester formation has been proposed by Kunugi *et al.*[2] and one of the present authors.[3] The former investigators found that the ester was formed by the reaction between an aldehyde and an alcohol. In a study of the action of the reduced copper catalyst on alcohols, one of the present authors reported that the ester was formed by a hemiacetal mechanism.

In the formation of ketones, Komarewsky *et al.*[4] found that, in the presence of a chromium oxide catalyst, primary alcohols were converted to ketones by the following mechanism: (1) the dehydrogenation of the alcohol to the aldehyde, (2) the aldol condensation of the aldehyde, (3) the removal of carbon monoxide from the CHO group of the aldol, leaving a secondary alcohol, and (4) the dehydrogenation of this alcohol to the ketone. Kagan *et al.*[5] found that ethyl acetate was an important intermediate when ethyl alcohol was converted to acetone. Matsota *et al.*[6] reported that aliphatic ketones were prepared by heating esters in the presence of manganese oxide at 400—500 °C. Bolotov *et al.*,[7] however, reported that ethyl acetate was not an intermediate in the formation of acetone. Geisler *et al.*[8] examined the catalytic ketonization of ethyl alcohol in the presence of water vapor, and found that the formation of the ketone was presented by the reaction equation as follows:

$$2C_2H_5OH + H_2O \rightarrow CH_3COCH_3 + CO_2 + 4H_2.$$

The present investigation has been undertaken in order to clarify the mechanism of the formation of the ester and the ketone.

Experimental

Reactants. The aliphatic alcohols such as ethyl alcohol, propyl alcohol, butyl alcohol, and isobutyl alcohol were purified, after being dried with calcium oxide or potassium carbonate, by distillation through a fractionating column. Propionaldehyde, ethyl acetate, propyl propionate, ethyl propionate, propyl acetate, isobutyl acetate, and ethyl isobutyrate were purified by drying with anhydrous sodium sulfate, followed by fractional distillation under atmospheric pressure. The purity of the reactants was confirmed by gas chromatographic analysis. (PEG-6000, DEGS, and PEG-1000 F columns.)

Catalyst. The catalyst was prepared by the same method as described in a previous paper.[9]

Apparatus and Procedure. The apparatus and the procedure employed were similar to those used in a previous investigation.[9] Experiments were performed at 250 and 300 °C under atmospheric pressure.

Identification and Analysis of the Reaction Products. The reaction products were separated by gas chromatography (PEG-6000, DEGS, and Tween-80 columns. For the determination of water, a 3 m column packed with Shimalite F impregnated with PEG-1000 was used.), and each constituent was identified by NMR and IR spectra. The gaseous products were analyzed by gas chromatography. (activated charcoal and silica-gel columns.) The quantitative analysis of liquid and gaseous products was performed by gas chromatography.

Results

Table 1 shows the influences of the molar ratio of the reactants and the reaction temperature on the yields of the products. The results obtained by passing a mixture of butyl alcohol and propyl alcohol or propionaldehyde over the catalyst are summarized in Table 2. Further, the results obtained by the reaction of isobutyl alcohol and propyl alcohol or propional-

---

** Present address: Department of Chemistry, Takamatsu Technical College, Takamatsu, Kagawa 760.

Table 1. The Cu-catalyzed reaction of the mixture of ethyl alcohol and propyl alcohol or propionaldehyde

Experiment No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Reaction temp (°C)	250	250	250	250	250	250	250	250	250	250	250	250	300	300
Reactant charged (g)														
Ethyl alcohol	20.10	14.13	11.64	7.91	5.92	4.06	—	15.54	11.79	9.59	5.55	—	7.76	7.62
Propyl alcohol	—	6.21	7.72	10.31	15.36	15.13	19.96	—	—	—	—	—	10.11	—
Propionaldehyde	—	—	—	—	—	—	—	6.69	7.49	11.97	15.47	16.19	—	9.85
Velocity (g/h)	7.2	6.5	6.6	6.1	6.8	6.5	7.2	7.0	6.5	6.9	6.9	7.1	6.5	6.7
Liquid products (g)	19.02	18.89	18.15	17.35	20.13	17.99	19.00	20.68	18.29	20.06	19.22	15.15	16.40	16.02
Composition of liquid products[a] (%)														
Acetaldehyde	18.1	13.8	9.9	6.9	6.1	3.4	—	12.4	9.9	8.3	4.1	—	12.4	12.9
Ethyl alcohol	61.7	31.6	24.0	16.2	14.6	10.8	0.5	34.0	25.3	21.9	12.2	—	7.3	16.9
Propyl alcohol	—	13.4	20.2	24.8	30.6	37.5	62.7	6.4	6.3	5.3	4.4	2.6	11.5	5.3
Propionaldehyde	—	5.5	6.4	8.4	12.7	13.1	15.4	15.4	21.2	38.7	57.7	95.0	18.0	35.0
Ethyl acetate	16.8	14.0	13.0	8.4	2.5	0.9	—	16.2	12.5	6.6	3.0	—	8.5	6.2
Propyl acetate	—	5.9	7.1	9.0	7.1	5.9	—	1.6	1.2	0.8	0.5	—	9.4	T
Propyl propionate	—	2.3	3.8	8.3	10.5	13.1	13.7	1.9	1.7	1.5	1.2	0	8.4	1.4
Ethyl propionate	—	3.5	4.6	5.2	3.9	2.9	—	5.9	12.7	10.4	10.0	—	5.2	6.6
Acetone	1.6	1.5	1.2	0.8	0.5	0.2	—	1.6	1.2	0.6	0.5	—	1.4	1.0
Ethyl methyl ketone	—	5.7	6.0	6.7	5.9	4.3	—	3.0	6.4	5.1	4.7	—	9.7	8.9
Diethyl ketone	—	1.2	1.6	3.4	4.0	6.1	6.4	T	T	T	T	—	5.5	0.2
Acetic acid	T	T	T	T	T	T	—	T	T	T	T	—	0.6	0.4
Propionic acid	—	0.2	0.2	0.3	0.4	0.4	0.5	0.4	0.4	0.5	0.8	2.4	0.3	0.9
Aldol	0.3	T	T	T	T	T	—	T	T	T	T	—	T	T
Crotonaldehyde	0.2	T	T	T	T	T	—	T	T	T	T	—	T	T
Butyraldehyde	0.2	T	T	T	T	T	—	T	T	T	T	—	T	T
2-Buten-1-ol	0.2	T	T	T	T	T	—	T	T	T	T	—	T	T
Butyl alcohol	0.4	T	T	T	T	T	—	T	T	T	T	—	T	T
Methyl alcohol	0.1	T	T	T	T	T	0.2	T	T	T	T	—	1.3	1.2
Water	T	T	T	T	T	T	T	T	T	T	T	T	T	T
Unidentified products	0.4	1.4	2.0	1.6	1.2	1.4	0.6	1.2	1.2	0.3	0.9	T	0.5	3.1

a) The yields of each compound produced were given by (grams of each compound per grams of total reaction product)×100(%). T=Trace.

Table 2. Cu-catalyzed reaction of the mixture of propyl alcohol or propionaldehyde and butyl alcohol (Reaction temp: 250 °C)

Experiment No.	15	16	17
Reactant charged (g)			
Propyl alcohol	8.36	—	—
Propionaldehyde	—	9.43	—
Butyl alcohol	10.21	12.12	19.98
Velocity (g/h)	6.4	6.8	7.2
Liquid products (g)	17.94	19.95	18.84
Composition of liquid products (%)			
Propionaldehyde	5.8	21.4	—
Propyl alcohol	29.3	14.7	0.2
Butyraldehyde	7.0	7.2	18.9
Butyl alcohol	31.7	39.9	64.0
Propyl propionate	3.5	0.2	—
Butyl propionate	4.1	3.7	—
Butyl butyrate	4.7	2.5	15.7
Propyl butyrate	4.4	0.4	—
Diethyl ketone	0.1	T	—
Ethyl propyl ketone	0.4	0.2	—
Dipropyl ketone	0.2	0.1	0.5
Propionic acid	0.2	0.6	—
Butyric acid	T	T	T
Ethyl alcohol	0.3	0.3	0.2
Methyl alcohol	T	0.1	0.1
Water	T	T	T
Unidentified products	8.3	8.7	0.4

T=Trace.

Table 3. Cu-catalyzed reaction of the mixture of propyl alcohol or propionaldehyde and isobutyl alcohol (Reaction temp: 250 °C)

Experiment No.	18	19
Reactant charged (g)		
Propyl alcohol	8.41	—
Propionaldehyde	—	9.47
Isobutyl alcohol	10.36	12.44
Velocity (g/h)	6.6	6.5
Liquid products (%)	17.71	20.75
Composition of liquid products (%)		
Propionaldehyde	6.1	23.1
Propyl alcohol	29.4	13.7
Isobutyraldehyde	6.3	6.0
Isobutyl alcohol	32.3	43.1
Propyl propionate	3.2	0.2
Isobutyl propionate	4.1	2.9
Isobutyl isobutyrate	4.6	2.2
Propyl isobutyrate	4.9	0.4
Diethyl ketone	0.1	T
Ethyl isopropyl ketone	0.6	0.2
Diisopropyl ketone	0.3	0.2
Propionic acid	0.3	0.7
Isobutyric acid	T	T
Ethyl alcohol	0.2	0.2
Methyl alcohol	T	T
Water	T	T
Unidentified products	7.6	7.1

T=Trace.

dehyde are summarized in Table 3. Tables 4 and 5 show the results of the catalytic decomposition of the esters. The yields of each compound shown in these tables are an average of two and three experiments under constant operating conditions.

Influence of the Molar Ratio of the Reactants on the Yields of Esters and Ketones. *a) Reaction between Ethyl Alcohol and Propyl Alcohol*: As may be seen from Table 1, the yields of esters and ketones depended on the molar ratio of the reactants as follows: 1) The yield of ethyl acetate increased with an increase in the molar ratio of ethyl alcohol to propyl alcohol. 2) The yield of propyl propionate decreased with an increase in the molar ratio of ethyl alcohol to propyl alcohol. 3) The maximum yields of propyl acetate and ethyl propionate were obtained when ethyl and propyl alcohols were mixed in the ratio of approximately 1:1. 4) Further, the yield of each ester was in the following order: propyl acetate>ethyl acetate, propyl propionate>ethyl propionate. 5) The yield of acetone increased with an increase in the molar ratio of ethyl alcohol to propyl alcohol, but the yield of diethyl ketone decreased. When the molar ratio of the reactants was about 1:1, the maximum yield of ethyl methyl ketone was obtained. As may be seen from Table 1, the yield of the unsymmetrical ketone was larger than that of the symmetrical ketone except in the case of a large excess of propyl alcohol.

From these results, it is considered that ethyl acetate and acetone may be formed from ethyl alcohol, that propyl propionate and diethyl ketone may be formed from propyl alcohol, and that propyl acetate, ethyl propionate, and ethyl methyl ketone may be formed by the reaction between ethyl alcohol and propyl alcohol.

When the mixture of two alcohols or an alcohol and propionaldehyde was passed over the catalyst, carbon monoxide, carbon dioxide, and hydrocarbon were detected as gaseous products, and it was found that the molar ratio of carbon monoxide to carbon dioxide was 3 : 1—2 in the cases of Experiment Nos. 2—6 in Table 1.

b) Reaction between Ethyl Alcohol and Propionaldehyde: As may be seen from Table 1, when propionaldehyde was used in place of propyl alcohol, the kinds of reaction products were the same as those obtained by passing the mixture of ethyl and propyl alcohols over the catalyst, but there were distinct differences in the yields of the ester and the ketone in the products. It was found that, when propionaldehyde was used in place of propyl alcohol, the yield of ethyl propionate increased remarkably, but the yield of propyl esters decreased, and little diethyl ketone was obtained. As is shown in Experiment No. 12 of Table 1, propionaldehyde did not condense to give the ester and ketone.

c) Reaction between Secondary Alcohol and Primary Alcohol or Propionaldehyde: When the mixture of a secondary alcohol and a primary alcohol or propionaldehyde was passed over the catalyst, the esters and the ketones were obtained. For example, when

Table 4. Cu-catalyzed decomposition of various esters

Experiment No.	20	21	22	23	24
Reaction temp (°C)	250	250	300	300	250
Reactant charged (g)					
Ethyl acetate	18.24	—	—	—	10.22
Propyl acetate	—	—	13.47	—	—
Ethyl propionate	—	—	—	12.57	—
Propyl propionate	—	18.08	—	—	—
Propyl alcohol	—	—	—	—	6.08
Hydrogen (l)	—	—	2.85	2.61	—
Velocity					
Liquid reactant (g/h)	6.6	7.0	7.1	7.1	6.5
Hydrogen (l/h)	—	—	2.85	2.61	—
Liquid products (g)	17.31	17.02	12.06	11.73	14.98
Composition of liquid products (%)					
Acetaldehyde	0.3	—	2.8	1.9	1.5
Ethyl alcohol	0.5	—	2.0	2.5	2.2
Propionaldehyde	—	0.3	4.4	3.5	6.0
Propyl alcohol	—	0.3	4.8	2.7	20.7
Ethyl acetate	97.9	—	1.1	0.3	50.7
Propyl acetate	—	—	79.3	0.3	6.4
Ethyl propionate	—	—	0.5	84.7	0.4
Propyl propionate	—	98.5	0.9	0.5	3.9
Acetone	0.5	—	0.2	0.1	1.9
Ethyl methyl ketone	—	—	3.7	3.1	4.1
Diethyl ketone	—	0.3	T	T	1.5
Acetic acid	0.4	—	T	T	T
Propionic acid	—	0.4	T	T	0.3
Water	T	T	T	T	T
Unidentified products	0.4	0.2	0.3	0.4	0.4

T=Trace.

propyl alcohol and isopropyl alcohol were used as the reactants, propyl propionate, isopropyl propionate, diethyl ketone, and acetone were obtained.

Influence of the Reaction Temperature on the Yields of Ester and Ketone. As may be seen in Experiment Nos. 4 and 13 of Table 1, the conversion of primary alcohols depended upon the reaction temperature, and the yields of aldehydes and ketones increased with a rise in the reaction temperature, but the yield of the ester was little affected.

Decomposition of Ester. When ethyl acetate was passed over the catalyst, acetone was obtained, and in the case of propyl propionate, diethyl ketone. Experiment Nos. 22 and 23 of Table 4 showed that the kinds of the reaction products obtained by using propyl acetate as the reactant were the same as those obtained by using ethyl propionate. Further, Table 5 showed that the kinds of the products obtained from isobutyl acetate were the same as those obtained from ethyl isobutyrate, when isobutyl acetate and ethyl isobutyrate were passed over the catalyst in the presence of hydrogen.

Experiment Nos. 20 and 21 of Table 4 showed that, when the ester type $C_nH_{2n+1}COOC_{n+1}H_{2n+3}$ such as $CH_3COOC_2H_5$, $C_2H_5COOC_3H_7$, and $C_3H_7COOC_4H_9$ was passed over the catalyst, a symmetrical ketone was produced. However, Experiment Nos. 22, 23, 25, and 26 of Tables 4 and 5 showed that, when the other esters were passed over the catalyst, the results were as follows: (1) most of the ketones formed were unsymmetrical ketones. (2) the yield of the ketone increased in the presence of hydrogen. (3) the yield of carbon monoxide was larger than that of carbon dioxide.

Discussion

The Formation Mechanism of Ester and Ketone Obtained by the Catalytic Reaction of Primary Alcohols. a) *Formation Mechanism of Ester*: Eto[10] reported that the copper catalyst strongly accelerated the ester formation by the Tischenko Reaction. Saito and Tanabe[11] also reported that the formation of the ester was similar to the Tischenko Reaction mechanism, when benzyl benzoate was formed from benzaldehyde in the presence of magnesium oxide or calcium oxide.

However, in the present research, propionaldehyde did not condense to give the ester. This indicates that the Tischenko Reaction type esterification does not take place under the present reaction conditions. Kunugi *et al.*[12] reported that the ester was not formed by the Tischenko Reaction mechanism, but by the reaction between an alcohol and an aldehyde. Dolgow[13] found that, when the mixture of alcohol or aldehyde and hydrogen was passed over the copper catalyst, an ester was obtained. He proposed a hemiacetal intermediate mechanism as the scheme of the

TABLE 5. THE Cu-CATALYZED DECOMPOSITION OF ISOBUTYL ACETATE AND ETHYL ISOBUTYRATE
(Reaction temp: 300 °C)

Experiment No.	25	26
Reactant charged (g)		
Isobutyl acetate	13.00	—
Ethyl isobutyrate	—	12.59
Hydrogen (l)	2.75	2.05
Velocity		
Liquid reactant (g/h)	7.1	7.1
Hydrogen (l/h)	1.5	1.1
Liquid products (g)	11.98	11.49
Composition of liquid products (%)		
Acetaldehyde	2.3	1.8
Ethyl alcohol	2.0	2.4
Isobutyraldehyde	3.6	1.7
Isobutyl alcohol	4.6	1.4
Isobutyl acetate	83.0	0.2
Ethyl acetate	1.0	0.2
Ethyl isobutyrate	0.4	86.1
Isobutyl isobutyrate	0.8	0.4
Isopropyl methyl ketone	2.2	1.7
Acetone	T	T
Diisopropyl ketone	T	T
Acetic acid	T	T
Isobutyric acid	T	T
Water	T	T
Unidentified products	0.1	4.1

T=Trace.

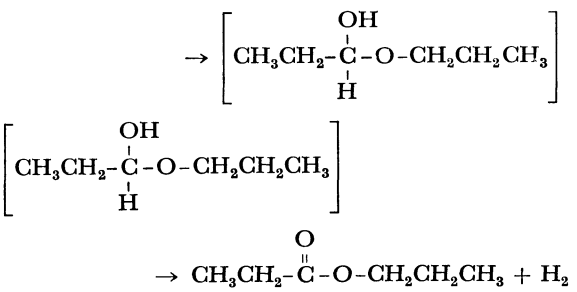
formation of the ester. It was reported by Tarama[14] that, when the hydrogenolysis of an ester was carried out, the ester was converted to two alcohols *via* a hemiacetal. Covert *et al.*[15] reported that a cyclic acetal was converted to ether, alcohol, and hydrocarbon *via* a hemiacetal.

As reported above, when propionaldehyde was used in place of propyl alcohol, the yield of propyl esters which appear to be produced by the participation of propyl alcohol was very small, suggesting that the ester is produced by the reaction between the aldehyde and the alcohol.

From these results, the formation mechanism of esters may be explained by the hemiacetal intermediate mechanism as follows:

$CH_3CH_2CH_2OH \rightarrow CH_3CH_2CHO + H_2$

$CH_3CH_2CHO + CH_3CH_2CH_2OH$



$$\rightarrow \left[\mathrm{CH_3CH_2\text{-}\overset{OH}{\underset{H}{C}}\text{-}O\text{-}CH_2CH_2CH_3}\right]$$

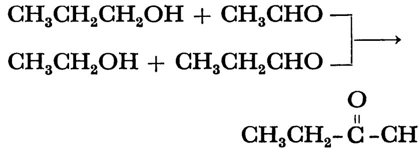
$$\left[\mathrm{CH_3CH_2\text{-}\overset{OH}{\underset{H}{C}}\text{-}O\text{-}CH_2CH_2CH_3}\right] \rightarrow \mathrm{CH_3CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2CH_2CH_3} + \mathrm{H_2}$$

b) Formation Mechanism of Ketone: Komarewsky *et al.*[16] reported that aldehydes and aldols seemed to be logical intermediates when the ketone was formed from primary alcohols, and that the order of the conversion of the reactants to the ketones was aldol> aldehyde>alcohol. Bolotov *et al.*[7] reported that the acetone was formed by the aldol condensation of acetaldehyde. Geisler and Danneberg[8] reported that ethyl alcohol was converted to acetone *via* the aldehyde and acid. Further, Kagan *et al.*[5] reported that, when ethyl alcohol was converted to acetone, ethyl acetate was an important intermediate in the chain of reactions involved. Dolgow and Golodnikow[17] showed that the ketone was obtained by the catalytic reaction of primary alcohol, and that the reaction was proceeded by an ester intermediate mechanism.

In the present research, however, as may be seen in Experiment No. 12 of Table 1, no ketone and aldol were produced from propionaldehyde. Aldol condensation products were not obtained by the catalytic reactions of the alcohols except ethyl alcohol. Therefore, aldol appears not to be an intermediate of the ketone formation from primary alcohol with the reduced copper catalyst.

From the experimental results obtained in the reaction between ethyl alcohol and propyl alcohol or propionaldehyde and by the decomposition of esters, the formation of ketones with the reduced copper catalyst may proceed along two paths.

I) One appears to be formed by the following scheme.



$$\left.\begin{array}{l}\mathrm{CH_3CH_2CH_2OH + CH_3CHO}\\ \mathrm{CH_3CH_2OH + CH_3CH_2CHO}\end{array}\right] \longrightarrow \mathrm{CH_3CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + CO + 2H_2}$$

II) Another may be accounted for by Kagan's Process[5] as follows:

$$2C_2H_5COOC_3H_7 \rightarrow C_2H_5COC_2H_5 + C_3H_7OH + C_3H_6 + CO_2 \ .$$

From the molar ratio of carbon monoxide to carbon dioxide, it is considered that, when the primary alcohol is converted to the ketone, the ketone may be produced by either Process I or II, but that Process I predominates. In the case of the decomposition of the esters, most of the ketone may be formed by Process I.

References

1) (a) R. E. Dunbar, *J. Org. Chem.*, **3**, 242 (1938); R. E. Dunbar and M. R. Arnold, *ibid.*, **10**, 501 (1945); (b) V. N. Ipatieff and V. Haensel, *J. Org. Chem.*, **7**, 189 (1942); (c) V. I. Komarewsky, C. F. Price, and J. R. Coley, *J. Am. Chem. Soc.*, **69**, 238 (1947); V. I. Komarewsky and J. T. Stringer, *ibid.*, **63**, 921 (1941); J. R. Coley and V. I. Komarewsky, *ibid.*, **74**, 4448 (1952); (d) M. Takayasu, *Nippon Kagaku Zasshi*, **64**, 457, 461, 676, 684 (1943); (e) K. Hoshiai, *Kogyo Kagaku Zasshi*, **54**, 238 (1951); **56**, 381 (1953); **57**, 76 (1954); (f) S. Kudo, *Kogyo Kagaku Zasshi*, **58**, 719 (1955); (g) T. Ishiguro and Otsuka, *Yakugaku Zasshi*, **78**, 454 (1958); (h) B. N. Dolgov, B. A. Bolotov, and L. A. Komissarova, *J. Appl. Chem. USSR*, **28**, 61 (1955); B. A. Bolotov, and P. M. Adrov, *ibid.*, **28**, 271 (1955); B. A. Bolotov, P. M. Adrov, and L. K. Prokhorova, *ibid.*, **28**, 489 (1955); B. A. Bolotov and N. A. R. Marshova, *Zh. Prikl. Khim.*, **30**, 286 (1957); B. A. Bolotov and L. K. Smirnova, *Zh. Obshch. Khim.*, **25**, 1987 (1955); (i) Kh. M. Minachev, G. A. Loginov, and

M. A. Markov, *Kinet. Katal.*, **7**, 904 (1966); (j) U. R. Rao, R. Kumar, and N. R. Kuloor, *I&EC Process Design and Development*, **8**, 9 (1969); (k) K. Tanabe, K. Saito, T. Iizuka, H. Hattori, T. Yamaguchi, M. Sakashita, and I. Matsuzaki, *Asahigarasu Kogyo Gijyutsu Shoreikai Kenkyu Hokoku*, **15**, 303 (1969); (l) E. Donath, *Chem.-Ztg.*, **12**, 1191 (1889).

2) T. Kunugi, T. Matsuura, and T. Kono, *Kogyo Kagaku Zasshi*, **71**, 1517 (1968).

3) K. Kawamoto and Y. Nishimura, *Bull. Chem. Soc. Jpn.*, **44**, 819 (1971).

4) V. I. Komarewsky and J. R. Coley, *J. Am. Chem. Soc.*, **63**, 700, 3269 (1941).

5) M. J. Kagan, I. A. Sobolew, and G. D. Lubarsky, *Chem. Ber.*, **68**, 1140 (1935).

6) N. P. Matsota and V. D. Mezhov, *Chem. Abstr.*, **75**, 88114x (1971).

7) B. A. Bolotov and S. N. Borisov, *Zh. Obshch. Khim.*, **27**, 1237 (1957); B. A. Bolotov and B. N. Dologov, *Chem. Abstr.*, **59**, 8579a (1963).

8) G. Geisler and R. Danneberg, *J. Prakt. Chem.*, **26**, 296 (1964); M. Raetzch and G. Geisler, *Z. Chem.*, **5**, 229 (1965).

9) S. Nakamura and K. Kawamoto, *Bull. Chem. Soc. Jpn.*, **44**, 1072 (1971).

10) K. Eto, *Yuki Gosei Kagaku Kyokai Shi*, **21**, 61 (1963).

11) K. Saito and K. Tanabe, *Nippon Kagaku Kaishi*, **1973**, 1845.

12) T. Kunugi, T. Kono, H. Yoshino, and Y. Shinohara, *Kogyo Kagaku Zasshi*, **71**, 1638 (1968); T. Kunugi and T. Kono, *ibid.*, **72**, 1282 (1969); T. Kunugi, T. Kono, and H. Yoshino, *Nippon Kagaku Kaishi*, **1972**, 2265; T. Kunugi, T. Kono, M. Yanagisawa, and H. Arai, *ibid.*, **1972**, 2271; T. Kunugi, T. Kono, and Y. Shinohara, *ibid.*, **1973**, 454.

13) B. N. Dolgow "Die Katalyse in der Organishen Chemie," Veb Deutscher Verlag der Wissenschaften, Berlin (1963), pp. 275—277.

14) K. Tarama "Hannobetsu Jitsuyoshokubai," Kagaku Kogyo Sha, Tokyo (1970), p. 293.

15) L. W. Covert, R. Connor, and H. Adkins, *J. Am. Chem. Soc.*, **54**, 1651 (1932).

16) V. I. Komarewsky, "Advanced in Catalyst and Related Subjects," Vol. VIII, ed by W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal, Academic Press, New York, N. Y. (1956), pp. 207—217.

17) B. N. Dolgow and G. V. Golodnikow, *Zh. Obshch. Khim.*, **24**, 987, 1167, 1364 (1954).