Oxidation of Methyl Ethyl Ketone to Diacetyl on V_2O_5–P_2O_5 Catalysts

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A V_2O_5–P_2O_5 catalyst with a P/V atomic ratio of 1.6 prepared by using oxalic acid as a reducing agent was found to be effective for the synthesis of diacetyl in the vapor-phase air-oxidation of methyl ethyl ketone (MEK). The selectivity to diacetyl was about 40 mol% at MEK conversions of up to 70%, and it decreased slightly with a further increase in the conversion. The selectivity for the oxidative C–C fission to form acetic acid and acetaldehyde varied from 58 to 56 mol% with an increase in the conversion. The rate was nearly proportional both to the oxygen concentration up to 20 vol% and to the MEK concentration up to 10 vol%, even at the low temperature of 140°C. The apparent activation energy was 7.6 kcal/mol. The addition of water vapor favors the oxidative fission against the diacetyl formation. The effects of reaction variables on the selectivity was also studied. A peroxide-like reaction mechanism was proposed.

INTRODUCTION

Methyl ethyl ketone (MEK) is converted very easily to acetic acid and acetaldehyde by an oxidative fission of the central C–C bond with an acidic metal-oxide catalyst, such as a MoO_3- or V_2O_5-based mixed oxide. This reaction has been considered to be an undesirable side-reaction of the partial oxidation of *n*-butenes to maleic anhydride (*1, 2*). However, in view of the formation of acetic acid from *n*-butenes (*3*), together with the oxidation of olefins to ketones which was found by Buiten (*4*), this reaction has been proposed by Yamashita *et al.* (*5, 6*) as one of the intermediate steps in the oxidation.

Besides acetic acid, acetaldehyde, and carbon oxides, diacetyl (2,3-butane dione; dimethyl glyoxal; CH_3–CO–CO–CH_3) is obtained in a small amount in the oxidation of MEK. Because of its chemical formula and its high reactivity on V_2O_5-based oxides, it was assumed to be an intermediate in the oxidation of MEK to acetic acid (*5, 6*).

Diacetyl has been manufactured by the reaction of MEK with ethyl nitrile (*7*) and used mainly as a perfume.

Some spinels containing cobalt have been reported to be selective for the formation of diacetyl from MEK when the extent of the reaction is low (*8*). It seems, however, hard to preserve a high selectivity at high levels of MEK conversion, because it has been predicted that such oxides have a high activity for the oxidation of diacetyl, too.

Recently, we found that V_2O_5–P_2O_5 catalysts are effective in the formation of diacetyl; this was predictable from the finding (*9*) that a considerable amount of diacetyl is formed in the oxidation of *n*-butenes on V_2O_5–P_2O_5 catalysts, which possess a high selectivity for the formation of maleic anhydride from *n*-butenes. It is interesting to note that the carbon skeletons of reactants are preserved both in the oxidation of *n*-butenes to maleic anhydride and in the oxidation of MEK to diacetyl.

In this study, we focused our attention on the formation of diacetyl from MEK and attempted to clarify the effects of catalysts

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and reaction variables, since no detailed in-
formation about this oxidation reaction has
yet been reported.

EXPERIMENTAL

Six preparative methods were used for
the $V_2O_5-P_2O_5$ catalysts: V-P(A) were pre-
pared without using a reducing agent, as
has been described in Refs. (*1, 2*); in the
same manner as the PVa catalysts in Ref.
(*10*); V-P(B) were prepared by using oxalic
acid, in the same manner as the PVb cata-
lysts in Ref. (*10*); V-P(C) were prepared by
using isobutanol as the solvent, according
to a patent (*11*); V-P(D) were prepared by
using lactic acid, as has been described in
Ref. (*12*); V-P(E) were prepared by using
HCl, as has been described in Ref. (*13*); V-
P(F) were prepared by using both oxalic
acid and HCl, as has been described in Ref.
(*14*). The other catalysts, consisting of Mo
O_3- or V_2O_5-based binary oxides and 12-
molybdophosphoric acid ($H_3PMo_{12}O_{40}$) and
its derivatives, were prepared as has been
described in previous papers (*15, 16*). All
of the catalysts were supported on natural
pumice in the 10–20 mesh-size range.

The oxidation of MEK was conducted in
a continuous-flow apparatus at atmospheric
pressure. The reactor was made of a steel
tube, 50 cm long and 1.8 cm i.d., mounted
vertically and immersed in a lead bath. Dry
air was fed in from the top of the reactor,
with MEK being introduced into the pre-
heating section by means of a micro liquid-
feeder. The reaction conditions were fixed
as follows unless otherwise indicated:
MEK concentration, 2.0 vol% in air; total
flow rate, 280 ml (at 20°C)/min (about 0.7
mol/h); amount of catalyst used, 30 g. The
effluent gas from the reactor was led suc-
cessively into three chilled water-scrubbers
to recover the water-soluble compounds.
At the end of 1 h, the content of the water-
scrubbers was collected (120 ml). The reac-
tion products were analyzed by gas chro-
matographs; a 1-m column of molecular
sieve 13X for CO; a 6-m column of propyl-
ene carbonate for CO_2, hydrocarbons, and

ethers; a 2-m column of PEG 20M at 100°C
for aldehydes, ketones, and alcohols; a 1-m
column of AT-1200 + H_3PO_4 at 130°C for
acids. The yield and selectivity of a particu-
lar product were defined as mole percent-
age yield and selectivity on a carbon-ac-
count-for basis.

RESULTS

*Oxidation of MEK on the V–P = 1/1.6
(B) Catalyst*

Preliminary catalyst-screening tests re-
vealed that the best results for the forma-
tion of diacetyl are obtained with the V–P
= 1/1.6 (B) catalyst. Thus, the oxidation of
MEK was studied with this catalyst.

Product distribution. The reaction was
conducted under the conditions presented
in the Experimental section. The major
products were diacetyl, acetic acid, and ac-
etaldehyde. The minor products were car-
bon oxides and propionaldehyde. Methyl
vinyl ketone and acrolein were detected
only in traces. The change in the conver-
sion (overall consumption) of MEK, the
yields of diacetyl and of the sum of acetic
acid and acetaldehyde, and the selectivities
to each product were studied by changing
the reaction temperature. The results are
shown in Fig. 1.

The selectivity to diacetyl is about 40
mol% at a MEK conversion of up to 70%,
but it falls slightly with a further increase in
the conversion. The yield of diacetyl
reaches 30 mol% at 260°C. On the other
hand, the selectivity to acetaldehyde tends
to increase, at the expense of a decrease in
the selectivity to acetic acid, with an in-
crease in the conversion, while the selectiv-
ity to the sum of acetic acid and acetalde-
hyde decreases only a little, from 58 to 56
mol%. The selectivities to propionaldehyde
and to carbon oxides are very low at low
levels of conversion, but they increase
gradually with the conversion.

Effect of the concentration of MEK. The
reaction was conducted at 120°C by chang-
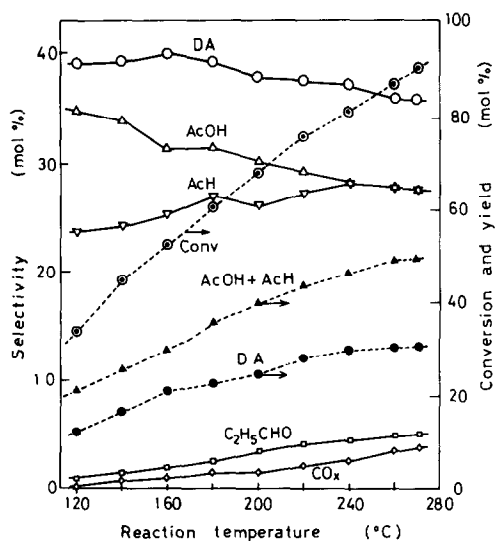ing the initial MEK concentration from 1.0

FIG. 1. Oxidation of MEK on the V–P = 1/1.6 (B) catalyst. DA, diacetyl; AcOH, acetic acid; AcH, acetaldehyde; CO_x, $CO + CO_2$.

FIG. 3. Effect of the MEK concentration on the selectivity. Symbols are the same as for Fig. 1.

to 9.7 vol% in air, while fixing the other conditions as presented in the Experimental section. The results are shown in Fig. 2. With an increase in the MEK concentration by an order of magnitude, the conversion decreases only a little, from 33 to 26%, indicating that the reaction rate is almost proportional to the MEK concentration up to about 10 vol%.

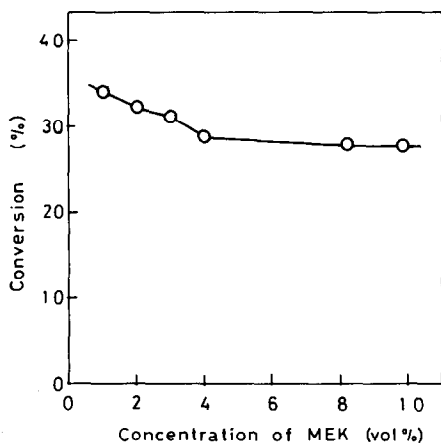In order to ascertain the effect on the selectivity another set of experiments was

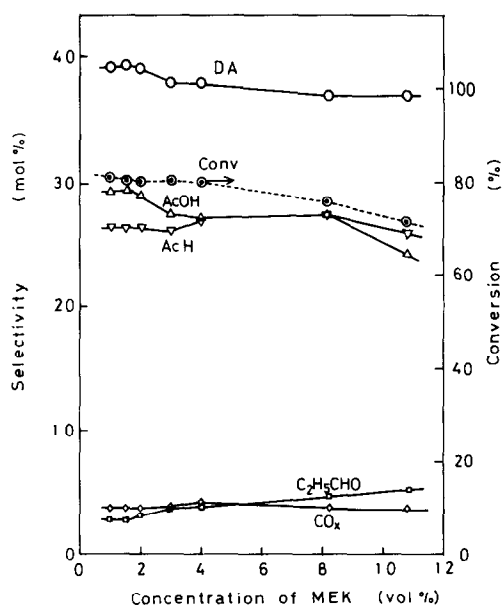FIG. 2. Effect of the MEK concentration on the rate.

conducted at the higher temperature of 250°C. The results are shown in Fig. 3. With an increase in the concentration by more than an order of magnitude, the change in the selectivity is small; diacetyl decreases from 38 to 36 mol%, propionaldehyde increases from 3 to 5 mol%, and carbon oxides and the sum of acetic acid and acetaldehyde remain unchanged at 4 and 54 mol%, respectively.

Effect of the concentration of oxygen. The initial concentration of oxygen was varied from 4.2 to 98 vol%. The change in the MEK conversion at 140°C is shown in Fig. 4. The conversion increases almost proportionally to the oxygen concentration at concentrations below 20 vol%, but it ceases to increase as the concentration increases to more than 50 vol%.

Figure 5 shows the MEK conversion and the selectivities to each product obtained from the reaction with neat oxygen (MEK concentration = 2.0 vol% in oxygen) in the temperature range from 120 to 220°C. From a comparison with the results obtained with air (Fig. 1), it was found that the formation of acetic acid and carbon oxides is en-
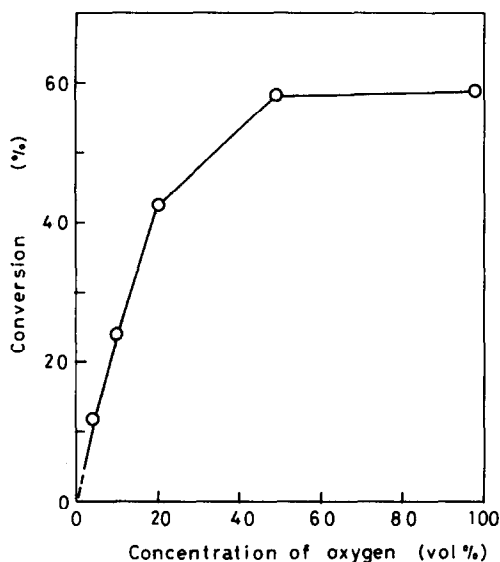
FIG. 4. Effect of the concentration of oxygen on the rate.

FIG. 6. Effect of the addition of water vapor. Symbols are the same as for Fig. 1.

hanced at the expense of a decrease in the formation of diacetyl, and that the consecutive decomposition of diacetyl is enhanced, with an increase in the oxygen concentration.

Effect of the addition of water vapor. The reaction was carried out at 180°C in the
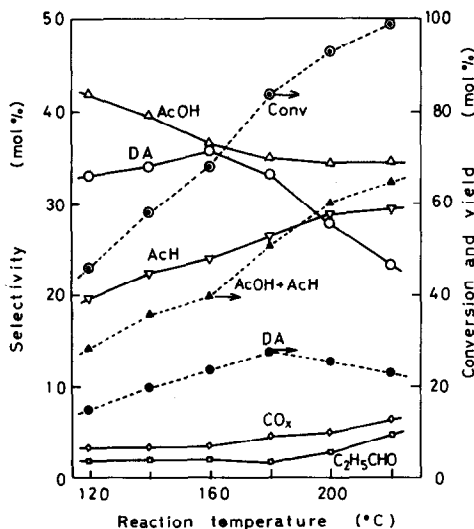

FIG. 5. Oxidation of MEK with oxygen on the V–P = 1/1.6 (B) catalyst. MEK–oxygen = 2/98 vol%; total flow rate, 280 ml (at 20°C)/min; catalyst, 30 g. Symbols are the same as for Fig. 1.
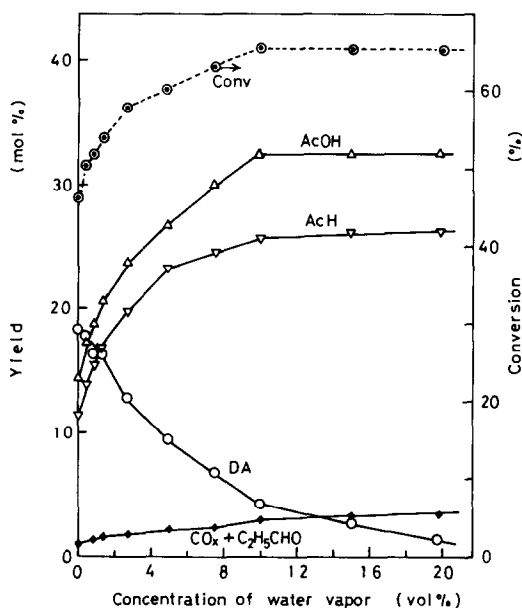
presence of water vapor in the range from zero to 19.7 vol% in the feed. The change in the MEK conversion and the yields of each product are shown in Fig. 6. With an increase in the amount of water vapor, the overall MEK conversion and the yields of acetic acid and of acetaldehyde increase, while the yield of diacetyl falls markedly.

In order to ascertain whether or not water vapor plays a role in promoting the consecutive decomposition of diacetyl, the change in the product distributions with a change in the extent of the reaction was studied in the presence of 10 vol% water vapor. As may be seen in Fig. 7, the selectivity to diacetyl is low, while it remains almost unchanged in the range from 6 to 7 mol%. These results suggest that the addition of water vapor directs the reaction to the oxidative C–C fission, but it does not promote the decomposition of diacetyl.

Effect of temperature. As may be seen in Fig. 1, about 33% of the MEK is converted at a low temperature of 120°C, while the conversion increases very slightly with a further elevation of the temperature. These findings seemed somewhat unusual. This
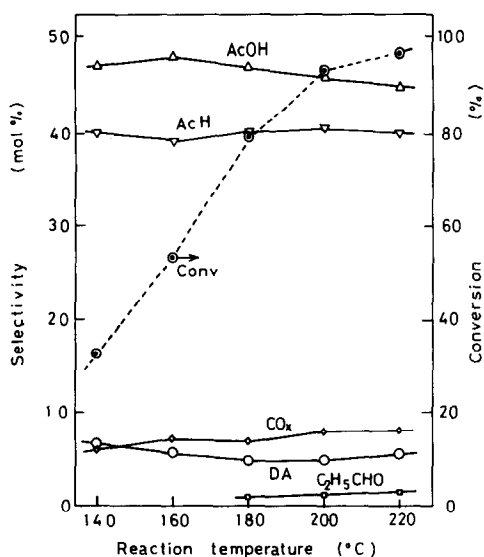
FIG. 7. Oxidation of MEK in the presence of water vapor. Symbols are the same as for Fig. 1.

led us to examine the temperature dependency of the reaction. The reaction was performed at 120, 160, 200, and 240°C and at different contact times. The contact time was varied by changing the amounts of catalyst (5, 10, 20, and 30 g), while fixing the total flow rate as 280 ml (at 20°C)/min. According to the first-order rate equation, the values of $\ln 1/(1 - x)$ are plotted against the nominal contact time, t (sec), where x represents the fraction of the converted MEK and where t is defined as the volume of the catalyst (ml) per unit of the flow rate of the feed (ml/sec). As may be seen in Fig. 8, relatively good linear relationship were obtained up to a 40% conversion for each temperature, suggesting the validity of the first-order approximation. Then the values of the first-order rate constant estimated from the initial slopes in Fig. 8 were plotted according to the Arrhenius equation. A reasonably straight line was obtained. The apparent activation energy calculated was 7.6 kcal/mol.

The effect of the temperature on the selectivity was also studied. Since the selectivity is influenced a little by the extent of the reaction (Figs. 1 and 5), the selectivities

were compared at fixed levels of MEK conversion, 50 and 70% (cf. Table 1). It was found that the selectivity to diacetyl decreases with an increase in the temperature.

Comparison of the Performances of Various Catalysts

Various MoO_3- or V_2O_5-based binary oxides and 12-molybdophosphoric acid and its derivatives were tested for ability to form diacetyl from MEK. The selectivities at a fixed level (50%) of MEK conversion are listed in Table 2. The reaction temperatures required to achieve the MEK conversion of 50% are also shown in the second column as an index reflecting the activity.

The results may be summarized as follows:

(i) The V–P catalysts show a higher selectivity for diacetyl formation than all the other catalysts tested.

(ii) The activity and the selectivity of the V–P catalysts vary markedly depending on the differences in the mode of preparation. The best results are obtained with the V–P (B) catalysts.

(iii) The MoO_3-based oxides show approximately the same level of selectivity, 11 to 18 mol%. The selectivities of heteropoly compounds are comparable with those of the MoO_3-based oxides.
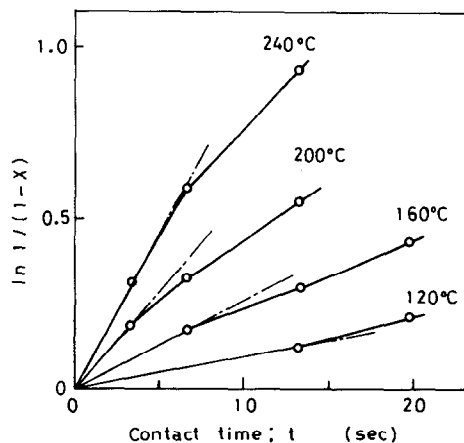

FIG. 8. Plots of $\ln 1/(1 - x)$ against t.

TABLE 1

Effect of the Temperature on the Selectivity to Diacetyl

Catalyst (g)	Temp. (°C)	Conv. (%)	Yield (mol%)	Selec. (mol%)	Temp. (°C)	Conv. (%)	Yield (mol%)	Selec. (mol%)
5	300	50	16	32	360	75	17	23
10	260	51	21	40	340	71	19	27
20	230	56	24	42	280	69	25	36
30	160	48	21	43	210	72	27	38

Note. Conv., overall conversion of MEK; Selec., selectivity to diacetyl.

(iv) The V–Sn and V–Ti catalysts possess a high activity and a high selectivity to acetic acid and acetaldehyde, while they show the lowest selectivity to diacetyl.

The change in the MEK conversion and the selectivities were studied by changing the reaction temperature only for the V_2O_5 and V–Ti catalysts (Fig. 9). With an increase in the temperature, the conversion increases more steeply than that observed

TABLE 2

Oxidation of MEK with Various Catalysts

Catalyst Atomic ratio		Temp. (°C)	Selectivity (mol%) at 50% conversion		
			Diacetyl	2AcOH or 2AcH	Others
Mo–V	8/2	240	14	73	13
Mo–Ti	6/4	230	16	69	15
Mo–Sn	7/3	240	18	68	14
Mo–Fe	7/3	260	15	69	16
Mo–Co	8/2	280	11	76	13
$H_3PMo_{12}O_{40}$		270	13	62	25
$Cs_2HPMo_{12}O_{40}$		245	10	72	18
$H_5PMo_{10}V_2O_{40}$		240	11	73	16
$Cs_{2.5}H_{2.5}PMo_{10}V_2O_{40}$		180	10	77	13
$H_3PMo_4W_8O_{40}$		300	14	56	30
V–S	7/3	250	14	74	12
V–W	7/3	210	6	82	12
V–Mo	8/2	190	8	82	10
V–Sb	9/1	210	14	74	12
V		220	11	76	13
V–Ti	5/5	180	6	88	6
V–Sn	5/5	180	6	89	5
V–K	9/1	240	16	73	11
V–K_2SO_4	7/3	220	15	68	17
V–P (A)	1/1.6	220	22	68	10
V–P (B)	1/1.6	160	40	57	3
V–P (C)	1/1.6	240	24	66	10
V–P (D)	1/1.6	260	25	64	11
V–P (E)	1/1.6	255	28	59	13
V–P (F)	1/1.6	260	33	57	10

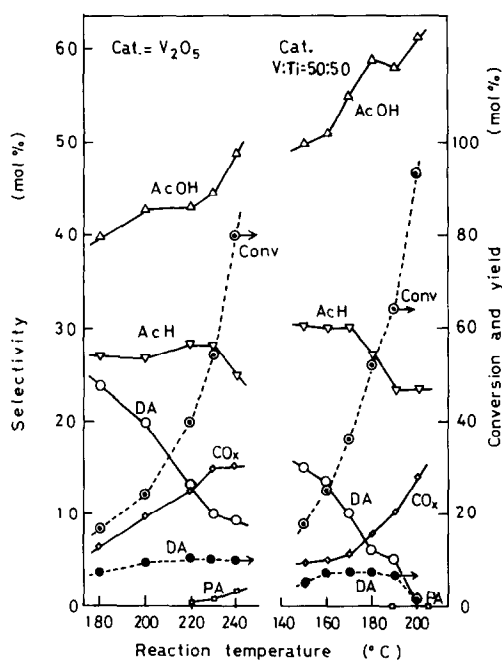*Note.* AcOH, acetic acid; AcH, acetaldehyde.

FIG. 9. Oxidation of MEK on the V_2O_5 and V–Ti = 50/50 catalysts. Symbols are the same as for Fig. 1.

when the reaction is conducted on the V–P (B) catalyst (Fig. 1); on the other hand, the selectivities to acetic acid and to carbon oxides increase at the expense of a decrease in the selectivity to diacetyl. These results indicate that the formation of diacetyl is depressed by its consecutive decomposition.

DISCUSSION

It is predictable that, because of the conjugation with the carbonyl group, MEK is oxidized to methyl vinyl ketone (MVK) by an allylic oxidation like the oxidations of olefins to 1,3-conjugated products. Indeed, MVK was obtained from MEK with a selectivity of 21 mol% on a Bi–Mo oxide at a high temperature of 450°C (17). However, on the V_2O_5–P_2O_5, MEK is oxidized, at a low temperature, to diacetyl, but not to MVK. Tests for the air-oxidation of MVK revealed that MVK is scarcely oxidized at all on the V_2O_5–P_2O_5 catalyst below 280°C, indicating that diacetyl is not formed via MVK. These findings suggest that the for-

mation of diacetyl occurs through a pathway different from that of ordinary allylic oxidations due to participation of lattice oxygen at higher temperatures.

An oxygen dependency similar to that observed in the oxidation of MEK (Fig. 4) is usually observed in oxidations of n-butenes on V–P oxide (1), V–Sn–W oxides (18), and the heteropoly compounds (16, 19), of butadiene on the heteropoly compounds (16, 19), of ethyl benzene on W–Ni oxide (20), and of o-xylene on V_2O_5 (21). This seems to be a common feature observed in oxidations with an acidic catalyst. Possibly, the surface of a catalyst is far from being saturated with oxygen because of its low affinity for oxygen. This may be the reason why these oxidations are usually performed in the presence of an excess of oxygen. The oxygen dependency does not necessarily prove the participation of molecular oxygen in the reaction. However, the present results are at least in conformity with this view.

The rate is nearly proportional to the concentration of MEK even at higher concentration levels and at a low temperature (Fig. 2). This feature is different from that observed in oxidations on acidic catalysts at higher temperatures (1, 14, 16, 19, 21). However, a good proportional relation was observed in the oxidation of n-butenes to acetic acid at temperatures below 250°C (18). This led us to consider that the first-order dependency is a feature observed commonly in oxidative C–C fission performed at low temperatures.

The apparent activation energy obtained is surprisingly low, 7.6 kcal/mol. The apparent activation energy in mild oxidations with V_2O_5-based oxides is in the range from 12 to 30 kcal/mol (22). For example, apparent activation energies of 17.5 (1) and 20 kcal/mol (14) were observed in the oxidation of n-butenes to maleic anhydride on V_2O_5–P_2O_5 catalysts. Interestingly, an apparent activation energy of 9.8 kcal/mol was observed in the oxidation of n-butenes to acetic acid (18). According to detailed

kinetic studies of the oxidation of *n*-butenes to acetic acid, Kaneko *et al.* (*18*) have concluded that the reaction is controlled by a surface reaction between adsorbed oxygen and physically adsorbed *n*-butenes. The participation of molecular oxygen was also assumed in the oxidation of MEK on cobalt-based oxides by Yamazoe *et al.* (*8*). In view of the low activation energy and the high extent of reaction achieved at a low temperature, the participation of molecular oxygen seems to be very probable.

Figure 1 reveals that the formation of diacetyl takes place in parallel with the oxidative C–C fission, and that the consecutive oxidation of products is small, though both reactions are somewhat enhanced under more severe conditions (Fig. 5 and Table 1). To check the reactivities of the products, a set of experiments was conducted using acetic acid (2.4 vol%), acetaldehyde

(2.1 vol%), and diacetyl (1.0 vol%) as the reactants, while fixing the other conditions as presented in the Experimental section. It was found that the consumption of acetic acid is negligibly small at 270°C, that 10% of the acetaldehyde is converted, mainly to acetic acid, at 270°C, and that about 12% of the diacetyl is converted to acetic acid, and about 6% of the diacetyl, to carbon oxides. These findings are in conformity with the results shown in Fig. 1.

The formation of acetic acid is sometimes greater than that of acetaldehyde, but it is hard to believe that this difference is to be ascribed to the consecutive oxidation of acetaldehyde to acetic acid, because the ratio of acetaldehyde to acetic acid increases with an increase in the extent of the reaction (Figs. 1 and 5).

The following peroxide mechanism emerges from the above considerations:
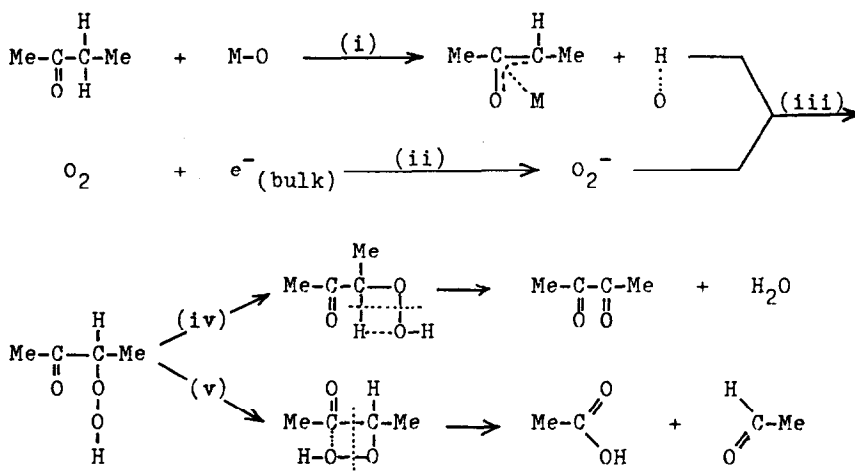
(i) The secondary C–H bonds in MEK are weakened due to conjugation with the carbonyl group, so the adsorption of MEK causes a hydrogen abstraction at this position, resulting in the formation of a conjugated complex, as has been proposed in the oxidation of propylene by Margolis (*22*) and by Daniel and Keulks (*23*).

(ii) Gaseous oxygen is adsorbed in a peroxide species, O_2^-.

(iii) The reaction of the conjugated complex and the O_2^- forms a peroxide species or an hydroperoxide. Then, the peroxide species or hydroperoxide proceeds via two parallel pathways, as has been proposed by Bretton *et al.* (*24*).

(iv) The fission of the O–O bond and adjacent C–H bond leads to the formation of diacetyl.

(v) The fission of the O–O bond and the

adjacent C–C bond leads to the formation of acetic acid and acetaldehyde in equimolar amounts.

Reactions similar to (iv) and (v) have been reported as nonradical rearrangements of hydroperoxide in the liquid phase with transition-metal ions (25, 26) and an alkali catalyst (27), respectively.

The rate-determining step is considered to be (iii) according to the first-order kinetics both on oxygen and on MEK. However, it should be noted that the ability of the above peroxide-like reactions to occur is to be ascribed both to the ease of C–H bond fission at the secondary C–H bonds adjacent to the carbonyl group and to the strong power of the catalyst for hydrogen abstraction, which may be related to the action of Lewis acid.

The addition of water vapor to the feed results in an increase in the conversion of MEK (Fig. 6). The promoting action of water vapor is usually observed in oxidations performed at lower temperatures, regardless of the participation of water in the reaction (16, 19). The effect on the selectivity is much more important (Figs. 6 and 7). The water plays a role in directing the reaction solely to the oxidative C–C fission, not in promoting the decomposition of diacetyl. It seems likely that Brønsted acid is connected with the selectivity, though it is difficult, at present, to explain its reason.

From a comparison of the results shown in Figs. 1 and 9 it is evident that the good performance of the V_2O_5–P_2O_5 catalyst is in part to be ascribed to its low catalytic activity for the decomposition of diacetyl.

Before the action of a catalyst for the reaction of MEK, the factor deciding the selectivity between the two parallel reactions, and the effect of the method of catalyst preparation can be discussed, detailed information on the acid–base, oxido-reduction, and O_2-adsorption properties of the V_2O_5–P_2O_5 system as well as its catalytic behavior, obtained in the oxidation of other organic compounds, should be collected. They will be studied in a subsequent work.

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