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Oxidation of Olefins with Mercuric Salts–Active Charcoal Catalysts

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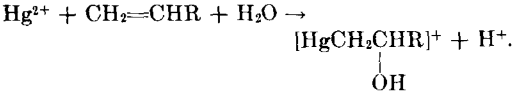
Catalytic reactions of olefins with mercuric salts supported on active charcoal in the presence of oxygen and steam yield unsaturated carbonyl compounds as major products. For proceeding the reaction catalytically, the active charcoal treated with nitric acid was essential as a carrier. The comparison with homogeneous oxymercuration on the kinetics, product distributions and reactivities of olefins suggested that the heterogeneous reactions proceed through each σ-complex and σ-allyl complex.

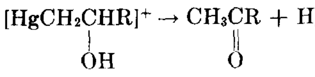
INTRODUCTION

A considerable number of studies has been devoted to the oxidation of olefins by mercuric salts. The addition of oxy salts of mercury to olefins to give β-oxyorganomercury compounds (σ-complex) is a well-known reaction (*1*, *2*).



$$Hg^{2+} + CH_2{=}CHR + H_2O \rightarrow [HgCH_2\underset{OH}{C}HR]^+ + H^+.$$

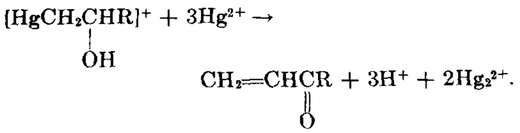
The stoichiometry, stereochemistry and kinetics of the reaction have been investigated (*2*–*4*). Further reaction of the σ-complex by thermal decomposition in aqueous solutions gave oxidized products such as saturated ketones (*5*).



$$[HgCH_2\underset{OH}{C}HR]^+ \rightarrow CH_3\underset{\overset{\|}{O}}{C}R + Hg^0 + H^+,$$

where R is H, alkyl or allyl.

On the other hand, the σ-complex which reacted with mercuric ion gave unsaturated ketone or aldehyde as a major product (*6*).



$$[HgCH_2\underset{OH}{C}HR]^+ + 3Hg^{2+} \rightarrow CH_2{=}CH\underset{\overset{\|}{O}}{C}R + 3H^+ + 2Hg_2^{2+}.$$

Although the stoichiometric oxidations of olefins with mercuric ion in solutions are known, the reoxidation of the reduced species of the metallic salts has not yet been found feasible in solutions. However, we found the oxidation of olefins with mercuric salts supported on active charcoal proceeds catalytically in the vapor phase (*7*).

In this paper we report the results of reactivities and product distributions on the oxidation of ethylene, propylene and butenes with various mercuric salt catalysts and discuss the reaction mechanisms by comparison with homogeneous oxymercuration.

EXPERIMENTAL METHODS

Materials. Ethylene, propylene, 1-butene, isobutene, *cis*-2-butene and *trans*-2-butene were obtained commercially from Takachiho Shoji Co. (Research Grade, minimum purity, 99.8 mol%). Allyl alcohol was obtained from Tokyo Kasei Co. Active charcoal, made from coconut, was obtained from Takeda Yakuhin Co.; the surface area was 952 m^2/g and was crushed to 10–20 mesh grain before use as carrier. The commercially available oxygen and nitrogen were purified by silica gel prior to use. Distilled water was used for the reaction.

Preparation of catalyst. Active charcoal was boiled with a 10% aqueous nitric acid solution for 3 hr and washed with boiling water repeatedly until the pH of rinsed water reached 4. Mercuric chloride–active charcoal catalyst was prepared in the following way. The pretreated active charcoal was immersed in the prescribed aqueous solution of mercuric chloride and was permitted to stand for 24 hr at 25°C. After adsorption of mercuric chloride on active charcoal, the catalyst was water-washed to a pH of 4 and dried at 150°C for 4 hr *in vacuo*. Mercuric acetate, mercuric sulfate, mercuric trifluoro acetate and mercuric bromide on active charcoal were prepared in the same way. For impregnating the charcoal with mercuric iodide the ethanol solution was used because mercuric iodide is not soluble in water. The amount of mercuric salts supported on active charcoal was calculated based upon chelate titration of the filtrate and the washed water, giving rise to 95–99%, usually.

Apparatus and procedure. The experimental apparatus was a conventional flow system. The reactor was a glass tube, 500 mm in length with an inside diameter of 16 mm, with a thermocouple sheath along the central axis. Five grams of mercuric salts–active charcoal catalyst was placed in the center and glass beads (2 mm in diameter) were packed above and below the catalyst bed. Water was fed with a microfeeder and was vaporized at the upper part of the reactor. The gaseous reactants, olefin and oxygen were supplied from the respective cylinders. After being measured separately, these reactants were mixed with each other. All the experiments were made under atmospheric pressure. W/F was between 10 and 20, where W is the catalyst weight and F is the total gas flow rate (mol/hr). The gaseous products from the reactor were cooled in a water condenser. Alcohols, ketones and aldehydes were analyzed by a gas chromatograph attached with a flame-ionization detector by use of a 3 m column packed with polyethyleneglycol 400 at 70°C. Carbon dioxide was analyzed also by gas chromatography using a silica gel column, 2 m in length at 80°C.

Results and Discussion

Mercuric salts supported on carriers such as alumina and silica gels have no catalytic activity for propylene oxidation below 200°C (*8*). Propylene was converted to oxidized compounds but 4% or less in conversion over the mercuric chloride supported on active charcoal so far as the latter is not treated by nitric acid. However, mercuric salts on the active charcoal, which had been treated with nitric acid at 95°C, were found to be active enough to give 10–15% conversion in oxidation of propylene (*8*). About 18 moles of methacrolein per 1 mole of mercuric chloride was formed in 16 hr (*7*). This result shows that mercuric salts–active charcoal catalyze oxidation of olefins.

The rates were measured for the respective product formation at 200°C for W/F 12.5 g-cat hr/mole over mercuric chloride catalysts (9.5 wt% as mercury) with varying partial pressures of oxygen, propylene and water, using nitrogen as the diluent.

$$V_{\text{acrolein}} = k_1[\text{propylene}][\text{O}_2] \quad k_1 = 0.172 \text{ mole/hr atm}^2 \text{ g-cat},$$

$$V_{\text{acetone}} = k_2[\text{propylene}][\text{H}_2\text{O}] \quad k_2 = 0.006 \text{ mole/hr atm}^2 \text{ g-cat},$$

$$V_{\text{CO}_2} = k_3[\text{propylene}][\text{O}_2] \quad k_3 = 0.015 \text{ mole/hr atm}^2 \text{ g-cat}.$$

Incidentally, the rate of methacrolein formation was first order with respect to both oxygen and isobutene and was independent of water (*7*).

The reactivities of the following olefins under the same experimental conditions were found to be in the order: isobutene > 1-butene > *cis*-2-butene > propylene > *trans*-2-butene > ethylene. This is in line with the order of rate constants in solutions of mercuric salts (homogeneous reaction): isobutene > 1-butene > propylene, which also parallels with the order of olefin oxidation by thalic ion (*9*). The products shown in Table 1 were obtained by olefin oxidation over mercuric chloride on active charcoal of our experiments under the conditions given. The formation of unsaturated alcohol such as allyl alcohol, methallyl alcohol, methylvinylcarbinol and crotonyl

TABLE 1
Reactivities and Product Distribution of Olefin Oxidation Over Mercuric Chloride–Active Charcoal Catalyst

Olefin	Conversion[a] (%)	Product distribution (%)							
		Methyl vinyl ketone	Methyl vinyl carbinol	Unsaturated aldehyde	Unsaturated alcohol	Saturated ketone	Saturated alcohol	Acetaldehyde	Carbon dioxide
Ethylene	0.049	0	0	0	0	0	0	0	100.0
Propylene	0.64	0	0	59.2[b]	3.2[c]	2.4[d]	12.9[e]	2.6	19.7
1-Butene	2.39	64.5	15.7	5.6[f]	4.4[g]	0.8[h]	0	0.3	4.1
cis-2-Butene	0.70	39.9	4.7	4.3[f]	3.6[g]	4.7[h]	24.7[i]	4.7	7.4
trans-2-Butene	0.49	36.9	4.7	10.0[f]	3.0[g]	3.9[h]	18.9[i]	4.7	14.0
Isobutene	21.3	0	0	78.9[j]	1.9[k]	0	7.8[l]	0.1	2.1

Experimental conditions: temp, 140°C; W/F = 18–19 g-cat hr/mol; reaction feed ratio, olefin:oxygen: water = 1.0:1.0:10.0; total pressure, 1 atm; catalyst, 5.0 wt%.

[a] Olefin basis.
[b] Acrolein.
[c] Allyl alcohol.
[d] Acetone.
[e] Isopropyl alcohol.
[f] Croton aldehyde.
[g] Crotonyl alcohol.
[h] Methylethylketone.
[i] *sec*-butyl alcohol.
[j] Methacrolein.
[k] Methallyl alcohol.
[l] *tert*-butyl alcohol.

alcohol are particularly interesting, because main products of the oxidation were dehydrogenated compounds of these unsaturated alcohols, namely acrolein, methacrolein, methylvinylketone and croton aldehyde. In other mercuric salt catalysts, the main products were almost the same as shown in Tables 2–4.

A high reactivity of isobutene compared with propylene, 1-butene, *cis*-2-butene and *trans*-2-butene was observed also in the oxidation of olefins by mercuric salts in solutions. The catalytic oxidation of olefins with mercuric chloride–active charcoal yield similar products as those obtained from oxymercuration in solutions. The rela-

TABLE 2
Oxidation of Propylene Over Various Mercuric Salts–Active Charcoal

Salt[a]	Propylene conversion (%)	Product distribution (%)						
		Acrolein	Allyl alcohol	Acetone	*i*-Propyl alcohol	Acetaldehyde	Carbon dioxide	Others
$HgCl_2$	3.5	77.6	4.6	0.9	3.2	1.4	10.3	2.0
$Hg(CH_3COO)_2$	4.1	80.8	4.3	1.0	0.4	1.4	10.2	1.9
$Hg(CF_3COO)_2$	2.5	46.8	2.5	0.2	1.2	0.7	14.3	34.8
$HgBr_2$	2.1	78.1	7.5	0.8	1.5	1.4	5.5	5.2
$HgSO_4$	3.6	41.0	2.7	6.3	36.9	0.6	6.9	5.6
HgI_2	2.8	61.5	4.2	0.1	0.4	6.3	21.1	6.5

Experimental conditions: 160°C; total pressure, 1 atm; mole ratio, propylene:oxygen:water = 1.0:1.0: 10.0; W/F = 14–15 g-cat hr/mol.

[a] Mercuric salts supported are 5.0 wt% as metallic mercury.

TABLE 3

Oxidation of Isobutene Over Various Mercuric Salts-Active Charcoal

Salt[a]	Isobutene conversion (%)	Product distribution (%)						
		Meth-acrolein	Methallyl alcohol	*tert*-Butyl alcohol	Acetone	Acrolein	Acetal-dehyde	Carbon dioxide
$HgCl_2$	10.55	66.7	1.5	23.2	3.0	2.0	0.2	3.4
$HgBr_2$	10.34	67.0	1.7	24.2	3.7	0	0.1	3.2
HgI_2	10.75	70.1	1.9	15.7	0.6	0	6.5	5.4

Experimental conditions: temp, 140°C; total pressure, 1 atm; mole ratio, isobutene:oxygen:water = 1.0:1.0:10.0; W/F = 13.3–13.7 g-cat hr/mol.

[a] Mercuric salts supported are 5.0 wt% as metallic mercury.

tive reactivities of olefin oxidation in various solutions were summarized in Table 5. The mercuric oxidation of olefins differs diametrically from oxidation of olefins with palladium chloride in the number of alkyl substituents (*10*). Longer and more highly branched substituents in general lead to great rates. The rate of the oxidation is determined by the position on the double bond and alkyl substituent rather than by the number of carbons. The reactivity of olefin oxidation catalysis by mercuric chloride agrees with that of the oxidation in solutions of mercuric salts.

The rates of acetone and acrolein formation in propylene oxidation increased with the increasing amount of mercuric salts supported on active charcoal as shown in Fig. 1. The rate of acetone formation remained constant above 3 wt%. However, the rate of acrolein formation increased linearly with the supported amount of mercuric salt up to 10 wt% as shown in Fig. 1. The rate of acetone formation is first order in the concentration of σ-complex and independent of mercuric concentration in solution (*5*). This suggests that only when σ-complex formation is dependent of the mercuric ion and formation of acetone from the σ-complex needs no

TABLE 4

Oxidation of Butenes Over Various Mercuric Salts-Active Charcoal

Salt[a]	Butene conversion (%)	Product distribution (%)						
		Methyl vinyl ketone	Methyl vinyl carbinol	Croton aldehyde	Crotonyl alcohol	Methyl ethyl ketone	Carbon dioxide	Others
1-Butene								
$HgCl_2$	5.15	69.3	9.2	13.2	2.4	0.1	4.4	1.5
$HgBr_2$	4.04	65.3	13.0	12.8	2.7	0.1	4.1	2.0
HgI_2	4.81	64.3	7.6	2.2	4.3	0	10.0	4.5
cis-2-Butene								
$HgCl_2$	1.94	68.0	6.5	7.2	2.0	1.1	7.7	7.7
$HgBr_2$	1.64	70.3	2.0	7.6	0.9	1.7	10.0	7.4
HgI_2	1.74	43.7	20.9	4.1	1.8	0.3	19.5	9.6
trans-2-Butene								
$HgCl_2$	0.72	59.9	2.9	9.0	1.6	3.3	15.2	8.1
$HgBr_2$	0.71	61.1	3.9	5.8	1.0	0	16.7	11.4
HgI_2	0.76	39.2	26.2	3.6	2.4	0.6	15.3	12.8

Experimental conditions: temp, 140°C; total pressure, 1 atm; mole ratio, butene:oxygen:water = 1.0:1.0:10.0; W/F = 13.0–13.7 g-cat hr/mol.

[a] Mercuric salts supported are 5.0 wt% as metallic mercury.

TABLE 5
RELATIVE REACTIVITIES OF OLEFINS

Olefin	$PdCl_4^{2-}$ Oxidation	Tl^{3+} Oxidation	$Hg(ClO_4)_2$ Hydroxy-mercuration	$Hg(NO_3)_2$[a] Saturated carbonyl formation	$Hg(CF_3COO)_2$[a] Unsaturated carbonyl formation	$HgCl_2$ Catalytic oxidation
Ethylene	3.8	6×10^{-3}	0.051	Very slow	—	0
Propylene	1.0	1.0	1.0	1.0	1.0	1.0
1-Butene	0.42	0.97	0.80	8.1	9.3	5.4
cis-2-Butene	0.32	0.35	0.058	4.4×10^3	—	0.93
trans-2-Butene	0.36	0.08	0.017	3.0×10^3	—	0.68
Isobutene	Very slow	1.2×10^3	Very fast	—	1.28×10^2	4.3×10^2
Ref.	*(10)*	*(9)*	*(2)*	*(5)*	*(6)*	This work

[a] Produced from σ-complex.

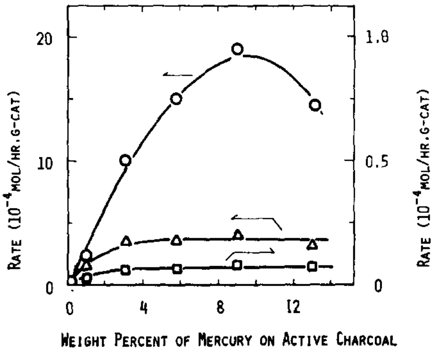


FIG. 1. Formation rate of products versus the amount of supported salt. Catalyst mercuric chloride supported on active charcoal; reaction temp, 200°C; total pressure, 1 atm; mole ratio, propylene:oxygen:water = 2.0:1.0:7.0; W/F = 15 — 17 g-cat hr/mol. (○) Acrolein; (□) acetone; (△) carbon dioxide.

more attack by mercuric ion *(5)*. On the other hand, acrolein formation is first order in the concentration of the σ-complex and mercuric ion *(6)*. These results show that the σ-complex adsorbed on the catalyst reacted with mercuric species near the σ-complex to produce the acrolein. Therefore, the rate of acrolein formation increased with increasing mercuric ion more than that of acetone formation.

Acetone formation is first order in olefin and water. The addition of olefins to oxy salts of mercury (oxymercuration) is known to give a σ-complex. The rate law in oxymercuration was found to be rate = $k[Hg^{2+}][\text{olefin}]$ *(2)*. The σ-complex is an intermediate for saturated ketone produced from olefin oxidation by mercuric ion *(5)*. The reaction rates of the redox decomposition were obtained as first order with respect to the σ-complex *(5)*. Since the reaction product in the D_2O solution was ketone containing no deuterium, hydrogen of σ-complex in redox decomposition of σ-complex transferred intramolecularly. The heterogeneous oxymercuration to form ketone is considered to proceed at the similar mechanisms in solutions.

$$HgX_2 + C_3H_6 + H_2O \overset{K}{\rightleftharpoons} \sigma\text{-complex} + HX,$$

$$\sigma\text{-complex} \xrightarrow{k} CH_3COCH_3 + Hg^0 + HX.$$

The concentrations of mercuric chloride and hydrogen chloride are assumed to be constant in the steady state owing to the reoxidation of catalytic sites by active charcoal and oxygen. The rate equation to yield acetone from propylene, oxygen and water, given as $v = k[\sigma\text{-complex}] = kK[HgX_2][C_3H_6][H_2O] = kK'[C_3H_6][H_2O]$, agrees with the experimental values in heterogeneous catalysis.

The following proposals have been made on the reaction mechanisms of oxymercuration of olefins in homogeneous system.

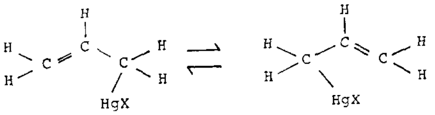
A. In the reaction of propylene with mercuric salts of a trifluoroacetate solution to give acrolein, σ-complex is intermediate and reaction kinetics for acrolein formation obey the following form *(6)*.

$$\text{rate} = k[\sigma\text{-complex}][Hg^{2+}],$$

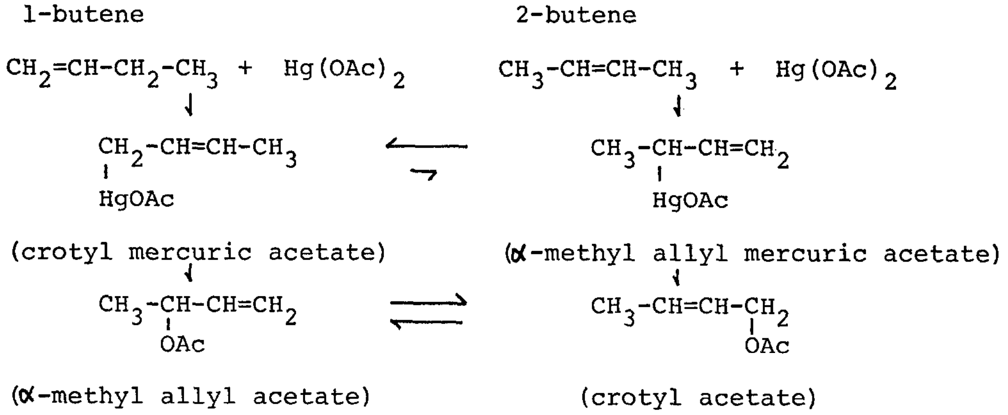
where σ-complex is (2-hydroxylpropyl) mercuric trifluoroacetate.

B. The order of rate constants of unsaturated carbonyl compounds produced from σ-complex in a trifluoroacetate solution is isobutene > 1-butene > propylene.

C. The oxidation of ^{13}C-labeled propylene ($^{13}CH_2{=}CH{-}CH_3$) with the mercuric ion perchloric acid gave two equal moles of $^{13}CH_2{=}CH{-}CHO$ and $CH_2{=}CH{-}^{13}CHO$ (*11*). This fact shows that the oxidation mechanism involves symmetrical allyl complex as an intermediate arising from dehydration of σ-complex, moreover the σ-allyl species was identified by NMR (*12*). Allyl mercuric chloride displays the NMR spectrum with the AX_4 proton pattern for rapidly equilibrating σ-allyl species



D. The NMR spectra of crotyl mercuric bromides show the crotyl isomer (I) with extremely small amount of α-methyl allyl isomer (II) under condition for rapidly allylic equilibration.



(I) (II)

E. Acetolysis of crotyl mercuric acetate gives 99% α-methyl allyl acetate under kinetically controlled conditions (*13*). The crotyl acetate formed by isomerization and its percentage increase with the progress of the reaction. The allylic acetate from the oxidation of the 1-butene, *cis*-2-butene and *trans*-2-butene are in a $Hg(OAc)_2$–HOAc solution are 98% α-methyl allyl acetate. After longer reaction time, an equilibrium distribution of butenyl acetate (ca. 35% α-methyl allyl acetate, 65% crotyl acetate) is obtained from the acid or $Hg(OAc)_2$ catalyzed isomerization (*14*). Rappoport, Winstein and Young (*14*) proposed the following mechanisms for the similar distributions of the allylic acetates in the oxidation of butenes and in the solvolysis of crotyl acetate and most of crotyl mercuric acetate isomers in butenyl system (*14*).

$Hg(OAc)_2$ reacted with crotyl mercurials and promoted demercuration as follows (*12*).

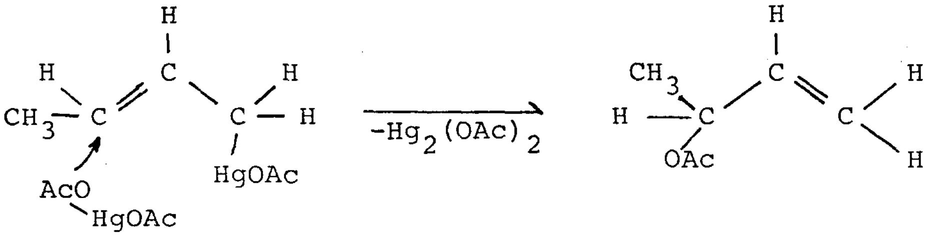


TABLE 6

OXIDATION OF ALLYL ALCOHOL

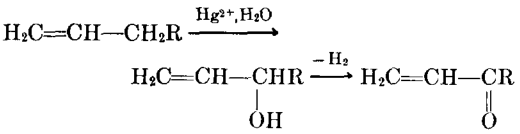
Catalyst	Yield of acrolein (%)
Active charcoal[a]	5.6
$HgCl_2$–active charcoal[b]	6.8

Experimental conditions: temp, 140°C; total pressure, 1 atm; mole ratio, allyl alcohol:oxygen: water = 1.0:1.0:10.0; W/F = 13 g-cat hr/mol.

[a] Active charcoal used treated with nitric acid.

[b] Mercuric chloride supported is 5.0 wt% as metallic mercury.

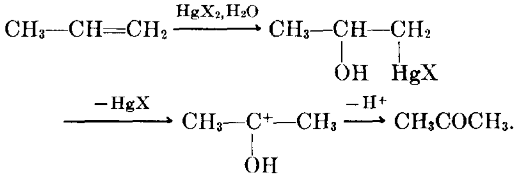
F. Unsaturated alcohols such as allyl alcohol, crotonyl alcohol and methylvinylcarbinol are obtained when terminal olefins are oxidized by aqueous mercuric sulfate, and the formation of unsaturated alcohols was proposed to be an intermediate step in the overall oxidation of olefins to unsaturated carbonyl compounds as follows (*15*).



$$H_2C{=}CH{-}CH_2R \xrightarrow{Hg^{2+},H_2O} H_2C{=}CH{-}\underset{OH}{\underset{|}{C}}HR \xrightarrow{-H_2} H_2C{=}CH{-}\underset{O}{\underset{\|}{C}}R$$

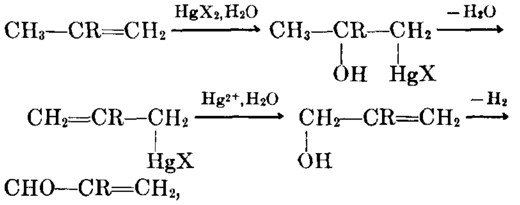
Based on the above-mentioned mechanisms of stoichiometric reaction in solutions, we can give an interpretation to the reaction mechanism of oxymercuration in heterogeneous catalysis. Allyl alcohol was dehydrogenated by oxygen on active charcoal or mercuric chloride–active charcoal catalyst to produce acrolein, as shown in Table 6. Allyl mercuric sulfate was demercurated in aqueous sulfuric acid to yield allyl alcohol. This reaction is similar to the allylic oxidation of olefins by mercuric acetate in acetic acid. The similar distribution of oxidation products in the stoichiometric reaction with mercuric ion in solutions and in the catalytic reaction over mercuric salt–active charcoal argues strongly for the same mechanism in both reactions. This conclusion gains support from the kinetical study about the oxidation of propylene and isobutene and from the reactivities between olefins. The oxidation mechanisms of propylene and isobutene on mercuric salts–active charcoal have been suggested;

1. Acetone formation



$$CH_3{-}CH{=}CH_2 \xrightarrow{HgX_2,H_2O} CH_3{-}\underset{OH}{\underset{|}{C}}H{-}\underset{HgX}{\underset{|}{C}}H_2 \xrightarrow{-HgX} CH_3{-}\underset{OH}{\underset{|}{C^+}}{-}CH_3 \xrightarrow{-H^+} CH_3COCH_3.$$

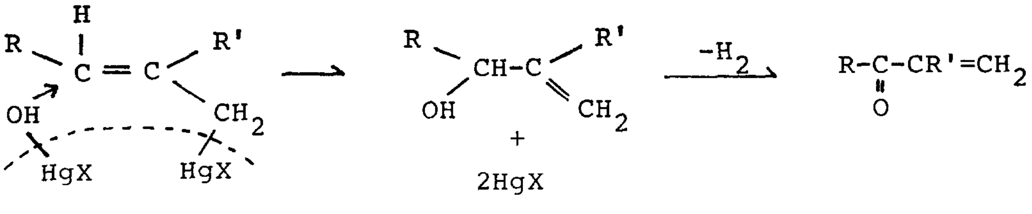
2. Acrolein or methacrolein formation



$$CH_3{-}CR{=}CH_2 \xrightarrow{HgX_2,H_2O} CH_3{-}\underset{OH}{\underset{|}{C}}R{-}\underset{HgX}{\underset{|}{C}}H_2 \xrightarrow{-H_2O} CH_2{=}CR{-}\underset{HgX}{\underset{|}{C}}H_2 \xrightarrow{Hg^{2+},H_2O} \underset{OH}{\underset{|}{C}}H_2{-}CR{=}CH_2 \xrightarrow{-H_2} CHO{-}CR{=}CH_2,$$

where R is hydrogen or methyl.

There is a considerable difference in the dependencies of the rates of formation of acetone and acrolein on the amount of mercuric salts on active charcoal, as shown in Fig. 1. The rate of acetone formation increases with increasing mercuric chloride up to 3 wt% but remains constant above 3 wt%. However the rate of acrolein formation increases with increasing mercuric chloride below 10 wt%. It suggests that σ-complex decomposed to yield acetone but σ-complex reacted again with mercuric ion to give acrolein. The reaction scheme is speculated from the acetoxylation of σ-allyl complex with mercuric ion (*12*) as follows



Since the formation rates of acrolein and methacrolein were found to be first order in olefin and oxygen and independent of water, it is proposed that the oxidation of unsaturated alcohol is the rate-determining step and the active species on the catalyst surface are seemingly in oxidative state due to the following facts: (a) The rate of acetone formation is first order in propylene and water, and independent of oxygen. (b) There are great differences in rates of oxidation between olefins. The observed kinetics of acrolein and methacrolein formation, which were independent of water, suggest that addition of hydroxy to olefin and dehydration of σ-complex to change σ-allyl complex was canceled about a contribution of water to this reaction. Since the unsaturated alcohols (allyl alcohol, methallyl alcohol, methylvinylcarbinol, crotonyl alcohol) were oxidized by adsorbed oxygen to give unsaturated carbonyl compounds, the observed kinetics is first order in oxygen.

The mechanism below was suggested from the product distribution of 1-butene, *cis*-2-butene and *trans*-2-butene oxidation.

$CH_2{=}CH{-}CH^{18}O$ was observed from the oxidation of propylene by $^{16}O_2$ and $H_2{}^{18}O$ on mercuric chloride-active charcoal, which was the catalyst of this work, and it was concluded that the oxygen transferred to the acrolein comes from the oxygen of water molecule (*16*).

Finally, the experimental findings of products and reactivity of the oxidation of olefins under heterogeneous system suggest that the reaction proceeds through a similar reaction mechanism as oxidation of olefins in aqueous solutions of mercuric salts. The mercuric ion, which had been reduced by olefin oxidation, were reoxidized by oxidizing sites produced by nitric acid treatment.

It is of interest to point out that a great number of homogeneous reactions can be applied to develop heterogeneous catalysis.

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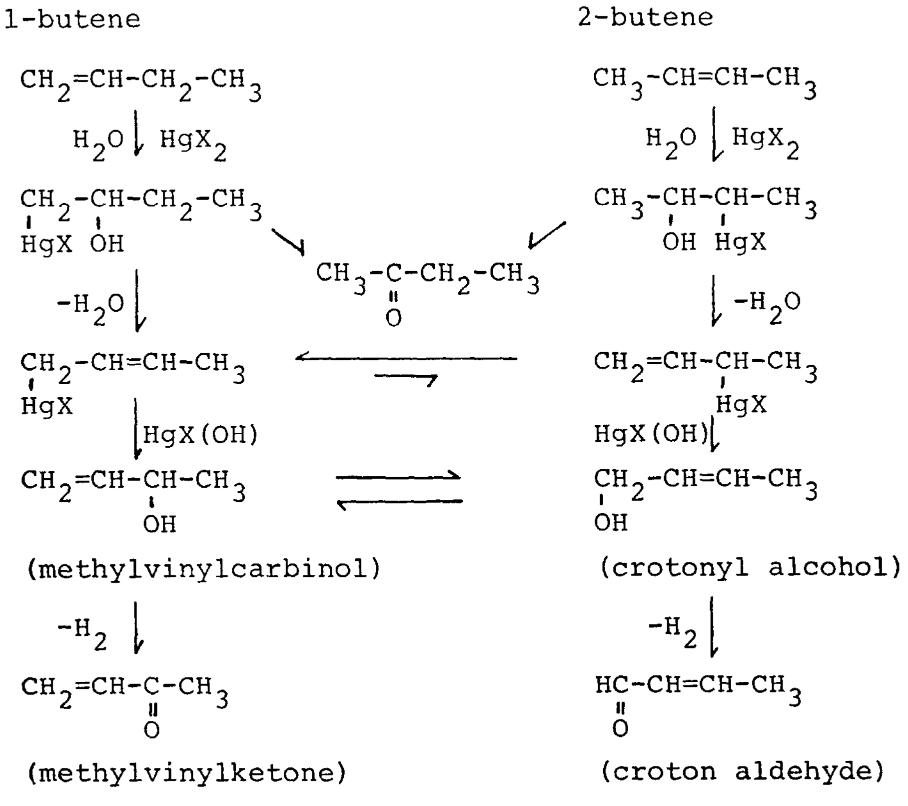

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