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The Liquid Phase Oxidation of Acrolein. III.*[1] Decompositions of Peracrylic Acid by Catalysts and with Acrolein

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Peracrylic acid was decomposed by four kinds of catalysts in a benzene solution at 30°C. The order of the catalysts' effect on the decomposition was: Mn>Co>Fe>Ni; this agreed, except for the reverse order of Co and Mn, with that of the effective catalysts in the oxidation of acrolein (Co>Mn>Fe>Ni). The empirical rate equation,

$$-\,d(CH_2{=}CHCOO_2H)/dt = k(CH_2{=}CHCOO_2H)^{0.58}(\text{catalyst})^{0.56}$$

was obtained from the decomposition by $Co(acac)_3$. On the other hand, from the stationary-state treatment of elementary steps adequate to the reaction and some assumptions, and from the experimental data, the following equation was derived:

$$-\,d(CH_2{=}CHCOO_2H)/dt = 1.3\times10^{-1}(CH_2{=}CHCOO_2H)(Co^{3+}) + 9.6\times10^{-3}(CH_2{=}CHCOO_2H)^{1/2}(Co^{3+})^{1/2}$$

The above two equations have been confirmed as agreeing with each other over the range of reaction conditions used. The interaction of peracrylic acid with acrolein was carried out in the absence of a catalyst under an oxygen or nitrogen atmosphere. In this case, there was formed a complex consisting of both peracrylic acid and acrolein. The complex was mainly decomposed through the ionic mechanism, but in part through the radical mechanism at a higher temperature, namely, through the homolytic cleavage of its peroxy group, followed by the induced decomposition of peracrylic acid. Furthermore, the formation mechanism of acrylic acid in the oxidation of acrolein was discussed in view of the activation energy of the decomposition of peracrylic acid.

It is now well known[1,2] that, in the autoxidation of aldehydes, aldehydes are oxidized to the corresponding peracids in the initial stage of the reaction, and are then converted to the corresponding carboxylic acids. Thus, in order to obtain a closer insight into the mechanism of the reaction, the decomposition of peracids in the absence of and in the presence of aldehydes has been separately investigated by many workers. According to the literature,[3] peracetic acid, which is easily synthesized from acetic acid or acetic anhydride and hydrogen peroxide, is decomposed by metal catalysts through a chain mechanism initiated by the following schemes:

$$CH_3COOOH + M^{(n+1)+} \longrightarrow CH_3COOO\cdot + M^{n+} + H^+, \text{ and}$$

$$CH_3COOOH + M^{n+} \longrightarrow CH_3COO\cdot + M^{(n+1)+} + OH^-.$$

Besides, peracetic acid reacts with acetaldehyde to give its more stable peroxide complex, which is then further decomposed to acetic acid or acetic anhydride.[4]

[*1] Part II: Reference 6.

[1] C. E. H. Bawn and J. B. Jolley, *Trans. Faraday Soc.*, **47**, 721, 735 (1951).

[2] M. J. Kagan and G. D. Lubarsky, *J. Phys. Chem.*, **39**, 837 (1935).

[3] C. E. H. Bawn, F. R. S., T. P. Hobin and L. Raphael, *Proc. Roy. Soc.*, **A237**, 313 (1956).

[4] B. Philips, F. C. Frostick and P. S. Starcher, *J. Am. Chem. Soc.*, **79**, 5982 (1957).

It has been reported in a previous paper[5] that peracrylic acid is an initial product in the oxidation of acrolein. In another paper,[6] it has been reported that peracrylic acid was prepared as a mixture with acrylic acid and decomposed by cobaltic acetylacetonate in various organic solvents; furthermore, the rates of the decomposition were compared with those of the oxidation reaction of acrolein. Therefore, it was considered that the rate-determining step in the oxidation of acrolein was the decomposition of the peracrylic acid formed.

In the present investigation, the decomposition of peracrylic acid by various metal-salt catalysts was carried out in a benzene solution, and the kinetics of the decomposition by cobaltic ions was studied in detail. The non-catalytic interaction of peracrylic acid with acrolein was also examined in order to survey the mechanism of the formation of acrylic acid in the oxidation of acrolein.

Experimental

Material. The preparation of peracrylic acid was carried out in the manner described in a previous paper.[5] The catalysts used in the reaction, cobalt(III)-, manganese(III)-, iron(III)- and nickel(II)-acetylacetonates, were synthesized and purified as in the literature.[5] Acrolein was purified as in the literature.[5]

Procedure. The apparatus and the procedure used in the catalytic decomposition of peracrylic acid have been described in a previous paper.[6] The non-catalytic interaction of peracrylic acid with acrolein was investigated in a benzene solvent under an oxygen or nitrogen atmosphere in the same apparatus. In this reaction, the concentration of peracrylic acid was about 1.0×10^{-1} mol/*l*, while the mole ratio of acrolein to peracrylic acid ranged from 6.94 to 10.61. In this case, acrolein and peracrylic acid reacted, and acrylic acid and the other products produced were quantitatively analyzed.

Analysis. The gaseous products of the catalytic decomposition were mainly analyzed by gas chromatography. The column conditions are shown below, along with those for the quantitative analysis of acids and aldehydes formed in the liquid phase.

All the peroxides in the liquid phase were estimated by an iodometry designed to determine the separate concentrations of hydrogen peroxide, peracrylic acid, and other peroxides.[7]

Hydrogen peroxide was first estimated by charging 1—2 m*l* of an accurately-weighed sample into an Erlenmeyer flask containing 150 m*l* of 5% sulfuric acid and sufficient cracked ice; the temperature of the mixture solution was maintained from 0 to 10°C, and it was titrated with 0.1 N ceric sulfate until the salmon color of the ferroin indicator disappeared. As the concentration of hydrogen peroxide in the feedstock of peracrylic acid was below 3×10^{-3} wt%, this step was omitted. To the resulting mixture there was then added 10 m*l* of a 10% potassium iodide solution, and thus iodine liberated was titrated with 0.1 N sodium thiosulfate. The concentration of the peracrylic acid was thus determined.

$$\text{wt\% of H}_2\text{O}_2=\frac{\text{Ceric sulfate (m}l\text{)}\times N\times17}{\text{Sample weight (g)}\times10}$$

$$\text{wt\% of peracrylic acid}=\frac{\text{Sodium thiosulfate (m}l\text{)}\times N\times44}{\text{Sample weight (g)}\times10}$$

Then the solution was heated for 5 to 10 min, and the further-liberated iodine was titrated with sodium thiosulfate. The active oxygen in the various peroxides other than hydrogen peroxide and peracrylic acid was calculated as follows:

$$\text{wt\% of active oxygen}=\frac{\text{Sodium thiosulfate (m}l\text{) used in this step}\times N\times8}{\text{Sample weight (g)}\times10}$$

In the above fomulas, N denotes the normality of the reagents.

From preliminary experiments, the titration was confirmed as suitable in this investigation. Peracrylic acid could be completely analyzed from 0 to 10°C, and any other peroxides which were perhaps formed during the decomposition were titrated in the last titration step. Moreover, the so-called "peroxide effects" as reported

	Compounds analyzed			
Conditions*	Carbon dioxide	Carbon monoxide	Hydrocarbon	Acids and aldehydes
Column (mesh)	silica gel (30—60)	Molecular sieve 5A	active alumina (60—80)	10% DOS on Diasolid S (80—100)
Column length (m)	1	3	2	3
Column temperature (°C)	room temp.	70	30	120
Helium flow (m*l*/min)	5	30	—**	30

* Thermal conductivity detector.
** Flame ionization detector.

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[5] A. Misono, T. Osa, Y. Ohkatsu and M. Takeda, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 2129 (1966).

[6] Y. Ohkatsu, M. Takeda, T. Hara, T. Osa and A. Misono, This Bulletin, **40**, 1413 (1967).

[7] F. P. Greenspan, *Anal. Chem.*, **20**, 1061 (1948).

[8] M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55**, 2468 (1933).

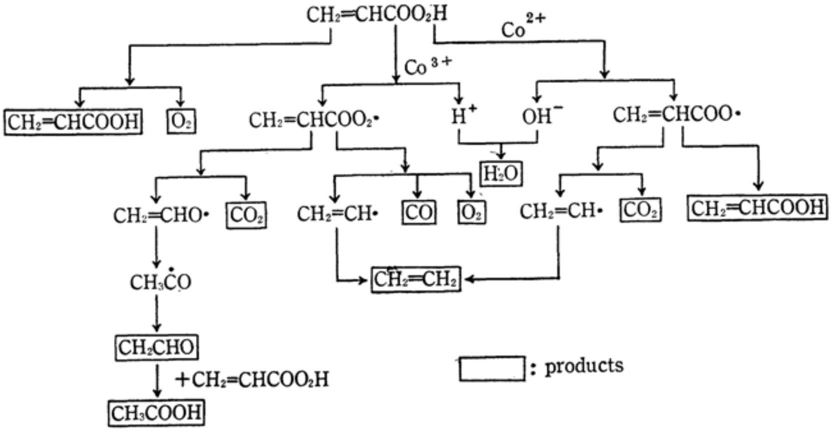

Fig. 1. Decomposition products of peracrylic acid.*

* Peracrylic acid concentration, 1.86×10^{-1} mol/l; catalyst concentration, 1.5×10^{-3} mol/l; in benzene under the nitrogen atmosphere at 30°C.

by Kharasch[8] were essentially negligible within the range of experimental error.

Results and Discussion

Peracrylic acid was decomposed by $Co(acac)_3$ in a benzene solution under a nitrogen atmosphere at 30°C, and the products in the gas, liquid, and solid phases were identified by means of their gas chromatographical retention times (Fig. 1). The main gaseous product, carbon dioxide, was then quantitatively analyzed (Table 1).

TABLE 1. CARBON DIOXIDE IN THE DECOMPOSITION OF PERACRYLIC ACID*

Time min	Carbon dioxide mol	Carbon dioxide mol/mol $CH_2=CHCOO_2H$
33	1.73×10^{-4}	3.72%
90	4.02×10^{-4}	8.60%
170	4.12×10^{-4}	8.86%

* Peracrylic acid concentration, 1.86×10^{-1} mol/l; $Co(acac)_3$ concentration, 7.2×10^{-4} mol/l; 30°C

Carbon dioxide, ethylene, carbon monoxide, and oxygen were found to be the reaction products in the gas phase. The amount of carbon dioxide was the largest, followed by the amount of ethylene. The carbon monoxide is considered to be formed by the decomposition of the acrylic peroxy radical. However, it was measured only a little, for the acrylic peroxy radical is mainly decomposed to an acetyl radical by decarboxylation. The formation of methane, ethane, butadiene, or any other lower hydrocarbons except ethylene was not observed. This may indicate that the acetyl radical formed is not further decomposed, and that the vinyl radical, formed by the decomposition of the acrylic peroxy radical or of the acrylic radical, produces ethylene and does not couple with another vinyl radical to form butadiene because of its low concentration.

In the liquid phase, acrylic acid, acetic acid, acetaldehyde, water and various peroxides were found. Acetaldehyde is considered to be formed from the acetyl radical mentioned above, and then to react with peracrylic acid to be converted into acetic acid.

Some polymers were observed in the solid phase. They are considered to be formed by the polymerization of compounds containing a vinyl double bond by the above various radicals.

The decomposition rates of peracrylic acid in the presence of $Co(acac)_3$, $Mn(acac)_3$, $Fe(acac)_3$, and $Ni(acac)_2$ are shown in Fig. 2. The order of the catalysts' effect on the decomposition was: Mn>Co>Fe>Ni; and this order agreed, except for the reverse order of Co and Mn, with that of the effective catalysts in the oxidation of acrolein; Co>Mn>Fe>Ni,[5] an order which was obtained from the induction periods of the formation of acrylic acid in the oxidation of acrolein. That is, it is mainly ascribed to the order of catalysts effective in the initiation reaction;

$$CH_2{=}CHCHO + M^{(n+1)} \longrightarrow CH_2{=}CH\dot{C}O + M^{n+} + H^+.$$

It may, therefore, be concluded that the catalysts effective in the decomposition are also effective in the initiation reaction. This explanation accords with that made in a similar investigation[9] with respect to the catalysts of both the decomposition of peracetic acid and the oxidation of acetaldehyde.

It is most characteristic of the catalytic decomposition of peracrylic acid that the polymerization

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[9] R. Oda, "Sanka" (Oxidations), Kagaku Kogyo Sha, Tokyo (1963), p. 126.

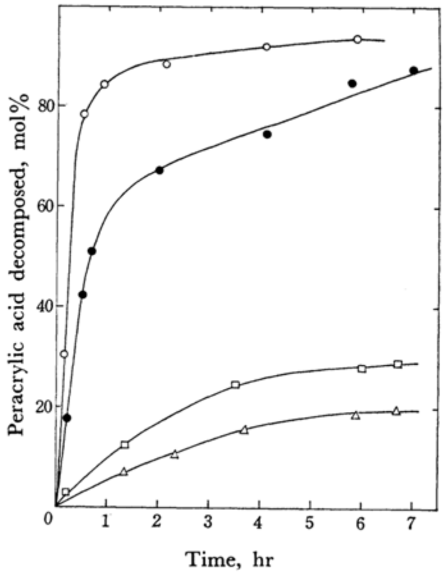

Fig. 2. Decomposition of peracrylic acid by catalysts.
Peracrylic acid concn.: 6.77×10^{-2} mol/l
Catalyst concn.: 1×10^{-3} mol/l; in benzene at 30°C

—○— Mn(acac)$_3$ —□— Fe(acac)$_3$
—●— Co(acac)$_3$ —△— Ni(acac)$_2$

TABLE 2. POLYMERS FORMED IN THE DECOMPOSITION*

Catalyst	Amount of polymer
Co(acac)$_3$	0.27 g
Mn(acac)$_3$	0.04 g
Fe(acac)$_3$	0.01 g
Ni(acac)$_2$	trace

* Peracrylc acid concentration, 4.9×10^{-3} mol (6.77×10^{-2} mol/l); catalyst concentration, 1×10^{-3} mol/l; in benzene solution at 30°C; time, 5 hr

of peracrylic acid and acrylic acid was promoted by the catalyst. In this case the catalyst was precipitated with the polymers to be inactivated, and could not be separated from them by any treatment. This means that peracrylic acid is coordinated with the catalyst, converting it into the acrylic peroxy radical or the acrylic radical under the coordination conditions which intiate the polymerization.¹⁰⁾

Table 2 shows the quantities of polymers formed in the decomposition by the above four catalysts. The amount of polymers decreased in the order: Co>Mn>Fe>Ni. This order has only small agreement with that given above. The catalyst accelerating the decomposition of peracrylic acid may naturally be considered to have a tendency to form polymers, because more radicals will be in the reaction solution when the decomposition rate is higher. However, this consideration alone cannot explain the difference between the orders of Co and Mn.

The Co(acac)$_3$-catalyzed decomposition of peracrylic acid was carried out in a benzene solution at 30°C over a range of catalyst concentrations from 3×10^{-5} to 1.5×10^{-3} mol/l and a range of peracrylic acid concentrations from 1.62×10^{-1} to 8.75×10^{-1} mol/l. The resulting empirical rate equation is shown to be:

$$-\frac{\mathrm{d(CH_2{=}CHCOO_2H)}}{\mathrm{d}t}=k(\mathrm{CH_2{=}CHCOO_2H})^{0.58}(\mathrm{catalyst})^{0.56}$$

It is taken for granted that the reaction proceeds through the following chain mechanism:

Initiation:

$$(1)\quad \mathrm{CH_2{=}CHCOO_2H + Co^{3+}} \overset{K_1}{\rightleftarrows} (\mathrm{CH_2CHCOO_2H{-}Co^{3+}}) \xrightarrow{k_1} \mathrm{CH_2{=}CHCOO_2\cdot + Co^{2+} + H^+}$$

$$(2)\quad \mathrm{CH_2{=}CHCOO_2H + Co^{2+}} \overset{K_2}{\rightleftarrows} (\mathrm{CH_2{=}CHCOO_2H{-}Co^{2+}}) \xrightarrow{k_2} \mathrm{CH_2{=}CHCOO\cdot + Co^{3+} + OH^-}$$

Propagation:

$$(3)\quad \mathrm{CH_2{=}CHCOO_2\cdot} \xrightarrow{k_3} \mathrm{CH_3\dot{C}O + CO_2}$$

$$(4)\quad \mathrm{CH_3\dot{C}O + CH_2{=}CHCOO_2H} \xrightarrow{k_4} \mathrm{CH_3CHO + CH_2CHCOO_2\cdot}$$

$$(5)\quad \mathrm{CH_2{=}CHCOO\cdot + CH_2{=}CHCOO_2H} \xrightarrow{k_5} \mathrm{CH_2{=}CHCOOH + CH{=}CHCOO_2\cdot}$$

Termination:

$$(6)\quad \mathrm{2CH_2{=}CHCOO_2\cdot} \xrightarrow{k_6} \text{inert compound.}$$

In the above scheme, the initiation reactions (1) and (2), consisting of the electron transfer by the metals, are adapted, as in many reports³⁾; they explain the impossibility of separating the catalyst from the polymers. The elementary steps (3) and (4) explain both the experimental results of the remarkable evolution of carbon dioxide (Table 1) and the formation of acetic acid. The step (5) is to be found in the usual propagation reaction, while the step (6) as the termination reaction is acceptable because of the higher concentration of the acrylic peroxy radical.

The application of the stationary-state treatment to the chain mechanism leads to the following decomposition rate equation:

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10) Y. Ohkatsu and A. Misono, unpublished report.

$$-\frac{d(CH_2{=}CHCOO_2H)}{dt} = (CH_2{=}CHCOO_2H)\{k_1K_1(Co^{3+}) + 2k_2K_2(Co^{2+}) + \frac{k_3}{k_6{}^{1/2}}(k_1K_1(Co^{3+}) + k_2K_2(Co^{2+}))^{1/2}(CH_2{=}CHCOO_2H)^{-1/2}\} \qquad (I)$$

As the concentration of cabaltous ions is negligible, as can be seen by the fact that the dark-green color of the solution, indicating the existence of cobaltic ions, was constant during the decomposition, the theoretical rate equation (I) of the catalytic decomposition of peracrylic acid may be replaced by:

$$-\frac{d(CH_2{=}CHCOO_2H)}{dt} = k_1K_1(CH_2{=}CHCOO_2H)(CO^{3+}) + \frac{(k_1K_1)^{1/2}k_3}{k_6{}^{1/2}}(Co^{3+})^{1/2}(CH_2{=}CHCOO_2H)^{1/2} \qquad (II)$$

The constants, k_1K_1 and $(k_1K_1)^{1/2}k_3/k_6{}^{1/2}$, were calculated as 1.3×10^{-1} and 9.6×10^{-3} respectively, by a trial-and-error method by putting the initial concentrations of the catalyst and peracrylic acid and the resulting initial decomposition rate in Eq. (II). Thus, the rate equation is given as:

$$-\frac{d(CH_2{=}CHCOO_2H)}{dt} = 1.3\times10^{-1}(CH_2{=}CHCOO_2H)(Co^{3+}) + 9.6\times10^{-3}(CH_2{=}CHCOO_2H)^{1/2}(Co^{3+})^{1/2} \qquad (III)$$

From a comparison of the decomposition rate observed with that derived from the theoretical Eq. (III) and shown in Table 3, Eq. (III) may be justified over the range of the reaction conditions used; accordingly, it also supports the empirical equation described above and the assumed elementary steps.

The interaction of peracrylic acid with acrolein was carried out in the absence of any catalyst and under an oxygen atmosphere at 20 to 40°C. The results are shown in Fig. 3. Immediately after the beginning of the reaction, the decomposition of peracrylic acid, the consumption of acrolein, and the formation of acrylic acid and, in some case, peroxides were observed, although peracrylic acid was decomposed by itself at 30°C after about a three hours' induction period. Moreover, even after ten hours, there was still no polymer visible in the reaction solution. In the case of 30°C, two moles of acrylic acid were produced by the decomposition of about one mole of peracrylic acid and the consumption of about one mole of acrolein, but no peroxides were detected in the reaction solution by iodometry titration. Thus, the formation

TABLE 3. RATES OF PERACRYLIC ACID DECOMPOSITION*

$CH_2{=}CHCOO_2H$ concentration ×10 mol/l	Co concentration ×10⁴ mol/l	Decomposition rate mol/min Theoretical ×10⁴	Decomposition rate mol/min Observed ×10⁴
1.62	6.75	1.14	1.13
3.24	6.84	1.71	1.70
8.75	6.76	3.10	3.00
1.82	0.588	0.327	0.315
1.86	0.300	0.234	0.232
1.86	4.69	1.08	1.07
1.82	6.76	1.22	1.12
1.86	15.0	1.95	1.90

* Decomposition of peracrylic acid in benzene solution under the nitrogen atmosphere at 30°C

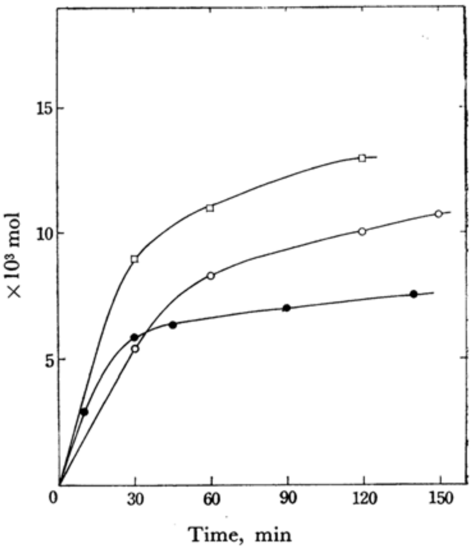


Fig. 3-1

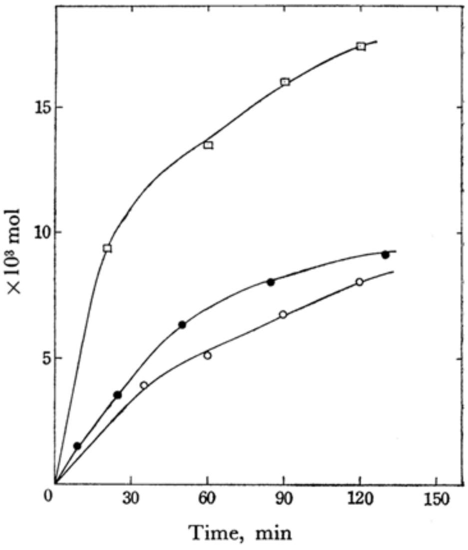


Fig. 3-2.

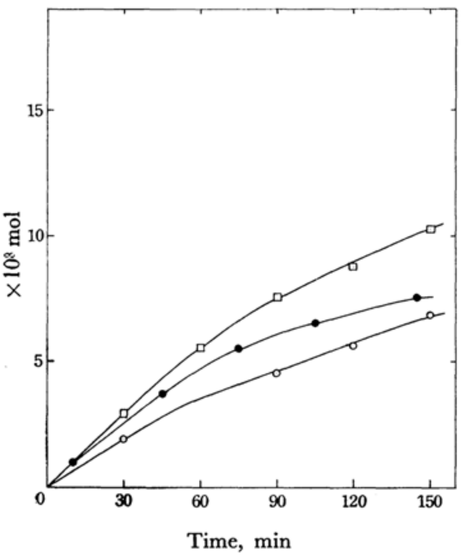


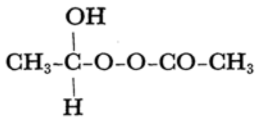
Fig. 3-3.

Fig. 3. Interaction of peracrylic acid with acrolein under the oxygen atmosphere at 40 to 20°C.

Peracrylic acid concn.: 1.08×10^{-2} mol/l
Acrolein concn.: 7.48×10^{-2} mol/l
—□— Acrylic acid formed
—○— Acrolein consumed
—●— Peracrylic acid decomposed
Reaction temp.: Fig. 3-1. 40°C
Fig. 3-2. 30°C
Fig. 3-3. 20°C

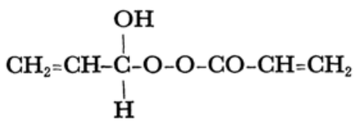
of acrylic acid in this reaction may be considered to be due to the decomposition of the peroxide complex, consisting of both peracrylic acid and acrolein, as has been widely established in the oxidation of acetaldehyde.1) At 20°C, acrylic acid corresponding to the sum of the peracrylic acid decomposed and the acrolein consumed was not formed; many peroxides were present in the reaction solution. These results mean that peracrylic acid is stable at 20°C and is decomposed *via* the complex. The small amount of acrylic acid at 40°C may be attributed to the formation of soluble polymers.

Assuming that the complex of peracrylic acid with acrolein is similar to acetaldehydemonoperacetate,



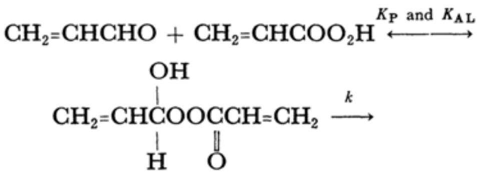
$$\mathrm{CH_3{-}\overset{OH}{\underset{H}{C}}{-}O{-}O{-}CO{-}CH_3}$$

through its configuration could not be determined, the complex may be given as follows:



$$\mathrm{CH_2{=}CH{-}\overset{OH}{\underset{H}{C}}{-}O{-}O{-}CO{-}CH{=}CH_2}$$

When the formation of acrylic acid proceeds by the following mechanism,



$$\mathrm{CH_2{=}CHCHO + CH_2{=}CHCOO_2H} \xleftrightarrow{K_P \text{ and } K_{AL}} \mathrm{CH_2{=}CH\overset{OH}{\underset{H}{C}}OO\underset{O}{\overset{}{\underset{\|}{C}}}CH{=}CH_2} \xrightarrow{k}$$

the values of kK_P and kK_{AL} are obtained (Table 4). In the above equation, K_P and K_{AL} denote the equilibrium constants based on the rates of consumption of peracrylic acid and acrolein as calculated from $-d(P)/dt = kK_P(AL)(P)$ and $-d(AL)/dt = kK_{AL}(AL)(P)$ respectively, in which AL is acrolein and P is peracrylic acid. If the reaction proceeds only through the decomposition of the complex, the value of $kK_P/kK_{AL} = d(P)/d(AL)$ must be equal to one. However, the experimental data show that the values are above one at all temperatures. Therefore, some other decomposition must be considered to occur in the reaction.

The same experiments were repeated under the same conditions except for the use of a nitrogen atmosphere in place of an oxygen atmosphere. In this case, white polymers were observed after 30 min, while no polymers were formed under an oxygen atmosphere; the solution turned entirely to gel after one hour. These results indicate that some radicals exist in the reaction solution, because oxygen is known to be an inhibitor of a radical polymerization. Accepting the well-established interpretation that the aldehyde-peracid complex is only ionically decomposed,1) the conspicuous formation of polymers in this reaction cannot be

TABLE 4. VALUE OF K_P AND K_{AL} IN THE INTERACTION OF PERACRYLIC ACID AND ACROLEIN

	Reaction temperature, °C		
	20	30	40
$-d(P)/dt$, mol/min	9.0×10^{-5}	15.0×10^{-5}	5.8×10^{-4}
$-d(AL)/dt$, mol/min	7.2×10^{-5}	11.9×10^{-5}	21.8×10^{-5}
kK_P	1.24×10^{-2}	2.00×10^{-1}	2.50×10^{-1}
kK_{AL}	9.87×10^{-1}	1.56×10^{-1}	2.84×10^{-1}
K_P/K_{AL}	1.26	1.28	2.64
$K_P/K_{AL}-1$	0.26	0.28	1.64

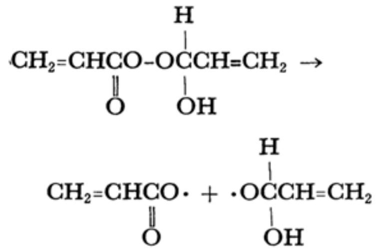
TABLE 5. RATES OF ACROLEIN CONSUMPTION AT DIFFERENT CONCENTRATIONS OF ACROLEIN TO PERACRYLIC ACID*

(AL)/(P)	$-d(AL)/dt$	kK_{AL}
10.61	8.34×10 mol/min	1.56×10^{-1}
6.94	11.9×10 mol/min	1.48×10^{-1}

* Reaction temperature, 30°C; in benzene solution under the oxygen atmosphere

explained. However, peracrylic acid did not immediately decompose by itself at 30°C.

Therefore, the formation of radicals may be elucidated as caused by the homolytic cleavage of the weakest bond in the peroxide complex, and the formation of polymers may be understood as follows:



$$\mathrm{CH_2{=}CH\underset{\underset{O}{\|}}{C}O{-}O\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}CH{=}CH_2} \rightarrow$$

$$\mathrm{CH_2{=}CH\underset{\underset{O}{\|}}{C}O\cdot} + \mathrm{\cdot O\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}CH{=}CH_2}$$

The $(kK_P/kK_{AL}-1)$ values in Table 4 may, then, correspond to the decomposition of peracrylic acid induced by the radicals which are produced in the above radical decomposition of the peracrylic-acrolein complex. This consideration well explains the findings that this radical decomposition increased with the increase in the reaction temperature, and that the polymerization occurred only under a nitrogen atmosphere. However, as the values at 20°C and 30°C were almost constant, the ratio of the radical decomposition of the complex to the ionic decomposition is considered to be small at these temperatures. Furthermore, at 30°C, as is shown in Table 5, the rate of acrolein consumed was higher at a lower ratio of the concentration of acrolein to peracrylic acid, but the values of kK_{AL} coincided with each other at different ratios. Accordingly, it may be estimated that acrolein is consumed only *via* the complex, which is decomposed ionically to acrylic acid, and that the complex is quite stable to the radical decomposition at 30°C.

The activation energy of the decomposition of peracrylic acid is calculated from the lines shown in Fig. 4. Line A plots the rates of the catalytic decomposition of peracrylic acid by $Co(acac)_3$. Line B plots the rates of acrolein consumption in the non-catalytic interaction of peracrylic acid with acrolein. From the slopes of Lines A and B, 14.4 and 10.2 kcal/mol are obtained respectively. The latter activation energy is perhaps that of the formation of acrylic acid through the peroxide complex of acrolein and peracrylic acid, since the rates of the reaction are based on those of the acrolein consumed.

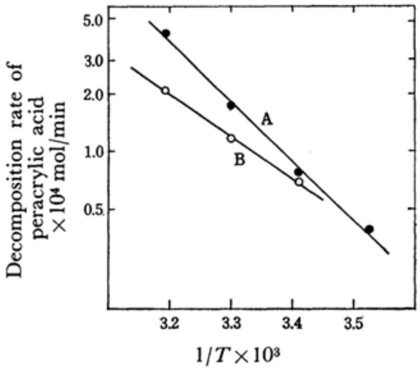


Fig. 4. Activation energies of the decomposition of peracrylic acid.
A Decomposition by $Co(acac)_3$
B Decomposition with acrolein

According to the results obtained in the oxidation of acrolein, acrylic acid may be mainly formed in two ways, by the decomposition of peracrylic acid by itself and by the decomposition of the complex. The latter decomposition is more likely than the former. However, in order to elucidate the formation of acrylic acid, the catalytic decomposition of the complex will also have to be invesigated.