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The Liquid Phase Oxidation of Acrolein. II.[*1] Solvent Effects in the Liquid Phase Oxidation of Acrolein and the Decomposition of Peracrylic Acid[*2]

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The liquid phase oxidation of acrolein and the decomposition of peracrylic acid with Co(acac)$_3$ in various solvents were investigated. The solvents of butyric and valeric acids gave the most desirable results with respect to the selective oxidation; for example, in butyric acid with 5×10^{-4} mol/*l* of Co(acac)$_3$ for 4 hr at 35°C, the conversion of acrolein and the selectivity of acrylic acid were 45.1% and 86.0%, respectively. The preferable solvent effects of C$_4$ and C$_5$ carboxylic acids were discussed in terms of the acidity and dielectric constant of the solvents, the oxygen solubility in the solvents and the interaction of the solvents with acrolein. Furthermore, from the comparison of solvent effects in the oxidation of acrolein with those in the decomposition of peracrylic acid, one of the rate determining steps in the oxidation was elucidated to be much concerned with the decomposition of peracrylic acid formed during the reaction.

Several investigations have been reported about solvent effects in a liquid phase oxidation. However, many of them relate to the oxidation of hydrocarbons and some are partly concerned with solvent effects in the oxidation of unsaturated aldehydes, such as acrolein and methacrolein. Thus, benzene,$^{1)}$ acetic acid,$^{2)}$ toluene$^{3)}$ and *t*-butyl alcohol$^{4)}$ have been used to obtain acrylic acid or methacrylic acid from the corresponding aldehyde in high selectivity, but no systematic investigation of solvent effects has been reported.

In general, solvent effects in the liquid phase oxidation are considered in three actions as follows: (1) solvents affect substrates and their peroxides directly, and change oxidation activities of the formers and decomposition activities of the latters; (2) solvents occupy coordination sites of the metal of a catalyst and change the activities of the catalyst; and (3) solvents act as a radical transfer.

The reactivities in the oxidation of acrolein in various solvents with Co(acac)$_3$ as a catalyst at 30°C or 35°C are investigated in this paper by determining the oxygen absorption rate, the conversion of acrolein, the yield of acrylic acid and the selectivity of acrylic acid. Butyric and valeric acids were found to be most effective in the autoxidation of acrolein, because in these solvents the reaction rates and selectivities of acrylic acid were higher than in any other solvents. Therefore, the relation between carbon numbers of lower aliphatic acids and oxygen absorption rates in those acids is discussed. Furthermore, decomposition of peracrylic acid with the same catalyst were carried out in many kinds of solvents and compared with the oxidation of acrolein.

Solvent effects are also discussed from the results of oxygen absorption rate, the dissolved amount of oxygen in solvents and the NMR spectra of acrolein in three solvents.

Experimental

Materials. Acrolein was purified and the catalyst, Co(acac)$_3$, was synthesized as in the previous paper.$^{5)}$

Solvents, such as methanol, monochloroacetic acid, formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, capric acid, benzene, toluene, cyclohexane, *n*-hexane, nitrobenzene, carbon tetrachloride, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, ethyl acetate and propionitrile, were used after purification, especially dehydration, by conventional methods.

Peracrylic acid was prepared as follows. To the mixture of 1.0 mol of acrylic acid and 1.0 mol of benzene, 1.2 mol of hydrogen peroxide (80%) was added in the presence of concentrated sulfuric acid (1.0 wt%). The solution was stirred for 30 hr at the room temperature and then the benzene phase, seprated from the water phase, was dried over anhydrous sodium sulfate to give 0.45 mol/*l* of peracrylic acid in benzene solution. The resulting peracrylic acid was used in its decomposition experiments.

[*1] Part I, Reference 7.

[*2] Presented at 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966.

1) W. Bauer and P. Weiseret, U. S. Pat. 1911219.

2) H. Schulz and H. Wagner, *Angew. Chem.*, **62**, 105 (1950).

3) J. M. Church, L. Lynu, *Ind. Eng. Chem.*, **42**, 768 (1950).

4) H. Shingu and T. Konaka, The 13th Annual Meeting of the Chemical Society of Japan, Preprints (1960), p. 305.

Procedure. The oxidation reaction was carried out with the same apparatus and method as described in the report.[5] The reaction conditions were: acrolein, 15 ml; solvent, 60 ml; reaction temperature, 30 and 35°C; catalyst concentration, 5.0×10^{-4} mol/l and 1.5×10^{-3} mol/l, if used.

The catalytic decomposition of peracrylic acid was carried out in an equipment shown in Fig. 1. The reactor of 80 ml capacity had a sampling outlet on the top and could be purged with nitrogen. At first, a solution, where a suitable amount of a catalyst, Co(acac)$_3$, was dissolved, was added to the mixture of peracrylic acid and a solvent with magnetical stirring. The reaction temperature was controlled within 30±0.1°C. The amount of decomposed peracrylic acid was determined by an iodometric titration at suitable reaction times.

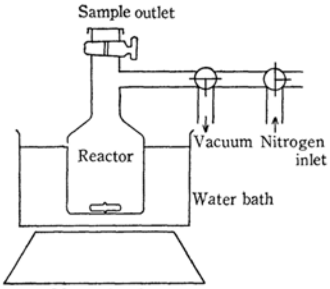

Fig. 1. An equipment for decomposition of peracrylic acid.

Measurements. The amount of oxygen dissolved in a solvent were determined by Sugawara's method.[6] The oxidation products of acrolein and the decomposition products of peracrylic acid were analysed mainly by gas chromatography.[7] Peracrylic acid and peroxides were determined according to the method by Greenspan *et al.*[8] Polymeric products in both the oxidation of acrolein and the decomposition of peracrylic acid were measured as follows: at the end of the reactions, the reactor was cooled rapidly and hydroquinone was charged. Then insoluble polymers containing oligomers were filtered, dried and weighed.

Results and discussion

The liquid phase oxidation of acrolein was carried out with Co(acac)$_3$ as a catalyst in many kinds of solvents at 30°C and the amount of oxygen absorbed was measured. The oxygen absorption rate, the conversion of acrolein and the selectivity of monomeric acrylic acid in seventeen solvents were shown in Table 1. A solvent and the catalyst were found to be necessary to obtain acrylic acid in the oxidation of acrolein, since monomeric acid was less produced without solvent and catalyst. The solvent, in which the maximum oxygen

Table 1. Solvent effect of the oxidation of acrolein

Solvent	$(dO_2/dt)_{max}$*	Conversion %	Selectivity %
Formic acid	1.8	20.2	22.8
Acetic acid	6.36	29.4	36.1
Propionic acid	7.63	31.3	—
Butyric acid	8.72	40.9	70.2
Butyric acid**	0.36	9.3	0.0
Valeric acid	8.12	39.7	36.6
Caproic acid	6.90	33.1	32.9
Capric acid	6.53	35.3	28.9
Benzene	5.82	39.6	32.3
Benzene**	0.36	8.8	0.0
Toluene	6.36	40.4	28.4
Carbon tetrachloride	4.45	39.2	30.9
Cyclohexane	3.09	32.2	23.7
n-Hexane	4.36	22.0	14.6
Nitrobenzene	2.18	34.7	7.6
Dimethyl sulfoxide	2.06	32.1	2.3
Water	0.26	—	—
—	9.08	80.3	5.6

Conditions: reaction temperature, 30.0°C
acrolein concentration, 3.0 mol/l
Co(acac)$_3$, 1.5×10^{-3} mol/l
reaction time, 2.0 hr
* $\times10^3 O_2$ mol/acrolein mol/min
** Uncatalyzed

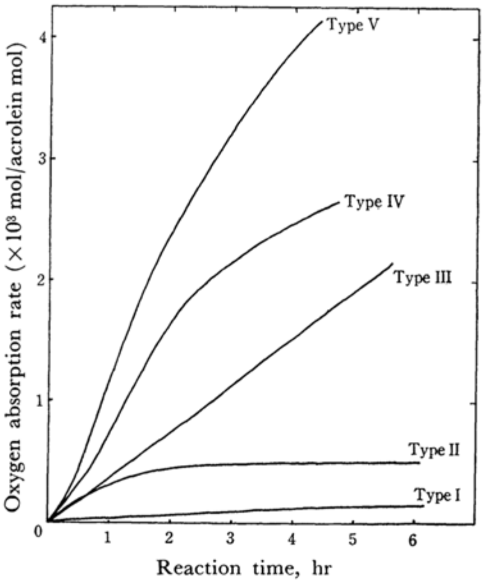

Fig. 2. The amount of oxygen absorbed.
Reaction conditions: reaction temperature, 30°C
acrolein concn., 3.0 mol/l
Co(acac)$_3$, 1.5×10^{-3} mol/l.

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[5] Y. Ohkatsu, T. Osa and A. Misono, This Bulletin, **40**, No. 9, in press.

[6] K. Kanehara, "Natural Gas Research and Sources," Asakurashoten, Tokyo.

[7] A. Misono, T. Osa, Y. Ohkatsu and M. Takeda, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 2130 (1966).

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

absorption rate was higher, in general, tended to promote the conversion of acrolein, but not always to increase the selectivety of acrylic acid. This may ascribed to the different amount of polymers formed during the reaction. Furthermore, solvents were classified into five types by the appearance of oxygen absorbed as shown in Fig. 2.

Type I. Water, Methanol, Monochloroacetic Acid and Formic Acid.

These solvents retarded the reaction velocity strongly and the oxidation proceeded undesirably. This may be attributed mainly to an interaption of the catalyst with solvents and a stop of the chain reaction by solvent reacting with propagating radicals, because monochloroacetic acid and formic acid having a large dissociation constant (the former: 1.55×10^{-3}, the latter: 1.77×10^{-3}) were reported to inactivate a catalyst and retard the reaction in the case of oxidation of various hydrocarbons.[9]

Type II. Cyclohexane and *n*-Hexane.

The oxidation reaction of acrolein in these two solvents proceeded considerably at the very early stage of the reaction. It was observed, however, that polymerization reaction occurred simultaneously and the resulting polymers made the catalyst precipitate. Therefore, the oxidation rate decreased gradually and became nearly zero in the later stage of the reaction. As reported by Hendly and Russel,[10] solvents of low polarity such as these solvents seem to have no particular interaction for the oxidation reaction.

Type III. Dimethyl Acetamide, Dimethyl Formamide, Dimethyl Sulfoxide and Nitrobenzene.

The amount of oxygen absorbed increased almost linearly as the reaction time went by and the conversion of acrolein was also observed. However, the monomeric acrylic acid was produced a very little (Table 1). Therefore, acrolein consumed may be attributable to the formation of polymers, including oligomers, composed of acrolein and/or acrylic acid rather than the production of monomeric acrylic acid. But the visible amount of precipitated polymers was not formed through the oxidation reaction. Some solvents are oxidized themselves and/or act as a retarder of radical polymerization. Though the content of nitrogen or sulfur in polymers soluble in the solvents was not analyzed, it is reasonable that radicals, such as $CH_2{=}CH\dot{C}O$ and $CH_2{=}CHCOO_2\cdot$, formed during the oxidation attack the nuclear of the solvents or their radicals and are trapped. Furthermore, these solvents of high polarities may occupy the coordination shell of the catalyst and vary the redox potential of the catalyst or disturb the coordination of reagents, resulting in the lower activity of the catalyst.[11] But the catalyst in these solvents did not precipitate even after five hours.

Type IV. Benzene, Toluene and Carbon Tetrachloride.

In these solvents, the velocity of the oxidation was very high, but went down rapidly after the middle stage of the reaction. This will probably be due to the inactivation of the catalyst. The inactivation of the metal catalyst in these neutral solvents has also observed by previous workers during the catalyzed autoxidation of tetralin,[12] *n*-decane,[13] and cumene.[14]

Type V. Butyric Acid and Valeric Acid.

The oxidation of unsaturated aldehydes was found to proceed suitably at the high oxidation rate and have the high selectivity of the corresponding acid in these lower carboxylic acid solvents. The rate of oxygen absorbed was kept high after five hours of the reaction time and this aspect was very different from the solvents of Type II and Type IV.

As the very good results were obtained by use of C_4 and C_5 aliphatic carboxylic acid solvents, a series of lower aliphatic acids were tested as a solvent. The maximum oxygen absorption rates in C_1—C_8 saturated aliphatic acids are shown in Fig. 3. The curve of the maximum rates was in a convex form, the peak of which stood at C_4 and C_5 acids. In order to explain this tendency, some reasons are considered: the higher pK_a of a solvent is, the more strongly a hydrogen bond between the carboxylic group of the solvent and the aldehyde group of acrolein will be able to be formed. Solvents having a higher dielectric constant are more ready to admix with and trap the water, formed during the oxidation, from the cirumstance of the catalyst, and consequently make its activity keep high, because excess water inactivates the catalyst and lessens the reaction rate. These two reasons suggest that the lower acids are preferably active to the oxidation. On the other hand, acrolein must approach the coordination shell of a catalyst and be coordinated with it in order that the reaction may start.[7] However, lower carboxylic acids with high pK_a will tend to approach the catalyst and disturb the coordination of acrolein. Therefore, higher acids will promote the oxidation reaction more than lower acids. As described hereinafter, moreover,

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[9] Y. Kamiya, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 1877 (1965).

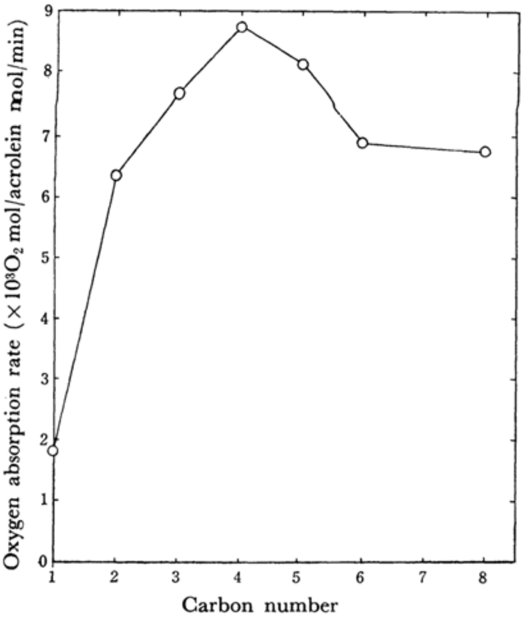
[10] D. G. Hendry and G. A. Russel, *J. Am. Chem. Soc.*, **86**, 2368 (1964).

[11] C. Nafre, *Bull. Soc. Chim. France*, 530 (1961).

[12] Y. Kamiya and K. U. Ingold, *Can. J. Chem.*, **41**, 2034 (1963).

[13] D. G. Knorre, Z. K. Maĭzus and N. M. Emanuel, *Zh. Fiz. Khim.*, **29**, 710 (1955).

[14] B. V. Erofeev, *ibid.*, **33**, 903 (1960).



Reaction conditions: Reaction temperature, 30°C
acrolein concn., 3.0 mol/*l*
$Co(acac)_3$, 1.5×10^{-3} mol/*l*

Fig. 3. Maximum oxygen absorption rates in C_1—C_8 saturated aliphatic carboxylic acids.

the solubility of oxygen in acid solvents forms the convex curve to the carbon number of the solvents. The curve had the peak at butyric acid and its inclination accorded with that in Fig. 3. The combination of these explanations may lead to consideration of results in Fig. 3.

An aspect of the oxidation of acrolein in butyric acid solvent, in which the highest maximum oxygen absorption rate was observed, was illustrated in Fig. 4. Full lines show the results in butyric acid and broken lines in benzene for comparison. Butyric acid was found to be considerably preferable in the oxygen absorption rate, the conversion of acrolein and the selectivity of acrylic acid, compared with benzene, which had been reported to be a suitable solvent for the oxidation of methacrolein1) and most effective on the liquid phase oxidation of acrolein.7) For example, when the concentration of $Co(acac)_3$ was 5×10^{-4} mol/*l* the reaction temperature was 35°C and the reaction time was 4 hr, the conversion of acrolein in butyric acid was 45.1% and the selectivity of acrylic acid was 86.0%, whereas in benzene, 25.8% and 47.0%, respectively. In benzene polymers were formed in considerable quantity, while in butyric acid they could be little produced, the activity of the catalyst was maintained and the oxidation reaction proceeded desirably even after six hours.

These optimum results are shown with those of in valeric acid in Table 2. When the results in Table 2 are compared with the corresponding results in Table 1, the oxygen absorption rate and the conversion of acrolein in the formers are lower in spite of a higher reaction temperature than those in the latters. But the selectivity of acrylic acid is generally higher. This is ascribed to the fact that the higher concentration of the catalyst makes the reaction rate and the conversion higher, but produces more amount of polymers, resulting in the lower selectivity of acrylic acid.

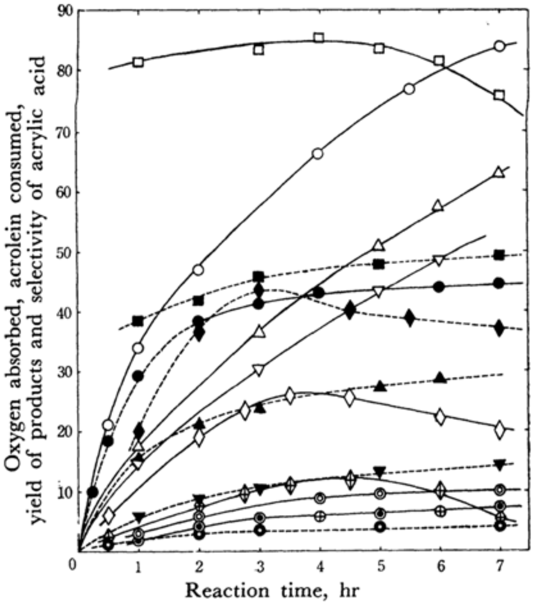


Fig. 4. Oxidation in butyric acid and benzene.
Reaction conditions:
reaction temperature, 35.0°C
acrolein, 3.0 mol/*l*
$Co(acac)_3$, 5×10^{-4} mol/*l*
□, ■: selectivity of acrylic acid (mol%)
○, ●: oxygen absorbed
($\times2\times10^2$ mol/acrolein mol)
△, ▲: acrolein consumed (mol%)
▽, ▼: yield of acrylic acid (mol%)
◇, ◆: yield of peracrylic acid (mol% × 10)
⊕ : yield of peroxide (mol% × 10)
◎, ⊙: yield of carbon dioxide (mol%)
⊕, ◉: yield of carbon monoxide (mol%)

TABLE 2. OPTIMUM RESULTS OF THE OXIDATION

Solvent	$(dO_2/dt)_{max}$*	Conversion %	Selectivity %
Butyric acid	4.38	45.1(27.3)**	86.0(82.7)**
Valeric acid	4.08	43.8(24.1)	72.6(69.8)
Benzene (control)	2.93	25.8(16.0)	47.0(42.1)

Conditions: reaction temperature, 35.0°C
acrolein concentration, 3.0 mol/*l*
$Co(acac)_3$, 5.0×10^{-4} mol/*l*;
reaction time, 4.0 hr

* $10^3\times O_2$ mol/acrolein mol/min

** Conversion and selectivity after two hours of the reaction time.

Peracrylic acid was decomposed with Co(acac)$_3$ as a catalyst in various solvents at 30°C to obtain results as shown in Fig. 5. Solvents such as dimethyl formamide and dimethyl sulfoxide were very effective on the decomposition of peracrylic acid. In butyric acid, 77.0% of peracrylic acid was decomposed after thirty minutes. On the other hand, the rate of decomposition in benzene was much slower. Thus, the order of solvents effective for the decomposition reaction was determined from the initial slope of the curves as follows:

dimethyl sulfoxide>dimethyl formamide>butyric acid>valeric acid>methyl acetate>carbon tetrachloride>acetic acid>tolunene>benzene>propionitrile.

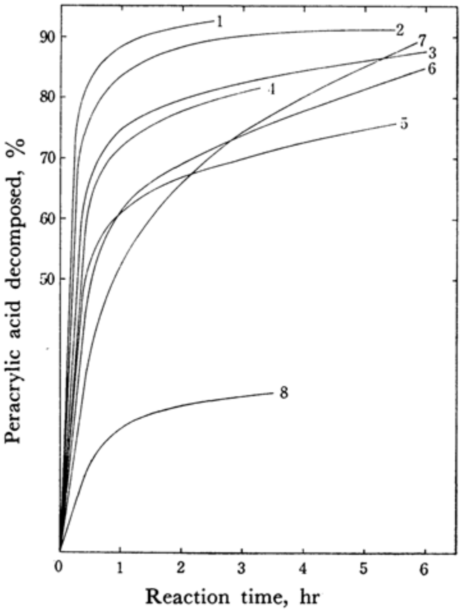


Fig. 5. Decomposition of peracrylic acid in various solvents.
Reaction conditions:
reaction temperature, 30°C
peracrylic acid, 6.67×10^{-2} mol/l
Co(acac)$_3$, 1.0×10^{-3} mol/l
1, dimethyl sulfoxide; 2, butyric acid; 3, valeric acid; 4, methyl acetate; 5, carbon tetrachloride; 6, acetic acid; 7, benzene; 8, propionitrile

The amount of polymers which were formed in the decomposition was very different by kinds of solvents. In such a non-polar solvent as carbon tatrachloride or benzene, in which polymers were apt to be formed, the catalyst was precipitated with the resulting polymers and lost its decomposition activity. On the other hand, in dimethyl sulfoxide and dimethyl formamide, polymers did not precipitate and the catalyst activity was kept in the course of the reaction, but oligomers were formed, because some polymeric substances could be separated by reduced vaporization of the liquid components in the presence of hydroquinone at 5°C. This accords completely with the formation of oligomers in the oxidation of acrolein in Type III solvents.

Almost all solvents, such as acetic acid, butyric acid, valeric acid and benzene, except carbon tetrachloride, dimethyl sulfoxide and dimethyl formamide, used in both the oxidation of acrolein and the decomposition of peracrylic acid had the same effect, that is the acceleration or the retardation of the both reactions (Fig. 6). But dimethyl formamide which is easily oxidized, dimethyl sulfoxide which has itself a high activity of the decomposition of peroxides,[15] and carbon tetrachloride which shows particular behaviors in the oxygen solubility (Fig. 8) are not included in the aforesaid solvents. This may mean that the rate-determining step in the oxidation of acrolein is much concerned with the decomposition of peracrylic acid formed during the oxidation at 30°C. This estimation is also supported by the linear increase of peracrylic acid in the early stage of the reaction (Fig. 4). That is to say that effects of a solvent are completely remarkable in the liquid phase oxidation of acrolein and especially in the decomposition of peracrylic acid.

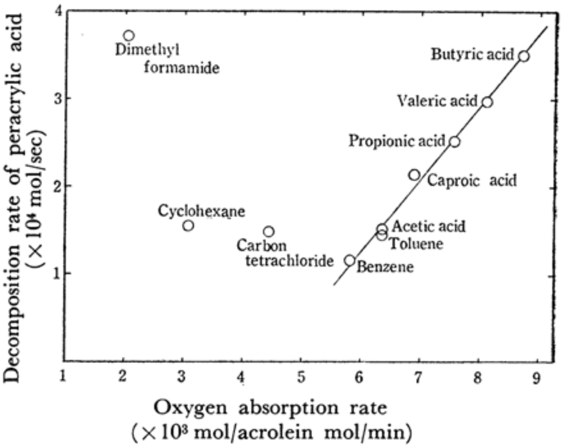


Fig. 6. Decomposition rate of peracrylic acid and oxygen absorption rate.
Reaction condition:
Decomposition of peracrylic acid:
reaction temperature, 30°C
peracrylic acid, 6.67×10^{-2} mol/l
co(acac)$_3$, 1.0×10^{-3} mol/l
Oxidation of acrolein:
reaction temperature, 30°C
acrolein concentration, 3.0 mol/l
Co(acac)$_3$, 1.5×10^{-3} mol/l

Figure 7 shows the NMR spectra of the solution of acrolein in benzene, acetic acid and butyric acid, that is chemical shifts due to the proton of

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15) R. Curci, *Tetrahedron Letters,* **1965**, 863.

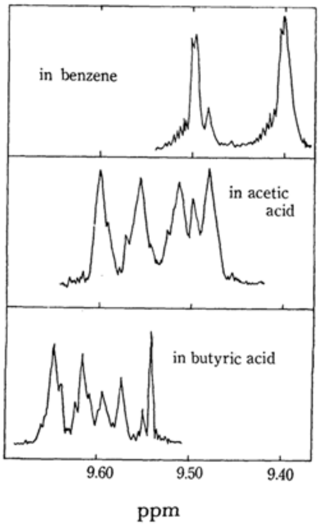

Fig. 7. NMR spectra of the aldehyde proton of acrolein in some solvents.

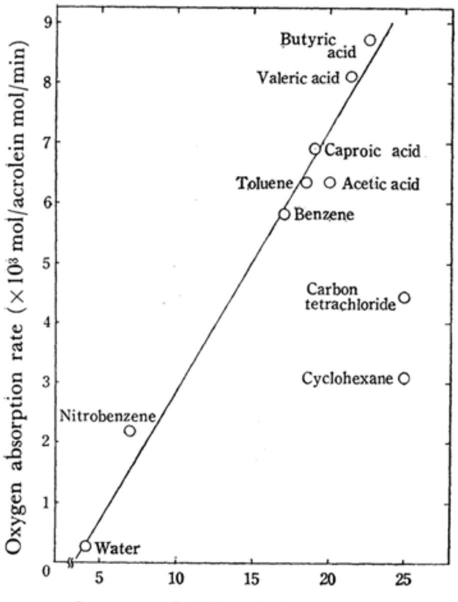

Fig. 8. Oxygen absorption rate and oxygen solubility.
Reaction conditions:
Oxidation of acrolein:
reaction temperature, 30°C
acrolein concentration, 3.0 mol/*l*
Co(acac)$_3$, 1.5×10^{-3} mol/*l*
Oxygen solubility:
measured at 30°C

the aldehyde group of acrolein. Though chemical shifts of the vinyl group in the above three solvents were not detected, shifts of the aldehyde proton were found out. The absorptions shifted to the lower magnetic field in the order of benzene, acetic acid and butyric acid. These spectra of the aldehyde proton are complicated and its fine structures are not clarified, but the order of shifts accorded with the tendency of the maximum oxygen absorption rates (Table 1), that is easiness of the reaction. Therefore, solvents may have some relation with the easiness of hydrogen abstraction of the aldehyde in the oxidation of acrolein.

Oxygen absorption rates at 30°C in butyric acid (the concentration of acrolein: 5×10^{-1}–10 mol/*l*; the concentration of the catalyst: $4\times10^{-5}-6\times10^{-3}$ mol/*l*; the oxygen pressure: $2\times10^{2}-7\times10^{2}$ mmHg) and in benzene (3–10 mol/*l*; $3\times10^{-5}-1\times10^{-2}$ mol/*l*; $2\times10^{2}-6\times10^{2}$ mmHg, respectively) were given respectively according to the following equation:

$$-dO_2/dt = k(\text{acrolein})^{0.82}(O_2)^{0.95}(\text{catalyst})^{0.26},$$

$$-dO_2/dt = k(\text{acrolein})^{1.22}(O_2)^{1.13}(\text{catalyst})^{0.47}.$$

In the experiments to obtain the equations, it was confirmed that the rate of oxygen dissolved was not a rate-determining step. That the oxygen absorption rates are proportional in about first order to the oxygen pressure, will suggest that the unpaired electron of the acyl radical formed in the chain propagation step of the oxidation of acrolein is not locarized and becomes stable, thereby reacting slowly with oxygen to become the peracid radical as follows:

$$CH_2{=}CH\dot{C}O + O_2 \xrightarrow{\text{late}} CH_2{=}CHCOO_2\cdot$$

Furthermore, the dissolved oxygen is considered to act as an inhibitor of the polymerization reaction, from the fact that the stop of bubbling of oxygen and the decrease of the stirring speed result in the formation of polymers. That is, the much dissolved oxygen may hasten the reaction of the above equation and the successive reactions by keeping the activity of a catalyst by hindering the precipitation of the catalyst with polymers.

The relation between the amount of oxygen dissolved and maximum oxygen absorption rates in various solvents is shown in Fig. 8. The linear relation was observed in solvents except carbon tetrachloride and cyclohexane. This supports the aforesaid effects of dissolved oxygen and means that the reaction rate depends extremely upon the solubility of oxygen in solvents.

Solvents may act as a radical transfer. The effect of solvents, especially lower carboxylic acids, have been studied on the oxidation of tetralin,[12] and *p*-xylene.[16] Mitskenvich[18] found that acetic

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[16] N. Ohta, Sunaoka and N. Ninai, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **63**, 768 (1960).

[17] N. I. Mitskevich, T. I. Soroko and B. V. Erofeen, *Doklady Akad. Nauk SSSR*, **115**, 103 (1957).

[18] K. Tokumaru, O. Simamura and M. Fukuyama, This Bulletin, **35**, 1673 (1962).

and butyric acids accelerated the oxidation of cumene and proposed that the radical R· produced from carboxylic acid RCOOH, acted as a hydrogen abstraction agent:

$$R\cdot + PhCHMe_2 \rightarrow RH + Ph\dot{C}Me_2.$$

Simamura[18] also reported that peracid was decomposed by the bimolecular decomposition with a solvent molecule SH:

$$RCO_3H + SH \rightarrow RCO_2\cdot + H_2O + S\cdot$$
$$S\cdot + RCO_3H \rightarrow RCO_2\cdot + SOH.$$

However, this mechanism seems to be doubtful at least for this oxidation of acrolein, since carboxylic acids are thought to be stable under the conditions used in this investigation and the effect of small amount of the additional acids was very small.

Ohta[16] proposed that carboxylic acids affected the molecules to be oxidized and consequently the oxidation proceeded easily, or the catalytic activity increased. In this experiment, one of effects of acid solvents may considered to be like that by Ohta.

Conclusion

In the liquid phase oxidation of acrolein, the best results were obtained by use of butyric acid or valeric acid as a solvent in all the reliable previous papers. Thus, the conversion of acrolein and the selectivity of acrylic acid in the former solvent were 45.1% and 86.0%, respectively, whereas in the latter solvent, 43.8% and 72.6%, respectively.

This reaction proceeds through the following steps:

$$CH_2{=}CHCHO + Co^{+3} \rightarrow CH_2{=}CH\dot{C}O + Co^{+2} + H^+ \quad (1)$$

$$CH_2{=}CH\dot{C}O + O_2 \rightarrow CH_2{=}CHCOO_2\cdot \quad (2)$$

$$CH_2{=}CHCOO_2\cdot + CH_2{=}CHCHO \rightarrow CH_2{=}CHCOO_2H + CH_2{=}CH\dot{C}O \quad (3)$$

$$\left.\begin{array}{l}\text{radicals} \rightarrow \text{inert compounds}\\ \text{radical} + M \rightarrow \text{polymers}\end{array}\right\} \quad (4)$$

(M: acrolein, acrylic acid, *etc.*).

In the initiation reaction (1), solvents, especially lower aliphatic acids, attack to the oxygen atom of the aldehyde of acrolein through the hydrogen bond, make the hydrogen abstraction of acrolein ease, and begin the reaction smoothly. Moreover, the reaction according to Eq. (1) proceeds by the coordination of acrolein with the metal of a catalyst. Thus, the solvents preferable to the coordination of acrolein are effective on the chain initiation reaction. That is to say that polar solvents are more useful for the above reaction than non-polar ones.

The catalyst kept its activity in a larger amount of dissolved oxygen, followed by the smooth proceeding of the reaction of Eq. (2). Thus solvents having high solubility of oxygen therein, for example butyric acid and valeric acid, are preferable to the reaction of Eq. (2).

Furthermore, solvents take part in the decomposition of peracrylic acid. Almost all solvents suitable to the decomposition of peracid, except solvents which are not inert to peracids, are generally useful ones in the oxidation of acrolein too. Especially butyric and valeric acids are preferable, since they are known to make the decomposition of peracid ease by a hydrogen bond between them and the peracid.

Polymers were produced by radicals formed during the oxidation of acrolein and the decomposition of peracrylic acid, and precipitated a catalyst with them. The precipitated catalyst was not separated from the polymers, however many kinds of solvents were used for washing the catalyst out. This may mean that the catalyst bonds chemically with the polymers, as described in the previous paper.[7] Therefore, solvents, in which the exchange of coordination of acrolein with the catalyst is rapidly carried out and acrolein does not stay long at the coordination shell of the catalyst, are prefered.

From consideration of each solvent effect as described above, butyric acid and valeric acid can be explained to be most useful in the oxidation of acrolein.