Kinetics of the Oxidation of Acrolein Initiated by Di-*t*-butyl Diperoxyoxalate

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The kinetics of the liquid-phase autoxidation of acrolein were studied using di-*t*-butyl diperoxyoxalate as an initiator. The ratios of the rate constants for the propagation *vs* the termination steps ($k_3k_6^{-1/2}$ and $k_2k_4^{-1/2}$) in the autoxidation mechanism were determined from the empirical rate equation thus obtained. The lower reactivity of acrolein was explained by comparing the ratios with those of saturated aldehydes.

There are only a few articles relating to the liquid-phase oxidation of α,β-unsaturated aldehydes to the corresponding carboxylic acids.[1-5] They refer mainly to the selective formation of the carboxylic acids and do not emphasize the kinetics and mechanisms. The absolute rate constants in the elementary steps of the oxidation or the ratio of the rate constants for the propagation *vs.* the termination steps have not yet been determined. In a series of studies of the liquid-phase oxidation of acrolein, we have mainly clarified the action of the metal-salt catalysts.[6-11]

In this paper, the kinetics of the autoxidation of acrolein initiated by a peroxy ester were studied. It is well known that di-*t*-butyl diperoxyoxalate (DBPO) is decomposed at room temperature in benzene or cumene to yield carbon dioxide and *t*-butoxy radicals.[12] It can be used as a radical initiator to be decomposed quantitatively in the liquid-phase oxidation. The ratios of the rate constants were first determined in the case of acrolein, and the lower reactivity of acrolein discussed in comparison with saturated aldehydes.

Experimental

The DBPO used as an initiator was prepared according to the method in the literature.[12] DBPO was usually stored in *n*-pentane below −25 °C. The crystals were filtered off just before an experiment and were dried *in vacuo* below 0 °C. An accurately-weighed amount of DBPO was used for the oxidation reaction.

The reaction apparatus used was the same as one described previously.[7] Carbon dioxide, evolved in the course of the reaction by the decomposition of DBPO and the reaction intermediates, was eliminated by placing the absorption tube packed with soda lime in a gas recycling system. It was also confirmed that other gaseous compounds did not affect the measurement of the absorbed oxygen. The total volume of the reaction solution was maintained at 75 ml, and the reaction was carried out under an atmospheric pressure by the dilution of the oxygen with nitrogen, if necessary. The partial pressure of oxygen was calculated after revision using the vapor pressure of acrolein.[13] The concentration of oxygen dissolved in a benzene solution under an atmospheric pressure of oxygen is given as 7.73×10^{-3} mol/l.[14] Besides, the stirring speed and the amount of oxygen flow were maintained so as not to have an effect on the reaction rate.[9]

All the peroxide products were estimated by iodometry; we thus obtained each concentration of hydrogen peroxide, hydroperoxides, and the other peroxides.[8,15] The concentration of hydrogen peroxide was below 3×10^{-3} wt% in any feedstock of the reaction solution, measured at the first step of the titration. Peracrylic acid and the peroxide complex (1:1 adduct from peracrylic acid and acrolein) could be completely analyzed at the second and the last steps, as has been reported previously.[8]

The formation rate of radicals by the decomposition of DBPO was measured by the method that Bawn and Mellish,[16] and Hammond *et al.*[17] used for benzoyl peroxide and azobisisobutyronitrile. DBPO was decomposed in benzene in the presence of diphenylpicryl hydrazyl (DPPH). The solution showed an absorption maximum at 520 nm which obeyed Beer's law throughout the range of concentrations used in the present work. The optical densities of the solution were measured at adequate intervals during the reaction by means of a spectrophotometer (Hitachi, ESP-2).

Results and Discussion

The oxidation of acrolein was carried out in benzene at 40 °C. In the absence of an initiator, the absorption of oxygen was not observed for 3 hr; this behavior was different from that of the oxidation of the corre-

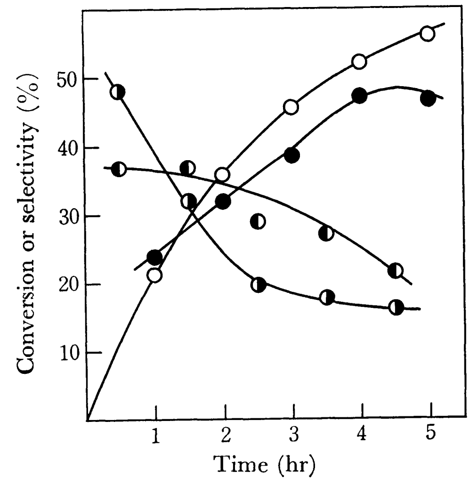


Fig. 1. Products in the oxidation of acrolein initiated by DBPO. Reaction conditions; [acrolein] 3.0 mol/l, [DBPO] 2.2×10^{-2} mol/l, 40 °C, in benzene. ○: conversion of acrolein, ●: selectivity of acrylic acid, ◑: selectivity of peracrylic acid, ◐: selectivity of the peroxide complex. Selectivities are based on consumed acrolein.

sponding saturated aldehydes. Oxygen was absorbed steadily without any induction period after the addition of DBPO. An aspect of the oxidation is illustrated in Fig. 1, with the selectivities of the products based on the acrolein consumed. The reaction intermediates, namely, peracrylic acid and the peroxide complex, remained rather stable at 40 °C, and 42% of the acrolein consumed was converted into these two kinds of peroxides at 4 hr. The formation of insoluble polymers was not observed throughout the oxidation.

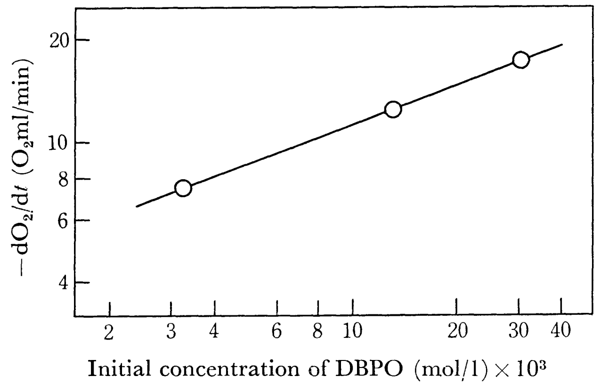


Fig. 2. Effect of DBPO on absorption rate of oxygen. Reaction conditions; [acrolein] 3.0 mol/l, [O_2] 5.1 × 10^{-3} mol/l, 40 °C, in benzene.

The initial concentration of DBPO showed a half-order dependence on the absorption rate of oxygen (Fig. 2). The orders of the dependence of the initial concentration of acrolein and of the partial pressure of oxygen were also found to be near 0.6 and 0.5 respectively. These results give the following rate equation, as will be discussed in detail below (Table 1):

$$-dO_2/dt = \frac{A[O_2][\text{acrolein}]}{[\text{acrolein}]+B[O_2]} \qquad \text{(I)}$$

where A and B are constants which depend neither on the concentration of acrolein nor on the oxygen pressure. Moreover, the A constant contains a term of the initiation rate, as will be explained below.

Equation (I) can be transformed into Eq. (II):

$$1/-dO_2/dt = 1/A[O_2] + B/A[\text{acrolein}] \qquad \text{(II)}$$

A linear relationship was obtained between $1/-dO_2/dt$ and both $1/[O_2]$ and $1/[\text{acrolein}]$, as is illustrated in Figs. 3 and 4 respectively. The values of A and B could be calculated from the lines of both figures; they accorded well as is shown below:

	A (s^{-1})	B
From Fig. 3	2.8×10^{-2}	6.8×10^{2}
From Fig. 4	2.8×10^{-2}	6.6×10^{2}
Average	2.8×10^{-2}	6.7×10^{2}

The observed absorption rate of oxygen accorded quite well with those calculated by means of the assumed rate Eq. (I) when the values of A and B were taken as 2.8×10^{-2} s^{-1} and 6.7×10^{2} (Table 1).

Assuming that the oxidation proceeds through the autoxidation mechanism shown below, the theoretical rate Eq. (III) may be derived by appling the stationary-state treatment:

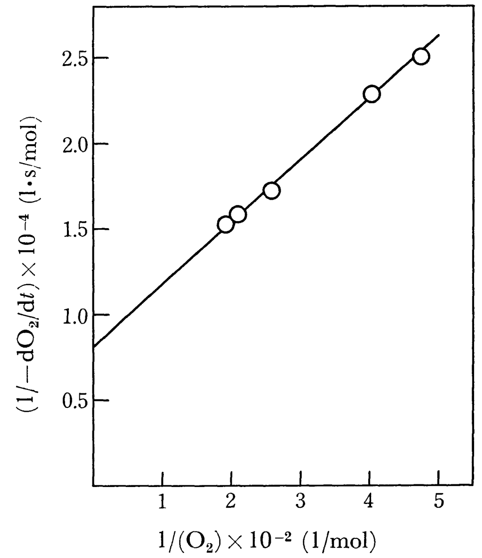


Fig. 3. Effect of oxygen pressure on absorption rate of oxygen. Reaction conditions; [acrolein] 3.0 mol/l, [DBPO] 3.4 × 10^{-3} mol/l, 40 °C, in benzene. Slope = $1/A = 0.35\times10^2$ s, $B/A[\text{acrolein}] = 0.80 \times 10^4$ l·s/mol.

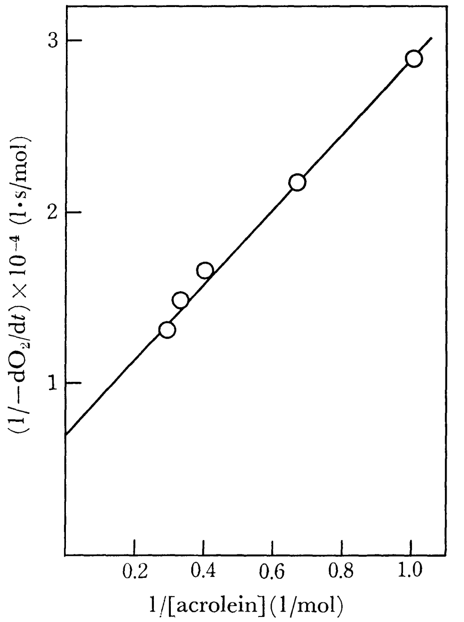


Fig. 4. Effect of acrolein on absorption rate of oxygen. Reaction conditions; [O_2] 5.1 × 10^{-3} mol/l, [DBPO] 3.4 × 10^{-3} mol/l, 40 °C, in benzene. Slope = B/A = 2.35×10^4 s, $1/A[O_2] = 0.70\times10^4$ l·s/mol.

$$RH \xrightarrow{R_i} R\cdot \qquad (1)$$

$$R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot \qquad (2)$$

$$RO_2\cdot + RH \xrightarrow{k_3} RO_2H + R\cdot \qquad (3)$$

$$2R\cdot \xrightarrow{k_4} \qquad (4)$$

$$R\cdot + RO_2\cdot \xrightarrow{k_5} \text{non-radical products} \qquad (5)$$

$$2RO_2\cdot \xrightarrow{k_6} \qquad (6)$$

where RH and R_i denote the acrolein molecule and

TABLE 1. EFFECT OF ACROLEIN AND OXYGEN PRESSURE ON ABSORPTION RATE OF OXYGEN

Concn. of acrolein mol/l	Oxygen pressure atm.	Concn. of oxygen mol/l×10^3	Absorption rate of oxygen mol/l s×10^5	
			Obsd	Calcd[a]
3.0	0.66	5.1	6.6	6.7
3.0	0.62	4.8	6.5	6.5
3.0	0.50	3.9	6.0	5.8
3.0	0.32	2.5	4.4	4.5
3.0	0.27	2.1	4.1	4.0
3.0	0.22	1.7	3.6	3.5
3.5	0.66	5.1	7.4	7.2
2.5	0.66	5.1	5.9	6.0
1.5	0.66	5.1	4.5	4.3
1.0	0.66	5.1	3.5	3.3

Reaction conditions; [DBPO] 3.4×10^{-3} mol/l, 40 °C, in benzene.

a) Calculated by the Eq. (I), where the values of A and B are $2.8\times10^{-2}\ \mathrm{s}^{-1}$ and 6.7×10^2, respectively.

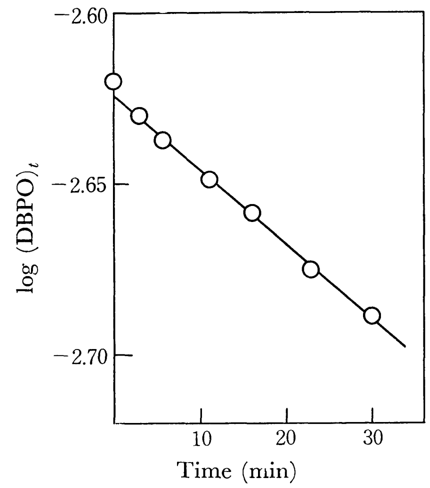


Fig. 5. Formation of t-butoxy radicals from the decomposition of DBPO. Reaction conditions; initial concentration of DBPO 2.40×10^{-3} mol/l, initial concentration of DPPH 1.82×10^{-3} mol/l, 40 °C, in benzene. $[\mathrm{DBPO}]_t=[\mathrm{DBPO}]_0-1/2\ \{[\mathrm{DPPH}]_0-[\mathrm{DPPH}]_t\}$. $[\mathrm{X}]_t$ and $[\mathrm{X}]_0$ denote the concentrations of X at $t=t$ and 0, respectively.

the rate of initiation respectively.

$$-\mathrm{dO_2}/\mathrm{d}t = \frac{R_i^{1/2}k_2k_3[\mathrm{RH}][\mathrm{O_2}]}{k_3k_4^{1/2}[\mathrm{RH}]+k_2k_6^{1/2}[\mathrm{O_2}]} \qquad \text{(III)}$$

The initiation reaction is considered to proceed in the following manner because the absorption rate in the absence of DBPO is negligible:[18)]

$$\mathrm{DBPO} \xrightarrow{k_{11}} 2t\text{-}\mathrm{BuO}\cdot + 2\mathrm{CO_2}$$

$$t\text{-}\mathrm{BuO}\cdot + \mathrm{RH} \xrightarrow{k_{12}} t\text{-}\mathrm{BuOH} + \mathrm{R}\cdot$$

Accordingly, R_i is given as the following expression and is dependent on neither the concentration of acrolein nor on the oxygen pressure:[18)]

$$R_i = 2ek_{11}[\mathrm{DBPO}]$$

The coefficient e is the efficiency of the radical initiator. In order to determine the value of ek_{11}, DBPO was decomposed in benzene at 40 °C in the presence of DPPH and the rate of decrease of DPPH was measured. According to Shine *et al.*,[19)] if the concentration of peroxide is higher than that of the hydrazyl, the yield of carbon dioxide is not affected by the presence of the hydrazyl. Therefore, the formation rate of t-butoxy radicals can be derived from the rate of decrease of DPPH under the present reaction conditions. From Fig. 5 the value of ek_{11} was determined to be $8.5\times10^{-5}\ \mathrm{s}^{-1}$ at 40 °C. Bartlett *et al.* measured the decomposition rate of DBPO in benzene by observing the decline of the absorption of the carbonyl frequency and found that the decomposition occurred through a uni-molecular mechanism.[12)] The rate constant of the decomposition at 40 °C can be calculated to be $10.5\times10^{-5}\ \mathrm{s}^{-1}$ from the reported values. The ratio of the two constants may correspond to an e value of 0.81 at 40 °C. Burnett *et al.* also determined the efficiency of azobisisobutyronitrile by DPPH-inhibitor techniques.[21)]

Therefore, A and B in Eq. (I) can be expressed by the rate constants of the elementary steps in the following manner, and the ratios of the constants, $k_3k_6^{-1/2}$ and $k_2k_4^{-1/2}$, at 40 °C can be determined in the oxidation of acrolein:

$$A = \{2ek_{11}[\mathrm{DBPO}]\}^{1/2}k_2k_4^{-1/2},\ B = k_2k_4^{-1/2}/k_3k_6^{-1/2}$$

$$k_3k_6^{-1/2} = 5.5\times10^{-2}\ (\mathrm{l}^{1/2}\cdot\mathrm{mol}^{-1/2}\cdot\mathrm{s}^{-1/2})$$

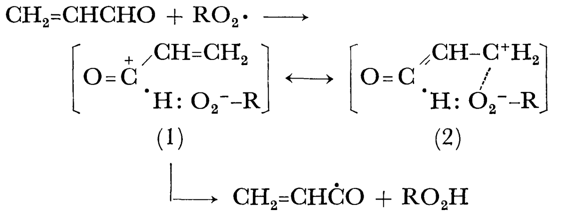
$$k_2k_4^{-1/2} = 3.7\times10\quad (\mathrm{l}^{1/2}\cdot\mathrm{mol}^{-1/2}\cdot\mathrm{s}^{-1/2})$$

The ratios of the rate constants, $k_3k_6^{-1/2}$, have been reported in many kinds of hydrocarbons; they seem to be dependent both on the property of the hydrogen being abstracted and on the structure and reactivity of the peroxy radicals.[20)] In the oxidation of acetaldehyde, $k_3k_6^{-1/2}$ has been reported to be 2.7×10^{-1} ($\mathrm{l}^{1/2}\cdot\mathrm{mol}^{-1/2}\cdot\mathrm{s}^{-1/2}$) at 0 °C.[22)] Considering that the activation energies of k_3 and k_6 are 2—4 and 0—2 kcal respectively,[23)] the ratio in acetaldehyde may be said to be 10 times larger than that in acrolein.

On the other hand, Zaikov *et al.* found that, in the oxidation of various aldehydes, the values of $k_3k_6^{-1/2}$ differed only slightly from one another because there were compensating changes for the rate constants of propagation and termination,[24)] the values of $k_3k_6^{-1/2}$ being substantially constant, independently of the kind of aldehyde. The termination rate constants, k_6, for acrolein and acetaldehyde may depend on the stability of these two kinds of acyloxy radicals formed in the tetroxide homolysis. Considering the more rapid decarboxylation of acetoxy radicals, the constant, k_6, of acrolein may be larger than that of acetaldehyde because of the existence of the conjugated double bond, as has been reported in the case between benzaldehyde and alkanals.[24)] The propagation rate constant, k_3, may be discussed in two ways; (1) the reactivity of aldehyde hydrogen, that is, the C–H bond strength and the steric effect, and (2) the reactivity of the attacking acylperoxy radicals. The bond strength is estimated to be 74 kcal for benzaldehyde and 88 kcal for acetaldehyde.[25)] The reason why compensating changes are found between benzaldehyde and alkanals may be mainly attributed to the difference in the bond strength. On the contrary, though the bond strength may be smaller for acrolein than for acetaldehyde because of the resonance stabilization of acryloyl radicals, the value of $k_3k_6^{-1/2}$ in the oxidation of acrolein is smaller than that of acetaldehyde or benzaldehyde. Russell claimed that the polar effect of acylperoxy radicals played an important role in the propagation step:²⁶⁾

$$RO_2\cdot + RH \xrightarrow{k_3} [RO_2^-:H\ R^+] \longrightarrow RO_2H + R\cdot$$

Such an intermediate complex will be elucidated in this oxidation. However, there may be two forms of complexes ((1) and (2)) which are stabilized by the existence of the conjugated C=C double bond:



$$CH_2{=}CHCHO + RO_2\cdot \longrightarrow \left[O{=}\overset{+}{C}\begin{matrix}CH{=}CH_2\\ \cdot H: O_2^-{-}R\end{matrix}\right] \longleftrightarrow \left[O{=}C\begin{matrix}CH{-}C^+H_2\\ \cdot H: O_2^-{-}R\end{matrix}\right]$$

(1) (2)

$$(1) \longrightarrow CH_2{=}CH\dot{C}O + RO_2H$$

The (2) complex is considered to be more stabilized than the (1) complex because of its electronic structure, and the (1) complex may produce an acryloyl radical and peracrylic acid faster than the (2) complex. This results in the lower reactivity for the abstraction of the hydrogen of acrolein as compared with that of the other aldehydes, such as acetaldehyde, with only one form of an intermediate complex. Besides, the steric hindrance may arise for acrolein in the abstraction reaction, because the rotation about the C–C single bond is restricted. The proportion of *s-trans* to *s-cis* isomers was reported to be 95: 5 at room temperature.²⁷⁾ As the sum of these effects, it may be possible to consider that k_3 does not compensate for the change of k_6 for acrolein, resulting in the following order with regard to the values of $k_3k_6^{-1/2}$:

$$\text{benzaldehyde} \fallingdotseq \text{acetaldehyde} > \text{acrolein}$$

There are no reports concerning the values of $k_2k_4^{-1/2}$. In the oxidation of saturated aldehydes, the rate-determining step is Step (3) and oxygen reacts with an acyl radical so fast that the absorption rate has no dependence on the oxygen pressure. However, the k_2 constant is considered to be smaller for acrolein because of the resonance stabilization, as has been reported in the case of allyl or benzyl radicals.²⁸⁾ The ratio of $k_2k_4^{-1/2}$ to $k_3k_6^{-1/2}$ reaches only 670 for acrolein. As the ratios of the concentrations of acrolein to dissolved oxygen are near 10^3 in the present work, the absorption rate has a certain dependence on the oxygen pressure. It has already been reported that a near-first-order dependence on the oxygen pressure can be observed in oxidations catalyzed by various metal salts.²⁹⁾ Brill and Lister also reported a first-order dependence in the catalyzed oxidation of methacrolein.²⁾ As the catalyzed oxidation proceeds through the same reaction mechanism except for the initiation step (1), part of the higher dependence on the oxygen pressure may be ascribed to the initiation step; that is, the abstraction of aldehyde hydrogen by a metal ion may be accelerated by the presence of oxygen.

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