KINETICS OF OZONATION OF ALDEHYDES IN RELATION TO THEIR OZONE-INITIATED AUTOXIDATION

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The rates of ozonation of aliphatic aldehydes and monosubstituted benzaldehydes are measured in carbon tetrachloride solutions, and the reaction order and the rate constants are determined on the basis of the theory of gas absorption accompanied by chemical reactions. It is found that the reaction is first order with respect to both ozone and benzaldehyde, and also that the second order rate constants for *n*- and *iso*-butyraldehydes are much higher than those for the substituted benzaldehydes studied. The order of reactivity of substituted benzaldehydes is anisaldehyde > *p*-tolualdehyde > benzaldehyde > *p*- and *m*-chlorobenzaldehydes > *p*- and *m*-nitrobenzaldehydes. It is also found that the rate of ozonation of substituted benzaldehyde follows Hammett's rule.

Furthermore, the kinetics of liquid-phase autoxidation of benzaldehyde with ozone-oxygen mixture is studied, and the observed oxidation rates are found to be approximately consistent with those predicted on the assumption that the reaction of ozone with aldehyde is an initiation reaction of the autoxidation.

Introduction

Ozonation of organic compounds has been the subject of many investigations, and recently has become very important in view of the use of ozone in wastewater treatment. Most of them, however, have dealt with product distribution, and the kinetics of ozonation was elucidated for relatively few organic compounds such as paraffin[11], olefin[10] and polyalkylbenzenes[6].

Ozone had been found to act as an initiator in the autoxidation of benzaldehyde with ozone-oxygen mixture[1] and the solvent effect on the yield of perbenzoic acid was also investigated[2]. Furthermore the ozone-initiated autoxidation of acetaldehyde to peracetic acid was also carried out commercially. This is well-known as AMP or UCC process[5]. To clarify the kinetics of the ozone-initiated autoxidation of aldehyde, it is necessary to investigate the mechanism of the initiation reaction, i.e., the reaction of ozone with aldehyde. With respect to the ozonation of aldehydes, White *et al.*[8] studied the reactivity of substituted benzaldehydes towards ozone, and reported the order of reactivity as follows; anisaldehyde > benzaldehyde > *p*-nitrobenzaldehyde. This result, however, was only qualitative because the rate constants were not determined.

This paper will present the rate constants of ozone-aldehyde reactions in carbon tetrachloride solutions determined on the basis of the theory of gas absorption accompanied by chemical reactions, and the reactivity of aldehyde will be described quantitatively. The applicability of Hammett's rule to the ozonation of monosubstituted benzaldehyde will be also examined. Furthermore, the kinetics of the ozone-initiated autoxidation of benzaldehyde with ozone-oxygen mixture will be also presented based on the proposed mechanism of the ozone-aldehyde reaction.

1. Experimental

The schematic diagram of the experimental apparatus is shown in **Fig. 1**. The reaction vessel (gas absorber) was a pyrex vessel, about 7.5 cm in diameter, equipped with two stirrers, one in the gas phase and the other (a teflon-coated magnetic stirring bar of 2 cm length) in the liquid phase. In most of the experiments, the stirring speed of the liquid n_L was adjusted at 150 rpm, and that in the gas phase n_G at 700 rpm. The vessel was charged with about 80 m*l* of aldehyde solution. After the solution was brought to the desired temperature, the mixture of ozone and oxygen was introduced into the reactor at a constant flow rate (about 250 m*l*/min) and the stirring was started. The concentration of ozone in the feed was 0.2–0.7 per cent. The gas was not bubbled into the liquid, but supplied over the free liquid surface across

which gas was absorbed into the liquid. The free surface was almost kept flat in the range of n_L of 150–300 rpm, and its interfacial area was 38.2 cm². The concentrations of ozone in the feed and effluent gas were measured by observing the absorbance at 255 nm with UV spectrometer equipped with a flow cell. A calibration chart of this absorption as a function of ozone concentration was prepared based on the usual analytical method which employs potassium iodide. The concentration of the effluent gas, which could be considered equal to that of the bulk gas in the reactor, reached a steady value within 5 min after the start of the experiments, and the absorption rate of ozone was calculated from the gas flow rate and the difference between the ozone concentrations in the feed and the effluent gas.

The amount of aldehyde consumed by the reaction with ozone and oxygen during one experiment was at most 3 per cent of that initially charged. Analysis of aldehyde was carried out using a gas chromatograph equipped with a flame ionization detector (column packing; polyethylene glycol 6000, 2 m, carrier gas; N_2, 30 ml/min, column temperature; 120°C). Peracid formed was determined by the usual iodometric titration. Materials used were prepared as follows. p-methoxy, p-methyl, p-chloro, m-chloro, p-nitro and m-nitrobenzaldehydes of G.R. grade supplied by Nakarai Chem. Co. were used without further purification. Other reagents were purified by simple batch distillation.

Solubility of ozone in carbon tetrachloride was measured. Bunsen's absorption coefficients (N cm³ O_3/cm³ solution·atm) were 3.52, 2.78, 2.18 and 1.96 at 0, 15, 25 and 30°C, respectively.

Diffusivity of ozone in carbon tetrachloride was estimated by the equation of Wilke and Chang[9] assuming that the molar volume of ozone is 1.5 times that of oxygen. The estimated values were 2.08×10^{-5}, 2.82×10^{-5} and 3.7×10^{-5} cm²/sec at 0, 15 and 30°C, respectively. Diffusivity of aldehyde was evaluated by the same method.

Gas-phase mass transfer coefficient k_G was measured by the absorption experiment of ozone into 0.5 N aqueous solution of potassium iodide at 25°C. In this absorption system, because of very rapid reaction of ozone, gas absorption rate was considered to be limited by the gas film resistance. This was confirmed by the observation that N_A was not affected by the liquid phase mass transfer coefficient k_L, or the stirring speed n_L. Thus, absorption rate was simply expressed by $N_A = k_G p_A$, and k_G could be calculated from this equation and is shown in **Fig. 2**.

Liquid phase mass transfer coefficient k_L was determined with oxygen–carbon tetrachloride system by the method of Teramoto et al.[7] and is shown in
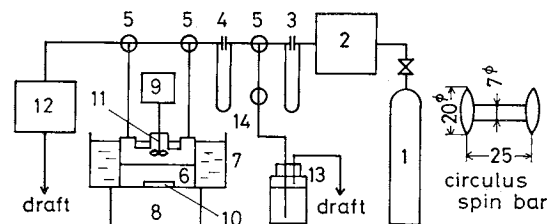
1: Oxygen cylinder
2: Ozone generator
3: Orifice flow meter
4: Capillary flow meter
5: Three way stopcock
6: Reaction vessel
7: Thermostat
8: Magnetic stirrer
9: Motor
10: Teflon-coated magnetic stirring bar in liquid phase
11: Stirrer in gas phase
12: UV spectrometer
13: Aqueous KI solution
14: Two way stopcock

In the experiment on ozone-initiated autoxidation of benzaldehyde, a condenser and an additional capillary flow meter were attached to the outlet of the reaction vessel.

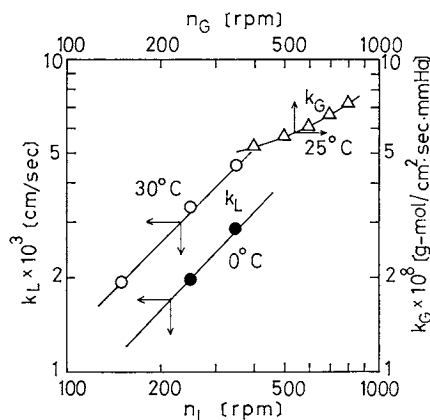Fig. 1   Schematic diagram of experimental apparatus

Fig. 2   Gas-phase and liquid-phase mass transfer coefficients

Fig. 2. The value of k_L for ozone-carbon tetrachloride system was estimated on the assumption that k_L is proportional to the square root of the diffusivity[12].

2. Ozonation of Aldehydes

2. 1   Ozonation of benzaldehyde

It was found that under the conditions studied, the absorption rate of ozone was not affected by n_L or k_L. Thus, the following equation could be applied to this reaction system[3].

$$N_A = \sqrt{2k A_i^{m+1} B_0^n D_A / (m+1)} \qquad (1)$$

The plot of N_A vs. A_i is shown in **Fig. 3**. A_i is the concentration of ozone equilibrium with p_{Ai} which is calculated by the following equation.

$$N_A = k_G(p_A - p_{Ai}) \qquad (2)$$

The slope of the plot, which is equal to $(m+1)/2$ according to Eq. (1), is unity. Thus the value of m is unity. **Figure 4** shows the plot of N_A vs. B_0 at $A_i = 2 \times 10^{-7}$ g-mol/cm³. Because the slope is 1/2, n
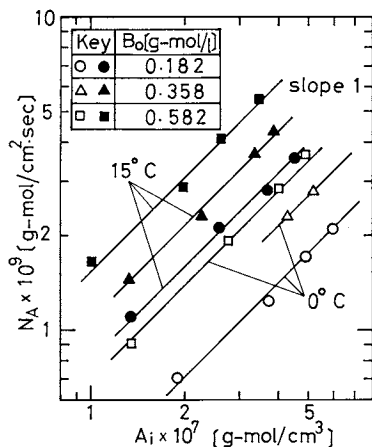
Fig. 3 N_A vs. A_i (benzaldehyde)
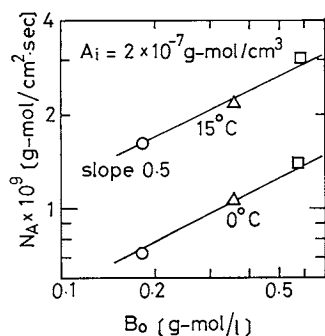

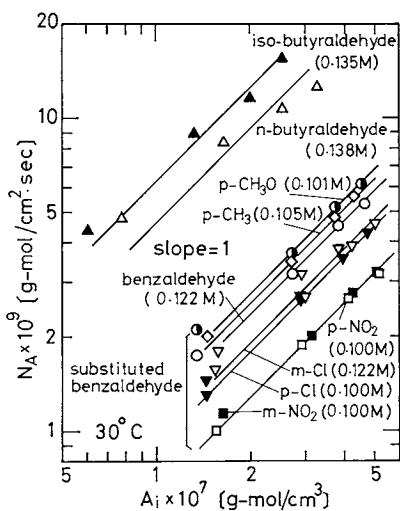Fig. 4 N_A vs. B_0 (benzaldehyde)

Fig. 5 N_A vs. A_i for various aldehydes

is unity. Thus it is concluded that the ozonation of benzaldehyde is first order with respect to both ozone and aldehyde. This result seems reasonable because the same reaction order has so far been reported for paraffin and olefin[10,11]. The rate constants calculated by Eq. (1) were 3.8, 12.9 and 29 l/g-mol·sec at 0, 15 and 30°C, respectively.

2. 2 Ozonation of substituted benzaldehydes and n- and iso-butyraldehydes

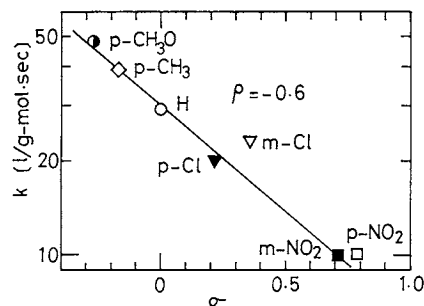The results at 30°C are shown in **Fig. 5**. It can be

Fig. 6 Applicability of Hammett's rule to ozonation of mono-substituted benzaldehyde

seen that the slopes for these aldehydes are about unity and the reactions are first order with respect to ozone. Although the value of n was not determined for these aldehydes, the rate constants were calculated assuming that n was also unity as in the case of benzaldehyde, and are shown in **Fig. 6**.

The necessary conditions for Eq. (1) to hold are as follows.

$$\gamma = \sqrt{2kD_A A_i^{m-1} B_0^n/(m+1)}/k_L > 3 \qquad (3)$$

$$r_B q_B = (D_B/D_A)(B_0/A_i) \gg \gamma \qquad (4)$$

It was confirmed that the values of γ calculated using these values of k for all experiments satisfied Eqs. (3) and (4), and that Eq. (1) could be successfully used in this study.

To examine the applicability of Hammett's rule to the ozonation of substituted benzaldehydes, log k is plotted against Hammett's substituent constant σ in Fig. 6. The data follow a straight line and the reaction constant ρ is found to be -0.6 from the slope. The negative value of ρ indicates that the rate determining step is not a nucleophilic ozone attack but an electrophilic ozone attack on aldehyde. The order of the reactivity of aromatic aldehyde with ozone is anisaldehyde $>$ p-tolualdehyde $>$ benzaldehyde $>$ p- and m-chlorobenzaldehydes $>$ p- and m-nitrobenzaldehydes, i.e., an aldehyde having an electron releasing group is more reactive than that having an electron attracting group. This result is in agreement with the qualitative result of White and Bailey[8].

As pointed out by White and Bailey, the rate determining step is supposedly the concerted hydride anion abstraction from the carbonyl group of the aldehyde by the positive end of ozone molecule and a simultaneous attack by the negative end of ozone on the carbonyl carbon.
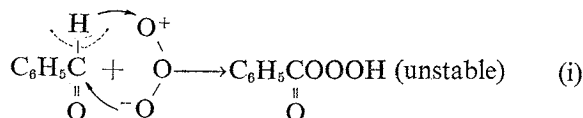
An electron releasing group on benzene ring increases the electron density on the carbonyl carbon and makes the abstraction of hydride anion easier and its

rate faster. The rates of aliphatic aldehydes are much faster than those of aromatic aldehydes, and the rate constants at 30°C are 520 and 720 l/g-mol·sec for n- and iso-butyraldehydes, respectively. This is because in the case of aliphatic aldehydes the alkyl group exerts the electron releasing effect directly to the carbonyl group.

3. Autoxidation of Benzaldehyde with Ozone–Oxygen Mixture in Carbon Tetrachloride Solution

It was found by Briner[1] that ozone acts as an initiator in the autoxidation of benzaldehyde with ozone–oxygen mixture; the kinetics of the reaction, however, has not been elucidated. To clarify the kinetics in connection with the mechanism of the ozone–aldehyde reaction above, further experiments were carried out. The apparatus used was similar to that presented above except that a teflon-coated "circulus spin bar" (BEL-ART PRODUCTS) shown in Fig. 1 was used for stirring liquid vigorously to cause sufficient entrainment of gas bubbles into the liquid phase from the liquid surface. The value of $k_L a$ for oxygen–carbon tetrachloride system measured by the method of Teramoto et al.[7] was about 800 1/hr. The absorption rate of oxygen was calculated from the difference in the gas flow rates measured at the inlet and outlet of the reactor by capillary flow meters. The flow rate of feed gas was 150 ml/min for all runs. At the beginning of the reaction, however, considerable fluctuation of the flow rate was observed. Therefore, measurements were carried out 1 min after the start of the reaction.

The hypothetical maximum physical transfer rate of oxygen which would be obtained if the concentration of oxygen in the bulk liquid were zero can be estimated by the following equation.

$$R_{G,\max} = k_{LG} a(C_i - 0) \tag{5}$$

Because $k_{LG} a$ is about 800 l/hr and C_i, the solubility of oxygen in carbon tetrachloride is about 0.012 g-mol/l at 30°C and 1 atm, $R_{G,\max}$ may be about 0.15 g-mol/l·min. The observed maximum absorption rate of oxygen was about 0.02 g-mol/l·min, and it was much smaller than $R_{G,\max}$. Thus, it was confirmed that the chemical reaction rather than the diffusion of oxygen was the rate-determining step.

As shown in Fig. 7 the absorption rate of ozone was found to be proportional to $[O_3]_0$, the concentration of ozone in the effluent gas and to be little dependent on the concentration of benzaldehyde. This suggests that ozone is absorbed in the region of "slow reaction" where the reaction proceeds mainly in the bulk liquid and the concentration of ozone there is significantly low compared with its gas-liquid interfacial concentration. The rate in this region is expressed as
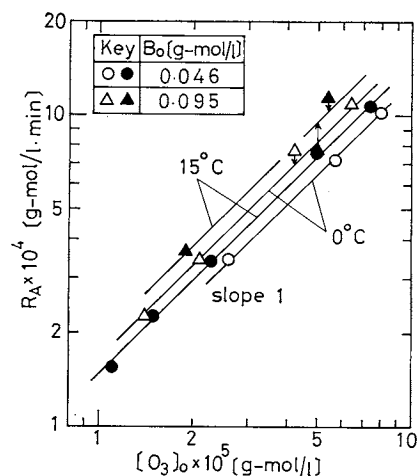

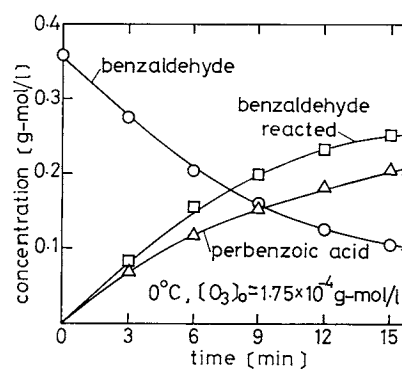Fig. 7 R_A vs. $[O_3]_0$ (benzaldehyde)

Fig. 8 Time-course of ozone-initiated autoxidation of benzaldehyde
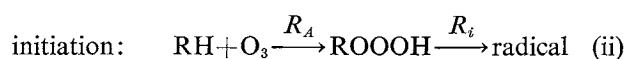
follows.

$$R_A = A_i/(1/k_{LA} a + 1/kB_0) \tag{6}$$

$$1/k_{LA} a > 1/kB_0 \tag{7}$$

It was confirmed that the experimental condition satisfied the relation of Eq. (7).

A typical time-course of the reaction is shown in **Fig. 8**. Markedly high yield of perbenzoic acid is characteristic of this reaction, and in the early stage of the oxidation, peracid is almost quantitatively produced. The plot of R_G vs. R_A shown in **Fig. 9** indicates that R_G is proportional to $R_A^{0.3}$. It is also shown that the value of R_G/R_A ranges from 3 to 22, which suggests that ozone is consumed in the initiation reaction followed by a chain reaction involving oxygen. The cross plot of Fig. 9 shows that R_G is approximately proportional to the concentration of benzaldehyde. Thus the following empirical rate equation was obtained.

$$R_G \propto B_0 R_A^{0.3} \tag{8}$$

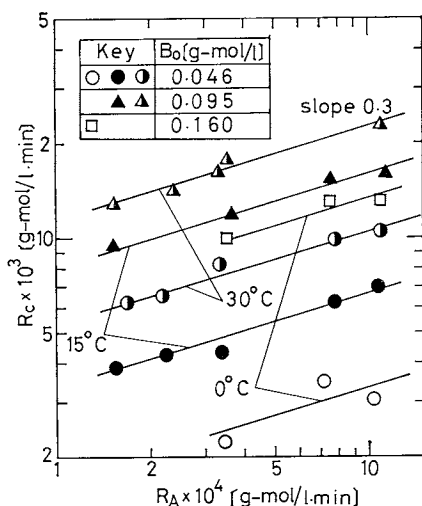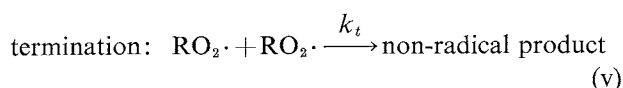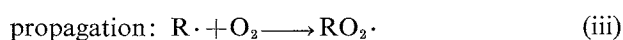A plausible mechanism of the ozone-initiated autoxidation is as follows;

initiation: $RH + O_3 \xrightarrow{R_A} ROOOH \xrightarrow{R_i} radical$ (ii)

Fig. 9 R_C vs. R_A (benzaldehyde)

propagation: $R \cdot + O_2 \longrightarrow RO_2 \cdot$ (iii)

$$RO_2 \cdot + RH \xrightarrow{k_p} ROOH + R \cdot$$ (iv)

termination: $RO_2 \cdot + RO_2 \cdot \xrightarrow{k_t}$ non-radical product (v)

where RH is benzaldehyde, ROOH is perbenzoic acid and R_i is the initiation rate. When the partial pressure of oxygen is sufficiently high as in the case of the present investigation, the oxygen absorption rate can be represented by the following equation on the basis of the quasi-steady state approximation.

$$R_c = (k_p / \sqrt{2k_t}) B_0 \sqrt{R_i}$$ (9)

If two radicals are assumed to form in the initiation,

$$R_i = 2eR_A$$ (10)

where e is the initiation efficiency defined as the ratio of the amount of ozone consumed effectively for producing radicals to total amount of ozone consumed. From Eqs. (9) and (10) it follows

$$R_C = (k_p / \sqrt{k_t}) B_0 \sqrt{eR_A}$$ (11)

from which it is expected theoretically that R_C is proportional to $B_0 R_A^{0.5}$. Comparison of Eq. (8) with Eq. (11) indicates that while the observed relation of R_C vs. B_0 is in agreement with that of Eq. (11), considerable discrepancy is recognized in the relation of R_C vs. R_A. Although the reason of this inconsistency is not clear, one plausible explanation for this is the decrease in e with an increase in R_A. As R_A increases, the concentration of radical increases, and the rate of induced decomposition of the peroxide ROOOH to non-radical products by the radicals also increases, which results in the decrease in e with increasing R_A. The values of e were calculated from Eq. (11) using the value of $k_p / \sqrt{2k_t}$ $(0.29 \ l^{1/2} \text{g-mol}^{1/2} \text{sec}^{-1/2 \ 4)})$ at 0°C and were found to range from 0.4 at high R_A to unity at low R_A.

The apparent activation energy of R_C was 6.5 kcal/g-mol which is in agreement with 6.3±1.2, the activation energy calculated from Eq. (11) by assigning the activation energies of $k_p / \sqrt{k_t}$ and R_A to 1.8±0.5[4) and 11.1±1.5 kcal/g-mol, respectively.

Conclusion

The rate constants of ozonation of aromatic and aliphatic aldehydes were determined based on the theory of chemical gas absorption. It was found that the reaction is first order with respect to both ozone and benzaldehyde, and also that the ozonation rate of monosubstituted benzaldehyde follows Hammett's rule with the reaction constant of −0.6. The reactivity of aliphatic aldehyde was found to be much higher than that of aromatic aldehyde studied, and these results were successfully explained by regarding hydride anion abstraction from carbonyl carbon as the rate-determining step. Furthermore, the kinetics of the liquid phase oxidation of benzaldehyde with ozone–oxygen mixture was found to be approximately consistent with that predicted on the basis that the reaction of ozone with aldehyde is an initiation reaction of the autoxidation.

Nomenclature

A	= concentration of ozone in liquid	[g-mol/cm³]
a	= gas-liquid interfacial area per unit liquid volume	[cm²/cm³]
B	= concentration of aldehyde	[g-mol/cm³]
C	= concentration of oxygen in liquid	[g-mol/cm³]
D	= diffusivity	[cm²/sec]
e	= initiation efficiency	[—]
k	= rate constant of ozone-aldehyde reaction	[l/g-mol·sec]
k_G	= gas-phase mass transfer coefficient	[g-mol/cm²·sec·mmHg]
k_L	= liquid-phase mass transfer coefficient	[cm/sec]
m	= reaction order with respect to ozone in ozone-aldehyde reaction	[—]
N	= gas absorption rate	[g-mol/cm²·sec]
n	= reaction order with respect to aldehyde in ozone-aldehyde reaction	[—]
n_G	= rotational speed of impeller in gas phase	[rpm]
n_L	= rotational speed of impeller in liquid phase	[rpm]
$[O_3]_0$	= concentration of ozone in effluent gas from reactor	[g-mol/l]
p	= partial pressure	[mmHg]
q_B	= B_0/A_i	[—]
R	= reaction rate	[g-mol/l·min]
r_B	= D_B/D_A	[—]
R_i	= rate of initiation	[g-mol/l·min]
γ	= $\sqrt{2kD_A A_i^{m-1} B_0^n/(m+1)}/k_L$	[—]
ρ	= Hammett's reaction constant	[—]

σ = Hammett's substitutent constant [—]

⟨Subscripts⟩

A = ozone
B = aldehyde
C = oxygen
i = gas-liquid interface
0 = bulk liquid

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