The Initiation Reaction of Autoxidation of Acrylaldehyde Catalyzed by Cobalt(III) Acetylacetonate

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The initiation reaction of autoxidation of acrylaldehyde with Cobalt (III) acetylacetonate, Co(III)(acac)_3 , was studied. The rate of initiation reaction was measured using the "DPPH technique". Acrylaldehyde was shown to have a much smaller rate of initiation than propionaldehyde. The rate dependence on the partial pressure of oxygen for autoxidation of acrylaldehyde was discussed by comparing the kinetic data of acrylaldehyde with those of propionaldehyde. Effects of solvents on the initiation reaction were also discussed in detail.

1. Introduction

It is well recognized¹⁾ that a transition metal ion having a higher valence is capable of abstracting the hydrogen atom directly from an aldehyde to initiate the autoxidation reaction:

The rate of initiation reaction of Eq. (1) can be calculated from the inhibitive period of autoxidation ("inhibitor method"), using an antioxidant such as 2,6-di-*tert*-butyl-4-methylphenol. The initiation rate can also be determined by titration of the concentration of a higher valent metal ion with time ("titration method"). These methods, however, are overly time consuming; moreover, the latter method is applicable only to a reaction system of slow rate of initiation reaction. When colorimetry is applied to the titration method, the relatively low absorption coefficient for *d-d* transition of a metal ion often leads to rather serious errors.

Thus, we have developed a new "DPPH technique", taking the advantage of α, α -diphenylpicrylhydrazyl (DPPH) possessing a higher absorption coefficient and reacting very rapidly with free radicals. This paper will discuss the DPPH technique in detail, with special reference to the initiation reaction of autoxidation of acrylaldehyde; it will also report solvent effects on the initiation reaction.

2. Experimental

Materials: The DPPH was used without any purification, and β -naphthol was recrystallized con-

ventionally. Acrylaldehyde and propionaldehyde were purified just before use as described previously²⁾. Cobalt(III) acetylacetonate, $[\text{Co(III)(acac)}_3]$, was prepared and purified according to the conventional method³⁾.

Solvents, such as cyclohexane, toluene, benzene, carbon tetrachloride, acetic acid, propionic acid, butyric acid, and valeric acid were used after purification.

Procedures: The hydrogen abstraction reaction of aldehydes with Co(III)(acac)_3 was carried out as follows: An aldehyde, DPPH (accurately weighed) and a solvent were charged into a reactor, and the solution was maintained at a fixed temperature. An accurately weighed amount of Co(III)(acac)_3 was added to the solution, and the reaction was started. The initial concentration of DPPH was adjusted equal to the molarity of Co(III)(acac)_3 . At appropriate time intervals, samples of the solution were taken for spectroscopic measurements. The atmosphere of air was used for the reaction system unless otherwise indicated.

The oxidation of acrylaldehyde was carried out as reported previously²⁾.

3. Results and Discussion

3.1 Scope and Limitation of the "DPPH Technique"

The DPPH, which gave a stable violet solution in benzene, reacted rapidly with the radicals formed by interaction of Co(III)(acac)_3 and aldehyde, accompanied by a sharp change in color. On the other hand, the DPPH solution remained stable for more than five hours at 40°C in absence of either the species, Co(III)(acac)_3 and aldehyde. In the visible spectroscopic measurement, DPPH showed a maximum absorption at 525 nm, which obeyed Beer's law over the range of concentra-

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tions used in this work. The molar absorption coefficient was calculated as 1.02×10^4 in the presence of equimolar Co(III)(acac)_3 , the coefficient being large enough to neglect the effect of the presence of Co(III)(acac)_3 which showed a slight absorption at 525 nm.

If the reaction is assumed to proceed according to steps (1) and (2),

the rate of formation of the radicals by step (1) can be replaced by $-d[\text{DPPH}]/dt$, because the rate constant, k_2 , of the second step is much larger than that of the first constant, k_1 , as reported in the literature⁴). Consequently, the absolute rate constant, k_1 , can be obtained in terms of the rate of decrease in the DPPH concentration. The rate as the stationary state rate, is graphically calculated by using the "tangential method".

The rate constants obtained by this method are shown in **Table 1** in which the corresponding constants obtained by the "inhibitor method", which is tried widely with confidence, are also listed for comparison. The values obtained by these two methods are found to be almost the same within the experimental errors. This indicates that the "DPPH technique" is reliable for the estimation of the initiation reaction of Eq. (1), that is, DPPH can quantitatively trap the free radicals formed by the interaction of aldehyde with Co(III)(acac)_3 .

3.2 Comparison of Initiation Reactions of Acrylaldehyde and Propionaldehyde

The hydrogen abstraction reaction of acrylaldehyde with Co(III)(acac)_3 was carried out in

Table 1 Rate Constants in the Hydrogen Abstraction of Aldehydes by Co(III)(acac)_3 in Benzene at 30°C

Aldehyde	Rate Constant k_1 ($\text{M}^{-1} \cdot \text{s}^{-1}$)	Method
Benzaldehyde	8.82×10^{-4}	1
"	9.12×10^{-4}	2
"	8.90×10^{-4}	3
Butyraldehyde	2.58×10^{-4}	1
"	2.30×10^{-4}	3
Acrylaldehyde	5.0×10^{-6}	1
"	6.1×10^{-6}	2

Method 1 : DPPH technique,

2 : Inhibitor method using β -naphthol

3 : Inhibitor method using 2,6-di-*tert*-butyl-4-methylphenol

Reaction conditions : [aldehyde] = 3.0 M,

[Co] = 1.5×10^{-3} M

benzene in the presence of DPPH under the atmosphere of air. The results obtained are shown in **Fig. 1**. The concentration of DPPH after the induction period in the initial stage decreased linearly with time at the stationary state.

Table 2 shows the dependence of the consumption rate of DPPH on the concentrations of both acrylaldehyde and Co(III)(acac)_3 . From the results, the rate was expressed as Eq. (3):

$$\begin{aligned} -d[\text{DPPH}]/dt &= d[\text{CH}_2=\text{CH}\dot{\text{C}}=\text{O}]/dt \\ &= k_{1,AL} [\text{CH}_2=\text{CHCHO}] [\text{Co(III)(acac)}_3] \end{aligned} \quad (3)$$

where $k_{1,AL}$ is the rate constant of Eq. (1) with acrylaldehyde as the substrate. Equation (3) indicates that acryloyl radical is formed by the bimolecular reaction of acrylaldehyde and Co(III)(acac)_3 . The calculated rate constant, $k_{1,AL}$, is also shown in **Table 2**. The constant, $k_{1,AL}$, was much lower than that of propionaldehyde ($k_{1,PA}$, see **Table 3**). The activation energy of the re-

Fig. 1 Hydrogen Abstraction of Acrylaldehyde by Co(III)(acac)_3 in Benzene

Table 2 Hydrogen Abstraction Reaction of Acrylaldehyde by Cobaltic Ion

$-d \text{ DPPH} / dt$ ($\text{M} \cdot \text{sec}^{-1}$)	Initial concentration of		Temperature (°C)	$k_{1,AL}$ ($\text{M}^{-1} \cdot \text{sec}^{-1}$)
	Acrylaldehyde (M)	Co(acac) ₃ (M)		
4.0×10^{-8}	6.0	1.5×10^{-3}	30	4.4×10^{-6}
2.4×10^{-8}	3.0	1.5×10^{-3}	30	5.3×10^{-6}
1.4×10^{-8}	2.0	1.5×10^{-3}	30	4.7×10^{-6}
4.4×10^{-8}	3.0	3.0×10^{-3}	30	4.9×10^{-6}
1.2×10^{-8}	3.0	7.5×10^{-4}	30	5.3×10^{-6}
6.0×10^{-9}	3.0	3.7×10^{-4}	30	5.4×10^{-6}
			average	5.0×10^{-6}
1.8×10^{-8}	3.0	1.5×10^{-3}	20	4.0×10^{-6}
3.5×10^{-8}	3.0	1.5×10^{-3}	40	7.8×10^{-6}

* Cald. from Eq. (3)

Table 3 Hydrogen Abstraction of Propionaldehyde with Co(III)(acac)₃ in Benzene at 30°C

Propionaldehyde ($\times 10$ M)	Co(III)(acac) ₃ ($\times 10^3$ M)	O ₂ ($\times 10^3$ M)	$-d[\text{DPPH}]/dt$ ($\times 10^8 \text{ M}\cdot\text{s}^{-1}$)	Induction Period (min)	$k_{1,PA}$ ($\times 10^5 \text{ M}^{-1}\cdot\text{s}^{-1}$)
2.8	1.5	7.7*	96.6	110	2.3
2.8	1.5	1.6	88.2	120	2.1
2.8	1.5	0.63	79.8	240	1.9
2.8	1.5	0.0	0.18	>1,500	—
2.8	3.0	7.7	193	86	2.3
5.6	1.5	7.7	194	40	2.3

* Corresponding to $[\text{Po}_2]=1 \text{ atm}$ Table 4 Correlation between Rates of Initiation Reaction and Autoxidation of Acrylaldehyde Catalyzed by Co(III)(acac)₃ at 30°C

Solvent	Dielectric Constant (D)	Rate of Initiation (R_1)* ¹ ($\times 10^5 \text{ M}\cdot\text{s}^{-1}$)	Rate of Autoxidation (Ro_2)* ² ($\times 10^4 \text{ M}\cdot\text{s}^{-1}$)	$Ro_2/R_1^{1/2}$ ($\times 10 \text{ M}^{1/2}\cdot\text{s}^{-1/2}$)
Cyclohexane	2.036	0.22	1.5	1.01
Carbon Tetrachloride	2.238	0.68	2.2	0.84
Benzene	2.28	0.51	2.9	1.28
Toluene	2.379	1.7	3.2	0.78
Valeric Acid	2.66	7.5	4.1	0.47
Butyric Acid	2.97	12	4.4	0.40
Propionic Acid	3.44	20	3.8	0.27
Acetic Acid	6.15	70	3.2	0.12

*¹) $[\text{Co(III)(acac)}_3] = [\text{DPPH}] = 1.5 \times 10^{-3} \text{ M}$, $[\text{AL}] = 3.0 \text{ M}$, 30°C*²) $[\text{Co(III)(acac)}_3] = 1.5 \times 10^{-3} \text{ M}$, $[\text{AL}] = 3.0 \text{ M}$, 30°C

[acrylaldehyde] : 3.0 M,
 [Co(III)(acac)₃] : $1.5 \times 10^{-3} \text{ M}$
 * : calculated by Eq. (3)

Fig. 2 Effect of Oxygen Pressure on the Hydrogen Abstraction of Acrylaldehyde by Co(III)-(acac)₃ in Benzene at 30°C

action was estimated to be 5.8 kcal/mol.

The rate of hydrogen abstraction reaction was found to increase with 1/2 order of the partial pressure of oxygen in the reaction system containing acrylaldehyde and Co(III)(acac)₃ (Fig. 2). In addition, the partial pressure influenced the length of the induction period of the initiation reaction considerably. No reaction with respect to acrylaldehyde started in the absence of oxygen.

On the other hand, the rate of hydrogen abstraction from the saturated aldehyde, propionaldehyde, was not affected by the partial pressure of oxygen, although the induction period became longer with lower partial pressure of oxygen, as was similar in the case of acrylaldehyde (Table 3).

The difference in the reactivities between acrylaldehyde and propionaldehyde cannot be fully explained. But this fact may be based on the difference in the electronic nature of the carbonyl groups of both aldehydes. The electron density of the carbonyl group of acrylaldehyde is lower than that of propionaldehyde because of the presence of the electron-withdrawing vinyl group. The former aldehyde, therefore, is more difficult to approach the Co³⁺ of the catalyst nucleophilically, resulting in the lower rate of initiation. For acrylaldehyde oxygen is assumed to accelerate the abstraction of the hydrogen atom from acrylaldehyde *via* route *a* based on the results and discussion mentioned above. On the other hand, for propionaldehyde, route *b* is considered to be more preferable to route *a* if any.

3.3 Solvent effect

As shown in **Fig. 3**, the initiation reaction of acrylaldehyde with Co(III)(acac)_3 under the atmosphere of air was affected considerably by the nature of the solvent. The induction period of the reaction was observed in most of the solvents examined, but not in carboxylic acids. The rate of initiation decreased in the order: acetic acid > propionic acid > butyric acid > valeric acid >> toluene > carbon tetrachloride > cyclohexane. Markedly higher rates were observed in carboxylic acids compared with the other solvents.

In the reaction containing intermediates of free radicals, the solvent effect is generally expressed by the Kirkwood equation:

$$\ln[k_{1,AL}/(k_{1,AL})_0] = -\frac{1}{kT} \left(\frac{D-1}{2D+1} \right) \left[\frac{\mu_A^2}{a_A^3} + \frac{\mu_B^2}{a_B^3} - \frac{\mu_{M^*}^2}{a_{M^*}^3} \right] + \frac{\phi_A + \phi_B - \phi_{M^*}}{kT} \quad (7)$$

in which D is the dielectric constant of the solvent, μ is the dipole moment, a is the radius, A and B are the reactants, and M is the activated complex derived from A and B . **Figure 4** shows, the initiation rate of reaction (1) against $D-1/(2D+1)$. It was found that the solvent effect can be arranged according to the Kirkwood equation (7), and that the solvents used could be classified into two groups: aprotic solvents such as benzene, toluene, cyclohexane and carbon tetrachloride (1st group), and protic solvents such as acetic acid,

[acrylaldehyde] : 3.0 M, 30°C
[DPPH] = [Co(III)(acac)₃] : 1.5 × 10⁻³ M,

Fig. 3 Solvent Effect in the Initiation Reaction of Autooxidation of Acrylaldehyde Catalyzed by Co(III)(acac)_3

propionic acid, butyric acid and valeric acid (2nd group). The slopes of the lines shown in **Fig. 4** seem to depend on the kinds of the solvent groups. Configurations of the intermediates of the initiation reaction, therefore, may depend on the solvent groups.

The effect of carboxylic acids on the initiation reaction was studied using mixtures of butyric acid and benzene as solvents. **Figure 5** shows the rate of initiation reaction against the molarity of butyric acid in the solvent mixture. Butyric acid of concentration below about 0.2 M affected the initia-

[acrylaldehyde] : 3.0 M,
[Co(III)(acac)₃] : 1.5 × 10⁻³ M, 30°C

Fig. 4 Correlation of Initiation Rates with Dielectric Constants of Solvents

[acrylaldehyde] : 3.0 M,
[Co(III)(acac)₃] : 1.5 × 10⁻³ M
○ : experimental, ● : calculated

Fig. 5 Rate of Initiation Reaction in the Mixture of Butyric Acid and Benzene at 30°C

要 旨

コバルト(III) アセチルアセトネートを触媒とするアクリルアルデヒドの自動酸化の開始反応

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遷移金属イオンを触媒とするアルデヒドの自動酸化反応は、高原子価金属イオンによる水素引き抜き反応によって開始される (Eq. (1) 参照)。この開始反応は、過去において、酸化防止剤を用いる「禁止剤法」や高原子価金属イオンを滴定定量する「滴定法」によって検討されてきた。しかしこれらの方法は時間がかかるなどのような欠点を有していた。本研究では、 α , α -ジフェニルピクリルヒドラジル (DPPH) を用いる新しい開始反応の検討法を開発し、この方法でアクリルアルデヒドの Co(III) (acac)₃ による開始反応を研究した。

本研究の実験条件下において、DPPH の分子吸光係数 (ϵ) は 1.02×10^4 であり、Co(III) (acac)₃ の存在によって影響されなかった。アルデヒド-Co³⁺-DPPH の系において反応が Eqs. (1), (2) に従って進み、(2) の反応速度が (1) の反応速度を無視できるほど速ければ、(1) の速度定数 k_1 は DPPH の消費速度から得ることができる。この方法で求めた数種のアルデヒドと Co(III) (acac)₃ の反応の速度定数 k_1 を Table 1 に示す。これには、現在最も普通に行われており、信頼性があるとされている禁止剤法で求めた k_1 も比較のために示してある。この結果から、両測定法による値は誤差範囲内で一致すること、すなわち DPPH 法が速度定数の決定に使用できることがわかった。

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アクリルアルデヒドに関する Eqs. (1), (2) による反応の様子を Fig. 1 に、また反応結果を Table 2 に示す。表から反応速度は Eq. (3) で表され、結果として速度定数 ($k_{1,AL}$) は 30°C で $5.0 \times 10^{-6} \text{M}^{-1} \cdot \text{sec}^{-1}$ であり、反応系の酸素圧が低下すると速度定数は 1/2 次の次数で低下し (Fig. 2)、無酸素の状態では反応が進行しなかった。一方プロピオンアルデヒドの場合の速度定数 ($k_{1,PA}$) (Table 3) は、30°C で $2.2 \times 10^{-5} \text{M}^{-1} \cdot \text{s}^{-1}$ とアクリルアルデヒドのそれより高く、酸素圧の影響を受けなかった。この両アルデヒドの Co(III) (acac)₃ に対する反応性の相違はアルデヒドのカルボニル基の電子密度の差に基づくものと推定された。

Eq. (1) による反応の溶媒効果をアクリルアルデヒドに対して検討した (Fig. 3)。これらの溶媒は、Kirkwood の溶媒効果の Eq. (7) によると、ベンゼン、トルエン、シクロヘキサンおよび四塩化炭素のような中性溶媒群 (第 1 群) と酢酸、プロピオン酸、酪酸および吉草酸のような酸溶媒群 (第 2 群) とに分類できることがわかった (Fig. 4)。一般に反応は酸溶媒中の方が速いが、これは Eqs. (10), (11) で示すようにアクリルアルデヒドが触媒のコバルトへ近づく (配位する) までの過程が H⁺ によって促進されるという仮定に基づいて解釈できた (Fig. 5 に、この仮定に基づく計算値と実測値が良く一致することを示してある)。

Keywords

Acrylaldehyde, Autoxidation, Cobalt (III) acetylacetonate, Diphenylpicryl hydrazyl technique, Initiation reaction