HETEROGENEOUS PHOTSENSITIZED OXYGENATION OF 2,3-DIMETHYL-2-BUTENE

TOSHIYUKI YOKOTA, YASUYUKI TAKAHATA, JUN HOSOYA,
KEIICHI SUZUKI AND KOJI TAKAHASHI

Department of Chemical Engineering, Yamagata University, Yonezawa 992

Key Words: Photo Oxygenation, Photosensitizer, 2,3-Dimethyl-2-Butene, Light Absorption Rate, Heterogeneous Photoreaction, Dye Supported Sensitizer

Photo-oxygenation of 2,3-dimethyl-2-butene was performed using dye-supported solid particles as photosensitizer. Quantitative effects of solid sensitizer concentration and of dye quantity supported on solid particles were investigated. The light absorption rate in the heterogeneous system was assessed by a Monte Carlo simulation. The reaction rate was proportional to the n -th order of light absorption rate, where n was a little less than unity, and to the 0-th order of butene concentration in a feed range of 5×10^{-1} – 2×10^2 mol/m³. The rate constant was a function of dye quantity supported on solid particles. This is due to the adsorbate-adsorbate interaction.

Introduction

There are two types of photosensitized reactions. One is a homogeneous system which uses a soluble sensitizer in the reactant solution and the other is a heterogeneous system which uses solid particles suspended in a reactant mixture as sensitizer. A heterogeneous system has the following advantages.^{5,6,7,9} A heterogeneous photosensitizer proves to be more stable. We can conveniently employ a much wider range of solvents according to the requirements of the reacting systems. In an oxygenation, we can select a solvent forming long-life singlet oxygen. The separation of the sensitizer from the products can be easy so that the sensitizer may be reused with little or no loss in efficiency.

Even though many advantages in a heterogeneous system have been pointed out, only a few kinetic analyses^{2,3} which treat the sensitizer activity and the sensitizer concentration quantitatively have been reported. One of the reasons is the difficulty in evaluating the light absorption rate accurately in a heterogeneous reaction system.

In this work, we employed the oxygenation of 2,3-dimethyl-2-butene to the corresponding hydroperoxide by dye-supported solid particles as photosensitizer,^{1,2} and performed a quantitative kinetic analysis. We assessed the light absorption rate in the liquid-solid oxygenation system by means of a new random-walk model^{10,11} which was proposed for a Monte Carlo simulation of light scattering in a multiphase system.

1. Experimental

1.1 Preparation of sensitizers

For the preparation of heterogeneous sensitizer we used two kinds of supporting particles: silica gel particles (average diameter 166 μ m) and acrylic ester resin beads (Amberlite XAD-7, average diameter 556 μ m), and three kinds of dyes: methylene blue (abbrev. MB), rose bengal (abbrev. RB) and eosin yellow (abbrev. EY).

To obtain methylene blue sensitizer we impregnated silica gel particles with a MB solution of known concentration for five hours in a rotavapor at room temperature and at atmospheric pressure.¹ Throughout the supportation reaction a buffer solution maintained the reactant at pH=4.4. The dye concentration measurement of the solutions before and after supportation reaction determined the supported methylene blue quantity.

We carried out the impregnation of acrylic beads with rose bengal or eosin yellow, using each methanol solution.⁹ After the supportation reaction for one hour at room temperature and atmospheric pressure, the beads were dried in an oven at 70°C for 6 hours. We determined the quantity of the supported dye by the desorption of the attached dye using proper solvents.

We proved that the dye supported on each particle did not dissolve in the solvent, which was selected for photo-oxygenation. We used benzene as the solvent for RB and EY sensitizer, and carbon tetrachloride for MB sensitizer.

1.2 Experimental apparatus and procedure

Figure 1 shows the apparatus for the photo-

Received August 29, 1988. Correspondence concerning this article should be addressed to T. Yokota.

Fig. 1. Schematic diagram of experimental apparatus

oxygenation. The reactor was a rectangular prism cell made of Pyrex glass ($2 \times 10^{-2} \times 2 \times 10^{-2} \times 3 \times 10^{-2} \text{ m}^3$) with a $4 \times 10^{-4} \text{ m}^2$ irradiated surface. The collimated light beam from a Sylvania JCD, 100V-300W lamp irradiated the reactor and the power to the lamp was adjusted to hold constant light intensity. A 30-minute lighting period before the reaction attained steady-state light intensity. A CdS photocell mounted in the lamp housing monitored the light intensity fluctuation and allowed manual regulation of the intensity.

We took a $6.4 \times 10^{-6} \text{ m}^3$ solution adjusted to a certain butene concentration with solid sensitizer in the reactor. A magnetic stirrer suspended the solid particles uniformly. Before the irradiation of the butene solution pure oxygen gas was fed for 15 minutes and during the irradiation it was fed at $5.5 \times 10^{-7} \text{ m}^3/\text{s}$ for RB and EY sensitizer and at $9.1 \times 10^{-7} \text{ m}^3/\text{s}$ for MB sensitizer. We ensured that each gas flow rate did not limit the overall reaction rate. To prevent butene vaporization caused by continuous oxygen feeding and by irradiation heat, we dipped the reactor in a water bath controlled at 5°C and connected it to a gas condenser cooled at -10°C . The temperature in the reaction mixture was kept at $8^\circ\text{C} \pm 0.5^\circ\text{C}$.

We determined the reaction rate by the measurement of butene concentration with gas chromatography. We also measured the produced allylic hydroperoxide by iodometric titration⁴⁾ and the results showed that the mass balance was held within 10% error.

We conducted the photo-oxygenation of 2,3-dimethyl-2-butene under various conditions to evaluate the influence of butene concentration, light intensity, sensitizer concentration and concentration of dye supported on the solid particles.

1.3 Determination of light intensity

To obtain a quantitative kinetics the rate of light absorption by sensitizer particles must be assessed precisely. For this assessment we determined the incident light intensity in advance. An accurate light intensity in a visible spectral range which was effective to dye-sensitized photoreaction was obtained by Reinecke's salt actinometry.⁸⁾ Two portions of fresh 1 mol/m^3 Reinecke's potassium salt solution were

prepared: one was fed for photoreaction in the reactor, which was to be used for photo-oxygenation, and the other was held for dark reaction. The spectrophotometry according to Wegner's procedure⁸⁾ determined the produced thiocyanate ion concentration after 1 minute exposure. Elimination of the thiocyanate ion released by a dark reaction from the irradiated sample determined the net photoreaction rate. The following equation gives the relation between photoreaction rate and an incident light intensity.

$$r_a = \frac{I_{o,t} A}{V} \sum \phi_\lambda (F_\lambda / F_t) (1 - e^{-\mu_\lambda l}) \quad (1)$$

Wegner⁸⁾ determined the quantum yield ϕ_λ 's and experimental measurements gave the incident light energy spectra (F_λ / F_t) and the attenuation coefficient μ_λ . The total incident light intensity could be determined by Eq. (1) from a photoreaction rate which corresponded with each power supply.

2. Results and Discussion

The widely accepted kinetic equation for the homogeneous photosensitized oxygenation via singlet oxygen is expressed by Eq. (2), based on the following sequential reaction scheme.^{1,2,5,7)}

In Eq. (2) R_o is the production rate of singlet oxygen, C_B is the butene concentration, and β is the ratio between the physical quenching constant of singlet oxygen k_5 and the chemical quenching constant k_4 .

At first we investigated the adoption of the above equation for the heterogeneous solid-liquid system. Integration of Eq. (2) yields Eq. (3) that evaluates the butene concentration change in a batch reactor.

$$(C_{B0} - C_B) + \beta \ln(C_{B0}/C_B) = R_o t \quad (3)$$

or

$$\frac{t}{1-X} = \frac{C_{B0} + \beta}{R_o} + \left(\frac{\beta}{R_o} \right) \left\{ \frac{\ln(1/X)}{1-X} - 1 \right\} \quad (4)$$

Figure 2 shows the butene concentration change which is expressed by Eq. (4) for EY sensitizer. For the low feed concentration of butene, the points lay on a straight line but for the higher feed concentration the data showed a convex downward trend. Calculating the kinetic constants in Eq. (2) from the slope and the intersection of the straight line for the feed concentration $C_{Bo}=1.01 \times 10^2 \text{ mol/m}^3$, we got β of 4.4 mol/m^3 , which was the same magnitude given in the literature,^{1,2,6)} and $R_o=3.9 \times 10^{-2} \text{ mol/m}^3 \cdot \text{s}$, which was almost the same as the initial reaction rate $r_o=3.7 \times 10^{-2} \text{ mol/m}^3 \cdot \text{s}$ derived from the butene concentration change.

Table 1 shows the initial reaction rates for various feed concentrations. The results showed that the oxygensation rate was constant in the range of butene concentration $5 \times 10^1 \sim 2 \times 10^2 \text{ mol/m}^3$. Because of low β compared to C_{Bo} , a zero-th order reaction rate proved valid in this experiment.⁷⁾

$$-r = R_o \quad (5)$$

The production rate of singlet oxygen was proportional to the light absorption rate by sensitizer. Then R_o is expressed as follows:

$$R_o = kQ = k \left(\frac{A}{V_R} I_{o,e} q \right) \quad (6)$$

where Q is the light absorption rate based on reactor volume, and q is the fraction of light absorption in a heterogeneous reactor. We defined the effective incident light intensity $I_{o,e}$ in Eq. (6) by considering dye absorbance as follows:

$$I_{o,e} = \frac{\int A b_\lambda I_{o,\lambda} d\lambda}{\int A b_\lambda d\lambda} \quad (7)$$

and

$$I_{o,\lambda} = (F_\lambda/F_o) I_{o,i} \quad (8)$$

We determined the total incident light intensity by chemical actinometry as described above.

We performed a series of experiments to investigate the effect of light intensity. The initial oxygensation rates were measured under various lighting conditions. Figure 3 shows the plot of the initial rate r_o vs. $I_{o,e}$. As indicated in this figure, the n -th power of $I_{o,e}$ fitted the data. In each sensitizer, n was a little less than unity.³⁾ This means that Eq. (2) does not always express satisfactorily the rate of the heterogeneous photosensitized oxygensation. Then we considered the following phenomenological or empirical equation for a heterogeneous system.

$$-r = KQ^n \quad (9)$$

Because the power of light absorption rate is less than unity, bimolecule termination steps for the excited chemical species might occur in addition to the single

Fig. 2. Butene concentration change expressed by Eq. (4)

Table 1 Effect of feed concentration on initial reaction rate

$C_{Bo} \times 10^{-2} [\text{mol} \cdot \text{m}^{-3}]$	$r_o \times 10^2 [\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}]$
0.57	3.95
1.01	3.72
1.32	3.49
1.72	3.90
2.58	4.08

Sensitizer: EY
 $S = 2.43 \times 10^2 \text{ m}^{-1}$
 $D = 7.11 \times 10^{-3}$
 $I_{o,e} = 18.5 \text{ J} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$

Fig. 3. Relationship between initial reaction rate and effective incident light intensity

termination steps described before. But we could not develop a detailed reaction mechanism for lack of other information.

To confirm the above phenomenological rate equation, we performed a series of experiments with various sensitizer concentrations, which produced various light absorption rates in the reaction mixture. We defined the sensitizer concentration $S [\text{m}^{-1}]$ as the surface area of sensitizer particles per unit volume of reacting liquid. At a constant light-intensity radiation and a feed butene concentration of $1 \times 10^2 \text{ mol/m}^3$, we determined the initial reaction rate as a function of S . Figure 4 shows the results.

Before the assessment of light absorption rate, we must estimate the fraction of light absorbed in the solid-liquid mixture. We did it for each reacting mixture by a statistical approach based on a new random-walk model.^{10,11)} The model assumes that scattering light rays will travel along one of six Cartesian coordinate directions randomly. After many

Fig. 4. Initial reaction rate vs. sensitizer concentration

Fig. 5. Light absorption fraction vs. sensitizer concentration

Fig. 6. Comparison of experimental and calculated butene concentrations for sensitizer concentration change

iterations of computation for a sufficient number of incident light rays which travel randomly in reaction mixture to reach a reactor boundary, we sum up the light energy absorbed by the suspended particles and obtain its fraction. The results are shown in Fig. 5 as a function of S . We could determine the light absorption rate from the results above together with the incident light intensities by chemical actinometry.

Based on Eq. (9), the initial reaction rate could evaluate the rate constant K using the light absorption rate and its power. The value of K for each sensitizer was as follows: $K = 7.26 \times 10^{-4} \text{ mol} \cdot \text{J}^{-n} \cdot \text{m}^{3(n-1)} \cdot \text{s}^{(n-1)}$ for RB, $K = 8.19 \times 10^{-4} \text{ mol} \cdot \text{J}^{-n} \cdot \text{m}^{3(n-1)} \cdot \text{s}^{(n-1)}$ for EY and $K = 3.94 \times 10^{-4} \text{ mol} \cdot \text{J}^{-n} \cdot \text{m}^{3(n-1)} \cdot \text{s}^{(n-1)}$ for MB. The solid lines in Fig. 4 show the reaction rates calculated by Eq. (9). We also performed an integral confirmation of the rate equation. The integral equation of Eq. (9) gave the butene concentration change in a batch reactor. Figure 6 shows a comparison of experimental and calculated butene concentrations. When the reaction proceeded to low butene concentration, the experimental data took slightly higher values than the estimated ones. This was caused by the zero-th order rate equation which was obtained by ignoring β in Eq. (9). The data for MB sensitizer were somewhat different from the predicted values for low S . This was caused by sensitizer deactivation

owing to fading of the supported dye. But most of the experimental data agreed well with the predicted butene concentration lines. Therefore, the formula of the rate equation and the values of K and n were confirmed to be valid.

We also investigated the effect of sensitizer size. Figure 7 shows the butene concentration change for RB sensitizer made from resin beads of $702 \mu\text{m}$ diameter. We assessed the light absorption rate in the reaction mixture with larger-size sensitizer and predicted the butene concentration change from the reaction rate of Eq. (9), in which the kinetic constant K and the exponent n were the values determined above. The solid curves in Fig. 7 show the predicted value. They agreed well with the experimental butene concentration.

We also investigated the effect of the dye quantity supported on solid particles. First we prepared a variety of sensitizers supporting different amounts of dye. The quantity of dye was denoted by D , which expressed grams of dye per gram of solid particles. Next, we submitted each sensitizer to the reaction mixture, which always had a certain initial butene content and a fixed S . The random-walk model estimated the light absorption rate in the reaction mixture for each sensitizer. Finally, we determined the kinetic constants in Eq. (9) from the initial reaction

rate derived from the reaction curve, the light absorption rate and the power n . They are shown in Fig. 8.

The rate constant decreased as D increased in every sensitizer. This means that higher-level supportation acts to lower the energy level and to shorten the lifetime of the excited-state sensitizers $^1\text{Sens}$ and $^3\text{Sens}$.¹⁾ In this experiment adsorbate-adsorbate interaction was responsible for the decrease of photosensitizing activity as Brkic *et al.*¹⁾ pointed out. Treating K as a function of D just like a curve in Fig. 8, we could predict the butene concentration change during photo-oxygenation. Figure 9 shows a comparison of predicted and experimental results. For the most part the agreement was satisfactory.

To test sensitizer stability we performed the following experiments. A fresh reaction mixture (a certain content of butene and new sensitizer in solvent) was irradiated and reached more than 90% conversion. The sensitizer particles were filtered out, rinsed with solvent and dried for reuse. A reaction

mixture containing the reused sensitizer was then illuminated. Comparing the reaction rates evaluated from the two reaction curves we examined the sensitizer stability. When the two initial reaction rates were the same, the sensitizer was at least stable during the reaction the first time.

As the above examination results, RB and EY sensitizers supported on acrylic beads were stable under our experimental conditions. But MB sensitizer supported on silica gel particles showed less activity, and an apparent fading of dye was observed in some experiments. This instability might be primarily related to a photo-oxidizing property of silica, namely, a support-adsorbate interaction.¹⁾

Conclusions

In this paper we reported the experimental results of a heterogeneous dye-sensitized photo-oxygenation of 2,3-dimethyl 2-butene, which was carried out to investigate quantitative effects of solid sensitizer concentration and of dye quantity supported on solid particles. We obtained the following results from the experiments.

- (1) Butene concentration did not affect the photo-oxygenation rate in a C_{B_0} range of $5 \times 10^{-1} - 2 \times 10^2 \text{ mol/m}^3$.
- (2) The photo-oxygenation rate was proportional

Fig. 7. Butene concentration change for RB sensitizer supported on $702 \mu\text{m}$ resin beads

Fig. 8. Kinetic constant vs. dye quantity of sensitizer

Fig. 9. Comparison of experimental and calculated butene concentrations for dye quantity change of sensitizer

to the n -th power of the light absorption rate, where n was a little less than unity.

(3) The light absorption rate estimated by the Monte Carlo simulation using the newly proposed random-walk model^{10,11)} could evaluate the quantitative effect of sensitizer concentration on heterogeneous oxygenation rate.

(4) Higher-level dye supportation acted to lower the photo-oxygenation rate. The adsorbate-adsorbate interaction was responsible for the decrease in activity of sensitizers.

Nomenclature

A	= radiation area	[m ²]
Ab_λ	= dye absorbance	[—]
C_B	= butene concentration	[mol·m ⁻³]
C_{Bo}	= initial butene concentration	[mol·m ⁻³]
D	= dye quantity supported on solid particles	[—]
F_λ/F_t	= spectral energy distribution of incident light	[—]
$I_{o,e}$	= effective light intensity	[J·m ⁻² ·s ⁻¹]
$I_{o,t}$	= total incident light intensity	[J·m ⁻² ·s ⁻¹]
$I_{o,\lambda}$	= incident light intensity at wave length λ	[J·m ⁻² ·s ⁻¹]
K	= rate constant	[mol·J ⁻ⁿ ·m ³⁽ⁿ⁻¹⁾ ·s ⁽ⁿ⁻¹⁾]
k	= rate constant	[mol·J ⁻¹]
l	= light path length	[m]
n	= power of light absorption rate	[—]
Q	= light absorption rate	[J·m ⁻³ ·s ⁻¹]
q	= fraction of light absorption	[—]
R_o	= production rate of singlet oxygen	[mol·m ⁻³ ·s ⁻¹]
r	= photo-oxygenation rate	[mol·m ⁻³ ·s ⁻¹]

r_a	= reaction rate of Reinecke's salt actinometer	[mol·m ⁻³ ·s ⁻¹]
r_o	= initial photo-oxygenation rate	[mol·m ⁻³ ·s ⁻¹]
S	= sensitizer concentration	[m ⁻¹]
t	= time	[s]
V	= feed volume of actinometer solution	[m ³]
V_R	= reactor volume	[m ³]
X	= C_B/C_{Bo}	[—]
β	= ratio k_4/k_5 in Eq. (2)	[mol·m ⁻³]
μ_λ	= attenuation coefficient	[m ⁻¹]
ϕ_λ	= quantum efficiency	[mol·J ⁻¹]

Literature Cited

- 1) Brkic, D., P. Forzatti and I. Pasquon: *J. Mol. Catalysis*, **3**, 173 (1977/78).
- 2) Brkic, D. and P. Forzatti: *Chem. Eng. Science*, **33**, 853 (1978).
- 3) Maemoto, A., A. Itaya and K. Okamoto: Preprint of the 49th Annual Meeting of the Society of Chem. Eng., Japan (Nagoya), G204 (1984).
- 4) Mari, R. D. and A. J. Graupner: *Anal. Chem.*, **36**, 194 (1964).
- 5) Matuura, T.: "Sanso Sanka Hannou," Maruzen (1977).
- 6) Okamoto, K.: *Kagaku Kougaku*, **43**, 497 (1979).
- 7) Schapp, A. P., A. L. Thayer, E. C. Blossey and D. C. Neckers: *J. Am. Chem. Soc.*, **97**, 3471 (1975).
- 8) Wegner, E. E. and A. W. Adamson: *J. Am. Chem. Soc.*, **88**, 394 (1966).
- 9) Williams, J. R., G. Orton and L. R. Unger: *Tetrahedron Lett.*, **46**, 4603 (1973).
- 10) Yokota, T., Y. Takahata, H. Nanjo and K. Takahashi: *J. Chem. Eng. Japan*, **22**, 548 (1989).
- 11) Yokota, T., Y. Takahata, Y. Ohto and K. Takahashi: *J. Chem. Eng. Japan*, **22**, 537 (1989).