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A Two-Color Laser Photolysis Method for Determining Reaction Rates of Short-Lived Intermediates by Product Analysis: Application to the *o*-Quinodimethane Problem - Supporting Information

[1] Derivation of eq 4 from eqs 1, 1', 2, and 3.

Equation 1' is converted to

$$[\mathbf{1}]_0 = \frac{[\mathbf{4}]_\infty}{a} \qquad (1'')$$

From eqs 1'' and 1, we obtain

$$[\mathbf{4}]_t = [\mathbf{4}]_\infty - a[\mathbf{1}]_t \qquad (1''')$$

When eqs 1''' and 2 are substituted to eq 3, we obtain

$$[\mathbf{4}]_\infty{}^{\mathrm{L}}{}_t = [\mathbf{4}]_\infty - a[\mathbf{1}]_t + a(1-b)[\mathbf{1}]_t$$

$$= [\mathbf{4}]_\infty - ab[\mathbf{1}]_t$$

$$\therefore\ [\mathbf{1}]_t = \frac{[\mathbf{4}]_\infty - [\mathbf{4}]_\infty{}^{\mathrm{L}}{}_t}{ab} \qquad (4)$$

[2] Derivation of eq 7 from eq 6.

Equation 6 is

$$-\frac{\mathrm{d}[\mathbf{1}]_t}{\mathrm{d}t} = k_1\,[\mathbf{2}]_t[\mathbf{1}]_t + k_2\,[\mathbf{1}]_t^2 \qquad (6)$$

When we put

$$u = \frac{1}{[\mathbf{1}]_t}$$

and substitute u to eq 6, we obtain a differential equation

$$\frac{\mathrm{d}u}{\mathrm{d}t} - k_1\,[\mathbf{2}]_t\,u = k_2 \qquad (9)$$

When $[\mathbf{1}]_t$ is a constant, eq 9 can be solved as

$$u = \frac{1}{[\mathbf{1}]_t} = \{C_1 + k_2 \int \exp(-W)\, dt\} \exp W \qquad (10)$$

where

$$W = \int k_1\, [\mathbf{2}]_t\, dt = k_1\, [\mathbf{2}]_t\, t + C_2$$

and C_1 and C_2 are constants. As

$$\int \exp(-W)\, dt = \int \exp(-k_1\, [\mathbf{2}]_t\, t - C_2)\, dt = -\frac{\exp(-k_1\, [\mathbf{2}]_t\, t - C_2)}{k_1\, [\mathbf{2}]_t} + C_3$$

where C_3 is a constant, eq 10 becomes

$$\frac{1}{[\mathbf{1}]_t} = [C_1 + k_2 \left\{ C_3 - \frac{\exp(-k_1[\mathbf{2}]_t\, t - C_2)}{k_1[\mathbf{2}]_t} \right\}] \exp(k_1\, [\mathbf{2}]_t\, t + C_2)$$

$$= (C_1 + k_2\, C_3) \exp(k_1\, [\mathbf{2}]_t\, t + C_2) - \frac{k_2}{k_1[\mathbf{2}]_t}$$

$$= (C_1 \exp C_2 + k_2\, C_3 \exp C_2) \exp(k_1\, [\mathbf{2}]_t\, t\,) - \frac{k_2}{k_1[\mathbf{2}]_t} \qquad (11)$$

At $t = 0$, $[\mathbf{1}]_t$ is $[\mathbf{1}]_0$, so that from eq 11

$$\frac{1}{[\mathbf{1}]_0} = (C_1 \exp C_2 + k_2\, C_3 \exp C_2) - \frac{k_2}{k_1[\mathbf{2}]_t}$$

$$\therefore\; C_1 \exp C_2 + k_2\, C_3 \exp C_2 = \frac{k_2}{k_1[\mathbf{2}]_t} + \frac{1}{[\mathbf{1}]_0} \qquad (12)$$

When we substitute eq 12 to eq 11, we obtain eq 7.

$$\frac{1}{[\mathbf{1}]_t} = (\frac{k_2}{k_1[\mathbf{2}]_t} + \frac{1}{[\mathbf{1}]_0}) \exp(k_1\, [\mathbf{2}]_t\, t) - \frac{k_2}{k_1[\mathbf{2}]_t} \qquad (7)$$