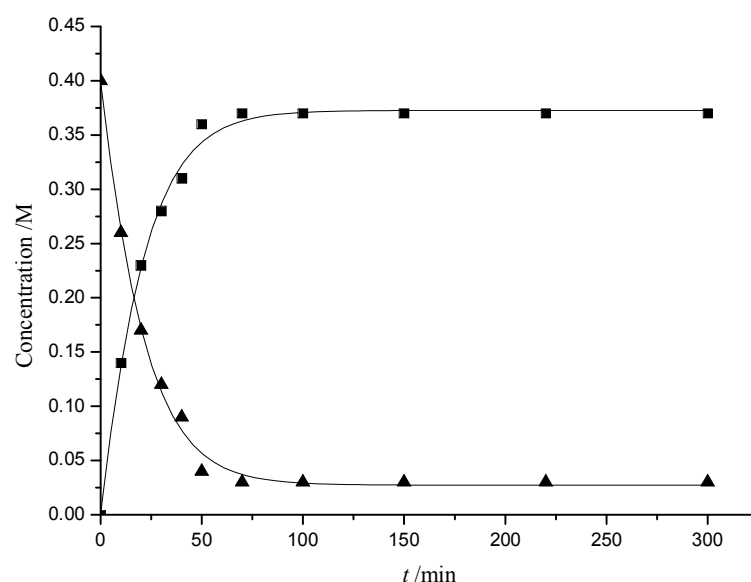


## Direct Oxidation of Secondary Alcohol to Ester by Performic Acid

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The organic peracid is expensive and unsteady. In order to investigate the exact kinetics, we readily prepared the performic acid from 30% H<sub>2</sub>O<sub>2</sub> and formic acid in this work. The variations of concentration of oxidative species in the reaction solution with reaction time were shown in figure 1S. From figure 1S, it can be seen that the performic acid could generate rapidly and arrive equilibrium within 60 min at 30 °C.



**Figure 1S.** The variations of concentration of oxidative species with time at 30 °C. ■ performic acid; ▲ H<sub>2</sub>O<sub>2</sub>  $c_0(\text{H}_2\text{O}_2) = 0.4 \text{ M}$ .

In order to investigate the reaction kinetics, we employed excessive concentration of performic acid over that of secondary alcohols to carry out the reaction. From figure 2S, it can be seen that the plots of  $\ln(c_0(\text{alcohol})/c_t)$  vs  $t$  were all straight lines and approximately passed the origin (the correlative coefficient were all more than 0.993), which indicated the reaction was first-order with respect to the concentrations of alcohols MVA, HMOPE, MPE, APE and cyclohexanol, respectively. Similarly, in order to investigate the "one step" reaction from ketone to ester, we carried out alone the oxidation of ketones by PFA, and it was found that the reactions were also first-order with respect to the concentrations of ketones (figure 3S).

Thus, according to scheme 1, the reaction rate equations can be written as follows:

$$\frac{dc_A}{dt} = -k_2 c_A c_P^\alpha - k_1 c_A c_P^\beta \quad (1)$$

$$\frac{dc_B}{dt} = k_2 c_A c_P^\alpha - k_3 c_B c_P^\gamma \quad (2)$$

$$\frac{dc_E}{dt} = k_1 c_A c_P^\beta + k_3 c_B c_P^\gamma \quad (3)$$

Where  $c_A$ ,  $c_B$ ,  $c_P$  and  $c_E$  were the concentration of reagents A (alcohol), B (ketone), P (performic acid) and product E (ester), respectively;  $k_1$ ,  $k_2$ ,  $k_3$  were the reaction rate constants as shown in scheme 1;  $\alpha$ ,  $\beta$  and  $\gamma$  were the power orders of concentration of performic acid.

$$\text{Let } k_1' = k_1 c_P^\beta, \quad k_2' = k_2 c_P^\alpha, \quad k_3' = k_3 c_P^\gamma, \quad k^* = k_1' + k_2' \quad (4)$$

By the Combination of Equations (1)-(4),  $c_A$ ,  $c_B$  and  $c_E$  can be expressed as

$$c_A = c_0 e^{-k^* t} \quad (5)$$

$$c_B = \frac{k_2' c_0}{k_3' - k^*} \left( e^{-k^* t} - e^{-k_3' t} \right) \quad (6)$$

$$c_E = c_0 - c_0 e^{-k^* t} - \frac{k_2' c_0}{k_3' - k^*} \left( e^{-k^* t} - e^{-k_3' t} \right) \quad (7)$$

Where  $c_0$  was the initial concentration of A. According to equations (4), we have

$$\ln k_2' = \ln k_2 + \alpha \ln c_P \quad (8)$$

$$\ln k_1' = \ln k_1 + \beta \ln c_P \quad (9)$$

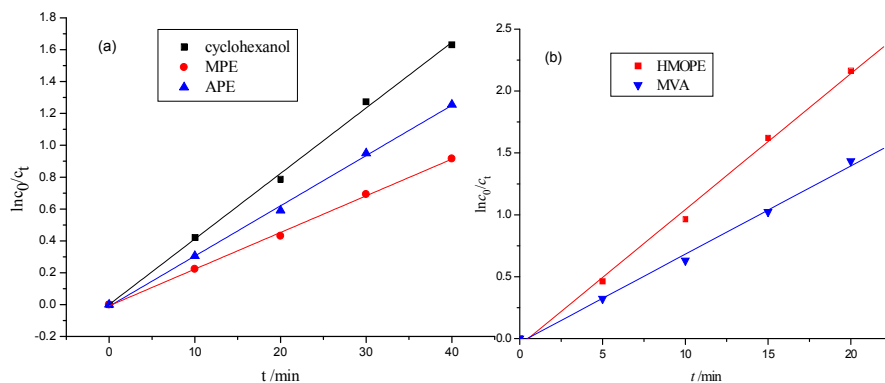
$$\ln k_3' = \ln k_3 + \gamma \ln c_P \quad (10)$$

Let  $k_3' = 0$ , Eqns (6) and (7) can be expressed as

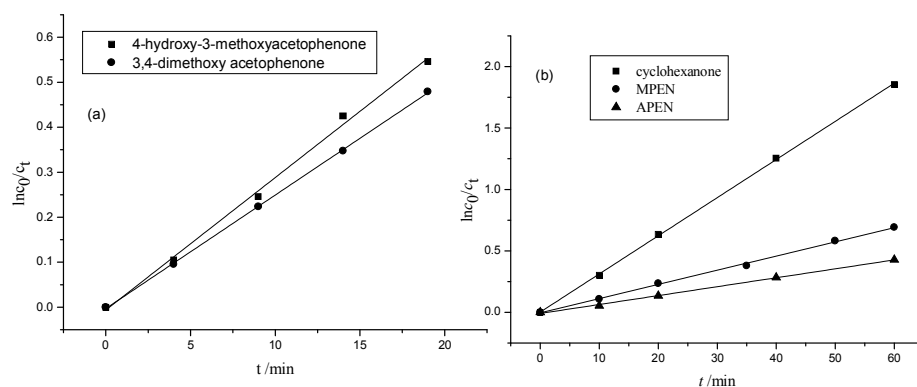
$$c_{B1} = \frac{k_2' c_0}{k^*} (1 - e^{-k^* t}) \quad (11)$$

$$c_{E1} = c_0 - c_0 e^{-k^* t} + \frac{k_2' c_0}{k^*} (e^{-k^* t} - 1) \quad (12)$$

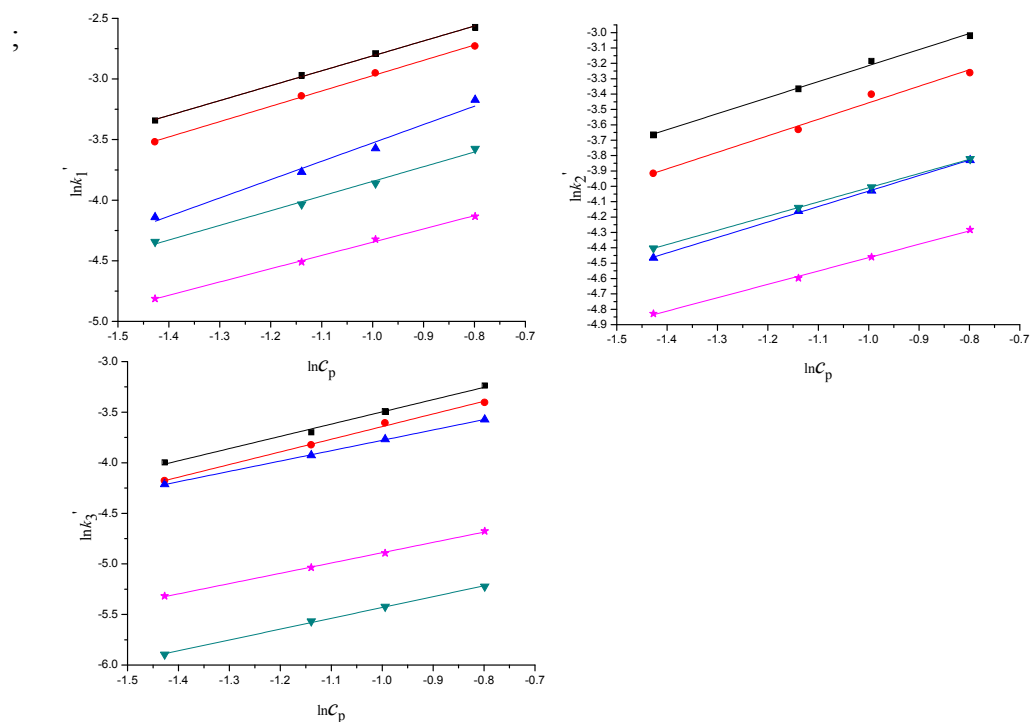
Where  $c_{B1}$ ,  $c_{E1}$  were the concentration of acetophenone and phenyl acetate.



**Figure 2S** Plots of  $\ln(c_0(\text{alcohol})/c_t(\text{alcohol}))$  vs reaction time for the oxidations of alcohols by PFA in formic acid. (a) 30 °C (b) 10 °C,  $c_0(\text{alcohol}) = 0.02 \text{ M}$ ,  $c_0(\text{PFA}) = 0.37 \text{ M}$

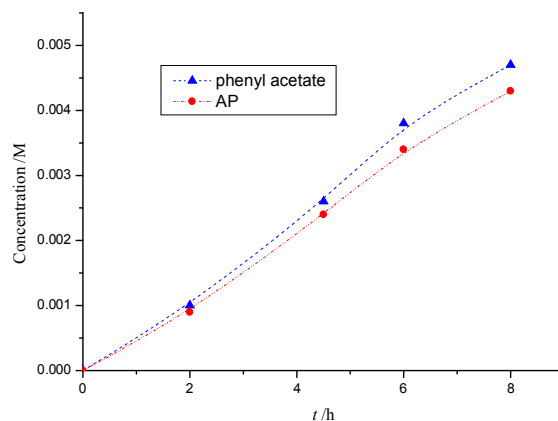


**Figure 3S** Plots of  $\ln(c_0(\text{ketone})/c_t(\text{ketone}))$  vs reaction time for the oxidations of ketones by PFA in formic acid. (a) 10 °C (b) 30 °C,  $c_0(\text{alcohol}) = 0.02 \text{ M}$ ,  $c_0(\text{PFA}) = 0.37 \text{ M}$

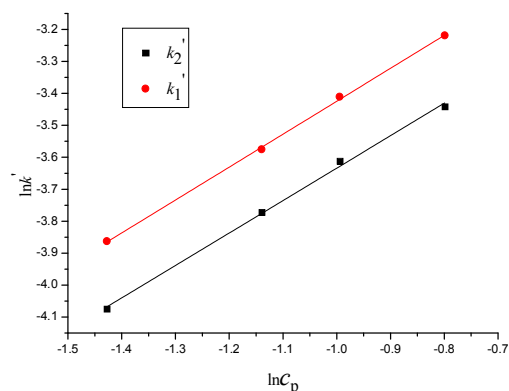


**Figure 4S** Plots of  $\ln k'$  vs  $\ln C_p$ . ■ HMOPE, ● MVA, ▲ cyclohexanol, ▼ MPE, ★ APE.

It can be seen that the plots of  $\ln k'$  vs.  $\ln c_p$  were all good linear relationship (all correlative coefficients  $r > 0.996$ ) for the oxidations of MVA, HMOPE, MPE, APE and cyclohexanol by performic acid.



**Figure 5S** The variations of concentration of AP and phenyl acetate vs. time.  
 $c_0(\text{PEA}) = 0.02 \text{ M}$ ,  $c_0(\text{PFA}) = 0.37 \text{ M}$ ,  $50 \text{ }^\circ\text{C}$



**Figure 6S** Plots of  $\ln k'$  vs  $\ln c_p$ .

It can also be seen that the plots of  $\ln k'$  vs.  $\ln c_p$  were all good linear relationship (all correlative coefficients  $r > 0.996$ ) for the oxidation of PEA by perbenzoic acid.

**Table 1S** The calculated reaction rate constants  $k_3$  and the powers orders  $\gamma$  for the oxidation of ketones by performic acid.

	$k_3 (\text{min}^{-1} \text{M}^{-\gamma_2})$	$\gamma_2$
HMOPE <sup>a</sup>	0.099	1.21
DMOPE <sup>a</sup>	0.092	1.22
cyclohexanone <sup>b</sup>	0.066	1.05
APEN <sup>b</sup>	0.016	1.07
MPEN <sup>b</sup>	0.023	1.06

<sup>a</sup>  $10 \text{ }^\circ\text{C}$ , <sup>b</sup>  $30 \text{ }^\circ\text{C}$ ,  $c_0(\text{alcohol}) = 0.02 \text{ M}$ ,  $c_0(\text{PFA}) = 0.37 \text{ M}$