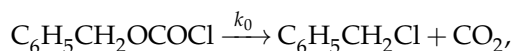


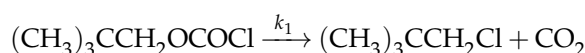
Instructions

1. The exam is for 75 min - an initial 15 min discussion period followed by 60 min writing period.
2. Writing is ONLY permitted during the second period.
3. Identify your discussion partner in your answer sheet.

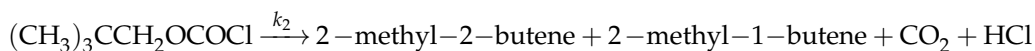
Questions 1– 3 relate to the kinetics of the gas-phase elimination reaction of benzyl chloroformate and neopentyl chloroformate which was reported recently in *Int. J. Chem. Kinet.* **47**, 104 (2015). Benzyl chloroformate, $C_6H_5CH_2OCOCl$, decomposes according to



while neopentyl chloroformate, $(CH_3)_3CCH_2OCOCl$, undergoes two parallel reactions



and

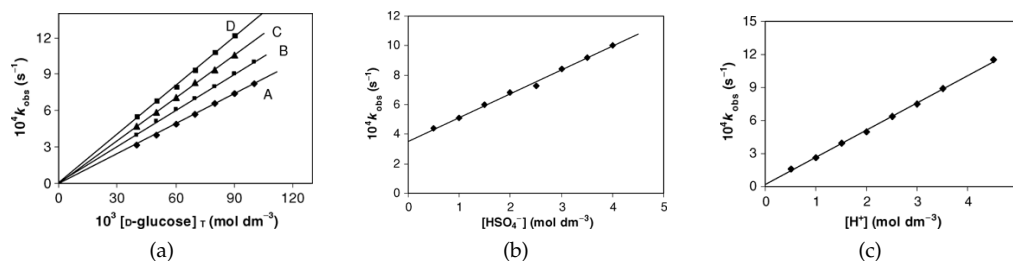


The authors report that $\log k_0 = 13.30 - 152.9 \text{ kJ mol}^{-1} \times (2.303RT)^{-1}$, $\log k_1 = 14.29 - 196.3 \text{ kJ mol}^{-1} \times (2.303RT)^{-1}$ and $\log k_2 = 12.12 - 178.2 \text{ kJ mol}^{-1} \times (2.303RT)^{-1}$.

1. For $C_6H_5CH_2OCOCl$, at a number of temperatures and over many half-lives, the ratio of the final pressure to the initial pressure is 1.96 ± 0.05 . What conclusion would you draw from this result? [5]
2. At 593 K, which product would predominate, neopentyl chloride or 2-methylbutenes? Why? [10]
3. Suggest possible experiment(s) to (a) confirm that neopentyl chloroformate forms neopentyl chloride and the two 2-methylbutenes in two separate processes and (b) account for the observation of 57% 2-methyl-2-butene and 43% 2-methyl-1-butene in the experiment at 593 K. [10]

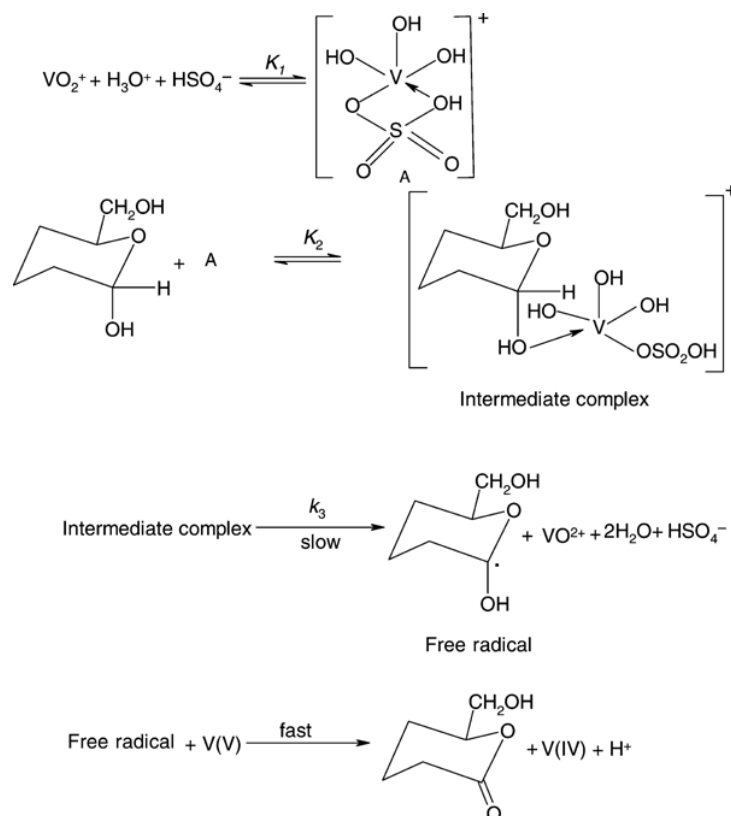
Information for questions 4– 7.

The effect of cationic surfactant, N-cetylpyridinium chloride (CPC), anionic surfactant, sodium dodecyl sulfate (SDS), and neutral surfactant, Triton X-100 (TX-100) on the oxidation of D-glucose by V^{5+} is reported in *Int. J. Chem. Kinet.*, **40**, 282 (2008). Figures (a), (b), and (c) show the variation of k_{obs} when $[D\text{-glucose}]$, $[HSO_4^-]$ and $[H^+]$, respectively, are varied (all other concentrations held constant). Lines A, B, C, and D in figure (a) are for different concentrations of micelles.



The kinetically active species of vanadium(V) is $[V(OH)_3HSO_4]^+$ which is formed in the equilibrium $VO_2^+ + H^+ + HSO_4^- \rightleftharpoons [V(OH)_3HSO_4]^+$. Moreover, it is believed that D-glucose and $[V(OH)_3HSO_4]^+$ are partitioned in the micellar phase where they react.

4. From the figures, what can you conclude about the rate law? Explain your reasoning. [10]
5. With a justification decide whether the mechanism given below explains the rate law that you deduced in question 4. [15]



6. What is the predicted order with respect to the oxidant and the reductant for this mechanism? [10]
7. The data reveal that SDS and TX-100 accelerate the rate, whereas CPC decreases it. Moreover, rate acceleration is higher in the case of SDS than TX-100. Explain these observations. [10]

Information for questions 8– 9.

Yasunaga *et. al.* (Bull. Chem. Soc. Japan **44**, 2308 (1971)) studied the hydrogen bond dimerization of benzoic acid by ultrasonic absorption. At 20 °C, they found that the forward, k_1 , and reverse, k_2 , rate constants were, respectively, $1.6 \times 10^8 \text{ s}^{-1}$ and $1.5 \times 10^7 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$.

8. Obtain an expression for the relaxation time, τ , for the dimerization process in terms of k_1 , k_2 , and any other relevant parameters. [15]
9. The authors state that $\frac{1}{\tau^2} = 8k_1k_2[C]_0 + k_1^2$, where $[C]_0$ is the total concentration of the acid. Deduce this expression from your result in question 8 and explain how you would determine the two rate constants from this expression. [10+5]