

Supporting Information for

Unveiling the Key Role of Excited-state Hydrogen Bonding in Homogeneous Photocatalytic CO₂ Reduction

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Supplement of experimental facility and details

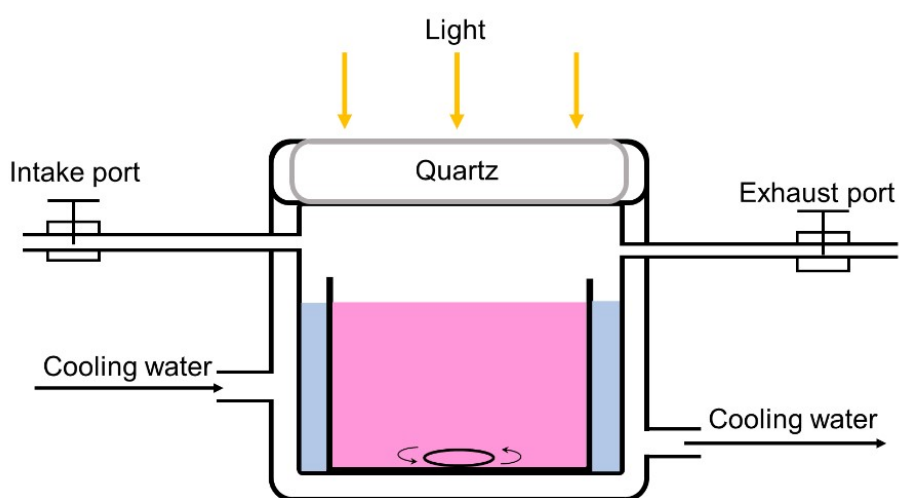
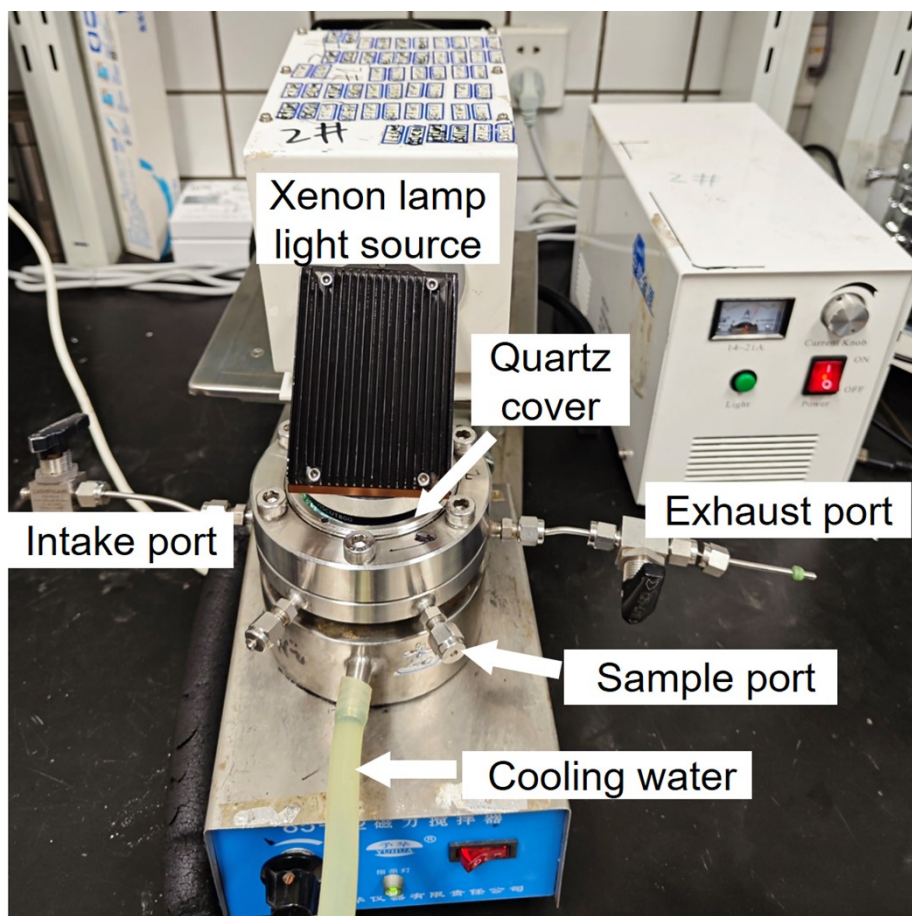


Figure S1. Schematic diagram of photocatalytic reaction device.

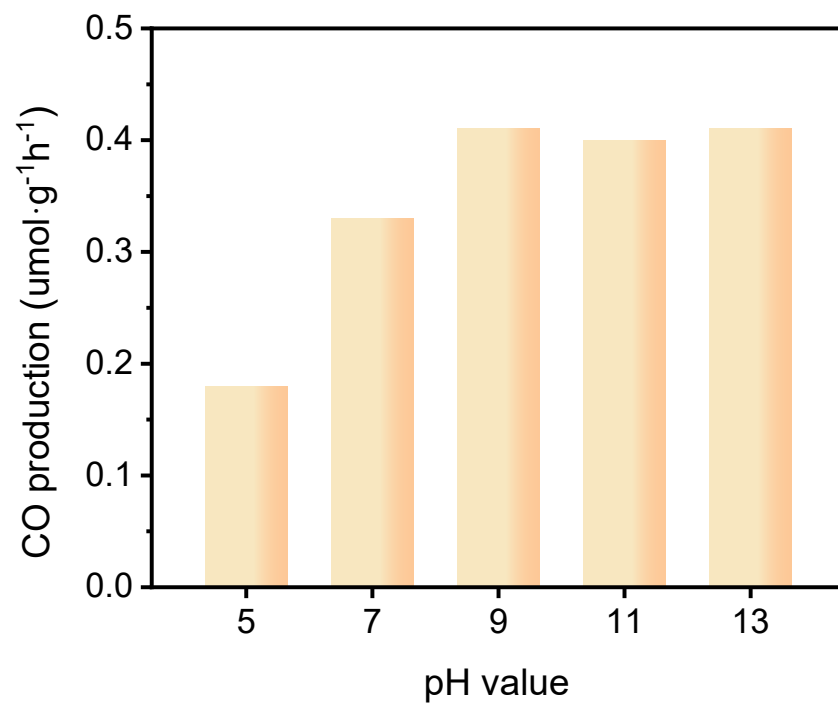


Figure S2. CO production versus pH value.

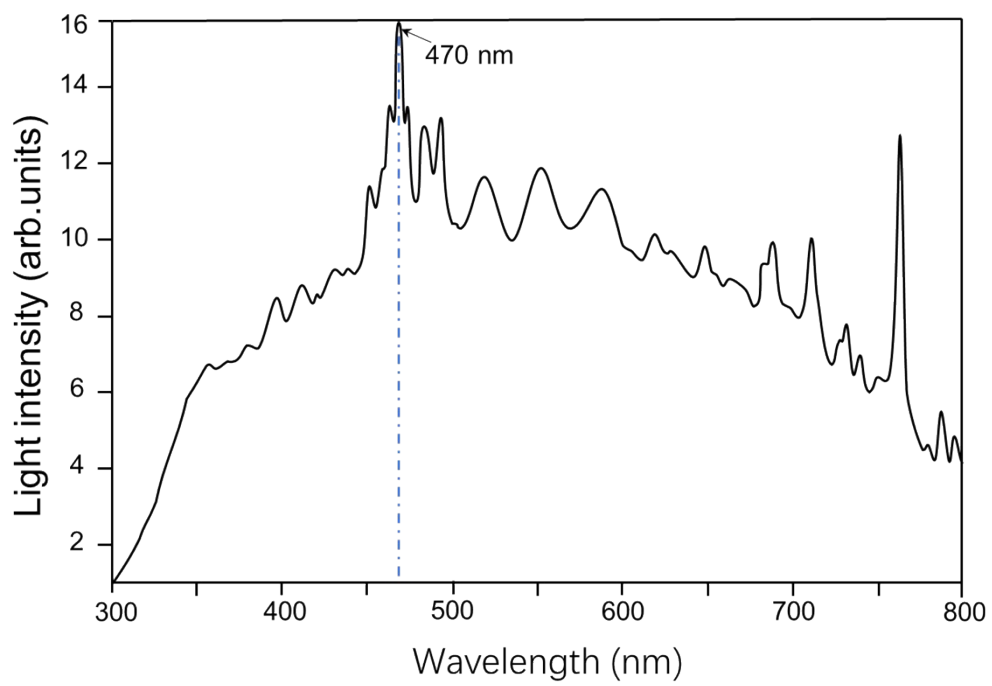


Figure S3. Xenon lamp spectrum

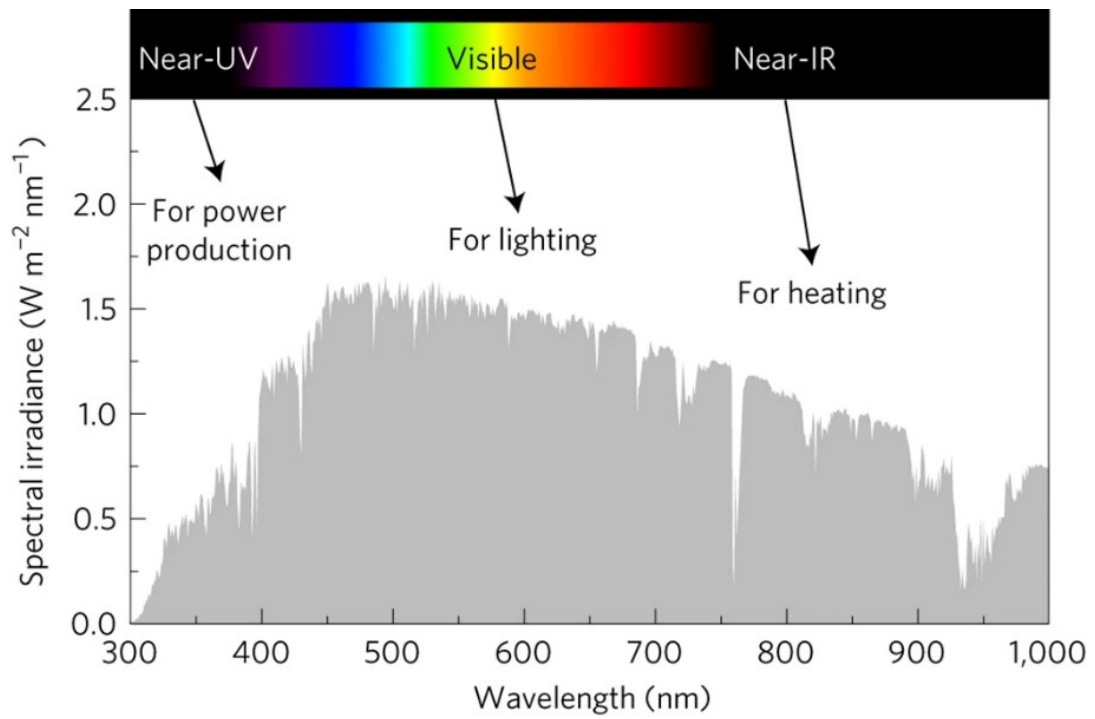


Figure S4. The solar spectrum.

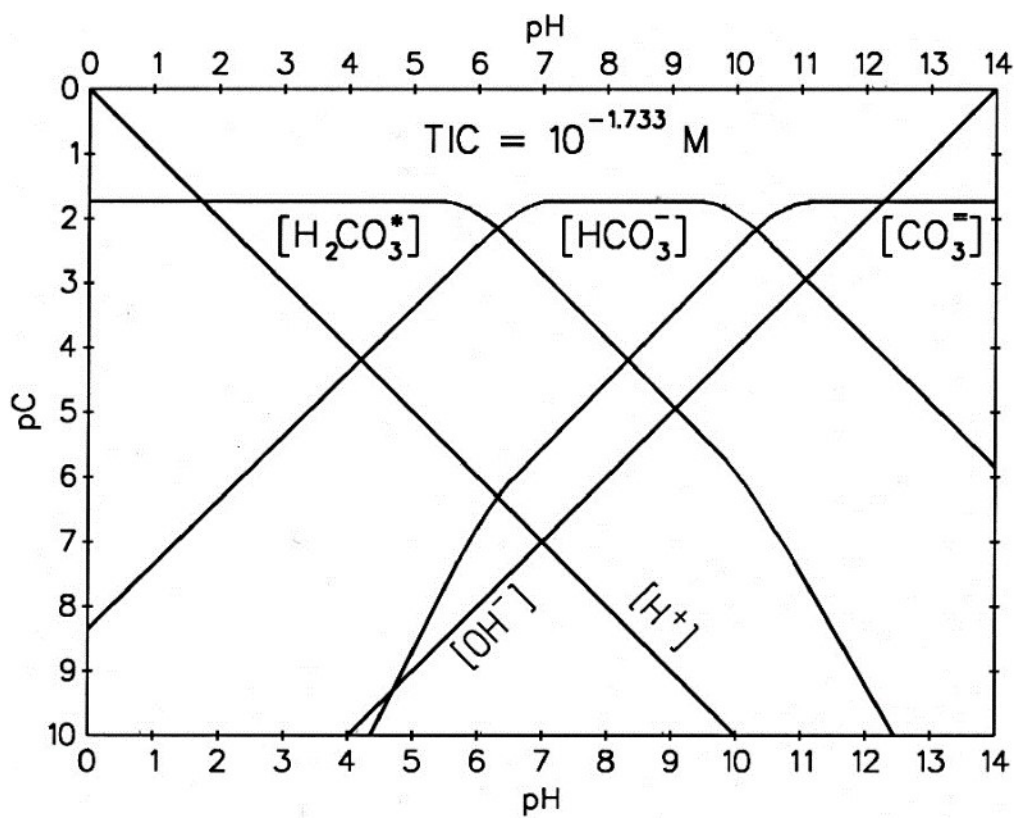


Figure S5. Graphical solution of carbonate equilibrium.

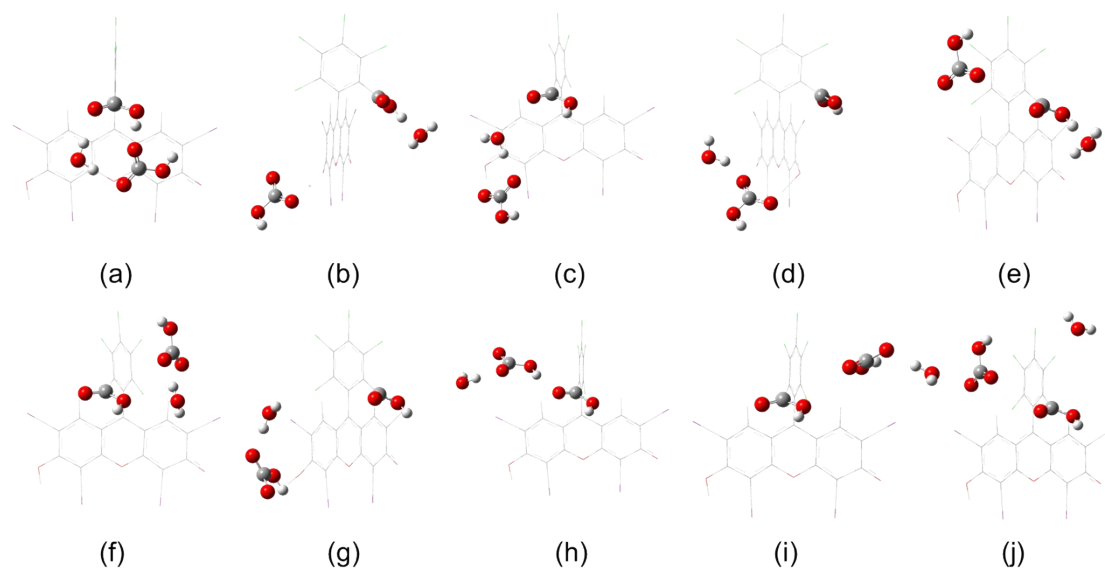


Figure S6. Structural models of different hydrogen bonding complexes.

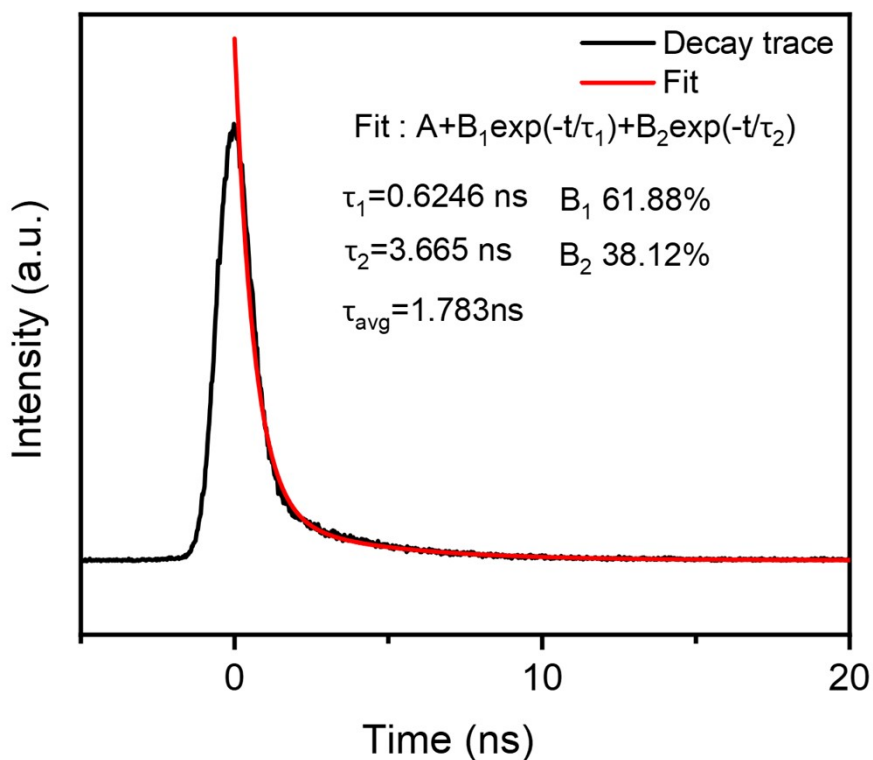


Figure S7. TRPL spectrum of Rose Bengal in water, $\tau_{avg} = 1.783$ ns

Photoluminescence decay lifetimes:

$y(t)=A+B_1\exp(-t/\tau_1)+B_2\exp(-t/\tau_2)$, ($B_1+B_2=1$) represents the fractional contributions of the time-resolved decay lifetimes τ_1 and τ_2 . The average decay lifetime τ_{avg} can be calculated

using the formula: $\tau_{avg} = B_1 \tau_1 + B_2 \tau_2$

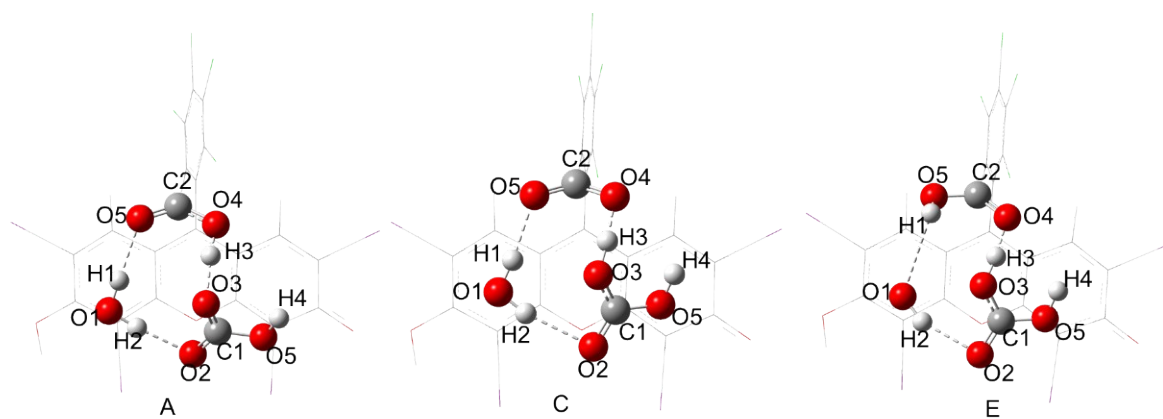


Figure S8. Structure of the hydrogen-bonded complexes of A C E.

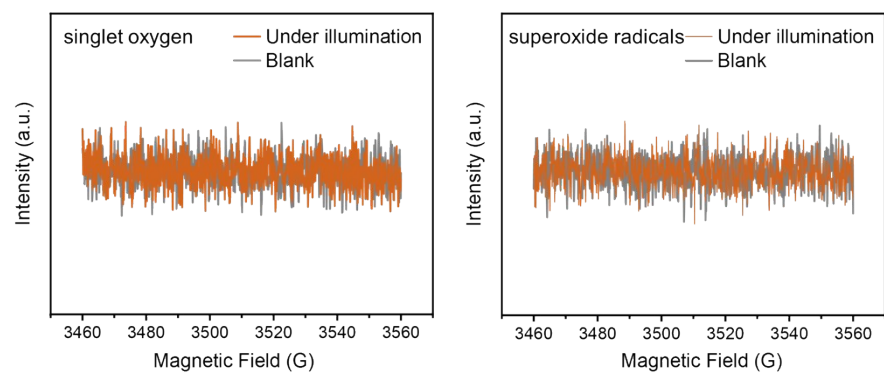


Figure S9. The ESR experiment of singlet oxygen and superoxide radicals.

Table S1. The relative energies of the different hydrogen-bonded complexes.

Structures	Relative energies (kal/mol)
a	0
b	7.25
c	8.49
d	9.42
e	9.58
f	9.80
g	11.30
h	12.83
i	13.55
j	17.03

Table S2. Hydrogen bond lengths, atom charge and electron spin population of the A C E hydrogen bond complex.

	A	C	E
lengths / Å	—	—	—
H1-O1	0.97	0.97	2.79
H1-O5	1.96	1.91	1.06
H3-O3	1.49	1.04	1.02
H3-O4	1.03	1.47	1.56
Charges	—	—	—
H1	0.272	0.280	0.344
O1	-0.628	-0.608	-0.447
H2	0.274	0.268	0.286
Spin population	—	—	—
H1	0.000	0.000	-0.001
O1	0.001	0.001	0.821
H2	0.000	0.000	-0.020

The reaction order is derived as follows:

The total reaction rate is determined by the rate of the rate-limiting step:

$$r = -dc \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O} \cdots \text{HO}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*} / dt = k_5 c \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O} \cdots \text{HO}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*} \quad (1)$$

For the absorption equilibrium formed by HCO_3^- , CO_2 , H_2O and the catalyst:

$$K_1 = c \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-} / c(\text{H}_2\text{O}) c(\text{TCTIF}-\text{COOH}) c(\text{HCO}_3^-) \quad (2)$$

For the equilibrium between $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-}$ And $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*}$:

$$K_2 = c \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*} / c \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-}$$

$$c \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*} = K_1 K_2 c(\text{H}_2\text{O}) c(\text{TCTIF}-\text{COOH}) c(\text{HCO}_3^-) \quad (3)$$

Then,

$$dc \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*} / dt = k_3 c \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*} - k_4 c \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*} = 0$$

$$k_3 c \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*} = k_4 c \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*} \quad (4)$$

For: $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O} \cdots \text{HO}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*}$

$$dc \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O} \cdots \text{HO}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*} / dt = k_4 c \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*} - k_5 c \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O} \cdots \text{HO}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*} = 0$$

$$k_4 c \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O}-\text{H} \cdots \text{O}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*} = k_5 c \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{O}=\text{C}-\text{O} \cdots \text{HO}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*} \quad (5)$$

For: $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{O} \cdots \text{HO}-\text{C}=\text{O} \cdots \text{HO}-\text{C}-\text{OH} \\ | \\ \text{TCTIF} \end{array} \right]^{-*}$

$$dc \left[{}^3 \left(\text{H}_2\text{O} \cdots \underset{\text{TCTIF}}{\text{HO}-\text{C}=\text{O}} \cdots \underset{\text{TCTIF}}{\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}} \right)^{-*} \right] / dt = k_5 c \left[{}^3 \left(\text{H}_2\text{O} \cdots \underset{\text{TCTIF}}{\text{H}-\text{O}-\text{C}=\text{O}} \cdots \underset{\text{TCTIF}}{\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}} \right)^{-*} \right] - k_6 c \left[{}^3 \left(\text{H}_2\text{O} \cdots \underset{\text{TCTIF}}{\text{HO}-\text{C}=\text{O}} \cdots \underset{\text{TCTIF}}{\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}} \right)^{-*} \right] = 0$$

Then

$$k_5 c \left[{}^3 \left(\text{H}_2\text{O} \cdots \underset{\text{TCTIF}}{\text{H}-\text{O}-\text{C}=\text{O}} \cdots \underset{\text{TCTIF}}{\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}} \right)^{-*} \right] = k_6 c \left[{}^3 \left(\text{H}_2\text{O} \cdots \underset{\text{TCTIF}}{\text{HO}-\text{C}=\text{O}} \cdots \underset{\text{TCTIF}}{\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}} \right)^{-*} \right] \quad (6)$$

According (3) (4) (5) (6),

$$k_3 K_1 K_2 c(\text{H}_2\text{O}) c(\text{TCTIF-COOH}) c(\text{HCO}_3^-) = k_5 c \left[{}^3 \left(\text{H}_2\text{O} \cdots \underset{\text{TCTIF}}{\text{H}-\text{O}-\text{C}=\text{O}} \cdots \underset{\text{TCTIF}}{\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}} \right)^{-*} \right] \quad (7)$$

For COOH⁻

$$dc(\text{COOH}^-) / dt = k_6 c \left[{}^3 \left(\text{H}_2\text{O} \cdots \underset{\text{TCTIF}}{\text{HO}-\text{C}=\text{O}} \cdots \underset{\text{TCTIF}}{\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}} \right)^{-*} \right] - k_7 c(\text{COOH}^-) + k_7 c(\text{CO}) c(\text{OH}^-) = 0$$

$$k_6 c \left[{}^3 \left(\text{H}_2\text{O} \cdots \underset{\text{TCTIF}}{\text{HO}-\text{C}=\text{O}} \cdots \underset{\text{TCTIF}}{\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}} \right)^{-*} \right] = k_7 c(\text{COOH}^-) - k_7 c(\text{CO}) c(\text{OH}^-)$$

Substitute into $K_7 = c(\text{CO}) c(\text{OH}^-) / c(\text{COOH}^-)$

$$k_6 c \left[{}^3 \left(\text{H}_2\text{O} \cdots \underset{\text{TCTIF}}{\text{HO}-\text{C}=\text{O}} \cdots \underset{\text{TCTIF}}{\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}} \right)^{-*} \right] = (k_7 / K_7 - k_7) c(\text{CO}) c(\text{OH}^-)$$

$$k_5 c \left[{}^3 \left(\text{H}_2\text{O} \cdots \underset{\text{TCTIF}}{\text{H}-\text{O}-\text{C}=\text{O}} \cdots \underset{\text{TCTIF}}{\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}} \right)^{-*} \right] = (k_7 / K_7 - k_7) c(\text{CO}) c(\text{OH}^-) \quad (8)$$

According (6) have

According (1)

$$r = -dc \left[{}^3 \left(\text{H}_2\text{O} \cdots \underset{\text{TCTIF}}{\text{H}-\text{O}-\text{C}=\text{O}} \cdots \underset{\text{TCTIF}}{\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}} \right)^{-*} \right] / dt = k_5 c \left[{}^3 \left(\text{H}_2\text{O} \cdots \underset{\text{TCTIF}}{\text{H}-\text{O}-\text{C}=\text{O}} \cdots \underset{\text{TCTIF}}{\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}} \right)^{-*} \right]$$

Substituting (7) and (8) into the left and right sides respectively

$$-(k_3 K_1 K_2 / k_5) dc \left[(\text{H}_2\text{O}) c(\text{TCTIF-COOH}) c(\text{HCO}_3^-) \right] / dt = (k_7 / K_7 - k_7) c(\text{CO}) c(\text{OH}^-)$$

Since TCTIF-COOH, H₂O and OH⁻ can be considered to be constant

$$-(k_3 K_1 K_2 / k_5) dc(\text{HCO}_3^-) / dt = (k_7 / K_7 - k_7) c(\text{CO}) c(\text{OH}^-)$$

$$dc(\text{HCO}_3^-) / dt = -k_5 (k_7 / K_7 - k_7) / k_3 K_1 K_2 c(\text{CO}) c(\text{OH}^-)$$

$$-k_5 (k_7 / K_7 - k_7) / k_3 K_1 K_2 c(\text{OH}^-) = k'$$

The concentration of the catalyst is constant,

$$dc(\text{HCO}_3^-) / dt = k' c(\text{CO})$$

The CO₂RR is a first order reaction for the product CO.