# Kinetics and Mechanism of the Oxidation of Formic and Oxalic Acids by Imidazolium Fluorochromate

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Kinetics and mechanism of oxidation of formic acid and oxalic acid by imidazolium fluorochromate have been studied in dimethyl sulphoxide. The main product of oxidation is carbon dioxide. The reaction is first order with respect to imidazolium fluorochromate. Michaelis-Menten type of kinetics were observed with respect to the reductants. The reaction is acid-catalyzed and the acid dependence has the form: $k_{obs} = a + b \, [H^+]$. The oxidation of $\alpha$-deuterioformic acid exhibits a substantial primary kinetic isotope effect ($k_H/k_D = 5.30$ at 298 K). The reaction has been studied in 19 different organic solvents and the solvent effect has been analyzed using Taft's and Swain's multiparametric equations. The temperature dependence of the kinetic isotope effect indicates the presence of a symmetrical cyclic transition state in the rate-determining step. Suitable mechanisms have been proposed.

**Key Words: Kinetics, Mechanism, Halorochromate, Organic acids, Oxidation.**

## INTRODUCTION

Halochromates have been used as mild and selective oxidizing reagents in synthetic organic chemistry[1-5]. Imidazolium fluorochromate (IFC) is one of such compounds used for the oxidation of benzylic alcohols[6]. We have been interested in the kinetic and mechanistic aspects of the oxidation by complexed Cr(VI) species and several reports on halochromates have already reported from this laboratory[7-10]. There seems to be no report on the oxidation aspects of organic acids by imidazolium fluorochromate. Therefore, we report in this paper the kinetics of oxidation of oxalic and formic acids by IFC in dimethyl sulphoxide as solvent. The mechanistic aspects are discussed. A suitable mechanism has also been proposed.

## EXPERIMENTAL

Imidazolium fluorochromate and $\alpha$-deuterioformic acid (DCO$_2$H or DFA) were prepared by the reported methods[1,11]. Due to the non-aqueous nature of the medium, toluene-*p*-sulphonic acid (TsOH) was used as a source of hydrogen ions. Toluene-*p*-sulphonic acid is a strong acid and in a polar solvent like DMSO it is likely to be completely ionized. Solvents were purified by the usual methods[12].

**Product analysis:** To determine the stoichiometry, an excess of IFC ($\times$ 5 or greater) was reacted with the organic acid in DMSO (100 cm$^3$) and the amount of residual IFC after the completion of reaction was measured spectrophotometrically at 352 nm. The results indicated 1:1 stoichiometry. No quantitative determination of carbon dioxide formed was carried out. The oxidation state of chromium in completely reduced reaction mixtures, determined by an iodometric method, was $3.95 \pm 0.15$.

**Kinetic measurements:** The reactions were followed under pseudo-first order conditions by keeping a large excess ($\times$ 15 or greater) of the organic acid over IFC. The temperature was kept constant to $\pm$ 0.1 ºC. The solvent was DMSO, unless specified otherwise. The reactions were followed by monitoring the decrease in the concentration of IFC spectrophotometrically at 352 nm for up to 80 % of the reaction. No other reactant or product has any significant absorption at this wavelength. The pseudo-first-order rate constants, $k_{obs}$, were evaluated from the linear (r = 0.995 - 0.999) plots of log [IFC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm$ 3 %. The second order rate constants were evaluated from the relation $k_2 = k_{obs}/$[reductant]. All reactions, other than those to study the effect of [H$^+$], were performed in the absence of TsOH.

## RESULTS AND DISCUSSION

**Stoichiometry:** The oxidation of organic acids leads to the formation of carbon dioxide. The stoichiometric determination indicated the following overall reactions:

$$(COOH)_2 + O_2CrFO^-ImH^+ \rightarrow 2CO_2 + H_2O + OCrFO^-ImH^+ \quad (1)$$

$$HCOOH + O_2CrFO^-ImH^+ \rightarrow CO_2 + H_2O + OCrFO^-ImH^+ \quad (2)$$

Imidazolium fluorochromate undergoes a two-electron change. This is in accord with our earlier observations with other halochromates also[7-10].

**Rate laws:** The reactions were found to be first order with respect to IFC. The reaction rate increases with an increase in [organic acid] but not linearly (Table-1). A plot of 1/[organic acid] *versus* $1/k_{obs}$ is linear (Fig. 1) with an intercept on the rate ordinate. Thus the reactions exhibited Michaelis-Menten type kinetics with respect to the organic acids. This indicates the following overall mechanism **3** and **4** and the rate law **5**.

### TABLE-1
### RATE CONSTANTS FOR THE OXIDATION OF OXALIC ACID AND FORMIC ACID BY IFC AT 298 K

| $10^3$ [IFC] (mol dm$^{-3}$) | [Organic acid] (mol dm$^{-3}$) | $10^4 k_{obs}$ (s$^{-1}$) Oxalic acid | Formic acid |
|---|---|---|---|
| 1.00 | 0.10 | 29.0 | 3.37 |
| 1.00 | 0.20 | 36.8 | 5.40 |
| 1.00 | 0.40 | 42.5 | 7.71 |
| 1.00 | 0.60 | 44.9 | 9.00 |
| 1.00 | 0.80 | 46.1 | 9.82 |
| 1.00 | 1.50 | 48.0 | 11.2 |
| 1.00 | 3.00 | 49.2 | 12.3 |
| 2.00 | 0.20 | 38.7 | 4.86 |
| 4.00 | 0.20 | 35.1 | 5.13 |
| 6.00 | 0.20 | 36.0 | 4.41 |
| 8.00 | 0.20 | 37.6 | 5.30 |
| 1.00 | 0.20 | 36.9* | 5.58* |

*Contained 0.001 mol dm$^{-3}$ acrylonitrile.
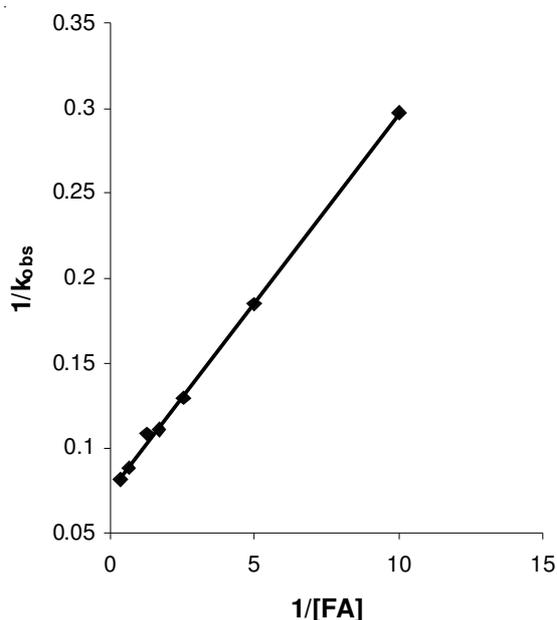


Fig. 1. Oxidation of formic acid (FA) acid by IFC: A double reciprocal plot

$$\text{Organic acid} + \text{IFC} \underset{}{\overset{K}{\rightleftharpoons}} [\text{Complex}] \quad (3)$$

$$[\text{Complex}] \xrightarrow{k_2} \text{Products} \quad (4)$$
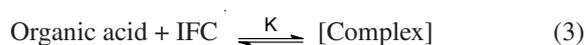
$$\text{Rate} = k_2 K[\text{IFC}] [\text{Organic acid}]/(1+K[\text{Organic acid}]) \quad (5)$$

The dependence of the reaction rate on reductant concentration was studied at different temperatures and the values of K and $k_2$ were evaluated from the double reciprocal plots. The thermodynamic and activation parameters, at 298 K, were also calculated from the values of K and $k_2$, respectively, at four different temperatures (Tables 2 and 3). Fig. 2 depicts a typical kinetic run.

### TABLE-2
### DEPENDENCE OF REACTION RATE ON HYDROGEN ION CONCENTRATION

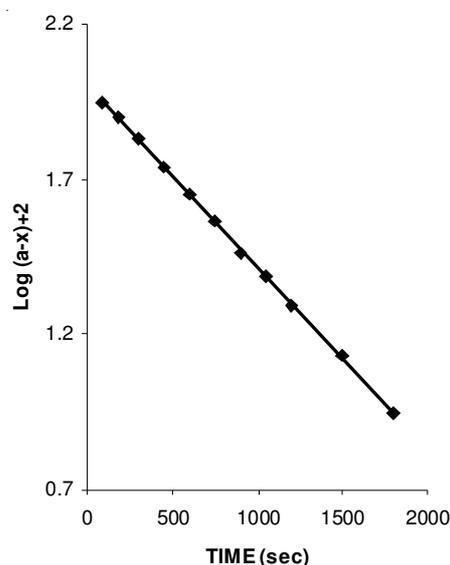| [IFC] = 0.001 (mol dm$^{-3}$) | [Acid] = 0.10 (mol dm$^{-3}$) | | Temp. = 298 (K) | | |
|---|---|---|---|---|---|
| Acid | 0.10 | 0.20 | 0.40 | 0.60 | 0.80 | 1.00 |
| | TsOH (mol dm$^{-3}$) | | | | | |
| OA ($10^4 k_{obs}$/s$^{-1}$) | 38.7 | 48.1 | 69.0 | 93.6 | 108 | 135 |
| FA ($10^4 k_{obs}$/s$^{-1}$) | 4.50 | 5.67 | 8.09 | 10.8 | 13.0 | 15.3 |

OA = Oxalic acid; FA = Formic acid



Fig. 2. Oxidation of formic acid acid by IFC: A typical kinetic run

**Induced polymerization of acrylonitrile:** The oxidation of organic acids by IFC, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate (Table-1).

**Effect of hydrogen ions:** The reaction is catalyzed by hydrogen ions. The hydrogen-ion dependence has the following form (Table-4). The values of a and b, for oxalic acid, are $2.75 \pm 0.21 \times 10^{-3}$ s$^{-1}$ and $10.6 \pm 0.34 \times 10^{-3}$ mol$^{-1}$ dm$^3$ s$^{-1}$, respectively ($r^2 = 0.9959$). The corresponding values for the oxidation of formic acid are $0.33 \pm 0.01 \times 10^{-3}$ s$^{-1}$ and $1.21 \pm 0.02 \times 10^{-3}$ ($r^2 = 0.9992$).

### TABLE-3
### FORMATION CONSTANTS AND THERMODYNAMIC PARAMETERS OF THE ORGANIC ACIDS-IFC COMPLEXES

| Acid | K (cm$^3$ mol$^{-1}$ s$^{-1}$) | | | | $-\Delta H^*$ (kJ mol$^{-1}$) | $-\Delta S^*$ (J mol$^{-1}$ K$^{-1}$) | $-\Delta G^*$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| | 288 K | 298 K | 308 K | 318 K | | | |
| OA | 29.7 | 13.5 | 7.47 | 3.33 | $58.4 \pm 0.8$ | $167 \pm 2$ | $8.93 \pm 0.6$ |
| FA | 4.14 | 3.33 | 2.61 | 2.01 | $19.2 \pm 0.3$ | $47 \pm 1$ | $5.45 \pm 0.2$ |
| DFA | 5.22 | 4.23 | 3.42 | 2.79 | $18.4 \pm 0.2$ | $42 \pm 1$ | $6.05 \pm 0.1$ |

| | TABLE-4 | | | | | | |
|---|---|---|---|---|---|---|---|
| | RATE CONSTANTS AND ACTIVATION PARAMETERS OF THE OXIDATION OF ORGANIC ACIDS BY IFC | | | | | | |
| Acid | $10^3 k_2$ (dm$^3$ mol$^{-1}$ s$^{-1}$) | | | | $-\Delta H^*$ (kJ mol$^{-1}$) | $-\Delta S^*$ (J mol$^{-1}$ K$^{-1}$) | $-\Delta G^*$ (kJ mol$^{-1}$) |
| | 288 K | 298 K | 308 K | 318 K | | | |
| OA | 24.3 | 50.4 | 108 | 207 | 52.2 ± 0.6 | 114 ± 2 | 86.1 ± 0.4 |
| FA | 6.84 | 13.5 | 28.8 | 54.0 | 50.4 ± 0.8 | 131 ± 3 | 89.3 ± 0.7 |
| DFA | 1.10 | 2.29 | 5.06 | 9.90 | 53.7 ± 0.7 | 135 ± 2 | 93.7 ± 0.6 |
| $k_H/k_D$ | 6.12 | 5.88 | 5.50 | 5.19 | – | – | – |

$$k_{obs} = a + b\,[H^+] \qquad (6)$$

**Kinetic isotope effect:** To ascertain the importance of the cleavage of the $\alpha$-C-H bond in the rate-determining step, the oxidation of $\alpha$-deuterioformic acid (DFA) was studied. The results recorded in Tables 2 and 3, showed that while the formation constant, K, for the ordinary and deuteriated formic acids have almost identical values, the rate constant for the decomposition of the complex, $k_2$, exhibited a substantial primary kinetic isotope effect ($k_H/k_D = 5.90$ at 298 K).

**Reactive oxidizing species:** The observed hydrogen-ion dependence suggests that the reaction follows two mechanistic pathways, one is acid-independent and the other is acid-dependent. The acid-catalysis may well be attributed to a protonation of IFC to yield a protonated Cr(VI) species which is a stronger oxidant and electrophile (eqn. 7).

$$[O_2CrFOImH] + H^+ \rightleftharpoons [HOCrOFOImH] \qquad (7)$$

Formation of a protonated Cr(VI) species has earlier been postulated in the reactions of structurally similar quinolinium fluorochromate[7] and PCC[8].

**Solvent effect:** The oxidation of formic acid was studied in 19 different organic solvents. The choice of solvents was limited due to the solubility of IFC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The kinetics were similar in all the solvents. The values of K and $k_2$ are recorded in Table-5. The formation constant of the intermediate complex, K, did not vary much with the solvent but the rate constant, $k_2$, exhibited much variation in values with different solvents.

The rate constants, $k_2$, in 18 solvents (CS$_2$ was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solvation energy relationship (eqn. 8) of Kamlet *et al.*[13].

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \qquad (8)$$

In this equation, $\pi^*$ represents the solvent polarity, (the hydrogen bond acceptor basicities and $\beta$ is the hydrogen bond donor acidity. $A_0$ is the intercept term. It may be mentioned

here that out of the 18 solvents, 12 have a value of zero for $\alpha$. The results of correlation analyses in terms of eqn. 8, a biparametric equation involving $\pi^*$ and $\beta$ and separately with $\pi^*$ and $\beta$ are given below as eqns. 9-12.

$$\log k_2 = -4.27 + 1.66(\pm 0.17)\pi^* + 0.15(\pm 0.14)\beta + 0.23(0.13)\alpha \qquad (9)$$
$$R^2 = 0.8879;\ sd = 0.16;\ n = 18;\ \psi = 0.37$$
$$\log k_2 = -4.33 + 1.57\,(\pm 0.17)\pi^* + 0.23\,(\pm 0.14)\beta \qquad (10)$$
$$R^2 = 0.8650;\ sd = 0.17;\ n = 18;\ \psi = 0.39$$
$$\log k_2 = -4.34 + 1.64\,(\pm 0.18)\pi^* \qquad (11)$$
$$r^2 = 0.8411;\ sd = 0.18;\ n = 18;\ \psi = 0.41$$
$$\log k_2 = -3.76 + 0.57\,(\pm 0.34)\beta \qquad (12)$$
$$r^2 = 0.1233;\ sd = 0.41;\ n = 18;\ \psi = 0.96$$

Here n = number of data points and $\psi$ is the Exner's statistical parameter[14].

Kamlet's[11] triparametric equation explains *ca.* 89 % of the effect of solvent on the oxidation. However, by Exner's[12] criterion the correlation is not even satisfactory. (cf. eqn. 9). The major contribution is of solvent polarity. It alone accounts for 84 % of the data. Both $\beta$ and $\alpha$ play relatively minor roles. The data on solvent effect were also analyzed in terms of Swain's equation[15] of cation- and anion-solvating concept of the solvents also 13.

$$\log k_2 = aA + bB + C \qquad (13)$$

Here A represents the anion-solvating power of the solvent and B the cation-solvating power. C = intercept term. (A + B) is postulated to represent the solvent polarity. The rates in different solvents were analyzed in terms of eqn. 13, separately with A and B and with (A + B).

$$\log k_2 = 1.13(\pm 0.04)A + 1.55\,(\pm 0.03)B - 3.91 \qquad (14)$$
$$R^2 = 0.9946;\ sd = 0.03;\ n = 19;\ \psi = 0.08$$
$$\log k_2 = 0.91\,(+0.51)A - 2.85 \qquad (15)$$
$$r^2 = 0.1556;\ sd = 0.41;\ n = 19;\ \psi = 0.94$$
$$\log k_2 = 1.47\,(\pm 0.20)B - 3.55 \qquad (16)$$
$$r^2 = 0.7568;\ sd = 0.22;\ n = 19;\ \psi = 0.51$$
$$\log k_2 = 1.41(0.06\,(A + B) - 3.90 \qquad (17)$$
$$r^2 = 0.9704;\ sd = 0.08;\ n = 19;\ \psi = 0.18$$

| | TABLE-5 | | | | |
|---|---|---|---|---|---|
| | FORMATION CONSTANTS AND RATE CONSTANTS FOR THE DECOMPOSITION OF FORMIC ACID-IFC COMPLEXES IN DIFFERENT SOLVENTS AT 298 K | | | | |
| Solvent | K (dm$^{-3}$ mol$^{-1}$) | $10^4 k_2$ (s$^{-1}$) | Solvents | K (dm$^{-3}$ mol$^{-1}$) | $10^4 k_2$ (s$^{-1}$) |
| Chloroform | 5.58 | 51.3 | Toluene | 5.44 | 12.0 |
| 1,2-Dichloroethane | 5.49 | 44.7 | Acetophenone | 4.58 | 57.5 |
| Dichloromethane | 5.04 | 55.0 | THF | 6.91 | 22.4 |
| DMSO | 3.33 | 135 | *t*-Butylalcohol | 5.50 | 25.7 |
| Acetone | 5.85 | 37.2 | 1,4-Dioxane | 4.95 | 20.0 |
| DMF | 5.67 | 77.6 | 1,2-Dimethoxyethane | 6.30 | 13.2 |
| Butanone | 5.55 | 27.5 | CS$_2$ | 5.56 | 6.46 |
| Nitrobenzene | 5.63 | 60.3 | Acetic acid | 4.81 | 20.9 |
| Benzene | 6.75 | 14.8 | Ethyl acetate | 4.47 | 18.2 |
| Cyclohexane | 5.13 | 1.51 | – | – | – |

The rates of decomposition of the complex in different solvents showed an excellent correlation in Swain's equation [cf. eqn. 14] with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for *ca*. 76 % of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for *ca*. 97 % of the data. In view of the fact that solvent polarity is able to account for *ca*. 98 % of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of log (rate) against the inverse of the relative permittivity is not linear ($r^2 = 0.4948$; sd = 0.32) ($\psi = 0.73$).

**Mechanism:** The presence of a substantial kinetic isotopic effect confirmed that an (-C-H) bond is cleaved in the rate-determining step. The observed kinetics indicate the formation of an intermediate complex in a rapid pre-equilibrium. However, the highly unfavourable entropy term obtained in the complex formation of oxalic acid-IFC reaction suggests that oxalic acid acts as a bidentate ligand and forms a cyclic intermediate complex. In the chromic acid oxidation also, the formation of a cyclic anhydride intermediate, oxalyl chromate, has been postulated[16]. The value of formation constant, 9.5 dm$^3$ mol$^{-1}$, reported by Hassan and Rocek[16] compares favourably with the values obtained in this investigation. The absence of any effect of a radical scavenger, acrylonitrile, indicates that a hydrogen abstraction mechanism, giving rise to free radicals, is unlikely.

For the formic acid oxidation, the cation-solvating power of the solvents plays a relatively more important role. Therefore, formation of an electron-deficient carbon centre in the transition state is indicated. Thus the decomposition of IFC-formic acid complex may involve a hydride ion transfer *via* an anhydride intermediate (**Scheme-I**).

Kwart and Nickle[17] have shown that a study of the dependence of the kinetic isotope effect on temperature can be gainfully employed to resolve this problem. The data for protio- and deuteriomandelic acids, fitted to the familiar expression $k_H/k_D = A_H/A_D \exp (E_a/RT)$[18,19] show a direct correspondence with the properties of a symmetrical transition state in which the activation energy difference ($E_a$) for $k_H/k_D$ is equal to the zero-point energy difference for the respective C-H and C-D bonds ($\approx 4.5$ kJ/mol) and the frequency factors and the entropies of activation of the respective reactions are nearly equal.

**Scheme-I**
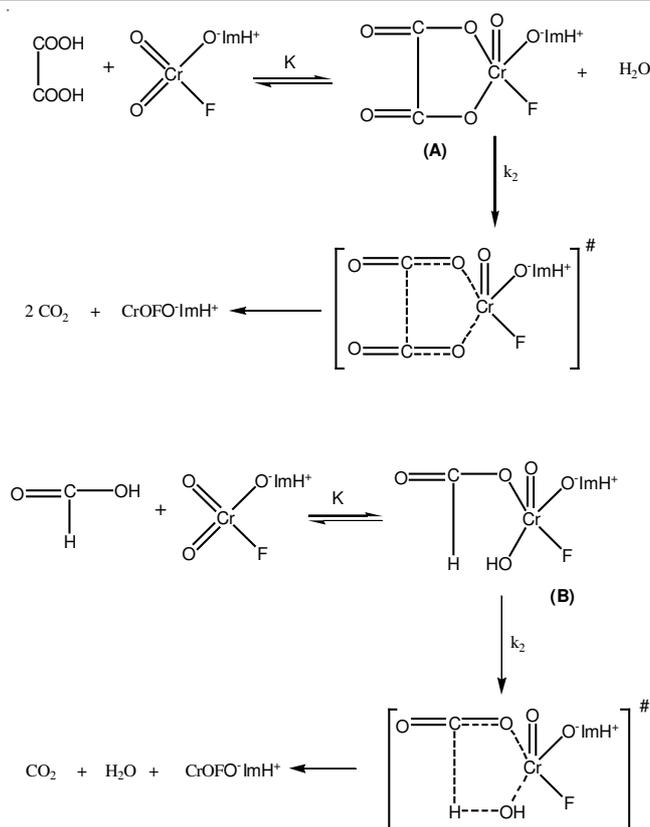
The observed dependence on the hydrogen-ion concentration in both the reactions shows there to be an additional acid-catalyzed pathway. This may be attributed to a rapid reversible protonation of the anhydride, with the protonated anhydride decomposing at a rate higher than the decomposition of the unprotonated anhydride (**Scheme-II**).

In the oxidation of these acids by IFC, PFC[20] and QFC[21] Michaelis-Menten- type kinetics, with respect to the reductants, were obtained, but with MCC[22] the reactions are of first order with respect to the reductants. It is possible that the values of the formation constants for the reductant-PCC complexes are very low. This resulted in the observation of second-order kinetics. No explanation of the difference is available presently. Kinetic isotope effects, solvent effects and the dependence of the hydrogen ions are of similar nature in all these reactions, for which essentially similar mechanisms have been proposed.
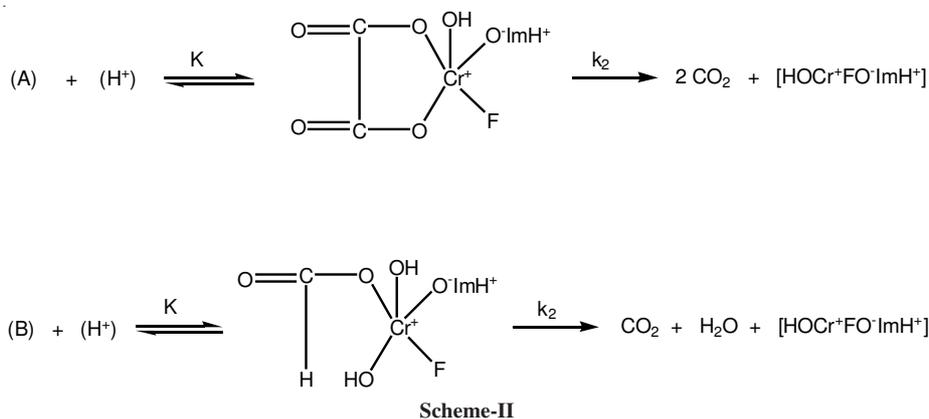
**Scheme-II**

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