

Kinetics and mechanism of the oxidation of formic and oxalic acids by benzimidazolium dichromate

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Manuscript received 25 May 2011, accepted 16 December 2011

Abstract : The oxidation of formic and oxalic acids by benzimidazolium dichromate (BIDC), in dimethyl sulfoxide, leads to the formation of carbon dioxide. The reaction is first order with respect to BIDC. Michaelis-Menten type kinetics were observed with respect to the organic acids. The values of the formation constants of the organic acid-BIDC complexes and the rates of their decomposition have been evaluated at different temperatures. Thermodynamic parameters of the complex formation and activation parameters for the decomposition of the complexes have been calculated. The reaction rate increases with an increase in hydrogen-ion concentration and the dependence has form : $k_{\text{obs}} = a + b [\text{H}^+]$. The oxidation of deuteriated formic acid indicated the presence of a substantial kinetic isotope effect. The reaction has been studied in nineteen organic solvents. An analysis of the solvent effect by solvatochromic equations indicated that though both the anion- and cation-solvating powers of the solvent contribute to the observed solvent effect, however, the role of cation-solvation is more. Suitable mechanisms have been proposed.

Keywords : Kinetics, mechanism, oxidation, formic acid, oxalic acid, benzimidazolium dichromate.

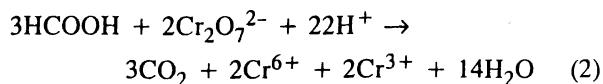
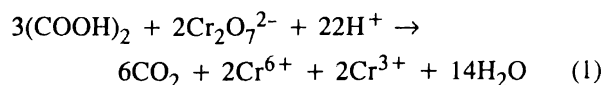
Introduction

Selective oxidation of organic compounds under non-aqueous conditions is an important transformation in synthetic organic chemistry. For this, a number of different chromium(VI) derivatives have been reported^{1,2}. In 1998, Meng *et al.*³ reported a new Cr^{VI} derivative – benzimidazolium dichromate (BIDC). It is neither hygroscopic nor light sensitive, therefore, it is more stable and easily stored as compared to other Cr^{VI} reagents. BIDC is reported³ to convert benzylic and allylic alcohols to corresponding carbonyl compounds in yield ranging from 75 to 98%. We have been interested in the kinetics and mechanism of the oxidation by BIDC and a few reports have emanated from our laboratory⁴⁻⁶. A perusal of literature showed that there seems to be no report on the kinetics and mechanism of the oxidation of formic and oxalic acids by BIDC. In this paper, we report the kinetics of the oxidation of formic (FA) and oxalic (OA) acids by BIDC, in dimethyl sulfoxide as solvent. Mechanistic aspects are discussed.

Results and discussion

The stoichiometric determination indicated the follow-

ing overall reactions for the oxidation of OA and FA respectively.



The reactions were found to be of first order with respect to BIDC. In individual kinetic runs, plots of log [BIDC] versus time were linear ($r^2 > 0.995$). Further, the pseudo-first order rate constants do not depend on the initial concentration of BIDC (Table 1). The order with respect to organic acid was less than one (Table 1). A plot of k_{obs} vs [Organic acid] is shown in Fig. 1. The downward curvature of the plots suggests the existence of a complex. A plot of $1/k_{\text{obs}}$ versus $1/[\text{Organic acid}]$ was linear with an intercept on the rate ordinate (Fig. 2). Thus, a Michaelis-Menten type kinetics were observed with respect to each FA and OA. This leads to the postulation of following overall mechanism and rate law :

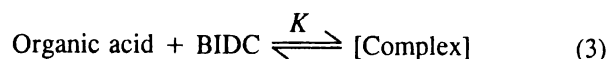


Table 1. Rate constants for the oxidation of organic acids by B IDC at 303 K

10^3 [B IDC] (mol dm ⁻³)	[Organic acid] (mol dm ⁻³)	[H ⁺] (mol dm ⁻³)	$10^4 k_{\text{obs}}$ (s ⁻¹)	
			FA	OA
1.0	0.04	0.1	1.75	18.1
1.0	0.06	0.1	2.45	22.5
1.0	0.10	0.1	3.56	26.9
1.0	0.20	0.1	5.48	32.4
1.0	0.30	0.1	6.78	34.5
1.0	0.60	0.1	8.63	37.5
0.2	0.20	0.1	5.53	31.8
0.4	0.20	0.1	5.41	32.0
0.6	0.20	0.1	5.60	32.8
0.8	0.20	0.1	5.45	32.3
1.0	0.60	0.1	8.59 ^a	37.9 ^a

^aContained 0.005 mol dm⁻³ acrylonitrile.

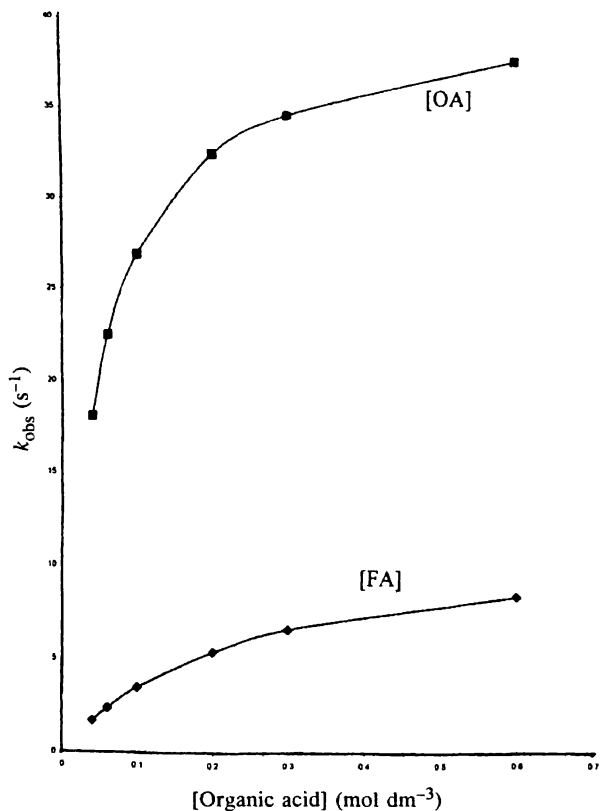


Fig. 1. A plot of $10^4 k_{\text{obs}}$ vs [Organic acid] : [B IDC] = 0.001 mol dm⁻³; [H⁺] = 0.1 mol dm⁻³; temperature 303 K.



$$\text{Rate} = \frac{k_2 K [\text{Organic acid}] [\text{B IDC}]_t}{(1 + K [\text{Organic acid}])} \quad (5)$$

or,

$$\begin{aligned} (\text{Rate}/[\text{B IDC}]_t)^{-1} &= 1/k_{\text{obs}} \\ &= 1/k_2 K [\text{Organic acid}] + 1/k_2 \end{aligned} \quad (6)$$

Here, $[\text{B IDC}]_t = [\text{B IDC}] + [\text{Complex}]$

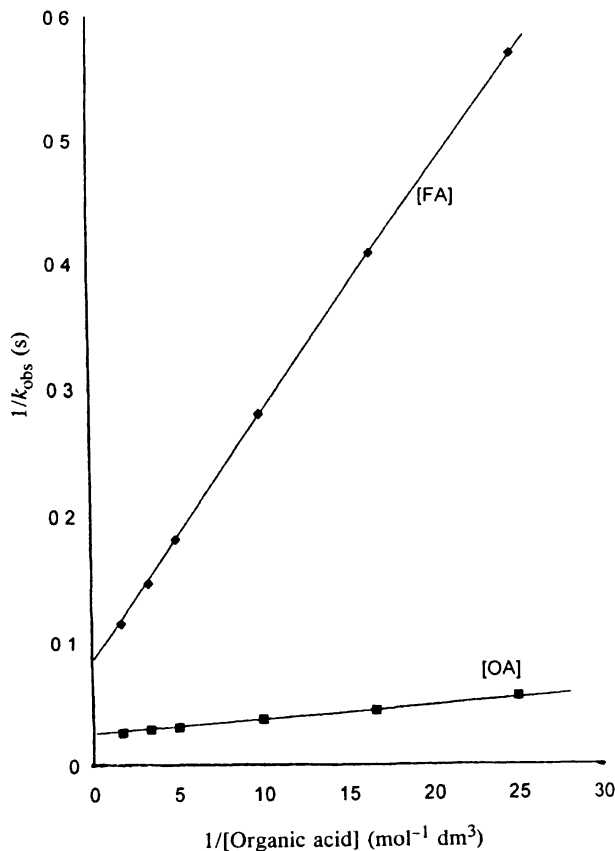


Fig. 2. A plot of $10^{-4} 1/k_{\text{obs}}$ vs $1/[\text{Organic acid}]$: [B IDC] = 0.001 mol dm⁻³; [H⁺] = 0.1 mol dm⁻³; temperature 303 K.

The dependence of k_{obs} on the concentration of organic acid was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots using eq. (6). The thermodynamic parameters for the complex formation and the activation parameters for the decomposition of complexes were calculated from the values of K and k_2 respectively, at different temperatures (Tables 2 and 3).

The oxidations of both FA and OA by B IDC, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. In blank experiments, with the substrate absent, no noticeable consumption of B IDC was observed. The addition of acrylonitrile had no effect on the rate of oxidation (Table 1). To further confirm the absence of

Table 2. Formation constants and thermodynamic parameters for organic acid-BIDC complexes

Organic acid	K (dm ³ mol ⁻¹) at temp. (K)				ΔH	ΔS	ΔG
	298	303	308	313	(kJ mol ⁻¹)	(J mol ⁻¹ K ⁻¹)	(kJ mol ⁻¹)
FA	5.88	4.30	3.13	2.30	-51.1 ± 0.3	-149 ± 2	-6.90 ± 0.3
OA	43.1	20.5	9.85	5.31	-111 ± 1.6	-334 ± 5	-11.8 ± 1.2
DFA	5.93	4.17	3.20	2.2.4	-51.9 ± 1.4	-151 ± 5	-6.90 ± 1.1

Table 3. Rates of decomposition and activation parameters for organic acid-BIDC complexes

Organic acid	k_2 (s ⁻¹) at temp. (K)				ΔH^*	ΔS^*	ΔG^*
	298	303	308	313	(kJ mol ⁻¹)	(J mol ⁻¹ K ⁻¹)	(kJ mol ⁻¹)
FA	7.46	11.9	17.7	26.5	62.6 ± 0.8	-95 ± 3	90.8 ± 0.7
OA	26.8	40.3	61.2	84.9	57.7 ± 1.2	-101 ± 4	87.7 ± 1.0
DFA	1.25	2.05	3.08	4.85	66.9 ± 1.1	-96 ± 3	95.3 ± 0.8
k_H/k_D	5.97	5.85	5.75	5.46			

free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol dm⁻³ of 2,6-di-*t*-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

The rates of oxidation of both FA and OA increase with an increase in the concentration of hydrogen ions and the dependence has the form : $k_{obs} = a + b [H^+]$ (Table 4). To ascertain whether the acidity is affecting the formation constant, K , of the complex and/or the rate

Table 4. Dependence of reaction rate on the hydrogen-ion concentration

	[Organic acid] = 0.60 mol dm ⁻³ , [BIDC] = 0.001 mol dm ⁻³ , Temp. 303 K					
[H ⁺] (mol dm ⁻³)	0.01	0.02	0.04	0.06	0.10	0.20
$10^4 k_{obs}$ (s ⁻¹) (FA)	1.20	2.00	3.37	5.33	8.63	16.7
$10^4 k_{obs}$ (s ⁻¹) (OA)	8.50	11.5	18.4	25.2	37.5	70.3

constant, k_2 , of decomposition of the complex, the dependence of the reaction rate on the concentrations of both FA and OA were studied at three different concentrations of hydrogen-ion. It was observed that the formation constant does not vary appreciably with the hydrogen-ion concentration, however, the rate of decomposition of complex increases (Table 5). Similar observations have been reported in the oxidation of organic acids by pyridinium fluorochromate (PFC).

To ascertain the importance of the cleavage of the α -C-H bond in the rate-determining step, the oxidation of DFA was studied. The results, recorded in Tables 2 and

Table 5. Dependence of substrate variation at different acidities^a
[BIDC] = 0.001 mol dm⁻³, Temp. 303 K

Organic acid (mol dm ⁻³)	$k_{obs} \times 10^4$ (s ⁻¹) at [H ⁺] (mol dm ⁻³)		
	0.02	0.06	0.10
(i) Formic acid			
0.04	0.41	1.08	1.75
0.06	0.56	1.57	2.45
0.10	0.83	2.20	3.56
0.20	1.30	3.35	5.48
0.30	1.53	4.19	6.78
0.60	2.00	5.33	8.63
K (dm ³ mol ⁻¹)	4.39	4.37	4.30
$10^4 k_2$ (s ⁻¹)	2.73	7.35	11.9
(ii) Oxalic acid			
0.04	4.90	12.0	18.1
0.06	5.96	15.1	22.5
0.10	7.38	18.0	26.9
0.20	8.70	21.8	32.4
0.30	9.68	23.0	34.5
0.60	10.3	25.2	37.5
K (dm ³ mol ⁻¹)	19.5	20.1	20.5
$10^4 k_2$ (s ⁻¹)	11.1	27.2	40.3

3, showed that the values of the formation constant, K , do not differ much for the ordinary and deuterated formic acid. However, the rate constant of decomposition of complex, k_2 , exhibited a substantial primary kinetic isotope effect ($k_H/k_D = 5.97$ at 298 K).

Solvent effect : The oxidation of formic acid by BIDC was studied in nineteen organic solvents. The solubility of the reactants and the reaction of BIDC with primary

and secondary alcohols limited the choice of solvents. There was no reaction with the chosen solvents. The kinetics were similar in all the solvents. The corresponding values of K and k_2 , are recorded in Table 6.

Table 6. Effect of solvent on the oxidation of formic acid by B IDC at 303 K

Solvent	K ($\text{dm}^3 \text{ mol}^{-1}$)	$k_2 \times 10^5$ (s^{-1})
Chloroform	4.78	33.5
1,2-Dichloroethane	4.85	34.3
Dichloromethane	4.11	35.1
DMSO	4.30	119
Acetone	5.89	27.3
Dimethylformamide	6.01	55.3
Butanone	4.45	18.7
Nitrobenzene	4.93	40.4
Benzene	5.99	7.70
Cyclohexane	5.01	0.51
Toluene	4.69	5.80
Acetophenone	5.03	38.6
Tetrahydrofurane	4.97	11.1
<i>tert</i> -Butyl alcohol	6.23	14.2
Dioxane	4.75	12.1
1,2-Dimethoxyethane	5.99	6.50
Acetic acid	4.49	9.40
Ethyl acetate	5.17	13.1
Carbon disulfide	5.71	2.70

B IDC seems to be an ionic compound as a result of proton transfer. To find out the state of B IDC in our reaction conditions, conductivity measurements have been carried out. It was observed that DMSO has very low conductivity and the addition of B IDC in DMSO shows negligible change in the conductivity value. Therefore, B IDC can be considered to be remained as non-ionised under our reaction conditions and does not dissociate as dichromate and benzimidazolium ions. No effect of added benzimidazolium ion on the rate of oxidation also supports the postulation that B IDC remain as non-ionised⁵. The crystal structure study of B IDC, reported by Meng *et al.*⁸ supports the non-ionic nature of the oxidant in the reaction system. The dichromate ion connects two benzimidazolium rings via hydrogen bonds. With the effective hydrogen donor (N-H) and hydrogen acceptor (O) in the molecule, B IDC forms a number of hydrogen bonds. Furthermore, an intermolecular hydrogen bridge

is remarkably formed between two neighboured dichromate ions. The molecules are then linked into infinite chains by these hydrogen bridges which controlled the releasing process of dichromate ions to reaction system and thus the compound behaves as non-ionic in our reaction system.

The data recorded in Table 6 indicate that the equilibrium constant, K , is fairly insensitive to the change in solvent, however, k_2 , varies appreciably. Therefore, the values of the rate constant of the decomposition of complexes, k_2 , in eighteen solvents (CS_2 was not considered as the complete range of the solvent parameters are not available), were correlated in terms of linear solvation energy relationship (LSER) of Kamlet *et al.*⁹. But the correlations were insignificant.

The data on solvent effect were then analyzed in terms of Swain's¹⁰ eq. (7), where A represents the anion-solvating power of the solvent and B the cation-solvating power; C is the intercept term, and $(A+B)$ is postulated to represent the solvent polarity.

$$\log k = aA + bB + C \quad (7)$$

The results of the correlation analyses in terms of Swain's eq. (7), individually with A and B , and with $(A+B)$ are given below.

$$\log k_2 = 1.41 \pm 0.01 A + 1.88 \pm 0.01 B - 5.43 \quad (8)$$

$$R^2 = 0.9997, sd = 0.01, n = 19, \psi = 0.018$$

$$\log k_2 = 1.14 \pm 0.62 A - 5.42 \quad (9)$$

$$r^2 = 0.1667, sd = 0.50, n = 19, \psi = 0.94$$

$$\log k_2 = 1.77 \pm 0.25 B - 4.97 \quad (10)$$

$$r^2 = 0.7485, sd = 0.28, n = 19, \psi = 0.52$$

$$\log k_2 = 1.72 \pm 0.06 (A+B) - 5.42 \quad (11)$$

$$r^2 = 0.9795, sd = 0.08, n = 19, \psi = 0.15$$

The data on solvent effect showed an excellent correlation in terms of Swain's eq. (7) with both anion- and cation-solvating powers contributing to the observed solvent effect. However, the cation-solvating power of the solvents plays a relatively more important role [cf. eq. (8)]. The solvent polarity, represented by $(A+B)$ accounted for ca. 98% of the data. In view of the fact ca. 98% of the data is accounted for by $(A+B)$, an attempt was made to correlate the data with relative permittivity of the solvents. A plot of $\log k_2$ against the inverse of the relative permittivity, however, is not linear ($r^2 = 0.6039$).

Mechanism : A one-electron oxidation, giving rise to

free radicals, is unlikely in view of the failure to induce polymerisation of acrylonitrile. BHT is an excellent trap for free radicals¹¹. The fact that BHT was recovered unchanged also goes against the occurrence of a one-electron oxidation. The observed Michaelis-Menten type kinetics with respect to both the organic acids led us to suggest the formation of 1 : 1 complex of the acid and BDC in a rapid pre-equilibrium. The observed acid-dependence of the reaction points to a rapid reversible protonation of the intermediate complex prior to its disproportionation. The analysis of the solvent effect indicated that the transition state of the decomposition of complex is more polar than the reactant. Further, the more importance of the cation-solvating power of the solvent suggested the formation of an electron-deficient centre in the transition state. The formation constant of the complexes of ordinary and deuteriated formic acid are almost similar, however, the rate of its decomposition exhibited a substantial kinetic isotope effect. This indicates that the C-H bond is cleaved in the rate-determining step. Thus, the decomposition of BDC-FA complex may involve a hydride-ion transfer. A hydride-ion transfer may take place either by an acyclic process or via concerted cyclic process. An analysis of the temperature dependence of the kinetic isotope effect by the method of Kwart and Nickle¹² showed that the loss of hydrogen proceeds through a concerted cyclic process. The data for protio- and deuterioformic acids were fitted to the familiar expression :

$$k_H/k_D = A_H/A_D \exp(-\Delta E_a/RT)$$

or,

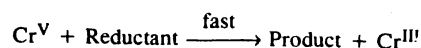
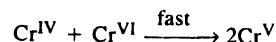
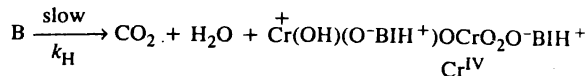
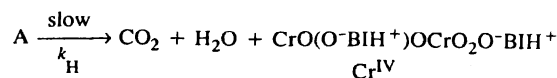
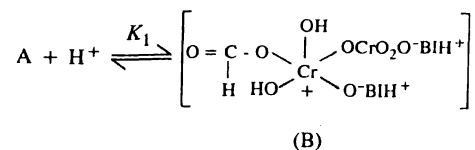
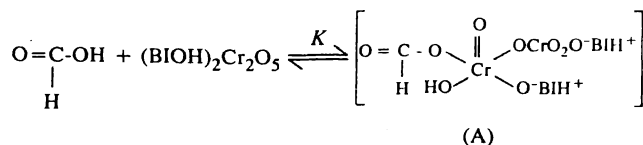
$$\log(k_H/k_D) = \log(A_H/A_D) - \Delta E_a/RT \quad (2)$$

The results showed that the activation energy difference for k_H/k_D is 4.40 kJ which agrees well with the zero-point energy difference for the respective C-H and C-D bonds (*ca.* 4.30 kJ mol⁻¹) and the entropy of activation of the respective reactions are nearly equal. This directly corresponds to the properties of a symmetrical transition state^{13,14}. Similar phenomenon have been observed earlier in the oxidation of alcohols by BDC⁵. Bordwell¹⁵ has given cogent evidence against the occurrence of concerted one-step bimolecular process of hydrogen transfer and it is clear that in the present reaction also, the hydrogen transfer does not occur by an acyclic bimolecular process. The only truly symmetrical processes involving linear transfer of hydrogen are intrinsically concerted sigmatropic reactions characterized by transfer with a cyclic transition state¹⁶. Therefore, one can safely con-

clude that in the oxidation of organic acid by BDC, the hydride-ion transfer occurs via an anhydride intermediate. The observed dependence on hydrogen-ion concentration, in both the reactions, shows that there are two paths of oxidation. One is an acid-independent path and another is acid-dependent. The hydrogen-ion effect may be attributed to a reversible protonation of the intermediate complex, with the protonated complex decomposing at a rate higher than the decomposition of the unprotonated complex. The highly unfavorable entropy term observed in the complex formation in the oxalic acid-BDC reaction suggests formation of a highly ordered complex. Thus, it seems that oxalic acid acts as a bidentate ligand and forms a cyclic complex. In the oxidation by pyridinium fluorochromate⁷ the formation of a cyclic anhydride intermediate, has been postulated. The formation constant of 25.7 dm³ mol⁻¹, reported by Asopa *et al.*⁷ at 303 K, compares favorably with the values, 20.5 dm³ mol⁻¹, obtained in the present investigation. The mechanisms depicted in Schemes 1 and 2 account for the experimental results. The rate laws based on the mechanisms (Schemes 1 and 2) proposed can be written as :

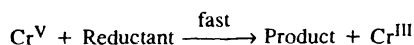
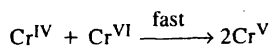
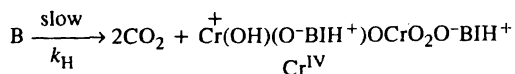
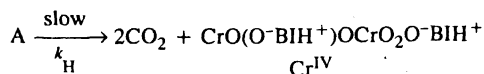
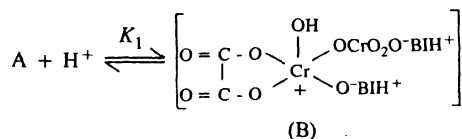
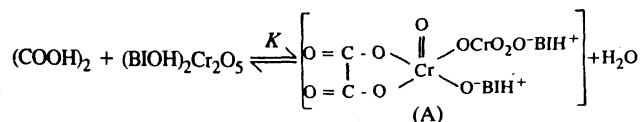
$$\text{Rate} = \frac{k_H K_1 K [\text{BDC}]_t [\text{Organic acid}] [\text{H}^+]}{1 + K [\text{Organic acid}]} \quad (13)$$

Comparing eqs. (4) and (12), we get $k_2 = k_H K_1 [\text{H}^+]$



BI = Benzimidazole

Scheme 1



BI = Benzimidazole

Scheme 2 .

The proposed mechanism is, however, supported by the observed negative entropy of activation. As the charge separation takes place in the transition state, the two ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy. The negative activation entropy additionally accounts for the influence of solvent.

Initially Cr^{VI} is reduced to Cr^{IV} . It is likely to react with another Cr^{VI} to generate Cr^{V} which is then reduced in a fast step to the ultimate product Cr^{III} . Such a sequence of reactions in Cr^{VI} oxidations is well known¹⁷.

Experimental

Materials : B IDC was prepared by the reported method³ and its purity was checked by an iodometric method. The organic acids were commercial products of the highest degree of purity available and were used as supplied. The solution of formic acid was standardized by alkalimetry while that of oxalic acid was prepared by direct weighing. α -Deuterioformic acid (DCOOH or DFA) was prepared by the reported method¹⁸ and its isotopic purity, ascertained by NMR spectra, was $94 \pm 5\%$. The solvents were purified by the reported methods¹⁹. Amongst

the solvents, CS_2 is a flammable liquid and is toxic. Toluene-*p*-sulphonic acid (TsOH) was used as a source of hydrogen ions.

Stoichiometry : The oxidation of oxalic and formic acids leads to the formation of carbon dioxide. No quantitative determination of carbon dioxide formed was carried out.

To determine the stoichiometry, B IDC (0.005 mol) and organic acid (0.001 mol) were made up to 100 ml in DMSO, in the presence of 0.5 mol dm^{-3} TsOH. The reaction was allowed to stand for 12 h to ensure the completion of the reaction. The residual B IDC was determined spectrophotometrically. Several determinations with different concentrations of organic acid showed that the reaction exhibited 2 : 3 stoichiometry i.e. two moles of B IDC were consumed with three moles of acid. The results with FA are presented in Table 7. B IDC, thus acts as a 3-electron oxidant and is reduced to Cr^{III} .

Table 7. Stoichiometry of the oxidation of formic acid by B IDC

10^3 [B IDC] (mol dm^{-3})	10^3 [Organic acid] (mol dm^{-3})	10^3 [Residual B IDC] (mol dm^{-3})	[Organic acid] [Consumed B IDC]
5.0	1.0	4.30	1.43
5.0	2.0	3.62	1.45
5.0	3.0	3.09	1.57
Mean = 1.48.			

Kinetic measurements : The reactions were carried out at constant temperature (± 0.1) under pseudo-first order conditions, by maintaining a large excess of the organic acid ($\times 15$ times or more) over B IDC. The solvent was DMSO, unless stated otherwise. The reactions were followed by monitoring the decrease in the concentration of B IDC at 364 nm for up to 80% of the reaction. The Beer's law is valid for B IDC within the concentration range used in our experiments. The pseudo-first order rate constant, k_{obs} , was evaluated from the linear ($r^2 > 0.995$) plots of $\log [\text{B IDC}]$ versus time. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 3\%$. In correlation analyses, we have used coefficient of determination (R^2 or r^2), standard deviation (sd) and Exner's parameter²⁰, ψ , as the measures of the goodness of fit.

Acknowledgement

We thank the University Grants Commission (India) and Council of Scientific and Industrial Research (India) for their financial support.

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