Kinetic and mechanistic studies of cerium(III)-catalysed oxidation of 4-oxo acids by bromate in acid medium: nonlinear Hammett plots

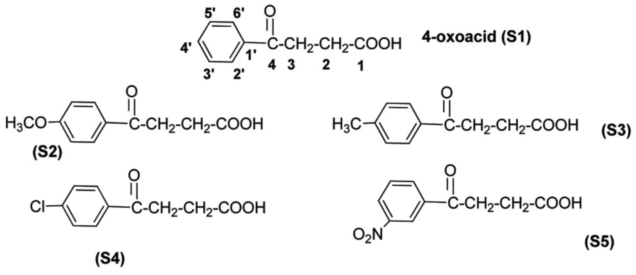
B. Suresh Babu[1], P. Sunitha Manjari[2] and Ch. Sanjeeva Reddy[1,]*

[1]Department of Chemistry, University College, Kakatiya University, Warangal 506 009, India
[2]Department of Chemistry, University College of Science, Saifabad, Osmania University, Hyderabad 500 004, India

The kinetic and mechanistic aspects of cerium(III)-catalysed oxidation of 4-oxo acids by bromate (uncontaminated with bromine) in an acid medium have been studied. The reaction exhibited first-order each in [bromate] and [acid], fractional order each in [oxo acid] and [cerium(III)], and also showed solvent isotope effect of 0.55 ($k(H_2O)/k\,(D_2O)$). The reaction did not induce polymerization and the induction period was not observed. The influence of ionic strength on the rate was negligible, while increase in reaction rate was found by lowering the dielectric constant of the medium. The reaction rate was affected by the presence of substituents in the reaction centre. Increase in the reaction rate by electron releasing substituents and decrease in the rate by the presence of electron-withdrawing substituents were observed. The Hammett plots were characterized by smooth curvature; however, linearity was observed using exalted σ values. A negative value for the reaction constant was observed. The isokinetic relationship was evaluated from the Arrhenius and Hammett plots. The formation of a ternary complex between oxidant, substrate and catalyst has been proposed in the mechanism. Based on the proposed mechanism, the rate law has been derived. The formation of a π-complex between Ce(III) and -ene of the enol form of oxo acid has been proposed. This reaction finds application in the synthesis of substituted benzoic acids and involves the phenomena of intramolecular catalysis and neighbouring group participation.

Keywords: Bromate oxidation, cerium(III) catalysis, isokinetic relationships, reaction mechanism, 4-oxo acids.

3-BENZOYL propionic acid (4-oxo-4-phenyl butyric acid) and its substituted compounds are commonly known as 4-oxo acids or γ-oxo acids. These compounds have versatile synthetic applications; they are the precursors for natural products like piperidines, pyrrolidines, lactams and substituted γ-butyrolactones[1]. The two functional groups – carbonyl and carboxy groups – present in these compounds are separated by two carbon atoms, such that they are independent of each other. However, these compounds exert intramolecular mechanism[2] and neighbouring group participation[3]. The formation of propanedioic acid and benzoic acid from enolization and selective oxidation, makes these substrates attractive and therefore they possess wide synthetic organic applications[4–6].



S1: Unsubstituted, **S2**: 4'-Methoxy, **S3**:4'-Methyl, **S4**:4'-Chloro, **S5**: 3'-Nitro

Oxidants such as potassium bromate and sodium bromate are innocuous, inexpensive, stable solids and easy to handle. Since bromide is the reduction product of bromate oxidation, which makes bromate oxidation environmentally benign compared to metal ion oxidations[7,8]. Cerium(III) has been used as a homogeneous catalyst in many redox reactions including the Belousov–Zhabotinsky (B–Z) oscillating reactions of various organic substrates involving bromate as an oxidant[9–11]. Generally Ce(III) ion catalysed B–Z oscillating reactions involve the formation of several organic intermediate free radicals, auto-catalysis and different oxidation states of the catalyst, hence complicated.

The role of substituents on the rate of reaction can be understood based on the Hammett equation. When the substituents influence the reaction rate in different ways, then it results in a nonlinearity in the plot between log k and σ (Hammett plot), which is attributed to change in the mechanism, change in the rate-determining step, or change in the nature of the transition state during the reaction, hence interesting to study the substituent effect.

The present system (oxidation of 4-oxoacids by Ce(III)) is neither isoenthalpic nor isoentropic, but exhibits a linear relationship between the activation enthalpy and

---

*For correspondence. (e-mail: csreddykuc@gmail.com) activation entropy in accordance with the compensation law known as isokinetic relationship.

$$\frac{\delta \Delta H^{\ddagger}}{\delta \Delta S^{\ddagger}} = \beta,$$

where $\Delta H^{\ddagger}$ is the enthalpy of activation and $\Delta S^{\ddagger}$ the entropy of activation and β is the isokinetic temperature, i.e. the temperature at which all the compounds have the same rate. At the isokinetic temperature, the variation of substituents has no influence on the free energy of activation. In an isoentropic oxidation reaction, the isokinetic temperature lies at infinity and is zero for an isoenthalpic series. In the former, only enthalpy of activation determines the reactivity and in the latter, the entropy of activation[12].

Experimental observations revealed that the reaction of 4-oxo acids with bromate in acid medium without a catalyst was slow, but was enhanced by the addition of smaller proportions of $Ce_2(SO_4)_3$. The present study, therefore will help understand the mechanism of Ce(III)-catalysed oxidation of 4-oxo acids by acidic bromate.

The main objectives of this study are to identify the reactive species of the substrate, catalyst and bromate, interpreting a possible mechanism for the reaction, obtaining an appropriate rate law, identifying the reaction products, evaluation of related kinetic and thermodynamic parameters, and verifying the linear free energy and isokinetic relationships.

Materials and methods

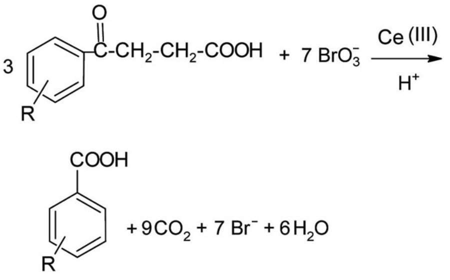
3-Benzoyl propionic acid and its substituted compounds (Aldrich, USA) were recrystallized twice from doubly distilled water. All other reagents were used after purification and their solutions were prepared using double-distilled water or pure acetic acid. D_2O (99.4% pure) was obtained from the Bhabha Atomic Research Centre, Mumbai. The stock solution of Ce(III) was made by dissolving $Ce_2(SO_4)_3 \cdot 8H_2O$ (Merck) in dilute acid and standardized using the method of Jeffery *et al.*[13].

Kinetic measurements

All the kinetic measurements were studied at pseudo-first order conditions with [oxo acid] $\gg$ [bromate]. Reaction was initiated by adding a known amount of bromate to the thermostated reaction mixture. The reaction was monitored by determining the unconsumed [bromate] using the iodometric method. The reaction was followed for at least 75–80% and rate constants (k, s^{-1}) were obtained by plotting log[bromate]$_t$ against time. There was no change in the observed rate constants in the presence of nitrogen atmosphere and the reported rate constants were obtained without nitrogen. Solutions were prepared fresh while performing the kinetic runs. Bromine production due to reaction between bromate and bromide and its further reaction with the substrate were completely reduced by the addition of mercuric acetate[14].

Stoichiometry and product analysis

Reaction mixtures containing different ratios of [bromate] to [4-oxo acid] with all other reagents, were kept for 12 h at 40°C. Estimation of [bromate] revealed the stoichiometry of the reaction according to eq. (1).



(1)

The observed stoichiometry was the same with all the phenyl substituted 4-oxo acids. The oxidation products were analysed. Benzoic acid, after separation by HPLC (melting point 121°C), was estimated quantitatively (92–96.6% yield) with a standard curve at 235 nm (λ_{max}). CO_2 was identified by bubbling N_2 gas through a U-shaped tube containing a saturated $Ba(OH)_2$ solution, which resulted in the formation of a white precipitate of $BaCO_3$. Formation of pale-yellow precipitate by the addition of silver nitrate solution confirmed the presence of bromide ions. Evolution of bromine did not occur, which further supported the formation of bromide ion.

It is pertinent to mention here that, under the kinetic conditions when [oxo acid] $\gg$ [bromate], the products of 4-oxo acids upon oxidation are benzoic and malonic acids. Malonic acid was identified by its melting point (135°C) and also tested with its characteristic spot test through conversion into barbituric acid[15]. Identification of the products, namely benzoic and malonic acids was also done by comparing the t_r (retention time) values of the authentic samples.

Results and discussion

In acid medium, production of molecular bromine (Br_2) due to autocatalytic bromate–bromide reaction was eliminated by the addition of $Hg(OAc)_2$, which forms non-ionizable Hg(II)-bromocomplexes[14]. No significant change in the reaction rate was observed, in the concentration range 0.001–0.01 M mercuric acetate. An optimum concentration of mercuric acetate (0.005 M) was employed to avoid all possible reactions due to bromine oxidation

Table 1. Factors influencing the rate of Ce(III)-catalysed oxidation of 4-oxo acids by bromate in acidic medium at 313 K

Non-variable constituent (mol dm^{-3})	Variable constituent (mol dm^{-3})	k^a (s^{-1}) × 10^4				
		-H	*p*-OCH_3	*p*-CH_3	*p*-Cl	*m*-NO_2
[Bromate]						
[Oxo acid] = 0.01	5.0 × 10^{-4}	3.82	57.57	7.67	0.77	0.39
[H_2SO_4] = 1.0	7.5 × 10^{-4}	3.83	57.56	7.65	0.79	0.38
[Ce(III)] = 0.0001	10.0 × 10^{-4}	3.84	57.57	7.67	0.79	0.38
AcOH–H_2O = 1 : 1 (% v/v)	15.0 × 10^{-4}	3.83	57.58	7.67	0.78	0.38
[$Hg(OAc)_2$] = 0.005	20.0 × 10^{-4}	3.83	57.57	7.67	0.79	0.38
[Oxo acid]						
[Bromate] = 0.001	5.0 × 10^{-3}	2.31	35.54	4.45	0.45	0.22
[H_2SO_4] = 1.0	7.5 × 10^{-3}	3.02	45.22	5.75	0.62	0.31
[Ce(III)] = 0.0001	10.0 × 10^{-3}	3.83	57.57	7.67	0.79	0.38
AcOH–H_2O = 1 : 1 (% v/v)	15.0 × 10^{-3}	4.81	72.14	8.95	0.96	0.45
[$Hg(OAc)_2$] = 0.005	20.0 × 10^{-3}	5.76	86.88	11.51	1.22	0.57
	30.0 × 10^{-3}	7.48	121.12	15.24	1.61	0.74
[Ce(III)]						
[Bromate] = 0.001	0.50 × 10^{-4}	2.78	38.54	5.87	0.55	0.23
[Oxo acid] = 0.01	1.00 × 10^{-4}	3.83	57.57	7.67	0.79	0.38
[H_2SO_4] = 1.0	2.00 × 10^{-4}	5.24	76.58	12.12	1.29	0.54
AcOH–H_2O = 1 : 1 (% v/v)	4.00 × 10^{-4}	7.58	106.25	17.24	1.68	0.78
[$Hg(OAc)_2$] = 0.005	8.00 × 10^{-4}	11.24	163.24	23.02	2.48	1.04
[H_2SO_4]						
[Bromate] = 0.001	0.50	1.94	28.84	4.36	0.46	–
[Oxo acid] = 0.01	0.75	3.01	40.73	6.02	0.68	0.28
[Ce(III)] = 0.0001	1.00	3.83	57.57	7.67	0.79	0.38
AcOH–H_2O = 1 : 1 (% v/v)	1.25	4.89	69.98	9.59	1.07	0.43
[$Hg(OAc)_2$] = 0.005	1.50	6.47	88.10	13.42	1.51	0.56
	2.00	8.70	112.71	19.05	1.81	0.83
AcOH–H_2O (% v/v)						
[Bromate] = 0.001	30–70 (53.18)*	1.64	25.58	1.91	0.47	0.16
[Oxo acid] = 0.01	40–60 (46.48)	1.91	35.43	2.87	0.58	0.21
[Ce(III)] = 0.0001	50–50 (39.78)	3.83	57.57	7.67	0.79	0.38
[H_2SO_4] = 1.0	60–40 (33.08)	5.75	86.36	11.51	1.17	0.54
[$Hg(OAc)_2$] = 0.005	70–30 (26.08)	7.67	116.25	15.28	1.81	0.76

[a]Reported rate constants are the mean of duplicate experiments.
*Values in parentheses indicate the dielectric constant of the medium.

produced from bromide ions. Therefore, the added mercuric ion acts as a bromide-ion scavenger.

Effect of concentration and other parameters

The rate of uncatalysed oxidation of 4-oxo acids by bromate (under the same reaction conditions) was slow, and followed first-order each in [bromate] and [oxo acid] and second-order in [H_2SO_4]. Appreciable increase in the reaction rate was observed by the addition of tracer amounts (0.0001 M) of cerium(III) sulphate, and the rate constants for Ce(III)-catalysed reactions were calculated from the following: $k_{\text{catalysed}} = k_{\text{overall}} - k_{\text{uncatalysed}}$.

At constant concentrations of acid, Ce(III) and $Hg(OAc)_2$, under the condition of [substrate] $\gg$ [bromate], the order of the reaction was found to be unity in $[\text{bromate}]_o$, as is evident from the slope values in Table 1, obtained from log$[\text{bromate}]_t$ versus time plots, which are found to be constant at different $[\text{bromate}]_o$.

At constant [bromate], acid and catalyst, the observed rate constant values were found to increase by changing the [substrate] (Table 1). Log k_c versus log [substrate] plots were linear and the order with respect to substrate was fractional (0.51–0.60). Further, the Michaelis–Menten plots of $1/k$ against 1/[substrate] were linear (Figure 1, $R^2 \geq 0.97$) with varying intercept and slope values, confirming order less than unity in [substrate]. However, the rate of uncatalysed reaction was very low under the same conditions and followed first-order kinetics in [oxo acid].

The reaction rate was studied by changing the concentration of Ce(III) from 5.0×10^{-5} to 80.0×10^{-5} mol dm^{-3}, maintaining the concentration of other reagents as constant (Table 1). The observed slopes of log k against log [Ce(III)] plots ($R^2 \geq 0.99$) suggest a fractional (0.50 ± 0.05) order in [Ce(III)]. The double reciprocal plots of $1/k_c$ versus 1/[Ce(III)] were straight lines with definite intercepts (Figure 2) for all the studied substrates.

The order of the reaction was found to be unity in [acid], as is evident from the linear plots of log k_c versus log [acid]. There was no significant effect of ionic strength on the rate of reaction (studied by varying $NaClO_4$); hence the ionic strength of the medium was not fixed at any constant value.

Dielectric constant of the medium (*D*) was varied by changing the solvent composition. The reaction rate increased with a decrease in dielectric constant of the medium (Table 1) and log k_c versus 1/*D* plots were linear with positive slopes.

In order to know the interference of free radicals in the reaction, acrylonitrile/acrylamide was added to the reaction mixture (in N_2 medium) during the reaction. No precipitate was formed, suggesting non-participation of free radicals in the reaction. This was further confirmed by studying the reaction at 0.05 M butylatedhydroxy toluene, which was recovered completely at the end of the reaction inferring the absence of free radicals.

Increase in the reaction rate was observed in the D_2O medium and $k(H_2O)/k(D_2O)$ ~0.45, at all the studied temperatures for all the studied 4-oxo acids (Table 2), suggesting that this is a proton-catalysed reaction.

The reaction was studied with all the substrates in the temperature range 298–323 K and the activation energies were calculated from the Arrhenius plot (Figure 3, $R^2 \geq 0.99$) of log k_c versus $1/T$. The thermodynamic parameters, viz. enthalpy of activation ($\Delta H^{\ddagger}$), entropy of activation ($\Delta S^{\ddagger}$) and free energy of activation ($\Delta G^{\ddagger}$) of the reaction were evaluated (Table 3). The isokinetic temperature (β) for the reaction was 384.16 K, obtained from the linear plot of $\Delta H^{\ddagger}$ versus $\Delta S^{\ddagger}$ (Figure 4 *a*; $R^2 = 0.989$). This is in accordance with the β value obtained from Exner's plot (Figure 4 *b*; $R^2 = 0.977$) of log *k* (323 K) against log *k* (313 K) (382.44 K).

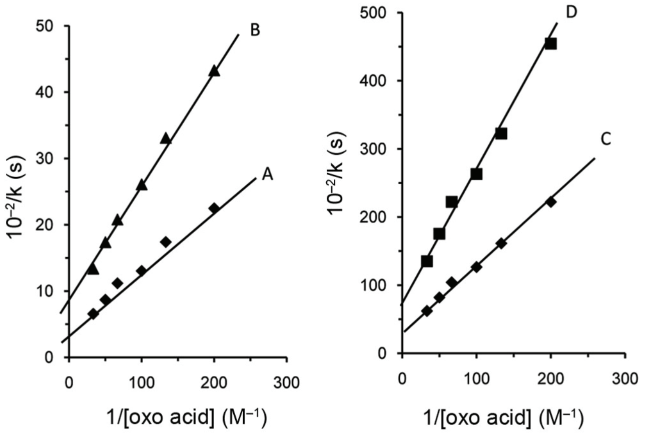


Figure 1. Representative Michaelis–Menten plots for Ce(III)-catalysed reactions. Conditions as in Table 1. (A) *p*-CH_3, (B) -H, (C) *p*-Cl and (D) *m*-NO_2.

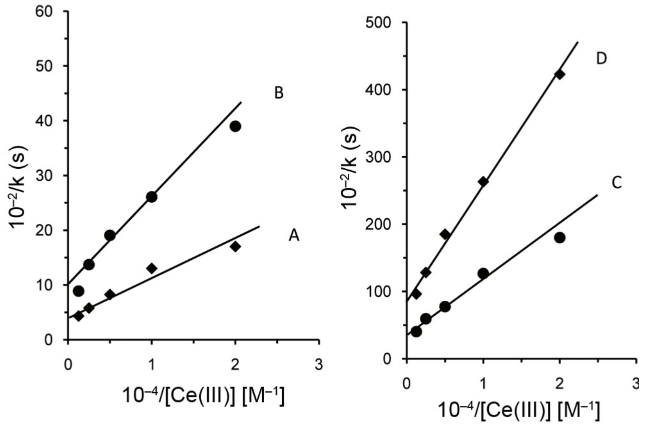


Figure 2. Plot of $1/k_c$ and 1/[Ce(III)]. Conditions as in Table 1. (A) *p*-CH_3, (B) -H, (C) *p*-Cl and (D) *m*-NO_2.

Table 2. Solvent isotope effect on the rate of Ce(III)–catalysed bromate oxidation of 4-oxo acids at 313 K

4-Oxo acid	$10^4 \times k$ (H_2O) (s^{-1})	$10^4 \times k$ (D_2O) (s^{-1})	k (H_2O)/k (D_2O)
–H	3.83	8.41	0.45
p-Methyl	7.67	16.67	0.46
p-Chloro	0.79	1.75	0.45
m-Nitro	0.38	0.84	0.45

Experimental conditions: [substrate] = 0.01 mol dm^{-3}, [bromate] = 0.001 mol dm^{-3}, [Ce(III)] = 1.0×10^{-4} mol dm^{-3}, [H_2SO_4] = 1.00 mol dm^{-3}, [$Hg(OAc)_2$] = 0.005 mol dm^{-3} and AcOH–H_2O = 1 : 1% (v/v). Reported rate constants are the mean of duplicate experiments.

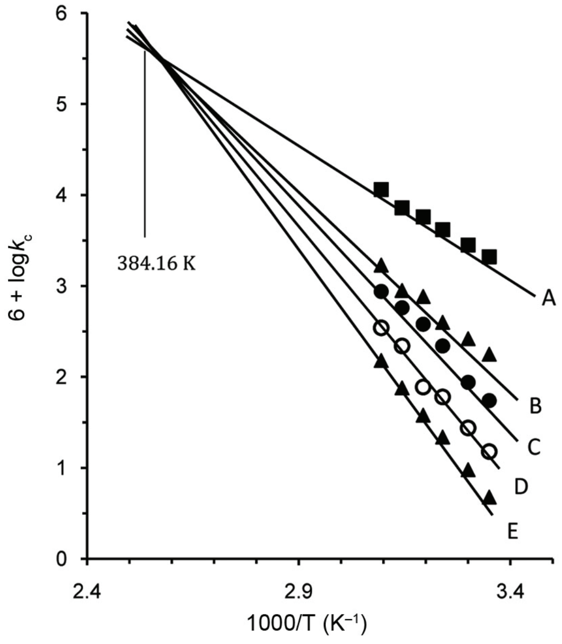


Figure 3. Arrhenius plots of log k_c versus $1/T$. Conditions as in Table 3. (A) *p*-OCH_3, (B) *p*-CH_3, (C) -H, (D) *p*-Cl and (E) *m*-NO_2.

Table 3. Rate constants at different temperatures and activation parameters at 313 K of Ce(III)-catalysed oxidation of 4-oxo acids by bromate in acid medium

	$10^5 \times k$ (s^{-1})				
Temperature (K)	-H	*p*-OCH_3	*p*-CH_3	*p*-Cl	*m*-NO_2
298	5.44	89.96	9.58	–	–
	(0.39)*	(14.43)	(1.13)	(0.26)	–
303	8.72	115.15	15.55	1.15	1.44
	(0.70)	(19.19)	(1.91)	(0.39)	–
308	21.83	255.58	33.11	3.09	2.55
	(1.35)	(28.78)	(3.19)	(0.71)	(0.17)
313	38.38	479.79	57.57	7.99	3.80
	(3.19)	(47.97)	(6.71)	(1.06)	(0.37)
318	57.57	639.72	115.15	15.99	7.67
	(4.79)	(57.57)	(11.19)	(1.72)	(0.71)
323	112.15	1115.25	223.87	38.01	21.15
	(9.59)	(67.17)	(17.61)	(3.59)	(1.43)
Ea (kJ/mol)	86.16	42.12	70.84	101.47	111.05
	(101.46)	(47.86)	(76.86)	(114.85)	(134.09)
$\Delta H^{\ddagger}$ (kJ/mol)	83.56	39.52	68.24	98.87	108.45
	(98.87)	(45.26)	(73.96)	(112.25)	(131.49)
$\Delta S^{\ddagger}$ (J/mol K)	–43.76	–161.79	–86.99	–8.03	16.67
	(80.26)	(–68.32)	(–69.47)	(9.5)	(66.27)
$\Delta G^{\ddagger}$ (kJ/mol)	97.25	90.22	95.43	101.38	103.23
	(73.74)	(66.64)	(71.79)	(70.98)	(76.21)

[Substrate] = 0.01 mol dm^{-3}, [$KBrO_3$] = 0.001 mol dm^{-3}, [H_2SO_4] = 1.0 mol dm^{-3}, [(Ce(III)] = 1.0×10^{-4} mol dm^{-3}, [$Hg(OAc)_2$] = 0.005 mol dm^{-3}, HOAc–H_2O = 1 : 1% (v/v).
*Values in parentheses indicate the rate constants (k_{un}, s^{-1}) and activation parameters of uncatalysed reactions.

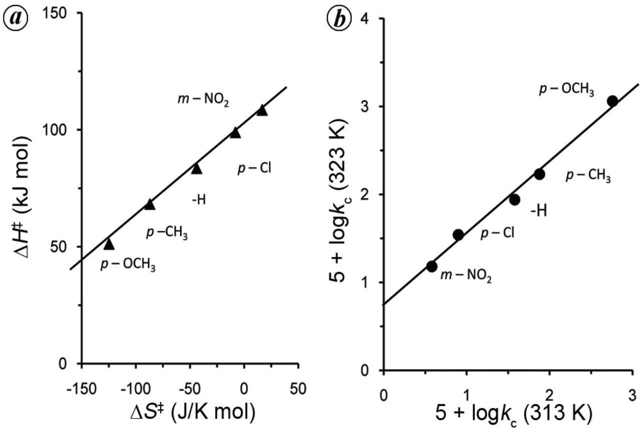


Figure 4. Plot of (***a***) $\Delta H^{\ddagger}$ versus $\Delta S^{\ddagger}$ and (***b***) log k_c (323 K) versus log k_c (313 K).

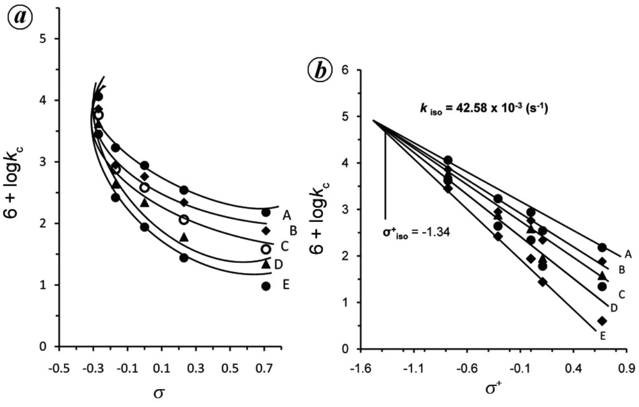


Figure 5. ***a***, Hammett plots between (***a***) log k_c and σ (***b***) log k_c and σ^+ at different temperatures. Conditions as in Table 3. (A) 323 K, (B) 318 K, (C) 313 K, (D) 308 K and (E) 303 K in both (***a***) and (***b***).

The influence of substituents on the reaction kinetics was studied at different temperatures using substrates with different substituents on the phenyl ring (Table 3). Changing substituent in the phenyl ring of 4-oxo acid changed the reaction rates. Electron-releasing substituents enhanced the rate of oxidation, whereas electron-withdrawing substituents retarded the rate. The Hammett's plot (linear free-energy relationship) was characterized by a smooth curve (Figure 5 *a*) which is expressed in terms of log k_c vs σ plot; however, when Brown and Okamoto's[16] exalted σ^+ values were used, linear plots with good correlation coefficients ($R^2 \geq 0.99$) were observed at the studied temperatures (Figure 5 *b*). The reaction constant (ρ) was negative and decreased with increase in temperature (–1.64, –1.59, –1.48, –1.35 and –1.29 at 303, 308, 313, 318 and 323 K respectively).

Catalysis of oxidation of 4-oxo acids involving cerium(III) as catalyst can be understood in two ways, one of which is the oxidation of 4-oxo acid by Ce(IV) ion resulting from bromate–cerium(III) auto-catalytic reaction.

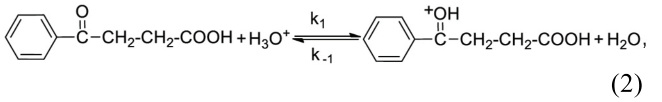
In the bromate–cerium(III) reaction, Yoshida and Ushiki[17] observed second-order in [bromate]$_o$, an induction period without mercury(II) acetate, and the reaction was independent of [Ce(III)]. On the other hand, in the present study. The reaction exhibited first-order kinetics in [bromate] in presence of mercuric acetate. The reaction rate increased with increase in [H_2SO_4], and no induction period was observed at varying concentrations of bromate, H_2SO_4, oxo acid and Ce(III).

Bromate cannot oxidize Ce(III) significantly in perchloric acid medium.[9,10,18]. This conclusion is also consistent with the complete failure to obtain oscillations in perchloric acid medium[9,10]. However, in the present study the oxidation rates obtained in the $HClO_4$ and H_2SO_4 media were comparable, and there was no evidence for free-radical formation. Generally, Ce(IV) oxidations of keto compounds occur through mechanism involving free radicals and oxidant attacks on the keto group of the substrate[19]. With these evidences oxidation of 4-oxo acids by the cerium(IV) formed is ruled out.

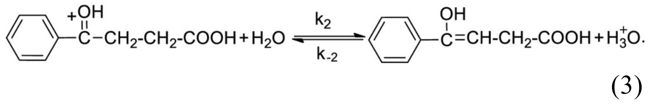
Complexation of Ce(III) and oxo acid is another alternative. The obtained data for all the substrates used suggest complexation between Ce(III) and oxo acid, which further reacts with bromate yielding products. The ultraviolet-visible spectra of oxo acid and oxo acid–cerium(III) mixture resulted in a hypsochromic shift of 5 nm from 275 to 270 nm and hypochromicity at 270 nm are the spectroscopic evidences for the complexation between Ce(III) and oxo acid. Figures 1 and 2 also illustrate the dependence of oxidation of oxo acids on [substrate] and [catalyst], following Michaelis–Menten kinetics. The reversible formation of Ce(III) complex with one mole of the substrate must precede the rate-determining oxidation step.

The negligible effect of the added acrylonitrile/acrylamide suggests the absence of free radicals in the reaction, ruling out the occurrence of reaction by one electron oxidation/reduction. Thus, the oxidation state of Ce(III) in the oxidation of 4-oxo acids by bromate in acidic medium remains unaltered. This is further supported by the absorption maximum of Ce(III), which remains the same during the course of reaction; the substrate forms preferably an outer-sphere complex with the catalyst Ce(III).

The oxo acids are weak acids with pKa of about 5–6 in aqueous solutions at 40°C (ref. 20), exist in undissociated form under acidic conditions and undergo enolization (eqs (2) and (3)). They follow push–pull or concerted mechanism.

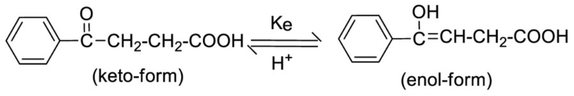


(2)



(3)

Thus, the enolization reaction is represented as

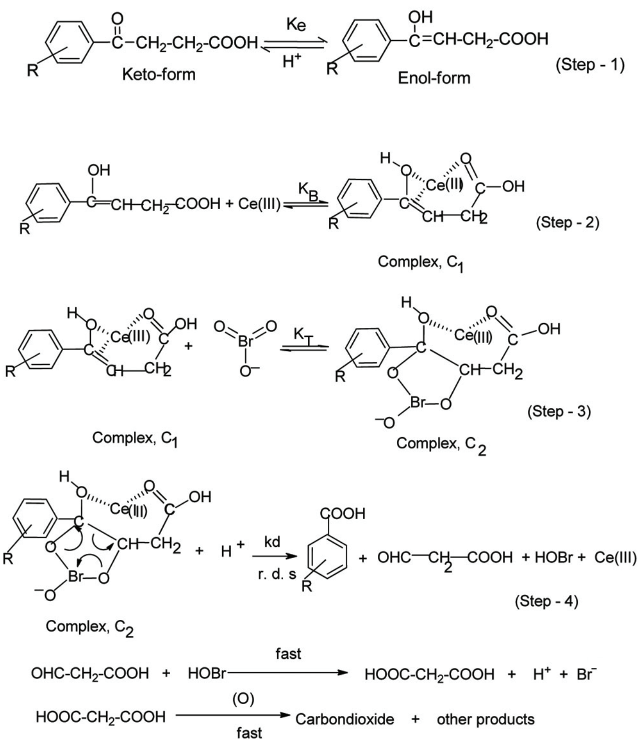


(4)

Reaction mechanism

In the present study, 'the rate of enolization determined by the bromination method[21] is greater than the rate of oxidation by a factor of 15–18. Hence, the step involving enol formation will not be the rate-determining step and the reaction may be visualized as proceeding via the enol-form of the oxo acid'[22]. In view of the above observations, a mechanism is proposed for the Ce(III)-catalysed oxidation of 4-oxo acids by bromate in acid medium (scheme 1).

The mechanistic pathway involves the formation of the outer-sphere complex of Ce(III) with the enolic-form of the oxo acid (complex **C**$_1$). This complex formation enhances the reactivity of C=C (ref. 23) and therefore, bromate attacks the C–C double bond of the substrate by concerted *cis*-1,3-cycloaddition and forms a five-membered cyclic bromate ester complex, **C**$_2$. The same was observed in the bromate oxidation of cinnamic acids[24] and in the pyridinium fluorochromate oxidation of 4-oxo acids[3]. The five-membered ring complex **C**$_2$ further undergoes decomposition involving C–C and O–Br bonds (in the rate-determining step), resulting in the formation of benzoic



Scheme 1.

acid and formyl acetic acid in the presence of H^+ ion. During the reaction the oxidation state of Ce(III) remains unchanged. The formed products were further confirmed by comparing with the retention time (t_r) of the authentic samples. Formyl acetic acid on further oxidation gives malonic acid and Br^- ion as final products. This reaction proceeds through neighbouring group participation and also involves intramolecular catalysis. The proposed mechanism is also in accordance with the observed stoichiometry.

Rate law and its verification

From the proposed mechanism (scheme 1), the rate law for the reaction was obtained. Rate in terms of bromate concentration can be expressed as in eq. (5).

$$\text{Rate} = \frac{-\mathrm{d}\left[\mathrm{BrO_3^-}\right]}{\mathrm{d}t} = kd\,[\text{complex C}_2][\mathrm{H^+}]. \tag{5}$$

On the basis of the equilibrium steps in scheme 1, eqs (6)–(8) can be obtained as follows

$$[\text{Complex C}_1] = K_\mathrm{B}K_\mathrm{e}\,[\text{oxo acid}][\text{Ce(III)}], \tag{6}$$

$$[\text{Complex C}_2] = K_\mathrm{T}K_\mathrm{B}K_\mathrm{e}\,[\text{oxo acid}][\text{Ce(III)}][\mathrm{BrO_3^-}]. \tag{7}$$

Using eqs (5)–(7) we get eq. (8).

$$\text{Rate} = \frac{-\mathrm{d}[\mathrm{BrO_3^-}]}{\mathrm{d}t} = kd\;K_\mathrm{T}K_\mathrm{B}\,K_\mathrm{e}\,[\text{oxo acid}]$$

$$\times\,[\text{Ce(III)}][\mathrm{BrO_3^-}][\mathrm{H^+}]. \tag{8}$$

Total concentration of bromate can be obtained by considering the complexed and uncomplexed forms of bromate which gives eq. (9).

$$[\text{Br(V)}]_\mathrm{T} = [\mathrm{BrO_3^-}] + [\text{complex } \mathbf{C}_2],$$

$$[\text{Br(V)}]_\mathrm{T} = [\mathrm{BrO_3^-}] + K_\mathrm{T}K_\mathrm{B}K_\mathrm{e}\,[\text{oxo acid}]$$

$$\times\,[\text{Ce(III)}][\mathrm{BrO_3^-}], \tag{9}$$

$$[\text{Br(V)}]_\mathrm{T} = [\mathrm{BrO_3^-}][1 + K_\mathrm{T}K_\mathrm{B}K_\mathrm{e}\,[\text{oxo acid}][\text{Ce(III)}]]. \tag{10}$$

Therefore

$$[\mathrm{BrO_3^-}] = \frac{[\text{Br(V)}]_\mathrm{T}}{1 + K_\mathrm{T}K_\mathrm{B}K_\mathrm{e}\,[\text{oxo acid}][\text{Ce(III)}]}. \tag{11}$$

The rate law in terms of total bromate concentration can be given as eq. (12).

$$\text{Rate} = \frac{-\mathrm{d}[\mathrm{BrO_3^-}]}{\mathrm{d}t}$$

$$= \frac{kdK_\mathrm{T}K_\mathrm{B}K_\mathrm{e}\,[\text{oxo acid}][\text{Ce(III)}][\text{Br(V)}]_\mathrm{T}}{1 + K_\mathrm{T}K_\mathrm{B}K_\mathrm{e}\,[\text{oxo acid}][\text{Ce(III)}]}. \tag{12}$$

The derived rate law (eq. (12)) is in accordance with the obtained experimental results, and adds evidence for the first-order dependence of rate on [acid] and [bromate] and fractional order in [oxo acid] and [Ce(III)]. The reaction occurred smoothly in the presence of added sulphuric acid and did not occur in the absence of sulphuric acid.

Upon rearranging eq. (12), we get

$$\frac{\text{Rate}}{[\text{Br(V)}]_\mathrm{T}} = k_\mathrm{c} = \frac{k\mathrm{d}K_\mathrm{T}K_\mathrm{B}K_\mathrm{e}\,[\text{oxo acid}][\text{Ce(III)}]}{1 + k\mathrm{d}K_\mathrm{T}K_\mathrm{B}K_\mathrm{e}\,[\text{oxo acid}][\text{Ce(III)}]}, \tag{13}$$

$$\frac{1}{k_\mathrm{c}} = \left[\frac{1}{k\mathrm{d}K_\mathrm{T}K_\mathrm{B}K_\mathrm{e}\,[\text{oxo acid}][\text{Ce(III)}]} + \frac{1}{kd}\right]\frac{1}{[\mathrm{H^+}]}. \tag{14}$$

When [acid] is 1.0 mol dm^{-3}, eq. (14) changes to eq. (15).

$$\frac{1}{k_\mathrm{c}} = \frac{1}{k\mathrm{d}K_\mathrm{T}K_\mathrm{B}K_\mathrm{e}\,[\text{oxo acid}][\text{Ce(III)}]} + \frac{1}{kd}. \tag{15}$$

According to eq. (14), the plot of $1/k_c$ versus $1/[H^+]$ should be linear passing through the origin, other conditions being constant. According to eq. (15), the plots of $1/k_c$ against 1/[oxo acid] (at constant [Ce(III)]) and $1/k_c$ against 1/[Ce(III)] (at constant [oxo acid]) should be linear with a definite intercept on the $1/k_c$ axis. The same was observed from the above plots, validating the proposed rate law and hence the proposed mechanism (scheme 1). The proposed mechanism is further supported by the solvent influence on the reaction rate. The enhancement in the reaction rate by decrease in the polarity of the solvent (Table 1), suggests that the intermediate complex $\mathbf{C}_2$ is less polar than the reactants due to dispersal of charge and gets stabilized in comparison with the reactants.

Linear free energy relationships

By changing the substituents at para position on the phenyl moiety of 4-oxo acids, the effect of substituents was studied. The rate of reaction increased by the presence of electron-donating substituents and decreased by the presence of electron-withdrawing substituents. The reactivity of the substituted 4-oxo acids at all the studied temperatures followed the order: *p*-methoxy $\gg$ *p*-methyl $>$–*H* $>$ *p*-chloro

>*m*-nitro oxo acid. Linear free-energy relationship for the reaction was verified from the plot of log k_c versus Hammett's sigma (σ), where a smooth concave downward curve was observed. The curvature is usually observed in the reactions when there is a change in the reaction mechanism, change in the rate-determining step and also when there is a change in the nature of transition state. However, the linearity of the Exner's plot (Figure 4 *a*) suggests that these reactions follow a similar mechanism[25]. Thus, the smooth curvature in the plot of log k_c versus σ (Figure 5 *a*) is attributed due to change in nature of the transition state as we move from electron-releasing to electron-withdrawing substituents, i.e. electronic perturbation effect[20]. There is a direct conjugation between the substituent and the reaction centre, due to which Hammett's sigma values are not applicable. Therefore, higher values of sigma, i.e. exalted Brown and Okamoto's[16] σ^+ values were used to fit all the points on the line. In the present study, this is observed, and the plot of log k_c versus σ^+ is linear at 303 K, with a slope value of –1.64. With increasing temperature, the reaction constant (ρ^+) decreases (in magnitude). The negative value of the reaction constant (ρ^+) and acceleration of reaction rate with electron-releasing substituents clearly show that the transition state approaches a carbocationic nature. The ρ^+ value (–1.64 to –1.29) might be related to the nature of the measured rate constant (k_c), which is a composite of various components such as enolization, complexation and oxidation.

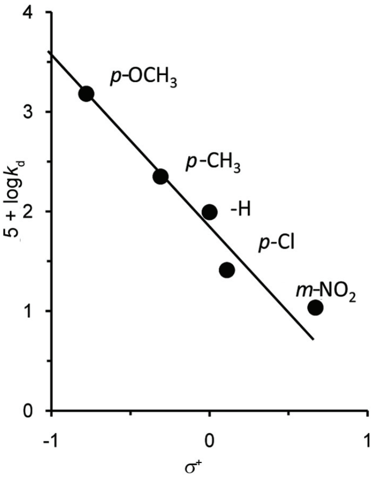


Figure 6. Plot of log *kd* versus σ^+.

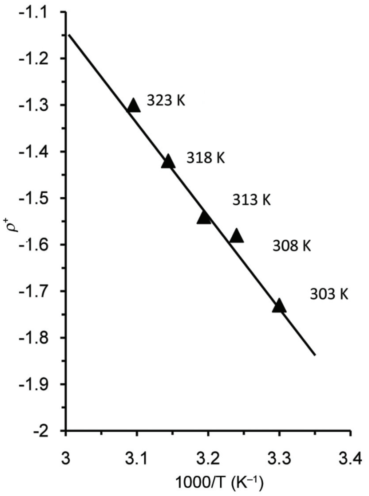


Figure 7. Plot of log ρ^+ versus $1/T$ at different temperatures.

The linear plot of log *kd* (*kd* values are obtained from the double reciprocal plots (Figures 1 and 2) versus σ^+ (Figure 6) rather than log *kd* versus σ provides further evidence for the electronic perturbation effect in the transition state.

Isokinetic relationship

The isokinetic temperature (β) was calculated from the slope of Exner's plot (375.44 K). It was found to be higher than the reaction temperature, indicating that the reaction rate is governed by enthalpy of activation. The Hammett reaction constant (ρ^+) decreases (in magnitude) with increase in temperature, from –1.64 at 303 K to –1.29 at 323 K. The Hammett lines intersect at a point corresponding to an σ^+_{iso} value of –1.34 and a k_{iso} value of 42.58×10^{-3} s^{-1}. An oxo acid with a substituent having this σ^+ value will be oxidized by bromate with the same rate at all temperatures. Such insensitivity of the reaction rate to temperature is an indication of the existence of isokinetic relationship[20].

A reacting system that has a common point of intersection in the Hammett plot is expected to have a common point of intersection in the Arrhenius plot as well[26]. From the plots of $\Delta H^‡$ against $\Delta S^‡$, and ρ^+ against $1/T$ (Figure 7), the T_{iso} value was found to be 384.16 K, which is in accordance with that obtained (382.44 K) from the slope of the Exner's plot (Figure 4 *b*). Anti-compensation effect was not observed, even though the rate constant is a composite of all the steps.

Conclusion

In the present study, Ce(III)-catalysed bromate oxidation of substituted 4-oxo-4-phenylbutanoic acids in the presence of bromo-complexing metal ion proceeded through a cyclic complex, which resulted in cleavage of the carbon–carbon bond, yielding benzoic acid (92–96.6%). From the Hammett plot, the reaction constant (ρ) is negative and decreases with increase in temperature. Electron donors enhanced the rate of reaction, while electron acceptors decreased the rate. The reaction centre was found to be carbocationic in nature. Isokinetic temperature was determined from Hammett and Arrhenius plots. To conclude, Ce(III) acts as an efficient catalyst in the oxidation of

4-oxo acids by bromate in acid medium. This reaction is an example of the neighbouring group participation and intramolecular catalysis in the oxidation of 4-oxo-4-arylbutanoic acids.

1. Fuentes, L. M., Gerald, L. and Larson, G. L., A facile synthesis of 4-oxo carboxylic acids from γ-butyrolactone. *Tetrahedron Lett.*, 1982, **23**(3), 271–274.
2. Bell, R. B. and Covington, D., Intra- and inter-molecular catalysis in the halogenation of some oxocarboxylic acids. *J. Chem. Soc., Perkin Trans 2*, 1975, **12**, 1343–1348.
3. Bhatt, M. V., Ravindranathan, M., Somayaji, V. and Rao, G. V., Aspects of tautomerism. 13. Alkaline hydrolysis of gamma-, delta- and epsilon-keto esters and their desoxy analogs. Geometrical constraints on keto participation. *J. Org. Chem.*, 1984, **49**(17), 3170–3173.
4. Kavitha, S., Pandurangan, A. and Alphonse, I., Kinetics and mechanism of oxidation of beta benzoylpropionic acids by pyridinium fluoro-chromate in aqueous acetic acid medium. *Indian J. Chem. A*, 2005, **44**(4), 715–718.
5. Farook, N. A. M., Kinetics and mechanism of oxidation of 4-oxoacids by *N*-bromosuccinimide in aqueous acetic acid medium. *J. Iran. Chem. Soc.*, 2006, **3**, 378–386.
6. Vannamuthu, I., Saleem Malik, V., Shafi, S. and Sheik Mansoor, S., Kinetics and mechanism of oxidation of 4-oxo-4-phenyl butanoic acid by benzimidazolium fluorochromate in presence of 1,10-phenthroline catalyst in acetic acid–water medium. *Der Pharm. Lett.*, 2015, **7**(3), 96–103.
7. Kudzanai Chipiso, A. and Simoyi, R. H., Kinetics and mechanism of oxidation of *d*-penicillamine in acidified bromate and aqueous bromine. *Aust. J. Chem.*, 2016, **69**, 1305–1313.
8. Olagunju, O. and Simoyi, R. H., Oxyhalogen–sulfur chemistry: kinetics and mechanism of oxidation of 1,3-dimethylthiourea by acidic bromate. *J. Phys. Chem. A*, 2017, **12**, 6366–6376.
9. Field, R. J., Koros, E. and Noyes, R. M., Oscillations in chemical systems. II. Thorough analysis of temporal oscillation in the bromate–cerium–malonic acid system. *J. Am. Chem. Soc.*, 1972, **94**(25), 8649–8644.
10. Noyes, R. M., Chemical oscillations and instabilities. 39. A generalized mechanism for bromate-driven oscillators controlled by bromide. *J. Am. Chem. Soc*., 1980, **102**(14), 4644–4649.
11. Hegedus, L., Wittmann, M., Noszticzius, Z., Van, S., Sirimungkala, A., Forsterling, H. D. and Field, R. J., HPLC analysis of complete BZ systems. Evolution of the chemical composition in cerium and ferroin catalysed batch oscillators: experiments and model calculations. *Faraday Discuss*., 2002, **120**, 21–38, and references therein.
12. Karunakaran, Ch. and Chidambaranathan, V., Linear free energy relationships near isokinetic temperature. Oxidation of organic sulfides with nicotinium dichromate. *Croat. Chem. Acta*, 2001, **74**(1), 51–59.
13. Jeffery, J. H., Bassett, J., Mendham, J. and Denney, R. C., *Vogel's Textbook of Quantitative Chemical Analysis*, ELBS, Longman, Essex, UK, 1996, 5th edn, p. 843.
14. Bailer, J. C., *The Chemistry of Coordination Compounds*, Reinhold, New York, USA, 1956, p. 787.
15. Fiegl, F. and Anger, V., *Spot Tests in Organic Analysis*, Elsevier, Amsterdam, The Netherlands, 1975, p. 459.
16. Brown, H. C. and Okamoto, Y., Electrophilic substituent constants. *J. Am. Chem. Soc.*, 1958, **80**(18), 4979–4987.
17. Yoshida, T. and Ushiki, Y., The kinetics of bromate–cerium(III) and –iron(II) reactions. *Bull. Chem. Soc. Jpn*, 1982, **55**(6), 1772–1776.
18. Rabai, G. and Hanazaki, I., pH Oscillations in the bromate–sulfite–marble semibatch and flow systems. *J. Phys. Chem.*, 1996, **100**(25), 10615–10619.
19. Krishnan, S. V. and Santappa, M., Oxidation of acetone and methylethyl ketone by ceric ions in aqueous solution. *Z. Phys. Chem*., 1958, **16**, 73–84.
20. Sanjeeva Reddy, Ch. and Sunitha Manjari, P., Homogeneous catalysis of oxovanadium(IV) in the oxidation of substituted 4-oxoacids by bromate in acid medium: a mechanistic study. *J. Mol. Catal A: Chem*., 2010, **328**, 76–87.
21. Nathan, W. S. and Waston, H. B., Constitutional factors controlling prototropic changes in carbonyl compounds. Part III. The prototropy of nuclear-substituted acetophenones. *J. Chem. Soc.*, 1933, 217–220.
22. Sunitha Manjari, P. and Sanjeeva Reddy. Ch., Aquachlororuthenium(III) catalysis in theoxidation of substituted 4-oxo-4-arylbutanoic acids by bromatein acid medium: a kinetic and mechanistic study and validity of linear free-energy relationships. *Trans. Met. Chem*., 2011, **36**(7), 707–719.
23. Tsurugi, H. and Mashima, K., Renaissance of homogeneous cerium catalysts with unique Ce(IV/III) couple: redox-mediated organic transformations involving homolysis of Ce(IV)–ligand covalent bonds. *J. Am. Chem. Soc*., 2021; article ASAP, doi:10.1021/jacs.1c02889.
24. Sanjeeva Reddy, Ch. and Sundaram, E. V., Mechanism of acid bromate oxidation of trans mono-substituted cinnamic acids: structure reactivity correlation – a non-linear Hammett's plot. *Tetrahedron*., 1989, **45**(7) 2109–2126.
25. Exner, O., Entropy–enthalpy compensation and anti-compensation: solvation and ligand binding. *Chem. Commun*., 2000, **17**, 1655–1656.
26. Schmid, R. and Sapunov, V. N., *Non-Formal Kinetics, Monograph in Modern Chemistry* (ed. Ebel, H. F.), Verlag Chemie, Weinheim, 1982, p. 21.

ACKNOWLEDGEMENTS. We thank the Council of Scientific and Industrial Research, New Delhi, for the award of a research fellowship (to S.B.) and the University Grants Commission, New Delhi, India for financial support in the form of one-time research grant (to C.S.R.).

Received 12 February 2021; revised accepted 12 June 2021

doi: 10.18520/cs/v121/i5/651-659