Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 80 (8) 1019–1034 (2015)
JSCS–4777
UDC 547.551.41+546.766+547.288.1+546.141:542.9:531.3
Original scientific paper

Dynamics of cetyltrimethylammonium bromide-mediated reaction of phenylsulfinylacetic acid with Cr(VI): Treatment of pseudo-phase models

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(Received 19 September, revised 28 December, accepted 31 December 2014)

Abstract: The influence of cetyltrimethylammonium bromide, CTAB, on the oxidative decarboxylation of phenylsulfinylacetic acid, PSAA, and several *meta*- and *para*-substituted PSAAs by Cr(VI) was investigated in 95 % H_2O–5 % CH_3CN medium. The rate profile displayed a peculiar trend with an initial rate increase at low CTAB followed by sharp rate inhibition at higher CTAB concentrations. The initial rate acceleration could be explained by strong binding of SO_4^{2-} on the positively charged micellar surface. The specific partitioning of PSAA in the micellar phase by hydrophobic interaction and the oxidizing species $HCrO_3^+$ in aqueous phase by electrostatic repulsion accounted for the rate retardation at higher CTAB concentrations. The Hammett plot with different substituted PSAAs showed excellent correlation affording negative ρ value, which supports the proposed mechanism involving the intermediate formation of sulfonium cation. The obtained ρ value in CTAB medium was found to be slightly lower than that in aqueous medium. Quantitative analysis of the rate data for the inhibition shown by CTAB was performed using the Menger–Portnoy and the Piszkiewicz pseudo-phase models. The binding constant for PSAA with micelles was evaluated from the Piszkiewicz cooperative model.

Keywords: phenylsulfinylacetic acid; Cr(VI); CTAB micellar effect; Hammett correlation; Piszkiewicz cooperative model.

INTRODUCTION

Surfactants and their micellar aggregates exhibit widespread applications in chemical, biochemical, pharmaceutical and industrial fields. Cationic surfactants are useful as antifungal, antibacterial and antiseptic agents and have attracted much attention with reference to their interaction with DNA and lipids.[1] The

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doi: 10.2298/JSC140916001S

fascinating feature of aqueous surfactant solution is their self-organization into micelles above the critical micellar concentration, *cmc*. This leads to micellar aggregates having an architecture in which the hydrophobic groups of surfactants occupy the interior while the hydrophilic head groups at the surface are in contact with bulk water. In the case of ionic micelles, the interface is charged giving rise to an electrical double layer with a potential difference up to hundred of millivolts between the micellar pseudo-phase and water. Thus, the electrostatic potential and polarity prevailing in the interior of the aggregate differ from those of the bulk aqueous phase.

The redox processes in micellar media are considered as models to obtain insight into the dynamics and mechanistic paths of several redox processes occurring in complex biological systems.[2–5] Micellar systems were used in a number of studies, including oxidation reactions, due to their effectiveness in altering the rate of the reactions by their inherent characteristics of their surface activity.[6–11] Micelles act as nano reactors that may drastically modulate the reactivity of entrapped reactants. The importance of micelles arise from the fact that micelle catalyzed reactions resemble enzyme catalyzed reactions in several aspects.[12] The investigation of coupled systems composed of electron transfer and micelle-forming surfactant may contribute in a unique way to the understanding of the redox processes. Ionic micelles typically catalyze the reactions of a reactive counter ion with hydrophobic substrates that bind to the micelles.[13–16] For bimolecular reactions, inhibition arises from the incorporation of one reactant into the micellar pseudo-phase and exclusion of the other from it.

Although there are several reports in the literature on the investigation of micellar effects on the redox reactions of organic sulfur compounds,[16–21] the corresponding study on sulfur-containing carboxylic acids is limited. Even though phenylsulfinylacetic acid (PSAA) shows a wide range of synthetic utility, no reports are available in the literature on the oxidation of PSAA except a few recent works.[22–25] Hence, this investigation of the redox reaction between PSAA and Cr(VI) in the presence of cationic surfactant cetyltrimethylammonium bromide (CTAB) is of great interest. The substituent and micellar effects are highlighted and the rate data in the presence of CTAB were subjected to Menger–Portnoy and Piszkiewicz kinetic pseudo-phase models.

EXPERIMENTAL

Preparation of phenylmercaptoacetic acids

Phenylmercaptoacetic acids, the precursors used for the synthesis of the PSAAs, were prepared from the corresponding thiophenols.[26,27] The appropriate amount of thiophenol (0.05 mol) dissolved in 10 mL of 20 % sodium hydroxide solution was mixed with 4.7 g of chloroacetic acid dissolved in 10 mL of water without allowing the temperature to rise and then the mixture was heated in an oil bath at 120–130 °C for 5 h. The solution was cooled, acidified with 50 % HCl and the phenylmercaptoacetic acid obtained as solid was recrystallized from

water. The melting points of phenylmercaptoacetic acids were determined and checked with the corresponding literature values.[28]

Preparation of phenylsulfinylacetic acids

PSAAs and ten *meta*- and *para*-substituted PSAAs were prepared by the controlled oxidation of the corresponding phenylmercaptoacetic acids using 30 % H_2O_2.[29] The temperature was maintained at 40 °C and the reaction mixture was stirred until all the H_2O_2 had been consumed. At the end of the reaction, a clear and colorless syrupy liquid was obtained which was kept overnight. After evaporation of water under reduced pressure, a white solid was obtained. The solid was digested with hot benzene for a few minutes and then recrystallized. For the recrystallization of *para*- and *meta*-methyl PSAAs, $CHCl_3$–petroleum ether (1:1) mixture was used, while ethyl acetate–benzene (1:1) solvent mixture was used for the recrystallization of PSAA and the other *meta*- and *para*-substituted PSAAs. The recrystallized PSAAs were dried and their melting points were determined and compared with the corresponding literature values.[28] The purity was also checked by LC-MS. The recrystallized samples were stored in a vacuum desiccator and used for kinetic studies.

Kinetic measurements

All the kinetic runs were performed under pseudo-first-order conditions by maintaining a large excess of PSAA over the concentration of Cr(VI). The progress of the reaction in CTAB medium was monitored by following the rate of decrease of [Cr(VI)] spectrophotometrically at 360 nm. In order to avoid solubility problems, the reaction was conducted in a 95 % water––5 % CH_3CN medium. Several researchers used similar solvent systems to study the micellar effect in the oxidation of organic sulfides.[17,21,30-32] As the reaction mixture in the presence of CTAB produced turbidity with perchloric acid, in order to circumvent the solubility problem, sulfuric acid and potassium sulfate were used to maintain the H^+ concentration and ionic strength, respectively.

RESULTS AND DISCUSSION

Effect of reactants on the reaction rate

The kinetic study at different initial concentrations of reactants, [Cr(VI)], [PSAA] and [H^+], at fixed concentrations of the other substances showed first--order dependence on Cr(VI), PSAA and H^+. The constancy of the pseudo-first--order rate constant values with increasing concentration of Cr(VI) in the presence of CTAB (Table I) and excellent linear plots of log [Cr(VI)] against time are in agreement with the first-order dependence of the reaction on the Cr(VI) concentration. The observed trend of the constant k_1 with varying Cr(VI) con-

TABLE I. Effect of the Cr(VI) and PSAA concentrations on the rate of the CTAB-mediated reaction. [H^+] = 0.50 mol dm^{-3}, [CTAB] = 5.0×10^{-2} mol dm^{-3}, I = 0.65 mol dm^{-3}

[PSAA] / 10^{-2} mol dm^{-3}	[Cr(VI)] / 10^{-4} mol dm^{-3}	k_1 / 10^{-5} s^{-1}	k_2 / 10^{-3} mol^{-1} dm^3 s^{-1}
3.0	5.0	3.16±0.01	1.05±0.03
5.0	5.0	6.03±0.01	1.21±0.02
7.0	5.0	7.86±0.01	1.12±0.01
10	5.0	11.6±0.02	1.16±0.02
5.0	3.0	6.31±0.01	1.26±0.02
5.0	7.0	6.15±0.02	1.23±0.04

centrations is contradictory with that of the reaction in the absence of micelles, where a negative effect with concentration of Cr(VI) was registerd.[23] The observed constancy of the k_1 values in the CTAB-mediated reaction indicates that dimer formation was prevented by the surfactant molecules.

The unit-order dependence on PSAA was evidenced by the unit slope of the double logarithmic plot of k_1 *vs.* [PSAA] and invariant second-order rate constant values at different PSAA concentrations (Table I). The first-order dependence with respect to H^+ in the presence of CTAB is assessed from the unit slope of the log–log plot of k_1 *vs.* $[H^+]$ and the constant values of $k_1/[H^+]$ (Table II).

TABLE II. Effect of the H^+ concentration and temperature on the rate of the reaction; [PSAA] = = 5.0×10^{-2} mol dm^{-3}, [Cr(VI)] = 5.0×10^{-4} mol dm^{-3}, [CTAB] = 5.0×10^{-2} mol dm^{-3}, solvent: 95 % H_2O–5 % CH_3CN (*V*/*V*)

$[H^+]$ / mol dm^{-3}	k_1[a]$\times10^5$ s^{-1}	$k_1\times10^4/[H^+]$ mol^{-1} dm^3 s^{-1}	*t* °C	k_2[b]$\times10^4$ mol^{-1} dm^3 s^{-1}
0.25	2.64±0.02	1.06±0.08	20	3.61±0.03
0.35	3.65±0.01	1.04±0.03	25	7.20±0.01
0.50	6.03±0.01	1.20±0.02	30	12.1±0.02
0.75	7.84±0.02	1.12±0.03	35	18.2±0.03

ΔH = 80.0±3.25 kJ mol^{-1}
ΔS = –37.3±11.3 J mol^{-1} K^{-1}

[a]I = 0.80 mol dm^{-3}; [b]I = 0.65 mol dm^{-3}, $[H^+]$ = 0.50 mol dm^{-3}

Effect of temperature and activation parameters

In order to evaluate the activation parameters, the reaction in CTAB medium was performed at four different temperatures, *viz*., 20, 25, 30 and 35 °C. The second-order rate constants, k_2 and the activation parameters, ΔS and ΔH were evaluated respectively from the intercept and slope of the Eyring plot of log k_2/T *vs.* $1/T$ and are presented in Table II. The value of the entropy of activation is useful for the interpretation of the structure of transition state. A comparison of ΔS with that of the reaction in aqueous medium (ΔS = –24.5 J mol^{-1} K^{-1}) shows that the reactant molecules tend to associate in a well-structured activated state in the micellar medium with less degrees of freedom.

Effect of variation of the CTAB concentration

In order to explore the role of the CTAB surfactant micelles on the reaction rate, the reaction was studied as a function of the CTAB concentration at constant concentrations of Cr(VI), PSAA and H^+ at 30 °C. The effect of the surfactant CTAB on the rate of the reaction and the calculated pseudo-first-order rate constants are presented in Table III. The variation of the CTAB concentration showed two distinct effects on the rate of the reaction, *i.e.*, an initial increase in rate up to 0.5×10^{-2} mol dm^{-3} followed by a steady downward trend. There was a well-defined maximum in the rate profile at 0.5×10^{-2} mol dm^{-3} of CTAB.

TABLE III. Effect of the CTAB concentration on the rate of the reaction. [PSAA] = 5.0×10^{-2} mol dm^{-3}, [Cr(VI)] = 5.0×10^{-4} mol dm^{-3}, [H^+] = 0.50 mol dm^{-3}, solvent: 95 % H_2O–5 % CH_3CN (*V*/*V*), *I* = 0.65 mol dm^{-3}

[CTAB] / 10^{-2} mol dm^{-3}	k_1 / 10^{-5} s^{-1}
0	8.35±0.02
0.10	8.72±0.01
0.25	9.37±0.02
0.50	10.9±0.04
0.75	10.2±0.07
1.0	10.0±0.02
2.0	8.22±0.04
3.0	7.13±0.03
5.0	6.03±0.01
7.0	4.93±0.02
9.0	3.82±0.02
10	3.31±0.05
12	2.50±0.03

Substituent effect

The study of the influence of substituents on the rate of a reaction often provides insight into the nature of the transition state and mechanism. To probe the reaction mechanism in the cationic micellar medium, the substituent effect was studied with several *meta*- and *para*-substituted PSAAs at 30 °C in the presence of CTAB. The investigation showed that the rate of the reaction was accelerated by electron-donating groups and retarded by electron-withdrawing groups present in the phenyl ring of PSAAs. This indicates that electron-donating substituents enhance the nucleophilicity of the sulfur and facilitate the attack by the oxidizing species in the rate-determining step. A Hammett plot (Fig. 1) drawn for the kinetic data (Table IV) obtained in CTAB medium at 30 °C shows excel-

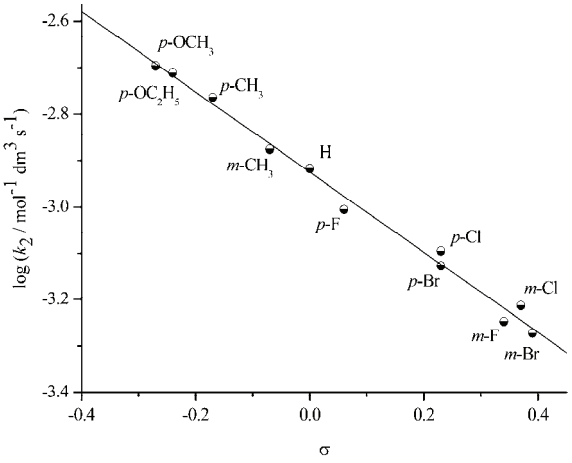


Fig. 1. Hammett plot for CTAB mediated reaction at 30 °C; ρ = = –0.864±0.03; r = 0.996.

lent correlation with the σ values affording negative ρ value (–0.864), which is lower in magnitude than that of the reaction in the absence of CTAB. This showed that the reaction in CTAB micellar medium was less sensitive to substituent effects, which is against the Reactivity–Selectivity Principle. However, the obtained ρ value is comparable with that of the reaction in the presence of sodium dodecyl sulfate (SDS).[25] The observed negative reaction constant supports the generation of an electron deficient sulfur center in the transition state and the linear relationship proves the operation of same mechanism in all the substituted PSAAs.

TABLE IV. Second-order rate constants for the reactions of substituted PSAAs with Cr(VI) in CTAB medium; [*X*-PSAA] = 3.0×10^{-2} mol dm^{-3}, [Cr(VI)] = 5.0×10^{-4} mol dm^{-3}, [H^+] = 0.50 mol dm^{-3}, I = 0.65 mol dm^{-3}, T = 30 °C

Cmpd. No.	X	k_2 / 10^{-4} mol^{-1} dm^3 s^{-1}	k_2^{CTAB}/k_2^{aq}.
1	*m*-Br	5.35±0.10	0.054
2	*m*-Cl	6.12±0.05	0.059
3	*m*-F	5.66±0.04	0.046
4	*p*-Cl	8.04±0.02	0.047
5	*p*-Br	7.47±0.02	0.041
6	*p*-F	9.88±0.01	0.041
7	H	12.1±0.02	0.039
8	*m*-CH_3	13.3±0.03	0.032
9	*p*-CH_3	17.2±0.02	0.032
10	*p*-OC_2H_5	19.4±0.05	0.033
11	*p*-OCH_3	20.1±0.02	0.029

Product analysis

The organic product of the reaction was identified from LC-MS and FT-IR spectral studies as (methylsulfonyl)benzene. The recorded LC-MS spectrogram shows that the product eluted at a retention time of 1.829 min ionized in the atmospheric pressure chemical ionization (APCI) (+) mode at *m*/*z* 157 with a relative abundance of 86 %, which corresponds to the mass of methyl phenyl sulfone (*m*/*z* = 156). The IR spectrum of the product showed strong absorptions for the symmetric and asymmetric stretching vibrations of the >SO_2 group at 1148 and 1290 cm^{-1}, respectively. The final product of Cr(VI) was identified as Cr(III) from the absorption spectrum of the reaction mixture after completion of the reaction, which displayed two absorption peaks in the region 410 and 580 nm (Fig. 2) corresponding to the d–d transitions of Cr(III). This finding is in contradiction with the results observed in the reaction without micelles when a blue shift was observed in the absorption peaks of Cr(III).[23] It was assumed that in the absence of CTAB, Cr(III) formed a complex with the organic product, methyl phenyl sulfone. In a CTAB micellar medium, methyl phenyl sulfone may be solubilized deep in the micelle by hydrophobic interaction while the Cr(III) ion

existed in the aqueous phase as the result of electrostatic repulsion. Thus, the methyl phenyl sulfone became inaccessible for complexation with and hence there was no shift in the characteristic peaks of the Cr(III) ion in the absorption spectrum of the product.

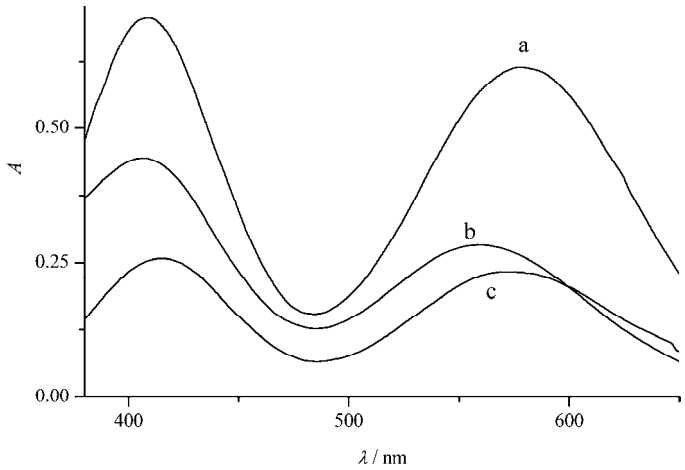


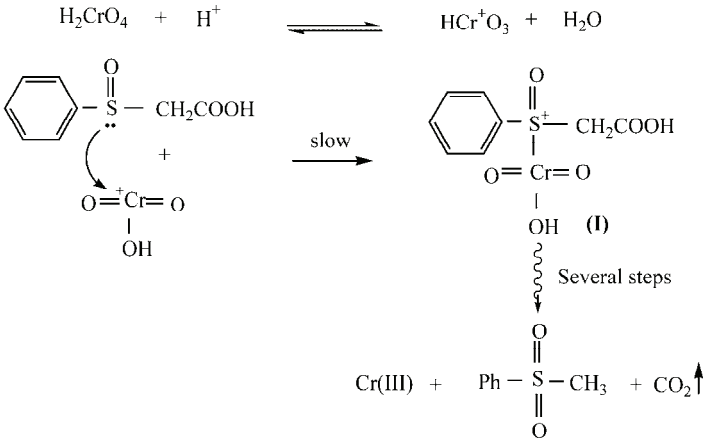
Fig. 2. Absorption spectrum of: a) free Cr(III) ion, b) the reaction mixture in CTAB after completion and c) the reaction mixture without CTAB after completion.

Reaction mechanism in micellar media

The kinetic results reveal that the redox reaction of PSAA and Cr(VI) follows the rate law:

$$-\frac{\mathrm{d[Cr(VI)]}}{\mathrm{d}t} = k[\mathrm{PSAA}][\mathrm{H^+}][\mathrm{Cr(VI)}] \quad (1)$$

From the kinetic evidence, it is clear that the redox reaction between PSAA and Cr(VI) in CTAB micelle follows unit-order with respect to Cr(VI), PSAA and H^+, as observed in the absence of micelles. Based on these kinetic observations, the substituent effect and the formation of methyl phenyl sulfone as the product, it is concluded that the same reaction mechanism as in aqueous medium,[23] was operative in CTAB micellar medium (Scheme 1). Scheme 1 satisfactorily explains the retardation effect observed in cationic micellar medium. The positive charge on the cationic micelle, CTAB prevents the approach of the protonated species of Cr(VI) and also disfavors the formation of positively charged sulfonium ion intermediate (**I**) in the rate determining step by coulombic forces. The observed micellar effect thus favors the proposed mechanism involving the formation of positively charged sulfonium ion intermediate because of nucleophilic attack of sulfur atom of PSAA on Cr of $HCrO_3^+$.



Scheme 1. Mechanism of oxidative decarboxylation of phenylsulfinylacetic acid.

To afford spectral evidence for the mechanism of the reaction of PSAA with Cr(VI) in micellar media, the reaction mixture in the presence of CTAB was scanned in the UV–Vis region at different time intervals (Fig. 3). The UV–Vis absorption spectra of the reaction mixture in CTAB micellar medium displayed a similar pattern of absorption peaks to that in the absence of micelles, which may be taken as positive evidence for the existence of the same type of intermediate both in the aqueous and micelle-mediated reactions. The change in the absorption spectra of Cr(VI) with PSAA, the significant hyperchromic shift and the widen-

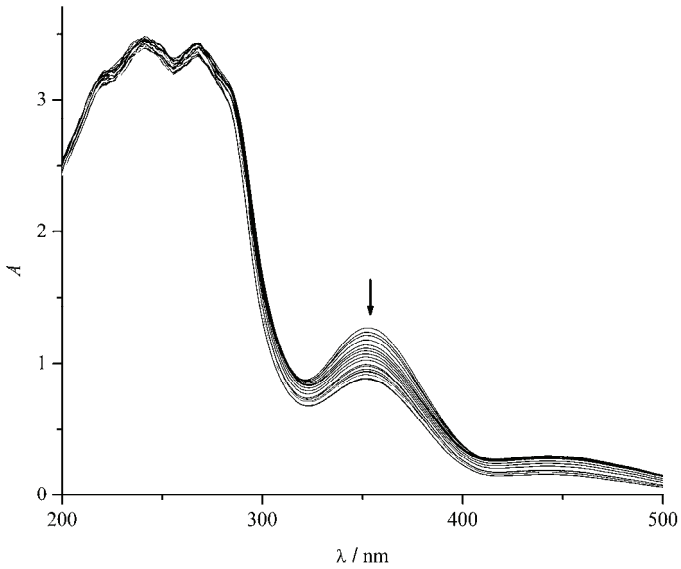


Fig. 3. Variation of absorbance of the reaction mixture with time. [PSAA] = 5.0×10^{-2} mol dm^{-3}, [Cr(VI)] = 5.0×10^{-4} mol dm^{-3}, [H$^+$] = 0.50 mol dm^{-3}, [CTAB] = 5.0×10^{-2} mol dm^{-3}.

ing of the peak in the region 200 to 300 nm for the reaction mixture (Fig. 3) also confirmed the existence of the Cr(VI)–PSAA complex (**I)** having a direct S–Cr bond, as in the case of the reaction in the absence of CTAB.

The UV–Vis absorption spectrum of Cr(VI) in CTAB medium showed a hyperchromic shift in the region of 200 to 300 nm and a hypochromic shift near 350 nm. Furthermore, a red shift of the wavelength from 351 to 360 nm was observed in the spectrum of Cr(VI) in CTAB medium, which indicates that the absorption spectrum of Cr(VI) was affected by the surfactant CTAB (Fig. 4). Although this spectrum appears to be similar to the one in SDS medium,[25] a notable difference in SDS medium was the observation of hyperchromic shifts in both the peaks of Cr(VI). The similarity of absorption spectra of the reaction mixture in both SDS and CTAB media demonstrated the involvement of the same transition state intermediate in both cases.

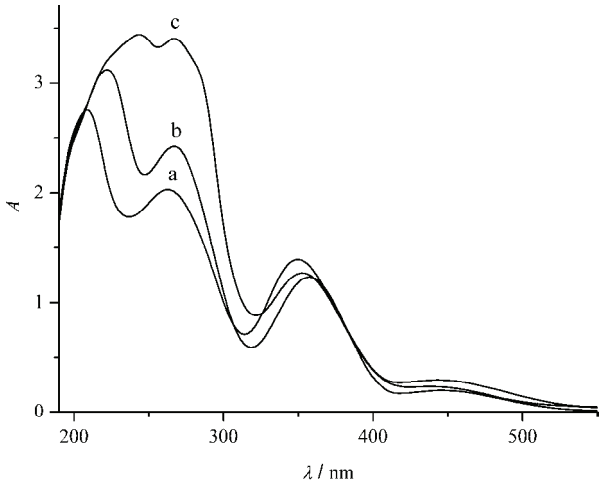


Fig. 4. Absorption spectra of: a) Cr(VI), b) Cr(VI) in CTAB and c) reaction mixture; [PSAA] = 5.0×10^{-2} mol dm^{-3}, [Cr(VI)] = 5.0×10^{-4} mol dm^{-3}, [H^+] = 0.50 mol dm^{-3}, [CTAB] = 5.0×10^{-2} mol dm^{-3}.

Interpretation of the micellar effect

The effect of ionic micelles on the reaction rate of bimolecular reactions is mainly due to the association or incorporation of reactants through electrostatic or hydrophobic interactions within the small volume of the self-assemblies.[12] In the present cationic micellar medium, the positively charged head groups of CTAB prevented the approach of the oxidizing species $HCrO_3^+$ by electrostatic repulsion and so the oxidizing species remained in aqueous phase. The other reactant PSAA that is neutral preferably partitioned in the micellar pseudo-phase of CTAB by hydrophobic interaction, and hence, became unavailable for the reaction with $HCrO_3^+$ in aqueous phase. Thus, the overall retarding effect obs-

erved with increasing CTAB concentration above 0.5×10^{-2} mol dm^{-3} was due to preferential partitioning of PSAA and $HCrO_3^+$ in the micellar pseudo-phase and aqueous medium, respectively, followed by a decrease in stoichiometric concentration of both reactants in both the phases. Consequently, the reaction rate in both aqueous and micellar phases decreased that led to an overall rate retardation. Moreover, during the course of the reaction, a positive charge developed on the sulfur due to electron transfer from the sulfur atom of PSAA to Cr(VI), which was prevented at higher concentrations of CTAB.

The increase in rate constant at low concentrations of CTAB up to 0.5×10^{-2} mol dm^{-3} is interesting and this may be due to a specific salt effect. As sulfuric acid and potassium sulfate are used, respectively, to maintain the H^+ concentration and ionic strength in the CTAB medium, the reaction mixture contained excess of SO_4^{2-}. The trend of binding efficiency of counter ions with micelles follows the Hofmeister series.[33] As SO_4^{2-} is positioned in the place of higher order in the Hofmeister series, the SO_4^{2-} has a high probability of binding with the positively charged CTAB. It was shown that strong binding of SO_4^{2-} to the micellar surface of cetyltrimethylammonium ion yields micelle properties which differ considerably from those with other counter ions.[34] Among the homologous of CTAX surfactants, X = Cl^-, Br^-, SO_4^{2-}, CTA sulfate is the only one that exhibits a positive enthalpy of micellization as a result of the strong and specific affinity of SO_4^{2-} for the micelle interface.[35] Furthermore, the micelle size and reactivity of CTAB aggregates were found to be affected by divalent counter ions, such as SO_4^{2-}, as a result of strong binding.[36,37]

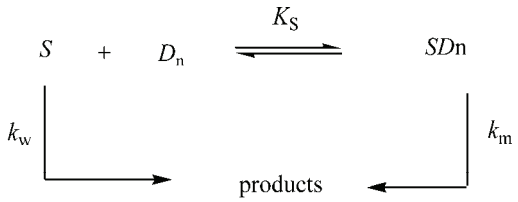
Based on these facts, it is assumed that complete neutralization of the positive charges on the CTAB micellar surface may occur at low concentrations of CTAB, *i.e.*, up to 0.5×10^{-2} mol dm^{-3}, as a result of strong binding of SO_4^{2-}. Under such condition, inclusion of $HCrO_3^+$ into CTAB micellar phase is possible. Thus, the accelerating effect observed in the region of low concentrations of CTAB may be due to increasing stoichiometric concentrations of both reactants in micellar phase, which favors the formation of the sulfonium ion intermediate. It is worth mentioning here that Kabir-ud-Din *et al.*[38] observed a substantial decrease in rate in the oxidation of oxalic acid by Cr(VI) in CTAB medium in the presence of added salt, Na_2SO_4. They explained the result based on the strong binding of SO_4^{2-} to CTAB, which prevents the inclusion of the reactive species $HCrO_4^-$.

Treatment of pseudo-phase models

Various models have been proposed to describe the variation of reaction rate in the presence of micelles. Among them, the pseudo-phase model is the most commonly used model to interpret the catalytic/inhibitory activity of micelles and to calculate binding parameters.

Menger–Portnoy model

The observed rate inhibition in the CTAB medium could be analyzed by considering the distribution pattern of reactants between the micellar and aqueous phases by application of the pseudo-phase kinetic model proposed by Menger and Portnoy and its modified forms.[39–42] This model considers the partitioning of the substrate between the aqueous and micellar pseudo-phases as given in Scheme 2 proposed by Menger and Portnoy.[39]



Scheme 2. Menger–Portnoy model.

From Scheme 2, the observed rate constant, k_ψ, is given by:

$$k_\psi = \frac{k_w + k_m K_S[D_n]}{1 + K_S[D_n]} \quad (2)$$

where D_n, S and SD_n represent micellar surfactant, free substrate and associated substrate, respectively, and k_w and k_m are the pseudo-first-order rate constants in aqueous and micellar phases, respectively, K_S is the binding constant of the substrate with the surfactant and $[D_n]$ is the concentration of the micellar surfactant, which is related to the stoichiometric concentration of the surfactant, $[D]_T$ and critical micelle concentration, *cmc* as $[D_n] = [D]_T - cmc$. The *cmc* value of CTAB was taken from the literature as 9.2×10^{-4} mol dm^{-3}.[43,44] The applicability of Menger–Portnoy model (Scheme 2) for the observed inhibitory effect of CTAB in the oxidative decarboxylation of PSAA was tested by modifying Eq. (2) as:

$$\frac{1}{(k_w - k_\psi)} = \frac{1}{(k_w - k_m)} + \frac{1}{(k_w - k_m)K_S[D_n]} \quad (3)$$

The modified Eq. (3) was successfully applied to various micellar inhibition reactions by different researchers.[45–47] Using the rate data, the values of $1/(k_w - k_\psi)$ were plotted against $1/[D_n]$ in the concentration range 2.0×10^{-2}–12×10^{-2} mol dm^{-3}. The Menger–Portnoy model is applicable to micellar inhibition only if the plot of $1/(k_w - k_\psi)$ *vs.* $1/[D_n]$ is linear with a positive slope and intercept.[48] In the present case, although the plot of $1/(k_w - k_\psi)$ *vs.* $1/[D_n]$ was linear, the plot afforded a negative intercept, showing its inadequacy to explain the micellar effect.

According to Rajasekaran *et al.*,[49] as double reciprocal plot is involved in this model, there exists some uncertainty in the intercept. In order to remove this uncertainty, they modified Eq. (3) to:

$$(k_\psi - k_w) = -\frac{(k_\psi - k_w)}{K_S[D_n]} + (k_m - k_w) \quad (4)$$

The plot of $(k_\psi - k_w)$ *vs.* $(k_\psi - k_w)/[D_n]$ should be linear and from the slope and intercept of the plot, the rate constant for the micellar phase, k_m, and the substrate–micelle binding constant, K_S could be evaluated. However, for the present reaction, the plot of $(k_\psi - k_w)$ *vs.* $(k_\psi - k_w)/[D_n]$ was non-linear (Fig. 5), which indicates the inapplicability of the Menger–Portnoy model to the inhibition of this reaction by CTAB.

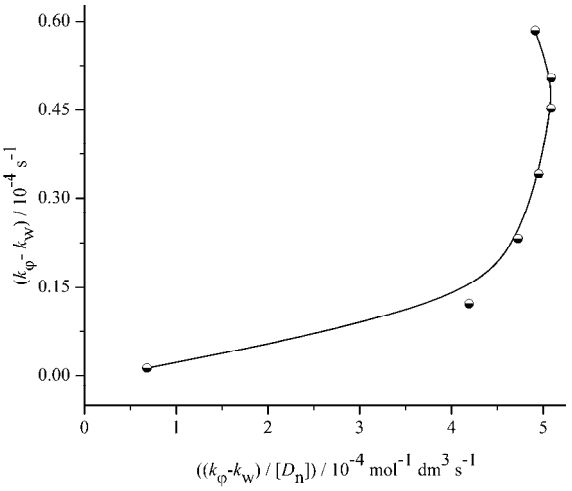


Fig. 5. Validity of Menger–Portnoy model.

Piszkiewicz cooperative model

Many micellar reactions were also explained by the cooperative model developed by Piszkiewicz,[50–52] which is analogous to the Hill model applied to enzyme-catalyzed reactions. This model was developed for micelle-catalyzed reactions showing a maximum rate followed by inhibition, as was observed in the present case. This model relates the cooperativity between a neutral species of the reaction and a surfactant to form the reactive micelles, as in Scheme 3 that was proposed by Piszkiewicz.[50]

From Scheme 3, the observed rate constant, k_ψ could be expressed as a function of the concentration of surfactant:

$$k_\psi = \frac{k_m[D]^n + K_D k_w}{K_D + [D]^n} \quad (5)$$

Equation (5) can be rearranged to:

$$\log \frac{(k_\psi - k_w)}{(k_m - k_\psi)} = n \log[D] - \log K_D \quad (6)$$

where, k_m is the rate constant at maximum surfactant concentration within the given range and $k_m \approx 0$ if the reaction is inhibited by surfactant.[19,49,53] n is the index of cooperativity that is a measure of the association of additional surfactant molecules to an aggregate in the whole surfactant concentration range, K_D is the dissociation constant of micellized substrate back to its free components and its inverse is K that is the association constant of the micelle–substrate complex. The advantage of the Eq. (6) is that it does not require knowledge of the *cmc* value of the surfactant used. Although Eq. (6) is generally used for micelle-catalyzed reactions, it was also applied to micellar inhibition reactions with certain modifications.[19,54–57]

Since CTAB retards the rate to a significant extent at high concentrations, it is assumed that the incorporation of positively charged oxidizing species, $HCrO_3^+$ into the positively charged micelle is negligible. Thus at higher CTAB concentrations, $HCrO_3^+$ is mainly solubilized in the aqueous phase and hence, it is presumed that $k_m \approx 0$. Under these conditions, Eq. (6) becomes:

$$\log \frac{(k_w - k_\psi)}{k_\psi} = n \log[D] - \log K_D \quad (7)$$

In the present reaction, the plot of log $[(k_w–k_\psi)/k_\psi]$ *vs.* log [CTAB] was found to be linear (Fig. 6, r = 0.996) in the rate retardation region of CTAB, 3.0×10^{-2}–12×10^{-2} mol dm^{-3}. The linearity of the plot obtained with the micelle support the positive cooperativity between PSAA and micelles to form reactive micelles, which indicates that the PSAA molecules are included into the micellar phase. The Piszkiewicz parameters, n and K_D determined, respectively, from the slope and intercept of the linear plot were n = 1.86 and $K_D = 9.11\times10^{-3}$. The association constant, K computed from the reciprocal of K_D was 109.82, which

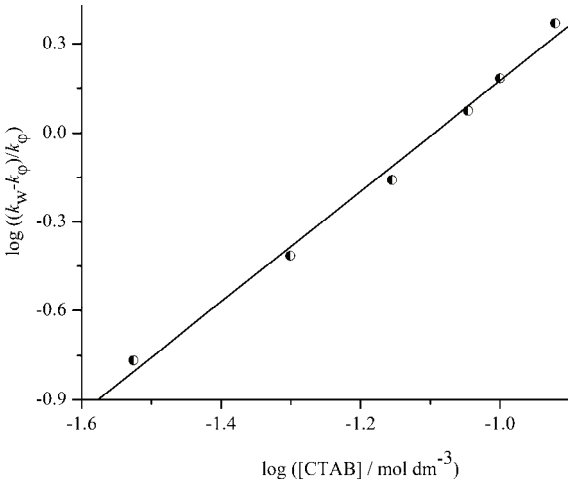


Fig. 6. Applicability of Piszkiewicz cooperative model.

indicates binding of PSAA to the micelles. The value of *n* greater than unity indicates positive cooperativity, *i.e.*, the binding of the first molecule of the substrate makes it easier for subsequent molecules to bind. Furthermore, the value of *n* is far less than the aggregation number (20 to 100) of the surfactants, which indicates the formation of catalytically productive sub-micellar aggregates.[38]

CONCLUSIONS

The CTAB mediated redox reaction of PSAA with Cr(VI) displayed two different effects, an initial increase in the rate constant followed by a sharp decrease with increasing concentration of CTAB. The observed trends of the rate constant were explained in terms of specific binding of SO_4^{2-} on the micellar surface and interactions such as electrostatic and hydrophobic. The kinetic data were treated for micellar effects with the Menger–Portnoy and Piszkiewicz pseudo-phase models. The results obtained from the kinetic studies were better fitted with the Piszkiewicz model and hence, the binding constant for PSAA with CTAB micelles was evaluated using this model.

ИЗВОД

ДИНАМИКА РЕАКЦИЈЕ ФЕНИЛСУЛФИНИЛАЦЕТАТНЕ КИСЕЛИНЕ СА Cr(VI) У ПРИСУСТВУ ЦЕТИЛТРИМЕТИЛАМОНИЈУМ-БРОМИДА: ТРЕТМАН ПСЕУДО-ФАЗНИМ МОДЕЛИМА

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Утицај цетилтриметиламонијум бромида (CTAB) на оксидативну декарбоксилацију фенилсулфинилацетатне киселине (PSAA) и неколико *мета*- и *пара*-супституисаних фенилсулфинилацетатних киселина (PSAA-а) са Cr(VI) је испитиван у раствору 95 % H_2O–5% CH_3CN. Почетна брзина реакције расте при малим [CTAB], а затим долази до наглог пада брзине реакције при већим [CTAB]. Раст почетне брзине може бити објашњен јаком везом између SO_4^{2-} и позитивно наелектрисане мицеларне површине. Специфична расподела PSAA у мицеларној фази услед хидрофобних интеракција, односно оксидујуће врсте $HCrO_3^+$ у воденој фази услед електростатичког одбијања, доводе до успоравања брзине при већим [CTAB]. Hammett дијаграм са различитим супституисаним PSAA-а је показао одличну корелацију негативне вредности ρ што подржава предложени мехнизам који укључује формирање интермедијера сулфонијум катјона. Добијена вредност ρ у CTAB средини је нешто нижа у поређењу са вредношћу добијеном за водену средину. Квантитатвина анализа података за инхибицију брзине реакције од стране CTAB је урађена применом Menger– Portnoy и Piszkiewicz псеудо-фазног модела. Константа везивања PSAA за мицелу је одређена на основу Piszkiewicz кооперативног модела.

(Примљено 19. септембра, ревидирано 28. децембра, прихваћено 31. децембра 2014)

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