

Micellar Effects on the Kinetics of Cerium(IV) Oxidation and the Cerium(IV)-Catalyzed Belousov–Zhabotinsky Reaction with Methyl-, Ethyl-, or Benzylmalonic Acid

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The kinetics of the oxidation of methyl- (MeMA), ethyl- (EtMA), or benzylmalonic (BzMA) acid by ceric ions and the Ce(IV)-catalyzed Belousov–Zhabotinsky (BZ) reaction with these substrates have been studied at 20.0 °C in stirred batch conditions in the absence and the presence of the cationic surfactant cetyltrimethylammonium nitrate (CTAN). Some measurements have also been performed using the anionic surfactant sodium dodecyl sulfate (SDS). Addition of increasing amounts of CTAN has a little inhibitory influence on the redox process with MeMA and EtMA, whereas it causes a significant enhancement with BzMA. Small decreasing rate effects are observed in the presence of SDS. In the absence of surfactants, the BZ systems with MeMA and EtMA show oscillatory behavior after an induction period, whereas no oscillations are found with BzMA. In the presence of CTAN all the systems exhibit oscillations after an induction period that is shortened markedly with increasing CTAN concentration and that, at constant [CTAN], increases in the order BzMA < MeMA < EtMA. Added CTAN also affects the oscillation period and the duration of the raising portion of an oscillatory cycle. The surfactant SDS affects these oscillatory parameters to a different extent. Explanations of the experimental results are provided.

Introduction

The organized surfactant assemblies are well-known to affect chemical equilibria and reactivities^{1–4} by selectively sequestering the reagent substrates by means of electrostatic and/or hydrophobic interactions. In the past, studies of the effects of different surfactant self-assembling systems (micelles,² vesicles,³ micro-emulsions⁴) on the kinetics of various chemical reactions have been performed by some of us, devoting particular attention to the type of interactions involved in the binding of the reactants to the micellar aggregates.

As a continuation of these studies, we have now begun to investigate the influence of micelle-forming surfactants on the Belousov–Zhabotinsky (BZ) oscillating reactions,^{5–8} that in the last years have received growing attention not only for the attempt to elucidate their complex mechanism^{9,10} but also for their relevance to the periodic phenomena observed in biochemistry¹¹ and in other fields.⁸ The chemical oscillating systems involve ionic reactants and intermediates, which are expected to interact with oppositely charged ionic micelles with likely consequent changes in both the reaction kinetics and the characteristic oscillatory properties. As far as we know, only a few systematic studies of the chemical oscillating reactions in organized surfactant systems^{12,13} so far exist.

The "classic" BZ oscillating reaction⁵ consists of the bromination and oxidation of malonic acid or its derivatives by bromate ions in strongly acidic aqueous medium, catalyzed by a one-electron redox couple. The most commonly used redox couple is Ce(IV)/Ce(III). Field, Körös, and Noyes¹⁴ proposed a mechanism (known as FKN mechanism) that describes the

fundamental processes involved in the BZ oscillating reaction. Models¹⁵ that substantiate the principal features of the FKN mechanism and take into account subsequent experimental results have been developed.

In this paper we report the results of the kinetic study of the cerium(IV) oxidation of three monosubstituted malonic acids RMA [R = Me (methyl), Et (ethyl), or Bz (benzyl)] and of the Ce(IV)-catalyzed BZ reaction with these substrates in the absence and the presence of varying amounts of the cationic micelle-forming surfactant cetyltrimethylammonium nitrate (CTAN). Some kinetic measurements have been carried out in the presence of the anionic surfactant sodium dodecyl sulfate (SDS). All the experiments have been performed spectrophotometrically in stirred batch conditions at 20.0 ± 0.1 °C in aqueous 1.00 mol dm⁻³ sulfuric acid solution.

The present work was stimulated by the observation,⁷ made during some preliminary kinetic measurements, that the BZ reaction with benzylmalonic acid (BzMA), unlike the MeMA- and EtMA-BZ systems, did not exhibit oscillatory behavior under the same experimental conditions, while oscillations took place in the presence of cationic CTAN micelles with an induction period that was shorter than those of the remaining systems tested.

Recently, Ruoff et al.¹⁶ used a potentiometric method to study the influence of oxygen or argon bubbling in the Ce(IV)-catalyzed BZ reaction with various substrates RMA [R = H, Me, Et, Ph (phenyl), and Bz] and also observed no oscillations in the case of BzMA either in oxygen or argon atmospheres. To our knowledge, no further investigations of the BZ reaction with benzylmalonic acid have been performed, while there exist several studies of oscillating chemical reactions with other substituted malonic acid derivatives. Ruoff et al.¹⁷ and Jwo et al.¹⁸ studied the BZ reaction with MeMA catalyzed by Ce(III) or the ferroin ion. Moreover, Jwo et al.¹⁹ investigated the Mn-

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TABLE 1: Observed Pseudo-First-Order Rate Constants k_{obs} (10^{-4} s^{-1}) for the Ce(IV) Oxidation of MeMA, EtMA, and BzMA at Varying Substrate Concentrations^a ($t = 20.0^\circ \text{C}$)

[RMA]/ $10^{-2} \text{ mol dm}^{-3}$	MeMA ^b	EtMA ^b	BzMA ^b
1.00	4.8	3.17	7.7
2.00	8.8	5.2	14.5
10.0	33	18.7	57
20.0	60	32.2	85

^a [Ce(IV)] = $4.00 \times 10^{-4} \text{ mol dm}^{-3}$, [H₂SO₄] = 1.00 mol dm^{-3} .^b $k_2 = 0.011 \pm 0.003$, 0.004 ± 0.002 , and $0.018 \pm 0.002 \text{ s}^{-1}$ for MeMA, EtMA, and BzMA, respectively; $K_m = 0.21 \pm 0.06$, 0.12 ± 0.06 , and $0.23 \pm 0.02 \text{ mol dm}^{-3}$ for MeMA, EtMA, and BzMA, respectively.

(II)-catalyzed oscillating reaction with MeMA, EtMA, or butylmalonic acid (BuMA). Jwo's group also studied the BZ reaction with PhMA²⁰ catalyzed by Ce(III), Mn(II), or ferroin ion and the Ce(III)- or ferroin-catalyzed BZ reaction with EtMA and BuMA.²¹

Experimental Section

Potassium bromate, Ce(SO₄)₂·4H₂O, MeMA, EtMA, BzMA, and sulfuric acid were of commercial analytical quality (Fluka) and used without further purification. Cetyltrimethylammonium nitrate was obtained from the corresponding bromide (Merck) by treatment with AgNO₃ and purified as described elsewhere.²² The cationic surfactant in nitrate form was used to avoid addition of bromide ions in the BZ systems. The presence of nitrate anions in solutions does not interfere with the kinetics studied. Sodium dodecyl sulfate (Fluka) was purified by recrystallization from ethanol. Stock solutions of sulfuric acid were standardized by acid–base titration. Deionized water from reverse osmosis (Elga, model Option 3) having a resistivity higher than 1 MΩ cm was used to prepare all solutions. Ce(IV)–RMA subsystems and oscillating mixtures for kinetic runs were obtained from stock solutions in 1.00 mol dm^{-3} sulfuric acid.

Kinetic experiments were carried out spectrophotometrically by recording the changes in the Ce(IV) absorbance at 350 nm with a computer-controlled Beckman model DU-640 spectrophotometer, equipped with thermostated compartments for 1.00 cm cuvettes and an appropriate magnetic stirring apparatus. All runs were carried out in stirred batch conditions.

The kinetics of the oxidation of the organic substrates by cerium(IV) were studied in the presence of a large excess of organic substrate over the Ce(IV) species. The observed pseudo-first-order rate constants, k_{obs} , were obtained from the linear least-squares fit of the plot of $\ln(A_t - A_\infty)$ vs time (A = absorbance) and were reproducible to within $\pm 3\%$. The k_{obs} values were found to be independent of the initial Ce(IV) concentration, and consequently, the oxidation rates are first order with respect to the oxidizing species. The surfactant concentrations used in all experiments were notably above the critical micelle concentrations²³ to make sure of the existence of micellar aggregates in solution.

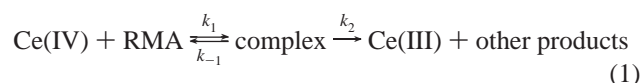
The temperature of the experiments was regulated to $20.0 \pm 0.1^\circ \text{C}$ with a thermostat Heto model DT HetoTerm. All the experimental data were processed with appropriate computer programs.

Results and Discussion

Kinetics of the Ce(IV)–Substrate Subsystems. We have first studied the kinetics of the cerium(IV) oxidation of the substituted malonic acid derivatives in the absence and the presence of the surfactants CTAN and SDS because this redox process is a component of the oscillatory BZ reaction. Table 1

collects the observed pseudo-first-order rate constants obtained for the three substrates in the absence of surfactant at various substrate concentrations. It can be noted that the k_{obs} values depend on both the RMA concentration and the type of the substituent group present in the parent malonic acid. At constant [RMA], the oxidation rate increases following the order EtMA < MeMA < BzMA, paralleling the electron-releasing properties of the substituent group as measured by the Taft^{16,24} constants σ^* .

For a given organic substrate the plot of k_{obs} against [RMA] is curved, whereas a linear trend with positive intercept is obtained when $1/k_{\text{obs}}$ is plotted as a function of $1/[RMA]$. These findings indicate that the reaction order with respect to substrate lies between zero and unity and that the oxidation process for all the three reducing agents examined can be interpreted by the sequential Michaelis–Menten-like mechanism given in eq 1. This mechanism involves^{21,25–29} the initial complex formation between the organic substrate and the reactive cerium(IV) species. Subsequently, the intermediate complex decomposes in the rate-determining electron-transfer step, yielding a free carbon radical and the cerium(III) species. The final reaction products are obtained by the subsequent fast oxidation of the organic radical. This type of mechanism has been proposed previously^{21,25–29} for the oxidation of a variety of organic substrates by cerium(IV) in sulfuric acidic media (i.e., malonic acid and its alkyl derivatives, tartronic, tartaric, citric, glycolic, benzoic, lactic, substituted mandelic acids, etc.).



According to the reaction mechanism (1) the rate constant k_{obs} is equal to $k_2[\text{RMA}]/(K_m + [\text{RMA}])$, where $K_m = (k_{-1} + k_2)/k_1$, and consequently, the $1/k_{\text{obs}}$ vs $1/[\text{RMA}]$ plot yields $1/k_2$ (=intercept) and K_m/k_2 (=slope). The k_2 and K_m values obtained from these plots are also reported in Table 1. It should be noted that, if the rate constant k_2 is much smaller than k_{-1} , the parameter K_m reduces to k_{-1}/k_1 and represents the reciprocal of the equilibrium constant for the intermediate complex formation.

For the Ce(IV)–MeMA reaction previously studied at 25°C in 1.00 mol dm^{-3} sulfuric acid medium, Ruoff and Nevdal²⁶ obtained k_2 and K_m values of $1.42 \times 10^{-2} \text{ s}^{-1}$ and 0.30 mol dm^{-3} , respectively, while Jwo's group²¹ found, using deaerated solutions, the somewhat different values of $3.54 \times 10^{-3} \text{ s}^{-1}$ and $4.07 \times 10^{-2} \text{ mol dm}^{-3}$, respectively. Taking into account the lower temperature used in the present work, our k_2 and K_m values are in good agreement with the data of Ruoff and Nevdal. Moreover, for the Ce(IV)–EtMA system, Jwo et al.²¹ estimated, under our experimental conditions, k_2 and K_m values of $3.05 \times 10^{-3} \text{ s}^{-1}$ and $9.38 \times 10^{-2} \text{ mol dm}^{-3}$, respectively, in fair agreement with our data. To our knowledge, no kinetic study of the Ce(IV)–BzMA system has been carried out before.

With regard to the reactive Ce(IV) species in eq 1, it has been previously suggested^{28,30} that, in sulfuric (or sulfate) acidic media with $[\text{HSO}_4^-]$ (or $[\text{SO}_4^{2-}]) \gg [\text{Ce(IV)}]$, cerium(IV) may exist in a number of sulfate and protonated sulfate complex forms, which may be neutral species [e.g., Ce(SO₄)₂] or bear either positive [e.g., Ce(HSO₄)₃⁺] or negative [e.g., Ce(SO₄)₃²⁻, H₂Ce(SO₄)₄²⁻] charges. From a kinetic point of view, the existence of various cerium(IV) complexes implies serious difficulties²⁸ for the identification of the actual reacting complex involved in the oxidation process. However, all these complexes do not seem to take part significantly in the overall redox rate^{26,28} and only limited complex species, usually the uncharged and

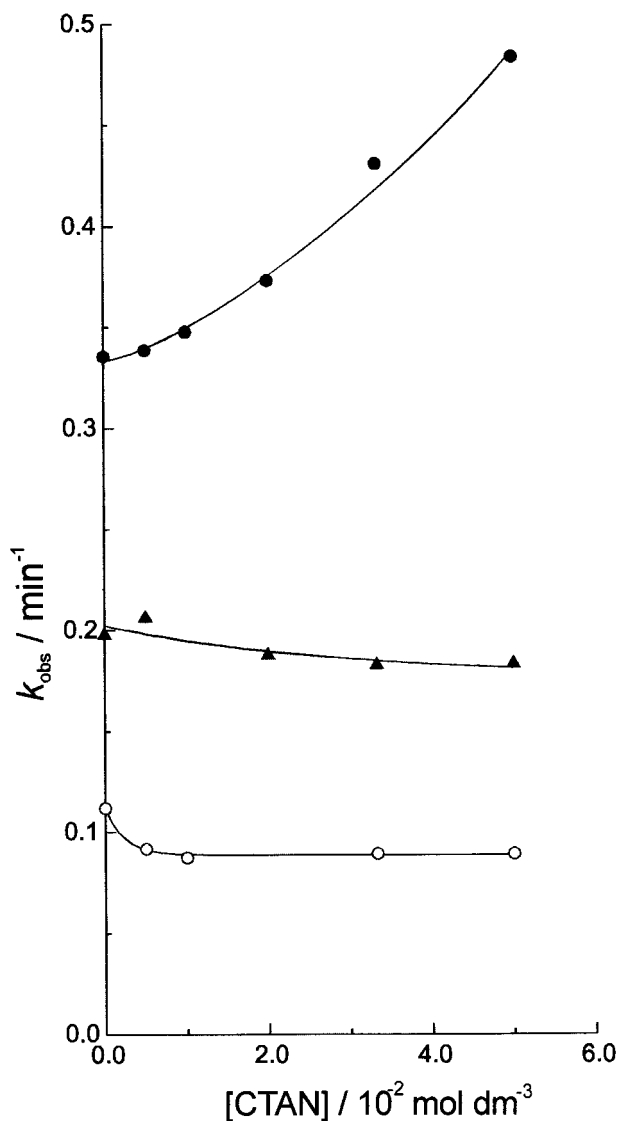


Figure 1. Plot of k_{obs} against [CTAN] for MeMA (▲), EtMA (○), and BzMA (●). $[\text{Ce(IV)}] = 4.00 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{RMA}] = 0.100 \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 1.00 \text{ mol dm}^{-3}$, $t = 20.0^\circ \text{C}$.

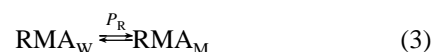
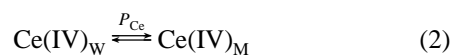
the anionic ones, have been assumed by different investigators as the reactive cerium(IV) species to account for the experimental rate equations obtained.

As to effects of added surfactants on the oxidation reactions under examination, Figure 1 shows that addition of increasing amounts of the cationic surfactant CTAN has little inhibitory influence on the redox process with MeMA and EtMA, whereas it causes a significant enhancement with BzMA. In the presence of the anionic surfactant SDS at the concentration of $5.00 \times 10^{-2} \text{ mol dm}^{-3}$ (equal to the highest [CTAN] used), a very small decrease in the rate constant can be observed with MeMA ($k_{\text{obs}} = 30.7 \times 10^{-4} \text{ s}^{-1}$) and EtMA ($k_{\text{obs}} = 17.2 \times 10^{-4} \text{ s}^{-1}$), but the oxidation rate is retarded to a larger extent with BzMA ($k_{\text{obs}} = 46 \times 10^{-4} \text{ s}^{-1}$).

The observed surfactant effects on the redox reactions can be qualitatively interpreted by the pseudophase model,^{1,2} bearing in mind that, in the presence of cationic CTAN micelles, hydrophilic negatively charged ions [HSO_4^- , SO_4^{2-} , and anionic reactive cerium(IV) species] will compete for binding to the micelle by exchanging the bound (nitrate) counterions, while cationic species [H^+ ; positively charged cerium(IV) species are very unlikely at the acid concentration used in this work] will

be confined to the intermicellar aqueous phase. The converse will occur with the anionic SDS micelles. On the basis of the $\text{p}K_{\text{a}}$'s for the first and second dissociations of the substituted malonic acid derivatives used,³¹ it is reasonable to consider the undissociated acids to be the predominant RMA species present in solution. It is well-known that hydrophobic interactions are primarily involved in the solubilization of uncharged molecules in the micellar pseudophase.

Therefore, if we consider in the CTAN medium the partitioning of both the anionic cerium(IV) species and the neutral substrates between water (w) and the micellar pseudophase (M) as shown in eqs 2 and 3, where the P 's indicate the partition



coefficients, the observed different trend of reactivity of the organic substrates may be ascribed to the different values of the partition coefficients P_{R} (the effects due to the Ce(IV) partitioning are the same with the three substrates).

In fact, BzMA, having the more hydrophobic character due to the benzyl group, would be the most solubilized substrate in the micellar phase as compared to the other reductants. An increase in the CTAN concentration would favor the micellar solubilization and, hence, the reaction between Ce(IV)_{M} and BzMA_{M} (micellar catalysis) that would contribute to an increasing extent to the overall oxidation process. A significant binding of BzMA to nonionic micelles of Triton X-100 [$\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4\text{O}-(\text{C}_2\text{H}_4\text{O})_9,10\text{H}$] and to sodium tetradecyl sulfate was observed before.³² In the case of MeMA and EtMA with lower hydrophobicity (then, with smaller P_{R} values), the substrate concentration in the micellar phase would not be sufficient to make appreciable the contribution of the micellar reaction to the overall redox process, which would proceed substantially in the aqueous phase. On the other hand, the distribution of the substrate MeMA or EtMA between the aqueous and micellar phases would cause a small reduction of the substrate concentration in water. This reduction would increase as [CTAN] increases and determine a small inhibitory surfactant effect on the reaction rate of these two compounds as indeed observed.

These suggestions are supported by the mentioned effects of the anionic surfactant SDS on the oxidation rate. In fact, in the micellar SDS medium only the substrate partitioning (eq 3) has to be taken into account and the same causes seen above for MeMA and EtMA would retard to a different extent, being larger with the more hydrophobic substrate, the redox processes that take place in the aqueous phase. Moreover, it should be noted that the different length of the hydrophobic alkyl chains of the two surfactants is also expected to affect the partition coefficients P_{R} differently and, hence, the extent of the retarding effects of these surfactants.

Finally, note that the opposite effects of the CTAN and SDS micelles on the reaction rate of BzMA substantiate the view that negatively charged cerium(IV) species are involved in the redox process.

Ce(IV)-Catalyzed BZ Systems. In this section we report the behavior of the BZ system with MeMA, EtMA, and BzMA catalyzed by cerium(IV) in the absence and the presence of the surfactants CTAN and SDS. To compare the various results obtained, we have always used the same initial concentrations for all the reactants involved [potassium bromate, RMA, Ce(IV), sulfuric acid].

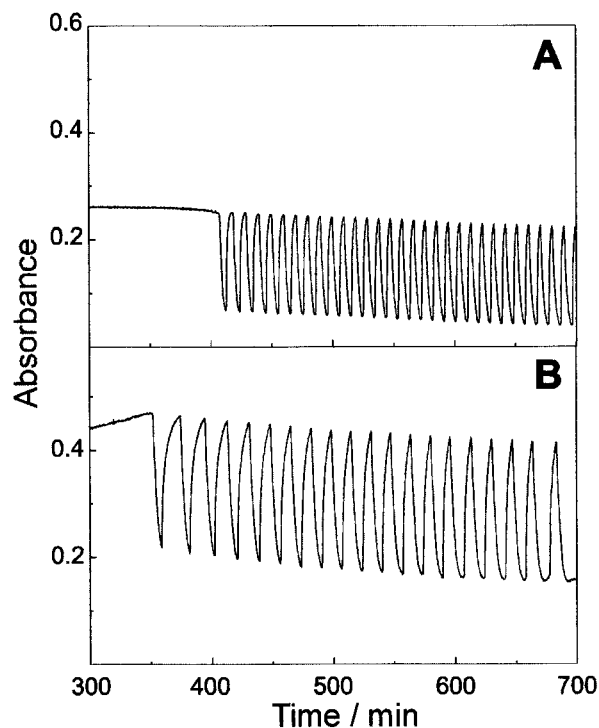


Figure 2. Time dependence of the Ce(IV) absorbance in the absence of surfactants for the BZ systems with MeMA (A) and EtMA (B). $[\text{Ce(IV)}] = 4.00 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{RMA}] = 0.100 \text{ mol dm}^{-3}$, $[\text{BrO}_3^-] = 3.00 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 1.00 \text{ mol dm}^{-3}$, $t = 20.0^\circ\text{C}$.

In the absence of surfactants, oscillations in the system with MeMA have been found to begin after an induction period (IP) of 410 min (Figure 2A), while with EtMA the oscillatory behavior is exhibited (Figure 2B) after 361 min (all the IP values reported in this work are the mean of five different experiments). By contrast, in the case of BzMA no oscillations have been observed, at least up to 120 h (5 days) of observation.⁷ Also, no oscillatory behavior with the latter substrate has been observed recently¹⁶ either in oxygen or in argon atmosphere by using a potentiometric technique.

In the presence of CTAN micelles all three substrates examined have exhibited oscillations after an induction period that depends on both the CTAN concentration and the nature of the substituent in the malonic acid derivatives. It is interesting to note that the most dramatic effect of the surfactant is observed with BzMA as substrate. The system begins to oscillate after an IP that is shorter than those of the other two substrates. Moreover, oscillations in the system soon decrease in amplitude and damp after a much shorter duration with respect to MeMA and EtMA oscillations. Typical oscillating patterns of the three systems in the presence of $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ CTAN are shown in Figure 3.

Figure 4 shows that an increase in the CTAN concentration reduces markedly the induction periods of the three BZ systems under study. Moreover, at each CTAN concentration examined, the effect of the substituent R on the induction period increases in the order $\text{BzMA} < \text{MeMA} < \text{EtMA}$. This sequence is the opposite not only to that observed in the absence of surfactant but also to the increasing electron-releasing properties of the substituents as measured by the Taft σ^* constants.

As to the influence of the anionic micelles of SDS, addition of $5.00 \times 10^{-2} \text{ mol dm}^{-3}$ surfactant (Figure 5) shortens the induction periods of the BZ systems with MeMA and EtMA (IP = 341 and 344 min with MeMA and EtMA, respectively)

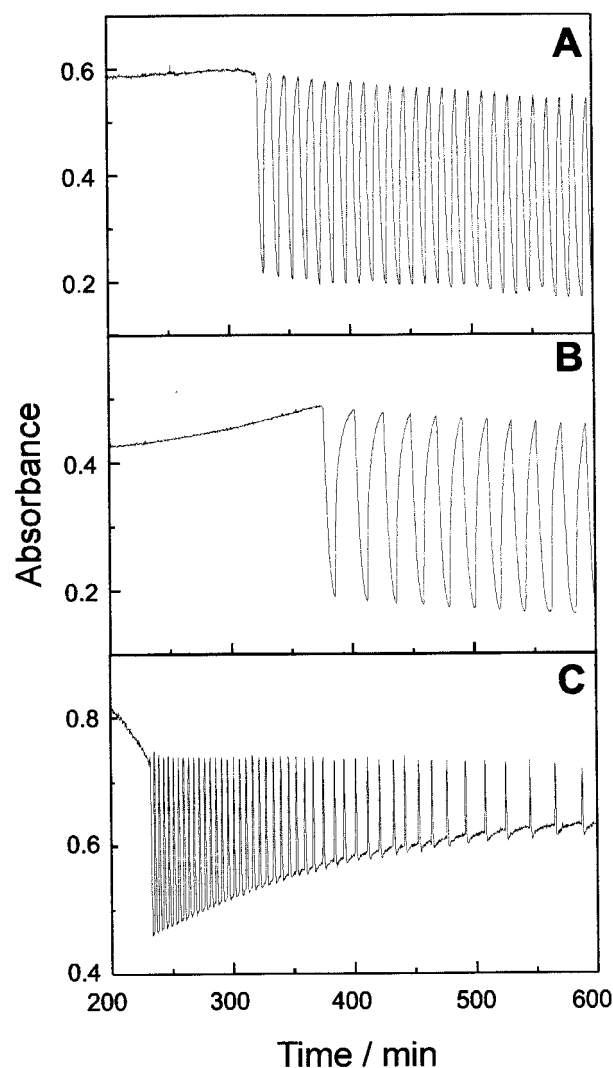
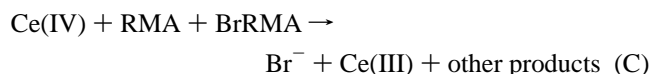


Figure 3. Time dependence of the Ce(IV) absorbance in the presence of $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ CTAN for the BZ systems with MeMA (A), EtMA (B), and BzMA (C). Experimental conditions are the same as in Figure 2.

as compared to the corresponding IP values without surfactant. In the case of BzMA, oscillations also occur, but the induction period (≈ 763 min) is much longer. Note that these IP values are much larger than those obtained for these substrates in the presence of CTAN at the same concentration (IP = 77, 164, and 189 min with BzMA, MeMA, and EtMA, respectively; cf. Figure 4).

We can provide some interpretation of the observed surfactant effects in the framework of the FKN¹⁴ mechanism proposed for MA as organic substrate. According to this mechanism, that can also be applied to the substrates RMA under study, the induction period is influenced by both the rate of formation of the bromomalonic acid derivative (BrRMA) and the rate of its oxidation by Ce(IV). The overall reaction represents^{14,15} process C, as labeled in the original paper,¹⁴ producing bromide ion,



which plays the fundamental role of the control intermediate in the oscillatory reaction (stoichiometric coefficients are omitted).

Because of the inductive effect of the bromo substituent, the bromo derivatives of all the three substituted malonic acids

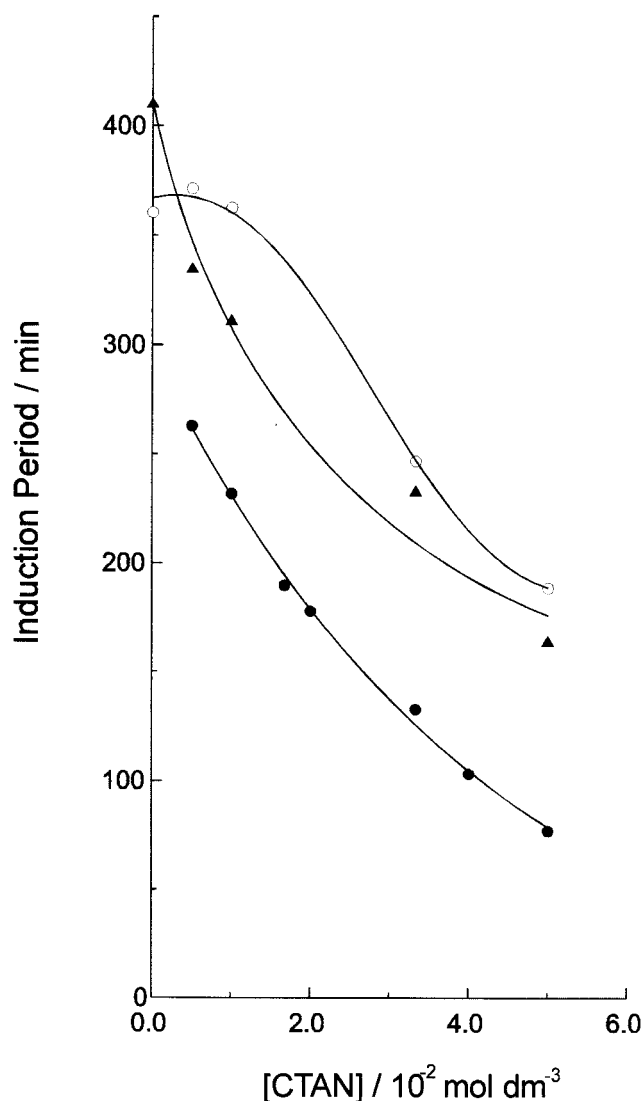


Figure 4. Plot of the induction period against [CTAN] for the BZ systems with MeMA (▲), EtMA (○), and BzMA (●). Experimental conditions are the same as in Figure 2.

should be stronger acids than the corresponding RMA ones and, consequently, monoanions¹² of the compounds BrRMA should be significantly present in solution, being able to associate with the cationic CTAN micelles but not with SDS micelles. Therefore, bearing in mind the considerations made in the previous section concerning the effect of CTAN on the rates of substrate oxidation by cerium(IV), in the presence of CTAN the bromide regeneration step (process C) involving the reactants in the micellar pseudophase would be favored and the induction periods reduced as [CTAN] increases. As to the observed effect of the added SDS micelles that do not bind anionic species, we expect no (appreciable) effect on process C.

An additional effect of the CTAN micelles is to favor the bromination of the substrates occurring via an enolization mechanism. In fact, the bromination process proceeds because of the attack of Br₂ on the enol form of the organic substrate,^{9,15} also leading to production of bromide ion. The rates of RMA enolizations have been estimated recently by Ruoff and al.,¹⁶ who have found that the log(*k*_{enol}) values show a linear dependence with Taft σ* constants, increasing then in the order EtMA < MeMA < BzMA. Since higher enolization rates imply shorter IP values, the opposite trend observed above for the induction period of these substrates in the presence of CTAN

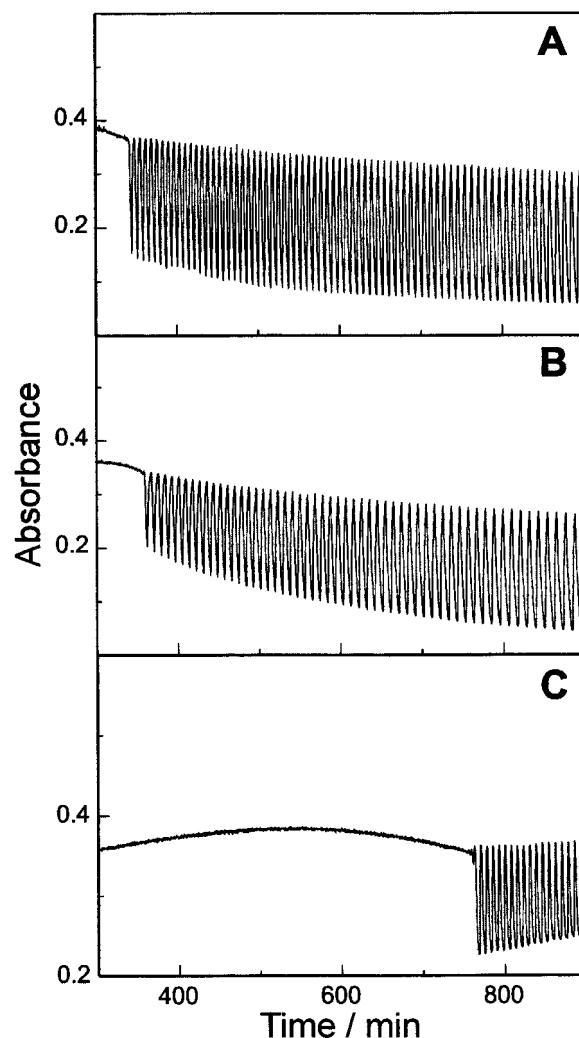


Figure 5. Time dependence of the Ce(IV) absorbance in the presence of $5.00 \times 10^{-2} \text{ mol dm}^{-3}$ SDS for the BZ systems with MeMA (A), EtMA (B), and BzMA (C). Experimental conditions are the same as in Figure 2.

micelles correlates well with the accelerating effect of these micelles on the enolization process.

Since both SDS and CTAN at the same concentration shorten to a different extent the induction periods of the substrates with respect to those without surfactants, we have to deduce that the two oppositely charged micelles affect the intermediate step(s) of the bromination process (e.g., the enolization one) and/or other intermediate step(s) by nonelectrostatic interactions with neutral species to a larger extent for the more hydrophobic CTAN surfactant.

The presence of CTAN micelles in the reaction medium determines, in addition to the above-mentioned effects on the induction period, effects on other oscillatory parameters of the systems under study. Figure 6 shows the influence of increasing CTAN concentration on the oscillation period (τ) for the three RMA substrates, whereas Figure 7 shows that on the duration of the raising portion (t_{rais}) of an oscillatory cycle, which corresponds to the oxidation phase Ce(III) → Ce(IV). The reported τ and t_{rais} values represent the means on the first five oscillatory cycles.³³ It can be seen that both τ and t_{rais} parameters increase as the CTAN concentration increases for MeMA and EtMA systems, but they decrease markedly in the case of BzMA, in all cases tending to reach a plateau at high CTAN concentrations. On the other hand, at a given [CTAN] value, the effect of the substituent R on both τ and t_{rais} values increases

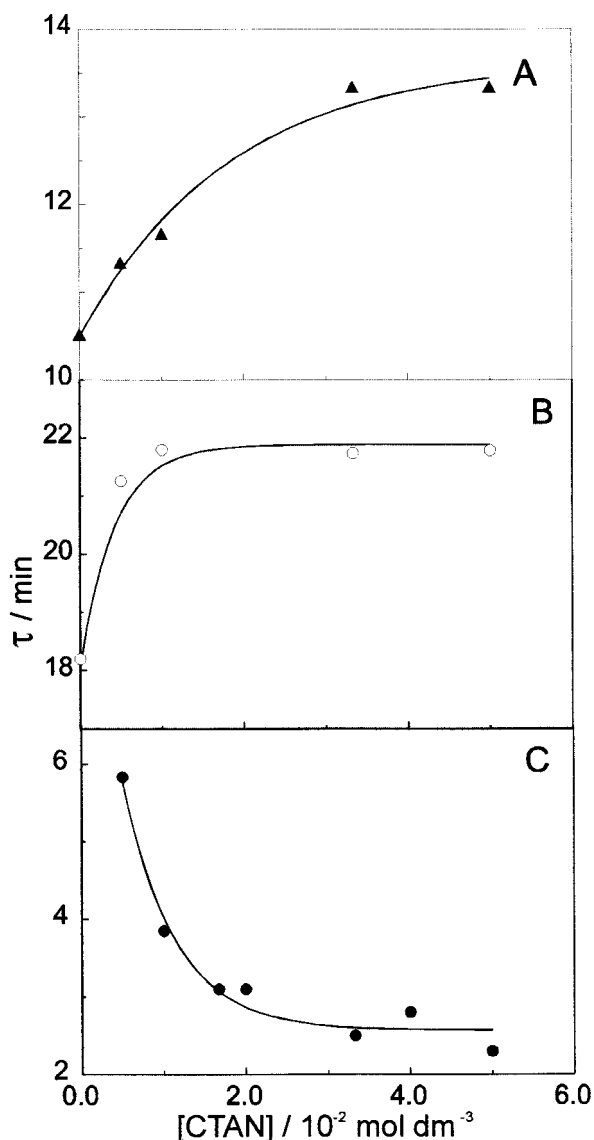


Figure 6. Plot of τ against [CTAN] for the BZ systems with MeMA (A), EtMA (B), and BzMA (C). Experimental conditions are the same as in Figure 2.

following the order BzMA < MeMA < EtMA. This is the same trend observed above for the substituent effect on the induction period of these substrates in the presence of CTAN.

In the presence of $5.00 \times 10^{-2} \text{ mol dm}^{-3}$ SDS, the estimated τ values are 7.0, 8.6, and 7.6 min with MeMA, EtMA, and BzMA, respectively, while the corresponding t_{rais} values are 3.0, 4.5, and 2.5 min. Both the τ and t_{rais} values found with MeMA and EtMA are smaller as compared to the corresponding data obtained either in the absence of surfactant or in the presence of $5.00 \times 10^{-2} \text{ mol dm}^{-3}$ CTAN (cf. Figures 6 and 7). By contrast, with the BzMA substrate the values of these two parameters are larger with respect to the corresponding values obtained with $5.00 \times 10^{-2} \text{ mol dm}^{-3}$ CTAN.

As a conclusion, the main findings of the present work show that the cationic CTAN micelles affect the cerium(IV) oxidation of substituted malonic acid derivatives and oscillatory parameters of the BZ systems with these substrates (i.e., induction period, oscillation period, duration of the raising portion of an oscillatory cycle) and that the benzyl-substituted malonic acid exhibits a peculiar kinetic and oscillatory behavior that can be mainly related to its greater hydrophobic nature compared to

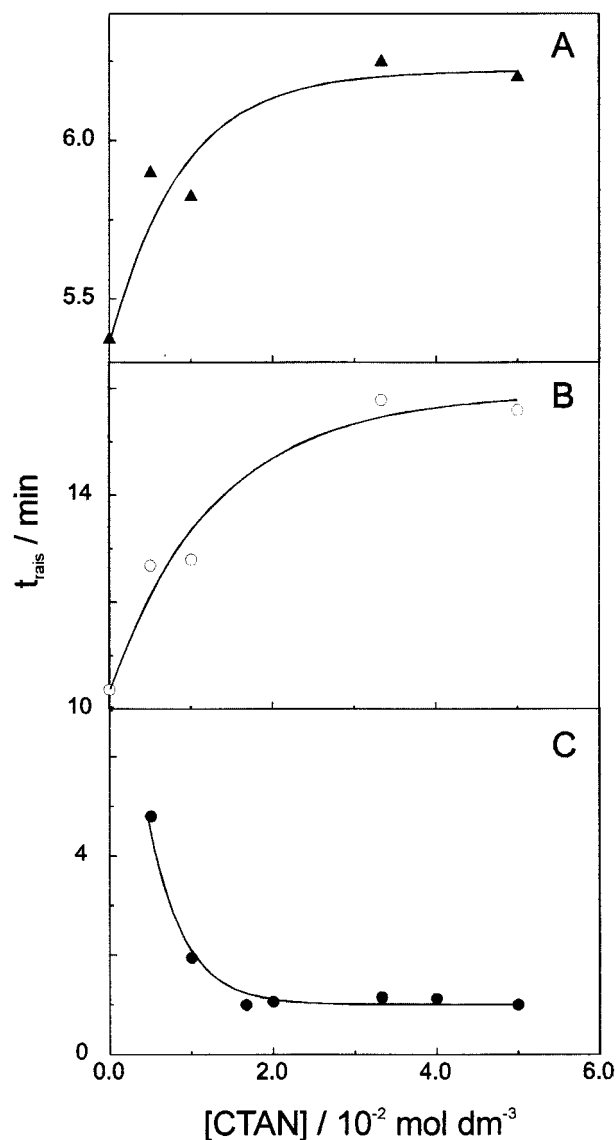


Figure 7. Plot of t_{rais} against [CTAN] for the BZ systems with MeMA (A), EtMA (B), and BzMA (C). Experimental conditions are the same as in Figure 2.

MeMA and EtMA. Effects of the anionic SDS micelles on these oscillatory parameters are observed to a different extent.

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