Bromination of benzoylacetone in cationic micelles. A strong inhibition effect

Emilia Iglesias* and Ana Domínguez

Departamento de Química Fundamental e Industrial, Facultad de Ciencias, Universidad de La Coruña, 15071 La Coruña, Spain. E-mail: qfemilia@udc.es

Received* (*in Montpellier, France*) *23rd March 1999, Accepted 16th June 1999

The bromination reaction of benzoylacetone in aqueous acid medium has been studied in the presence of cationic micelles of tetradecyltrimethylammonium bromide. The reaction involves enolization of the ketone, followed by electrophilic bromination of the enol. The presence of cationic micelles strongly modifies both the Br_2/Br_3^- equilibrium towards the formation of tribromide ion and the keto-enol equilibrium of benzoylacetone towards increasing enol concentration. As the enol is the reactive species in electrophilic substitutions, in the presence of cationic micelles it would be expected that bromination by Br_3^- would occur in the micellar phase, in accordance with previous studies on bromination of alkenes. In contrast, the kinetic results are quite satisfactorily explained by assuming bromination of the enol by molecular bromine, in water as in the micellar pseudophase. The optimized reactivity in water is higher than that in the micellar phase, a less polar medium than bulk water, and bromination is medium dependent because the solvent assists the departure of bromide ion.

Aqueous micelles induce changes in a wide variety of ground- and excited-state reactions and equilibria.[1,2] Micellar effects have generally been discussed in terms of a pseudophase model, which assumes that, for most thermal reactions, equilibrium is maintained between water and micelles, which are regarded as a medium distinct from the bulk solvent.[3] We have recently shown that aqueous micellar solutions strongly affect the keto-enol equilibrium of benzoylacetone,[4] BZA (1-phenyl-1,3-butadione), by taking up the enol tautomer of BZA, which predominates in aprotic, nonpolar and aprotic nonpolar solvents stabilized by intramolecular hydrogen bonding. The study of the influence of micelles on the generation of bromine from bromate in acid medium[5] indicates that the presence of cationic micelles displaces the equilibrium $Br_2 + Br^- \rightleftharpoons Br_3^-$ (K_T) almost completely towards the formation of tribromide ion.This equilibrium is medium dependent[6] such that the tribromide ion concentration increases in nonpolar solvents (*e.g.* the equilibrium constant K_T varies from 16, 92, 177, to 400 mol^{-1} dm^3 on going from water, acetic acid, methanol, and ethanol, respectively). This effect is also observed in the presence of cationic micelles, since the maximum absorption band due to Br_3^- centred in water at around 266 nm shifts to 271 nm in the presence of cationic micelles, as a result of the low polarity of the micellar interphase, and also the absorbance intensity due to Br_3^- increases by more than threefold with respect to the absorbance in water. Both observations indicate that the presence of micelles shifts the equilibrium Br_2/Br_3^- towards tribromide ion formation because of several effects operating in the same direction, such as the preferential solubilization of Br_3^- in a low polar medium; the high concentration of Br^- at the surface of TTABr micelles, and the affinity of the polarizable Br_3^- for a cationic micelle. These previous observations are of key importance in the understanding of the kinetic results obtained in the bromination of benzoylacetone in acid medium in the presence of micellar solutions of tetradecyltrimethylammonium bromide, TTABr. There are several studies on the halogenation of enols in water,[7] but there is a lack of similar studies in aqueous micellar media. Nevertheless, it is possible to find some references on bromination studies of alkenes in micellar[8] or microemulsion[9] media.

Experimental

All reagents were available at very high purity grades and were used as supplied (BZA and TTABr were Aldrich products and the rest of the reagents were Merck products). Bromine solutions were prepared daily in distilled water, either directly from pure bromine and standardized by thiosulfate titration or generated[5] from bromate as a primary standard ($BrO_3^- + 5\ Br^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O$). Absorbance measurements were recorded with a Kontron-Uvikon (Model 942) double-beam spectrophotometer provided with a thermostated cell holder. Bromination reactions of benzoylacetone were monitored at 25 °C by stopped-flow spectrophotometry, noting the disappearance of the absorbance due to tribromide ion at 271 nm. Kinetics were studied by following the integrated method, fitting the experimental data, absorbance *vs.* time, to eqn. (1), where A_0, A, and A_∞ are the mean absorbance readings at times 0, t, and ∞, respectively, and k_0 represents the pseudo-first-order rate constant.

$$A = A_\infty + (A_0 - A_\infty)\ e^{-k_0 t} \quad (1)$$

The initial concentration of Br_2 ($<10^{-5}$ mol dm^{-3}) was always smaller than that of the other reagents, and the observed decrease in absorbance was of the order of 0.2 absorbance units. The quoted values of k_0 are mean values of at least four separate measurements. Good reproducibility of k_0 and a perfect fit of A *vs.* t traces to eqn. (1) were obtained in all cases. (As an example of representative results, which have been measured under the following experimental conditions: $[BZA] = 8.6 \times 10^{-5}$ mol dm^{-3}, $[Br_2] = 8.0 \times 10^{-6}$ mol dm^{-3}, $[HBr] = 0.015$ mol dm^{-3}, we report: (*i*) $k_0 = [126.2 \pm 0.2;\ 121.5 \pm 0.3;\ 122.8 \pm 0.3;\ 126.4 \pm 0.3]$ s^{-1} at $[TTABr] = 3.3 \times 10^{-3}$ mol dm^{-3} and (*ii*) $k_0 = [3.812 \pm 0.006;\ 3.848 \pm 0.005;\ 3.809 \pm 0.006;\ 3.796 \pm 0.006]$ s^{-1} at $[TTABr] = 0.132$ mol dm^{-3}.)

Results

Bromine–tribromide ion equilibrium

In previous studies[5] we showed that in the presence of 0.05

Table 1 Variation of the absorbance at $\lambda = 266$ and 271 nm of aqueous acid solutions ([HBr] = 0.0167 mol dm^{-3}) of bromine ([Br_2] = 2.0 × 10^{-5} mol dm^{-3}) as a function of TTABr concentration

[TTABr]/10^{-3} mol dm^{-3}	A_{266}	A_{271}
0.0	0.1877	—
0.55	0.1924	0.1969
0.77	0.3772	0.3820
1.1	0.6336	0.6679
1.65	0.7965	0.8545
2.2	0.8090	0.8713
3.3	0.8122	0.8744
4.4	0.8267	0.8919
6.6	0.7985	0.8811

mol dm^{-3} of TTABr the bromine generated in the oxidation of BrO_3^- by Br^- (0.025 mol dm^{-3}) in an acid medium ([H^+] = 0.025 mol dm^{-3}) is almost entirely in the form of Br_3^-, which must be located at the micellar interphase. Table 1 reports the absorbance readings at 266 and 271 nm of an aqueous solution of bromine (2.2 × 10^{-5} mol dm^{-3}) in the presence of [HBr] = 0.0167 mol dm^{-3} as a function of [TTABr]. Under these conditions, the critical micelle concentration, CMC, of TTABr is reported[10] to be 1.01 × 10^{-3} mol dm^{-3}, but the data in Table 1 indicate a strong absorbance increase due to Br_3^- ($\varepsilon_{266} = 4.0 \times 10^4$ mol^{-1} dm^3 cm^{-1})[11] at [TTABr] even below the CMC. This effect cannot be attributed to the increase of [Br^-] introduced with the surfactant, since the process $Br_2 + Br^- \rightleftharpoons Br_3^-$ has an equilibrium constant of 16.1[11] or 16.8[12] mol dm^{-3} at 25 °C and at an ionic strength of 1.0 or 0.54 mol dm^{-3}, respectively. Therefore, the only possible explanation for the absorbance increase below the CMC should be the formation of submicellar aggregates, which could be understood by considering the high polarizability of the Br_3^- ion. The conclusion that can be drawn from these results is that in the presence of cationic micelles of TTABr, we can assume that bromine is virtually completely in the Br_3^- form.

Keto-enol equilibrium of BZA

Fig. 1 shows the effect of increasing [TTABr] on the absorbance of BZA (8.2 × 10^{-5} mol dm^{-3}) at the two main absorption bands in the UV spectrum: at $\lambda = 312$ nm, due to the enol tautomer ($\varepsilon_E = 13\,900$ mol^{-1} dm^3 cm^{-1}),[4] the absorbance increases, that is the enol concentration increases with

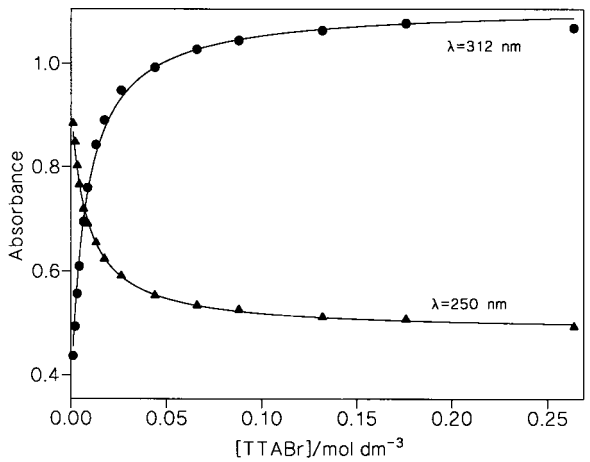
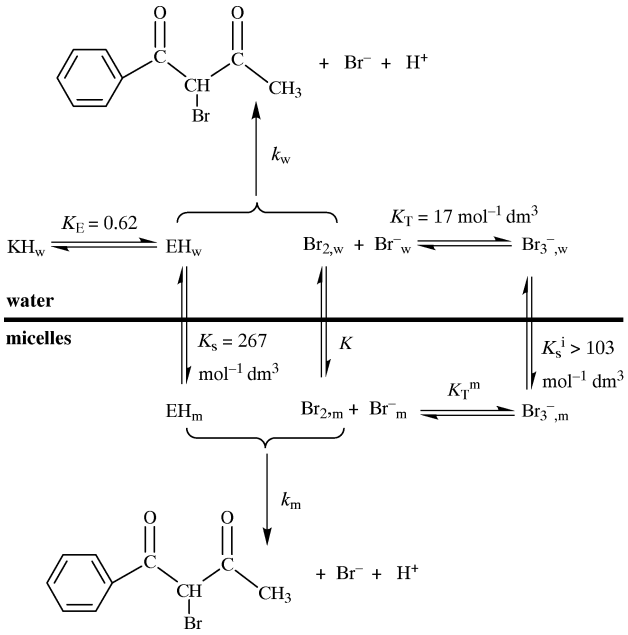


Fig. 1 Experimental absorbance values of aqueous solutions of benzoylacetone ([BZA] = 8.2 × 10^{-5} mol dm^{-3}) obtained as a function of TTABr concentration at [HCl] = 0.033 mol dm^{-3}. Solid lines are theoretical fits from the model.



Scheme 1

surfactant concentration; whereas the absorption band at $\lambda = 250$ nm, mainly due to the keto tautomer ($\varepsilon_K = 13\,850$ mol^{-1} dm^3 cm^{-1}, $\varepsilon'_E = 6000$ mol^{-1} dm^3 cm^{-1}),[4] decreases on increasing the surfactant concentration as a consequence of the keto-to-enol conversion, because of the preferential solubilization of the latter in the micellar phase. Taking into account Scheme 1 and considering that: $A_{312} = l \cdot \varepsilon_E([EH]_w + [EH]_m)$ and $A_{250} = l \cdot \varepsilon_K[KH]_w + l \cdot \varepsilon'_E([EH]_w + [EH]_m)$, with EH and KH being the enol and keto tautomers of BZA, respectively, and with the subscripts w and m denoting water and micellar pseudophases, respectively, the expressions for the concentrations of KH and EH are those reported in eqns. (2) and (3).

$$[KH]_w = \frac{[BZA]_t/(1 + K_E)}{1 + K_E K_s[TTABr]_m/(1 + K_E)} \quad (2)$$

$$[EH]_w = \frac{[BZA]_t \cdot K_E/(1 + K_E)}{1 + K_E K_s[TTABr]_m/(1 + K_E)};$$

$$[EH]_m = \frac{[BZA]_t \cdot K_E K_s[TTABr]_m/(1 + K_E)}{1 + K_E K_s[TTABr]_m/(1 + K_E)} \quad (3)$$

Solid lines in Fig. 1 are theoretical fits of the resulting equations from the model to the experimental absorbance data (A_{312} or A_{250}) against the micellized surfactant concentration ([TTABr]$_m$ = [TTABr]$_t$ − CMC). The determined values for the unknown parameters were $K_E = 0.62$ and $K_s = 267$ mol^{-1} dm^3.

Kinetic results

The influence of [BZA] on the bromination reaction was examined in the presence of HBr at two TTABr concentrations. The obtained results, displayed in Fig. 2, show that the reaction is first order in [BZA] and also that cationic micelles of TTABr strongly inhibit the bromination reaction. The slopes of the linear plots were determined to be (4.89 ± 0.04) × 10^5 and (2.9 ± 0.6) × 10^5 mol^{-1} dm^3 s^{-1}, when [TTABr] = 0.010 or 0.024 mol dm^{-3}, respectively, that is the second-order rate constant is nearly halved by an increase of 2.4 in the surfactant concentration.

The influence of the acidity was analysed at [TTABr] = 0.013 mol dm^{-3} in the range of [H^+] = (0.5–3.5) × 10^{-2} mol dm^{-3} and with the total Br^- concentration (equal to [Br^-]$_{ad}$ + α[TTABr]$_m$ + CMC) kept constant at 0.035 mol dm^{-3}. The obtained values for the pseudo-first-

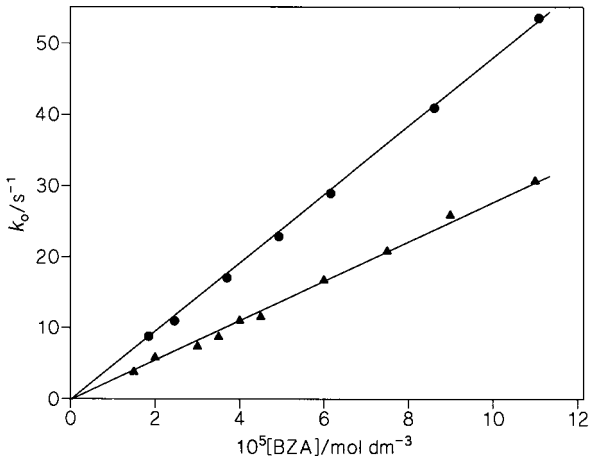


Fig. 2 Influence of BZA concentration on the pseudo-first-order rate constant of the bromination of BZA in aqueous micellar solutions of TTABr at (●) [TTABr] = 0.010 mol dm^{-3}, [HBr] = 0.015 mol dm^{-3} and (▲) [TTABr] = 0.0240 mol dm^{-3}, [HBr] = 0.010 mol dm^{-3}.

Table 2 Influence of the acidity of the medium (controlled with HBr) on the observed rate constant of the bromination ([Br_2] ≈ 3.5×10^{-6} mol dm^{-3}) of benzoylacetone ([BZA] = 3.6×10^{-5} mol dm^{-3} with [Br^-]$_{ad}$ = [HBr] + [NaBr] = 0.035 mol dm^{-3} and [TTABr] = 0.013 mol dm^{-3}

[H^+]/mol dm^{-3}	k_0/s^{-1}
0.005	10.70
0.010	10.33
0.015	10.34
0.020	10.17
0.025	10.31
0.035	10.24

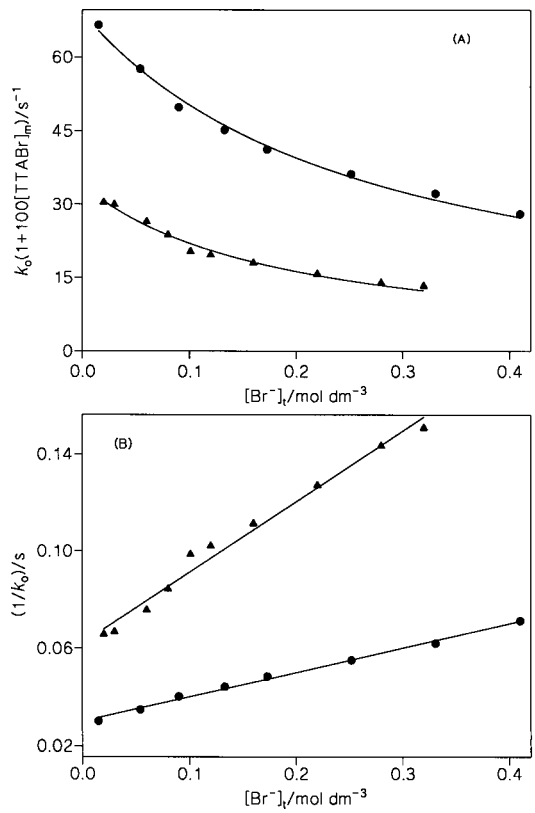


Fig. 3 Influence of bromide ion concentration on the observed rate constant of the bromination of BZA in the presence of [TTABr] = 0.010 mol dm^{-3} at (●) [BZA] = 8.2×10^{-5} mol dm^{-3}, [HBr] = 0.015 mol dm^{-3} and (▲) [BZA] = 3.5×10^{-5} mol dm^{-3}, [HBr] = 6.0×10^{-3} mol dm^{-3}. Plots of (*A*) k_0^{cor} and (*B*) $1/k_0$ *vs.* [Br^-]. Solid lines are theoretical fits from the model.

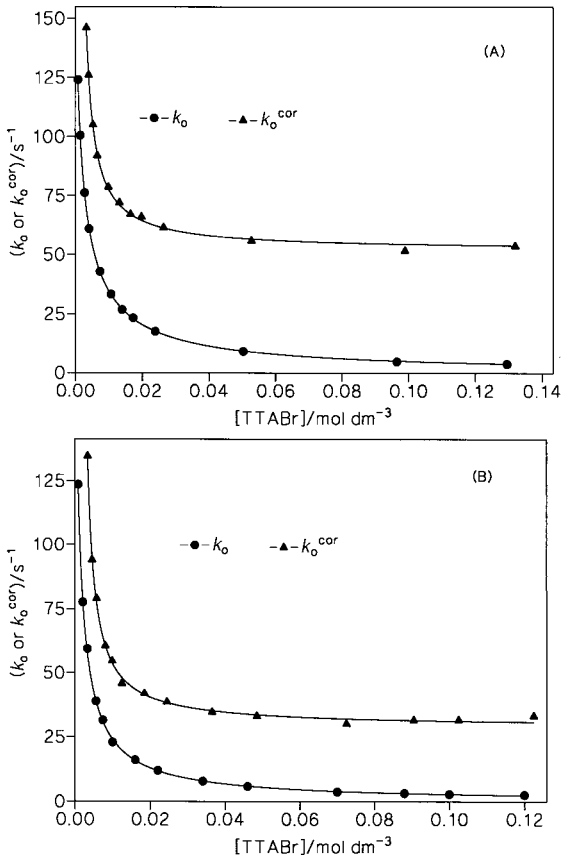


Fig. 4 (●) Variation of the observed rate constant, k_0, as a function of [TTABr] obtained at (*A*) [BZA] = 8.2×10^{-5} mol dm^{-3}, [HBr] = 0.015 mol dm^{-3}, and (*B*) [BZA] = 7.5×10^{-5} mol dm^{-3}, [HBr] = 0.032 mol dm^{-3}. (▲) Plot of $k_0^{cor} = k_0 \cdot \{1 + [TTABr]_m K_E K_s/(1 + K_E)\}$ *vs.* [TTABr], with CMC = 1.0×10^{-3} mol dm^{-3} and with $K_E K_s/(1 + K_E)$ = 100 mol^{-1} dm^3.

order rate constant, displayed in Table 2, indicate that the rate constants are independent of the acidity.

The influence of Br^- concentration was studied at [TTABr] = 0.010 mol dm^{-3} and at [HBr] = 0.015 or 6.0×10^{-3} mol dm^{-3}. In both experimental situations, k_0 decreases as [Br^-] increases. The experimental results are reported in Fig. 3, along with the reciprocal plot of $(k_0)^{-1}$ against [Br^-].

Finally, we studied the influence of surfactant concentration at several HBr concentrations. Fig. 4 shows typical results obtained at [H^+] = 0.015 and 0.032 mol dm^{-3}. As can be seen, on increasing TTABr concentration, k_0 decreases by more than 100-fold. The same figure also shows the variation of k_0^{cor} (where the expression for k_0^{cor} is given in the caption).

Discussion

Many enolization studies have been carried out from the halogenation reaction of the corresponding substrate,[13] because depending on the experimental conditions it is possible to change the rate-limiting step from that of enolization to reaction of the enol. Low halogen concentrations and/or working with substrates having considerable enol content, will favor the reaction of the enol as the rate-limiting step.

This study was performed with [BZA] > [Br_2], and given that benzoylacetone is around 40% enolized in water and even more so in the presence of micelles (see Fig. 1), it would be expected, for this substrate and under the experimental conditions of this work, that we would find a fully first-order dependence on bromine. This condition is fulfilled in every kinetic experiment, and the pseudo-first-order rate constant,

k_0, also increases linearly with [BZA] (see Fig. 2), indicating that the bromination reaction is first order in substrate concentration, $k_0 = k_2$ [BZA].

Even though under the acidity conditions used in this work (pH <2) the benzoylacetone enolate concentration would be expected to be very small ($pK_a^E = 8.27$ and $pK_a^K = 8.50$)[4,14] the higher reactivity of the enolate than the enol form, often found in nitrosation studies,[15] would make the enolate a likely candidate in bromination. Nevertheless, the lack of acidity dependence found in this study (Table 2) ruled out this possibility.

Previous studies on alkene bromination[8] have assumed the possibility of reaction by molecular bromine and by tribromide ion. In water, Br_2 is more reactive than Br_3^- towards most alkenes, but reactivity differences are not large. The huge inhibition of the reaction by cationic micelles, with respect to reaction in water, was explained on the basis that Br_3^- (the only brominating agent assumed to be in the micellar phase) is 5–6 orders of magnitude less reactive than in water. In contrast, the study of the bromination reaction of *cis*-4-cyclohexene-1,2-dicarboxylic acid dimethyl ester in water gives $k = 1.06 \times 10^6$ and $k' = 3.28 \times 10^5$ mol^{-1} dm^3 s^{-1} for the reactions of Br_2 and Br_3^-, respectively. On the other hand, the data of Williams' group on the halogenation of reactive enols[7] were interpreted on the basis of a bromination reaction by molecular bromine, which was diffusion controlled. Finally, the linear dependence of $1/k_{obs}$ against [Br^-], found by Ruasse *et al.*[9] on the bromination of oct-1-ene in anionic microemulsions, was attributed to a negligible reaction of Br_3^- with the substrate. A similar explanation is given by Lennox and McClelland,[16] who attributed the monotonic decrease of the second-order rate constant of the alkene bromination in non-ionic micelles of Brij-35, as the bromide concentration is increased, to the conversion of the electrophile bromide into the *unreactive* tribromide form. In line with this, the influence of Br^- concentration in bromination studies in aprotic solvents affords an expression for the observed rate constant of the form $k_{obs}(1 + K_T[Br^-]) = k + k'K_T[Br^-]$ with k being the corresponding rate constant for the addition of molecular bromine to alkene, whereas k' has been frequently attributed to the reaction by Br_3^-. Nevertheless, the meaning of k' has been questioned very recently by Ruasse,[17] who proposes that k' should be attributed to a salt effect on the free bromine reaction and/or bromide assisted bromine addition, both processes being kinetically indistinguishable; this author goes even further and concludes by questioning the electrophilic character of tribromide ion.

The above considerations, along with the results of Fig. 3, where the reciprocal plot of $(k_0)^{-1}$ shows a linear dependence upon [Br^-] when the bromination of BZA is studied in the presence of 0.010 mol dm^{-3} of TTABr, and other reasons (*vide infra*), lead us to propose the reaction mechanism of Scheme 1, in which only bromination by molecular bromine is take into account, eqn. (4).

$$\text{rate} = k_w[EH]_w[Br_2]_w + k_m[EH]_m[Br_2]_m \quad (4)$$

By considering the possible equilibrium steps existing in the BZA and Br_2 systems, both in water and in micellar pseudophases, as shown in Scheme 1, the mass balance equations on total BZA and bromine lead us to eqn. (5) with $[Br^-]_{w,t} = [Br^-]_{ad} + CMC + \alpha[TTABr]_m$ and with α ($=0.24$)[18] being the micellar ionization degree:

$$k_0 = \frac{K_E[BZA]_t/(1+K_E)}{1 + K_s K_E[TTABr]_m/(1+K_E)} \times \left\{ \frac{k_w + k_m K K_s[TTABr]_m}{1 + K_T[Br^-]_{w,t} + (K + \alpha K_T + K_s^i K_T[Br^-]_{w,t})[TTABr]_m} \right\} \quad (5)$$

(We recall that $k_0\{1 + K_s K_E[TTABr]_m/(1 + K_E)\} = k_0^{cor}$.) This equation predicts the observed behaviour of Fig. 2 and 3, and also the lack of acidity dependence. Fig. 4 shows the variation of the pseudo-first-order rate constant as a function of surfactant concentration. As K_E and K_s were previously determined from absorbance measurements, then it is also possible to plot k_0^{cor} against [TTABr], which was done in Fig. 4. The lines correspond to the theoretical fits of the model to the experimental points, for which the general expression of $k_0^{cor} = \delta(k_w + B[TTABr]_m)/(C + D[TTABr]_m)$ was used, with the values of $\delta = \{K_E[BZA]_t/(1 + K_E)\}$ and $C = (1 + K_T[Br^-]_{w,t})$ being introduced as known parameters. As can be seen, a good fit is obtained in every case (data obtained at [HBr] = 0.017 and 9.0×10^{-3} mol dm^{-3} are not shown) and the corresponding optimized parameters of k_w, B, and D obtained from the fitting process are collected in Table 3.

The value of k_w cannot be determined experimentally because the reaction in water is very fast. The optimized value, taken as the average of the results given in Table 3, is $k_w = 1.9 \times 10^7$ mol^{-1} dm^3 s^{-1}, which agrees quite well with the bimolecular rate constant obtained in the BZA-enol nitrosation[19] by NO^+, that is in an electrophilic substitution like bromination, with $k_{NO} = 5.5 \times 10^7$ mol^{-1} dm^3 s^{-1} being the corresponding rate constant; however, NO^+ (or NO^+OH_2) is a better electrophile than Br_2. These results are also in accordance with the value of 2.3×10^7 mol^{-1} dm^3 s^{-1} obtained in the bromination of oct-1-ene in water at 25 °C.[9] We must notice that the reaction center –C(OH)=CH– in BZA has an alkene-like character.

From the optimized values of B ($=k_m K K_s$) and by assuming the molar volume V of the micellar phase where the reaction takes place[20] to be 0.17 dm^3 mol^{-1}, we can determine that $k_2^m K = 1.2 \times 10^6$ mol^{-2} dm^6 s^{-1} (mean value from the four measurements) with k_2^m ($=k_m \cdot V$) being the second-order rate constant in the micellar pseudophase. If it were assumed that the bromination in the micellar phase was promoted by Br_3^- (contrary to the experimental observed linear dependence of $1/k_0$ *vs.* [Br^-]) and if one assumed a value for k_2^m as low as 5–6 orders of magnitude smaller than the value obtained in water (as is the case for alkenes[8]), then the association constant of molecular bromine to TTABr micelles would be as high as $K = (0.5–5) \times 10^4$ mol^{-1} dm^3, which would not be in agreement with the experimentally observed displacement of the Br_2/Br_3^- equilibrium toward the tribromide ion in the presence of cationic micelles. In contrast, if we assume that the bromination in the micellar phase is promoted by bromine, the following argument applies. In the bromination

Table 3 Experimental conditions used in the study of the influence of TTABr concentration on the bromination of BZA and values of the optimized parameters k_w, B and D determined by fitting the experimental data of k_0 *vs.* [TTABr]$_m$ to eqn. (5) with $K_E = 0.62$, $K_s = 267$ dm^3 mol^{-1} and CMC $= 1.0 \times 10^{-3}$ mol dm^{-3}

[BZA]/mol dm^{-3}	[HBr]/mol dm^{-3}	$k_w/10^7$ s^{-1} dm^3 mol^{-1}	$B = (k_2^m/V)K \cdot K_s/10^9$ dm^6 mol^{-2} s^{-1}	D/dm^3 mol^{-1}
7.5	0.032	1.4 ± 0.4	1.75 ± 0.1	1730 ± 12
7.5	0.017	1.6 ± 0.1	1.43 ± 0.1	1310 ± 20
8.5	0.015	1.34 ± 0.04	2.57 ± 0.05	1520 ± 20
7.5	0.009	3.2 ± 0.1	1.69 ± 0.2	1730 ± 80

of oct-1-ene, Ruasse *et al.*[9] determined a value of 2×10^5 mol^{-1} dm^3 s^{-1} for the bimolecular rate constant in SDS (sodium dodecylsulfate) micelles. This value decreases to 1.5×10^4 mol^{-1} dm^3 s^{-1} in anionic microemulsions, that is in a less polar medium than the interface of SDS micelles. If one considers that the lower reactivity of bromine in a less polar medium than water is because of the absence of any external assistance to the bromide departure, and, in the presence of TTABr micelles, also because of the saturated micellar interface with Br^- ions, then, taking into account the higher stabilization of the Br^- leaving group by cationic micelles with regard to anionic ones, we can assume a minimum value of $k_2^m = 1.2 \times 10^5$ mol^{-1} dm^3 s^{-1}. From this figure we can determine $K = 10$ mol^{-1} dm^3, a value that is quite acceptable taking into account the hexane–water transfer coefficient of bromine[21] (about 60), but the micellar interface of TTABr micelles is more polar (more water content) than hexane.

The above estimated value of K, combined with the average value detemined for the optimized parameter D, implies that $K_s^i = (3–11) \times 10^3$ mol^{-1} dm^3, which is the association equilibrium constant of tribromide ion to TTABr micelles. These values are in perfect agreement with K_s^i value estimated from absorbance measurements in this work (Table 1) and also with previous estimations.[8a]

Conclusions

Bromination of benzoylacetone is strongly inhibited by the presence of TTABr, a cationic surfactant forming micelles. Even though the presence of micelles increases the enol amount of BZA, which is the reactive tautomer in bromination, the concomitant increase in the concentration of the unreactive tribromide ion, along with the lower reactivity in the less polar medium of the micellar interphase, accounts for the experimentally observed reduction of the reaction rate by more than 100-fold. Experimental data are mechanistically explained by considering the fast distribution of bromine, tribromide, and enol species between water and micellar phases, and with the rate-limiting steps being the addition of bromine to the double bond of the enol tautomer, either in the reaction between both reagents residing in water or in the micellar interphase.

Acknowledgements

Financial support from the Dirección General de Investigación Científica y Técnica of Spain (Project PB96-1085) is gratefully acknowledged.

References

1 J. H. Fendler and E. J. Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York, 1975.
2 (*a*) C. A. Bunton and G. Savelli, *Adv. Phys. Org. Chem.*, 1986, **22**, 231; (*b*) C. A. Bunton, F. J. Nome, F. H. Quina and L. S. Romsted, *Acc. Chem. Res.*, 1991, **24**, 357.
3 (*a*) C. A. Bunton, in *Kinetics and Catalysis in Microheterogeneous Systems*, eds. M. Grätzel and K. Kalyanasundaran, Surfactant Science Series, Marcel Dekker, New York, 1991, vol. 38, p. 13; (*b*) H. Chaimovich, R. M. V. Aleixo, I. M. Cuccovia, D. Zanette and F. H. Quina, in *Solution Behavior of Surfactants*, eds. K. L. Mittal and E. J. Fendler, Plenum Press, New York, 1982, vol. 2, p. 949.
4 E. Iglesias, *J. Phys. Chem.*, 1996, **100**, 12592.
5 A. Domínguez and E. Iglesias, *Langmuir*, 1998, **14**, 2677.
6 E. Bienvenue-Goëtz, R. Msika and J. E. Dubois, *J. Chim. Phys. Phys.-Chim. Biol.*, 1980, **77**, 803.
7 (*a*) D. L. H. Williams and A. Graham, *Tetrahedron*, 1992, **48**, 7978; (*b*) A. R. Eberlin and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1043; (*c*) A. R. Eberlin and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1996, 883; (*d*) D. L. H. Williams and L. Xia, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1429; (*e*) M. J. Hynes and E. M. Clarke, *J. Chem. Soc., Perkin Trans. 2*, 1994, 901.
8 (*a*) G. Cerichelli, C. Grande, L. Luchetti and G. Mancini, *J. Org. Chem.*, 1991, **56**, 3025; (*b*) G. Cerichelli, C. Grande, L. Luchetti and G. Mancini, *J. Org. Chem.*, 1987, **52**, 5167; (*c*) M. T. Bianchi, G. Cerichelli, G. Mancini and F. Marinelli, *Tetrahedron Lett.*, 1984, **25**, 5205.
9 M.-F. Ruasse, I. B. Blagoeva, S. Krys and M.-A. Sebastian-Cambarro, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1283.
10 N. M. van Os, J. R. Haak and L. A. M. Rupert, *Physico-Chemical Properties of Selected Anionic, Cationic and Nonionic Surfactants*, Elsevier, Amsterdam, 1993, p. 113.
11 T. X. Wand, M. D. Kelley, J. N. Cooper, R. C. Beckwith and D. W. Margerum, *Inorg. Chem.*, 1994, **33**, 5872.
12 D. B. Scaife and H. J. V. Tyrell, *J. Chem. Soc.*, 1958, 386.
13 (*a*) J. Toullec, in *The Chemistry of Enols*, ed. Z. Rappoport, John Wiley & Sons, Chichester, England, 1990, ch. 6; (*b*) J. Toullec, *Adv. Phys. Org. Chem.*, 1982, **18**, 1; (*c*) R. P. Bell and G. G. Davis, *J. Chem. Soc.*, 1965, 353.
14 J. W. Bunting, J. P. Kanler, R. Nelander and Z. Wu, *Can. J. Chem.*, 1995, **73**, 1305.
15 (*a*) M. A. C. Reed and D. L. H. Williams, *J. Chem. Res.*, 1993, (*S*) 342; (*b*) P. Hervés-Beloso, P. Roy and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1991, 17; (*c*) P. Roy and D. L. H. Williams, *J. Chem. Res.*, 1988, (*S*) 122.
16 R. B. Lennox and R. A. McClelland, *J. Am. Chem. Soc.*, 1986, **108**, 3771.
17 M.-F. Ruasse, *Adv. Phys. Org. Chem.*, 1993, **28**, 207.
18 E. Iglesias, *Langmuir*, 1998, **14**, 5764.
19 E. Iglesias, *J. Chem. Soc., Perkin Trans. 2*, 1997, 431.
20 C. A. Bunton, N. Carrasco, S. K. Huang, C. H. Paik and L. S. Romsted, *J. Am. Chem. Soc.*, 1978, **100**, 5420.
21 I. Tohyama and K. Otozai, *Fresenius Z. Anal. Chem.*, 1978, **293**, 282.

Paper 9/02390I