# Effect of Cetyltrimethylammonium Micelles with Bromide, Chloride, and Hydroxide Counterions on the Rates of Decomposition of Para-Substituted Aryl-2,2,2-trichloroethanols in Aqueous NaOH

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The effect of cetyltrimethylammonium micelles with bromide, chloride, and hydroxide counterions, CTAX, X = Br, Cl, OH, on the decomposition of aryl-2,2,2-trichloroethanols was determined. This reaction follows an (Elcb)R type mechanism, i.e., rapid reversible deprotonation of the alcohol by OH<sup>-</sup> followed by rate determining loss of trichloromethyl carbanion to give the benzaldehyde product. In the presence of surfactants, despite the 3-5-fold decrease in the rate constant for the unimolecular decomposition of the alkoxide ion in the micellar phase,  $k_m$ , the dependence of  $k_m$  on substituents effects (values of  $\rho$  of -0.49, -0.46, and -0.45 were obtained from the corresponding Hammett plots for CTABr, CTACl, and CTAOH) is similar to that observed in water ( $\rho = -0.5$ ). The observed inhibition can be rationalized in terms of charge stabilization of the ground state, i.e., quaternary ammonium ions interact more strongly with alkoxy anions than with trichloromethyl carbanions.

## Introduction

The effect of ionic micelles on rates and equilibrium constants of relatively slow, thermal chemical reactions have been studied extensively.<sup>1-5</sup> Several models are available for interpreting these effects, and they often provide excellent qualitative and good quantitative fits of observed rate constants and apparent equilibrium constants over a wide range of experimental conditions (e.g., surfactant concentration, salt concentration and type and pH).<sup>6-11</sup> Micellar induced changes in observed rates of unimolecular reactions are usually attributed to the lower polarity of the micellar surface compared to water, and depending upon the reaction studied, micellar rate constants for completely bound substrates can be greater or less than the rate constants in water.<sup>12</sup>

The rates of bimolecular reactions between organic substrates and inorganic ions are also affected by the medium properties of the micellar surface, but they also depend upon how strongly organic substrates and reactive ions bind to micellar surfaces. The binding of organic molecules depends primarily upon the balance of their hydrophobicity and the polarity of their reactive functional groups. The binding of inorganic ions depends upon their charge and hydration forces, i.e., ions of opposite charges, counterions, are strongly bound, ions of like charge, co-ions, are repelled, and the specificity of the interaction is greater for more poorly hydrated ions. Thus cationic micelles speed reactions between organic substrates and anionic nucleophiles, e.g., OH-, by binding and concentrating the reactants within the much smaller volume of the micellar pseudophase. Conversely, cationic micelles inhibit reactions of organic substrates with cationic electrophiles, such as  $H_3O^+$ , by compartmentalization, i.e., binding the substrate but not the electrophile.

A large fraction of the studies in surfactant solutions are focused on single-stepped reactions, but only a small amount SCHEME 1<sup>a</sup>



$$^{a}$$
 X = H (I), CH<sub>3</sub> (II), OCH<sub>3</sub> (III), Cl (IV), NO<sub>2</sub> (V).

of modeling work has been done on more complex multistepped reactions,<sup>13-15</sup> so we decided to explore the effect of cationic micelles on the decomposition of para-substituted aryl-2,2,2trichloroethanols. The mechanism of this reaction, Scheme 1, is an (Elcb)R type, i.e., rapid reversible deprotonation of the alcohol by OH<sup>-</sup> followed by rate-determining loss of trichloromethyl carbanion to give the benzaldehyde product.<sup>16</sup> We also decided to study the decomposition rates with a variety of para-substituents because only a few substituent effect studies in micelles have been published that compare micellar rate constants which have been obtained from simulations that correctly account for the effects of substrate binding constants and surfactant, salt concentration, and buffer effects on the observed rate constants.<sup>14,15</sup> Indeed, all the substituted trichloroethanols are completely micellar bound and deprotonated at moderate surfactant and NaOH concentrations in the absence of buffers which permits direct estimates of their micellar rate constants for the rate-determining step without using any additional parameters.

On the basis of earlier results in cationic micelles<sup>13,17</sup> and the predictions of the PPIE model,<sup>2-5</sup> we expected cetyltrimethylammonium micelles with bromide, chloride, and hydroxide counterions, CTAX, X = Br, Cl, OH, to increase the extent of deprotonation of the trichloroethanols. Earlier results with 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol which decom-

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poses by the same mechanism as the trichloroethanols used here reacts more rapidly in methanol than water.<sup>18</sup> This result suggested that the rate constant for the decomposition step, Scheme 1, should be larger in micelles than water because of the lower polarity of the micelle surface, but, surprisingly, all three cationic surfactants inhibit instead of catalyze this step.

### **Experimental Section**

Materials. Cetyltrimethylammonium bromide, CTABr (Aldrich), was recrystallized repetitively from acetone/ethanol mixtures.<sup>19</sup> Cetyltrimethylammonium chloride, CTACl, was prepared and purified by Sepulveda's method.<sup>20</sup> Cetyltrimethylammonium hydroxide, CTAOH, was prepared by ion exchange from CTABr<sup>21</sup> and concentrations of CTAOH stock solutions were determined by titration with HCl using phenolphthalein as an indicator. The critical micelle concentration, cmc, for each surfactant at ambient temperature was estimated from the intersection point in its surface tension-log surfactant concentration profile. All the surface tension profiles are without minima, indicating the absence of hydrophobic impurities, and the cmc's for the surfactants are as follows: CTABr, 0.88 mM (lit. 0.8 mM at 25 °C);<sup>22</sup> CTACl, 1.1 mM (lit. 1.3 mM at 30 °C);<sup>22</sup> CTAOH 1.2 mM. Preparation, purification, and analysis of substrates 1-phenyl-2,2,2-trichloroethanol (I), 1-(p-methylphenyl)-2,2,2-trichloroethanol (II), 1-(p-methoxyphenyl)-2,2,2-trichloroethanol (III), 1-(p-chlorophenyl)-2,2,2trichloroethanol (IV), and 1-(p-nitrophenyl)-2,2,2-trichloroethanol (V) have been previously described.<sup>16</sup> Reagent grade NaOH (Merck) was used as received. All solutions were prepared using distilled, demineralized water which was boiled and cooled under nitrogen to remove dissolved CO<sub>2</sub>.

Methods. Rates of formation of the benzaldehyde products from substituted ethanols I–V were followed spectrophotometrically at the wavelength maximum of each benzaldehyde<sup>16</sup> by using a Shimadzu Model UV 210-A spectrophotometer fitted with a thermostated water-jacketed cell holder. Reaction was initiated by injection of 25  $\mu$ L of ca. 50 mM stock solutions of substrates I–V in ethanol (stored in the freezer) into 3 mL aqueous solutions of surfactant and NaOH equilibrated at 40 ± 0.1 °C. Absorbance versus time data were stored directly on a microcomputer using a Microquimica 12 bit A/D interface board. First-order rate constants,  $k_{obs}$ , were estimated from linear plots of  $\ln(A - A_t)$  against time for at least 90% reaction using an iterative least-squares program; correlation coefficients, r, were >0.999 for all kinetic runs. Surface tensions were obtained by using a Fisher Du-Nuoy tensiometer.

#### **Results and Discussion**

Figure 1 shows the effect of added NaOH on  $k_{obs}$  for substrates I–V in aqueous solution. Values of  $k_{obs}$  for each substrate increase rapidly with added NaOH and approach a plateau above ca. 100 mM NaOH. Decompositions of the trichloroethanols follow an (Elcb)R type mechanism and the dependence of  $k_{obs}$  on NaOH concentration in aqueous solution in the absence of surfactant can be fitted by using eq 1, where

$$k_{\rm obs} = k_{\rm w} K[OH^{-}]/(1 + K[OH^{-}])$$
 (1)

K is the preequilibrium constant for deprotonation (the reciprocal of the basicity constant) and  $k_w$  is the first-order rate constant for decomposition of the alkoxide ion to the benzaldehyde product. Table 1 lists values for K,  $k_w$ , and  $pK_a$  for substrates I-V obtained from the slopes and intercepts of plots of  $1/k_{obs}$  versus  $1/[OH^-]$ , the double reciprocal form of eq 1.



Figure 1. Effect of the sodium hydroxide concentration on the rates of decomposition of p-substituted-aryl-2,2,2-trichloroethanols at 40 °C. ( $\bigcirc$  p-H; ( $\triangle$ ) p-CH<sub>3</sub>; ( $\square$ ) p-CH<sub>3</sub>O; ( $\bigcirc$ ) p-Cl; ( $\blacksquare$ ) p-NO<sub>2</sub>.

TABLE 1: Rate Constants  $k_w$ , Preequilibrium Constants, K, and  $pK_a$  Values of Ethanols I–V in Water at 40.0 °C

substrate	$10^4 k_{\rm w},  {\rm s}^{-1}$	<i>K</i> , M <sup>-1</sup>	pKa	
I	$34.5 \pm 0.3$	$68 \pm 8$	12.17	
II	$37.9 \pm 0.2$	$66 \pm 7$	12.18	
III	$41.0 \pm 0.2$	$84 \pm 7$	12.08	
IV	$33.5 \pm 0.3$	$103 \pm 8$	11.99	
v	$15.0 \pm 0.5$	$250 \pm 20$	11.60	



**Figure 2.** Effect of cetyltrimethylammonium micelles with  $(\bigcirc)$  bromide,  $(\triangle)$  chloride, and  $(\Box)$  hydroxide counterions on the rates of decomposition of para-substituted-aryl-2,2,2-trichloroethanols at 40 °C. (2A) *p*-H; (2B) *p*-CH<sub>3</sub>; (2C) *p*-OCH<sub>3</sub>; (2D) *p*-Cl.

Figure 2 shows that micellized CTABr, CTACl, and CTAOH inhibit decomposition of substrates I–IV in 120 mM NaOH. Note the that cationic surfactants reduce  $k_{obs}$  from three to five fold. The results in Figure 2 can be interpreted using the pseudophase ion exchange, PPIE, model, Scheme 2.

Both the rapid reversible deprotonation and rate-determining decomposition steps will be affected by CTAX micelles. The quantitative treatment for the effect of aqueous micelles on the apparent acidity (and basicity) constants of weak acids and on the rates of unimolecular reactions using the PPIE model is well developed,<sup>1</sup> and here we simply summarize their application to these decompositions. The local concentration of counterions at micellar surfaces is typically 1-2 orders of magnitude greater than the concentration in the aqueous phase. In aqueous 120 mM NaOH, substrates I–IV are at least 90% deprotonated, and

SCHEME 2



**TABLE 2:** Values of  $K_s$  and  $k_m$  Obtained from the Data Simulations

surfactant	substrate	Ks	$10^{4}k_{\rm m}$
CTABr	I	5800	$5.86 \pm 0.53$
	II	7000	$6.97 \pm 0.99$
	III	5200	$9.68 \pm 1.26$
	IV	6200	$5.22 \pm 0.34$
CTACl	Ι	4300	$7.35\pm0.53$
	II	5200	$8.30\pm0.55$
	III	3400	$10.0\pm1.53$
	IV	5200	$5.75\pm0.42$
CTAOH	I	4200	$8.89\pm0.33$
	II	5500	$11.57\pm0.75$
	III	4000	$14.34 \pm 1.99$
	IV	4800	$8.43\pm0.54$

because the interfacial  $[OH^-]$  will be on the order of 1 M, micellar bound substrates will be completely deprotonated. Thus  $k_{obs}$  depends primarily upon the distribution of the alkoxide ions between aqueous and micellar pseudophases and  $k_{obs}$ -surfactant profiles can be fitted with eq 2, which is the form typically used for spontaneous reactions in micellar solutions, after correction for the extent of deprotonation of the trichloroethanols in the aqueous phase (i.e., eq 1):

$$k_{\rm obs} = K[OH_w^{-}](k_m K_S C_d + k_w) / \{1 + K[OH_w^{-}](1 + K_S C_d)\}$$
(2)

where  $k_w$  and  $k_m$  are, respectively, the first-order rate constants for the decomposition of an alkoxide ion in water and in micelles, and  $C_d$  is the stoichiometric concentration of surfactant in micellar form, i.e.,  $C_d = C_T - \text{cmc}$  where subscript T indicates the stoichiometric surfactant concentration.  $K_S$  is the binding constant of an alkoxide ion to the micelles (eq 3), and K corresponds to the preequilibrium constant in water (eq 4).

$$K_{\rm S} = [\mathrm{RO}_{\rm m}^{-}]/[\mathrm{RO}_{\rm w}^{-}]C_{\rm d}$$
(3)

$$K = [RO_w^{-}]/[ROH_w][OH^{-}]$$
(4)

Values of  $k_m$  and  $K_s$  are obtained by an iterative routine, i.e., by adjusting the value of  $K_s$  until the average deviation in  $k_m$ needed to fit all the data points is at a minimum. Note that at high surfactant concentrations when virtually all the alkoxide ion is bound,  $K_sC_d \gg 1$  and  $k_{obs} \approx k_m$ . Table 2 summarizes the values of  $K_s$ ,  $k_m$ , and the minimum deviation in  $k_m$  for the



**Figure 3.** Plot of log  $k_m$  for the decomposition of para-substitutedaryl-2,2,2-trichloroethanols versus  $\sigma$  at 40 °C in the presence of different surfactants: ( $\bullet$ ) CTABr; ( $\triangle$ ) CTACl; ( $\Box$ ) CTAOH. The dependence of log  $k_w$  on substituent ( $\bigcirc$ ) has been included for comparison purposes.

unimolecular decompositions of the alkoxides of substrates I-IV in each surfactant.

A value of  $\varrho = -0.5$  was obtained from Hammett plots, Figure 3, for  $k_w$  in water for the trichloroethanols using values of  $\sigma$  (correlation coefficient r = 0.966), a result which is consistent with the expected rate acceleration by electrondonating substituents on the ring. Indeed, literature values<sup>16</sup> of -0.58 and -0.81 have been reported for trichloroethanols and tribromoethanols, in aqueous solutions at 25.0 °C, respectively. The increase in K corresponds to a decrease in  $pK_a$ (Table 1) of the trichloroethanols with electron-withdrawing substituents, because  $pK_a = pK_w + pK$ , and yielded a value of  $\varrho = -0.56$  (graph of  $pK_a$  vs  $\sigma$  not shown, with correlation coefficient r = 0.985) which is similar to that reported earlier for the trichloroethanols at 25.0 °C ( $\varrho = -0.72$ ).<sup>16</sup>

In the presence of surfactants, despite the 3-5-fold decrease in the absolute value of the rate constant for the unimolecular decomposition of the alkoxide ion, a similar dependence of the rate constants  $k_m$  on substituents effects is observed. Indeed, values of  $\rho$  of -0.49, -0.46, and -0.45 were obtained from the corresponding Hammett plots, Figure 3, for CTABr, CTACl, and CTAOH respectively.

Comparison of  $k_w$  (Table 1) and  $k_m$  (Table 2) values shows that the rates of decomposition of the alkoxide ions are inhibited about 3-5-fold in micelles for all four substituents, and inhibition increases somewhat with counterion polarizability  $(Br^- > Cl^- > OH^-)$ . These effects are difficult to interpret. A number of spontaneous decompositions have been studied in micelles of various structures and charge types and no predictable pattern has emerged in micellar effects on these reactions. Indeed, examining spontaneous decompositions which have been carried out in CTABr micelles,<sup>23-27</sup> one finds rate changes that vary from rate accelerations (for anionic decarboxylations<sup>23,24</sup> and spontaneous decompositions of aryl sulfate monoanions<sup>25</sup> and aryl and acyl phosphate dianions<sup>26</sup>) to the 3-5-fold inhibition observed with substituted aryl-2,2,2-trichloroethanols. No general pattern is apparent between reaction type and the effects of cationic, anionic, zwitterionic, or neutral micelles on the spontaneous decompositions. What emerges from a dispassionate, classical rapid arm flapping physical organic analysis of the results is that chemical reactivity in micelles reflects the unique characteristics of micellar surfaces which cannot be modeled only by the properties of bulk solvents. Spontaneous decompositions which are speeded by CTABr micelles fit the traditional explanation for micellar (and solvent polarity) effects on reactivity; i.e., that the lower polarity of micellar surfaces. as estimated by micropolarity probes,<sup>28</sup> stabilizes charge delocalized transition states, relative to more charge localized ground states. However, this explanation can not easily be applied to inhibited spontaneous decompositions because some of these reactions also involve changes in charge delocalization. Correia and co-workers<sup>29</sup> invoked the unique structural characteristics of micellar surfaces, i.e., the high local concentration of charged organic ions created by micelle formation. They interpreted the inhibition of the decomposition of *m*-nitrophenyl-9-fluorene carboxylate by CTABr micelles by assuming that the ground state carbanion formed by deprotonation of the substrate at the micellar surface is more stabilized by the trimethylammonium head groups of CTABr than is the transition state in which the charge is being transferred to the oxygen of the *m*-nitrophenoxy group. This explanation is consistent with the rate enhancement they observed for the same reaction in anionic micelles and the absence of any rate effect in nonionic micelles. However, this explanation cannot be applied to the decompositions of the alcohols in Table 2 because charge is being transferred from an alkoxy oxygen to trichloromethylcarbanion and the micellar rate constants also depend some what on counterion type. Here one could invoke charge stabilization of the ground state as well but for the opposite reason; i.e., quaternary ammonium ions interact more strongly with alkoxy anions than with trichloromethyl carbanions. A more complete picture of aggregate effects on spontaneous decompositions awaits a better understanding of the relative contribution of medium and specific effects on chemical reactivity.

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