Effect of Normal and Functional Micelles in Elimination Reactions of Polyhalogenated Pesticides

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The dehydrochlorination of pesticides of the DDT family in the presence of functional and cationic micelles has been studied. Catalytic factors of (2 620 ± 504), (2 190 ± 404), and (1 470 ± 215)-fold were observed for 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane (DDT), 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethane (DDD), and 1-chloro-2,2-bis-(*p*-chlorophenyl)ethane (DDM) respectively, when hexadecyldimethyl-(2-hydroxyethyl)ammonium bromide (CHEDAB) was used as catalyst. Hexadecyltrimethylammonium bromide (CTAB) also showed catalytic effects (417 ± 77), (208 ± 40), and (70 ± 14)-fold increases for DDT, DDD, and DDM, respectively, though smaller than those observed with CHEDAB. The higher catalytic activities of CHEDAB are explained in terms of the participation of the alkoxide moiety.

As part of our systematic effort to arrive at models for the biological degradation of chlorinated pesticides we have previously reported the results of the reaction of DDT-type compounds with vitamin B_{12s} [1,2] and vitamin B_{12r}.[3] It was shown that the decomposition of polyhalogenated hydrocarbon pesticides is vitamin B_{12r}-mediated [3] and the experimental results also provided additional evidence for the involvement of metal centres in the dechlorination of 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane (DDT). On the other hand, the interaction of 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethane (DDD) with vitamin B_{12s} resulted in the formation of *trans*-4,4'-dichlorostilbene through a mechanism involving a Co–Cl α-elimination yielding a carbene or a carbenoid intermediate, which then rearranged to the product.[1,2]

It is well known that micelles play an important role in the enhancement of the rate of chemical reactions. The micellar catalytic effects in bimolecular reactions are generally explained in terms of a favourable partition of the substrate and reactant between the aqueous and micellar phases.[4–11] For example, the decomposition of Dicofol has been studied in the presence and absence of micelles.[12,13] In water and water–methanol the reaction proceeds *via* an *E*1cB mechanism and results in the formation of 4,4'-dichlorobenzophenone and chloroform.[12] This reaction was also studied in the presence of hexadecyltrimethylammonium bromide (CTAB) and hexadecyldimethyl-(2-hydroxyethyl)ammonium bromide (CHEDAB) [13] and catalytic factors of 200- and 345-fold, respectively, were observed. Sodium dodecyl sulphate inhibited the reaction and dodecylcarnitine chloride did not affect the rate significantly. Catalysis by cationic surfactants was inhibited by the addition of salts. Their effectiveness in inhibiting the reaction decreased in the order NaCl > NaBr > $NaNO_3$ > Na_2SO_4. The numerical values obtained for the activation parameters with CTAB [13] were similar to those observed in ethanol-rich mixtures [12] and to other micelle-catalysed reactions.

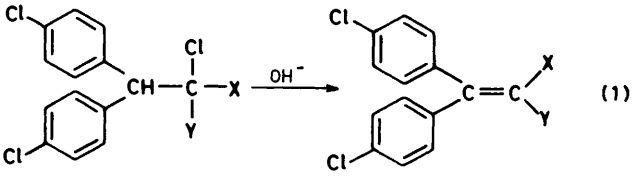
The present work reports the results obtained for the dehydrochlorination of DDT, DDD, and 1-chloro-2,2-bis-(*p*-chlorophenyl)ethane (DDM) in basic aqueous solutions containing cationic and functional surfactants.

Results and Discussion

The dehydrochlorination reactions of DDT, DDD, and DDM with base [equation (1)] were studied in water–ethanol and in aqueous solutions containing micelles of CTAB and CHEDAB.

Due to the extremely low solubility of the polyhalogenated hydrocarbons in water [14] (*ca.* 10^{-10}M) it was not possible to determine directly the rate constants for the dehydrochlorination reactions. Indeed, values for the second-order rate constants in water were obtained by extrapolation of experimental results determined for water–ethanol solutions. In all cases the organic cosolvent was used up to the lowest possible concentration allowed by solubility considerations. Table 1 contains the experimental results determined for various water–ethanol proportions. Extrapolation of these rates yielded values of (2.10 ± 0.25) × 10^{-3}, (4.74 ± 0.50) × 10^{-4}, and (1.02 ± 0.13) × 10^{-4} l mol^{-1} s^{-1} for the second-order rate constants of DDT, DDD, and DDM in water, respectively.

The non-ideality of the solvent mixture was accounted for by following the treatment of Gutbezahl and Grunwald [15] which applies to dilute alcoholic alkoxide solutions.[16] Values of log $k_2/f(OH)$ were constant within the limits of experi-



(1)

DDT, X = Y = Cl
DDD, X = Cl, Y = H
DDM, X = Y = H

DDE, X = Y = Cl
DDMU, X = Cl, Y = H
DDNU, X = Y = H

Table 1. Second-order rate constants for the reaction of DDT, DDD, and DDM with hydroxide ion in water–ethanol mixtures at 25 °C

Ethanol content (% v/v)	10^4k_2/l mol^{-1} s^{-1}		
	DDT	DDD	DDM
20	38.0 ± 3.1	9.20 ± 0.65	2.01 ± 0.08
25	44.0 ± 4.0		
30	58.8 ± 4.1	12.2 ± 1.1	2.79 ± 0.10
40	63.3 ± 4.2	14.4 ± 1.0	3.24 ± 0.19
50	77.5 ± 3.9	20.3 ± 1.2	3.48 ± 0.30
60	102 ± 6.1	21.3 ± 1.3	4.75 ± 0.26
70	127 ± 5.8		5.77 ± 0.35
75		36.6 ± 2.4	
80	173 ± 9.1	44.2 ± 3.3	7.32 ± 0.50
85	213 ± 11		
90	264 ± 13	73.4 ± 3.5	11.6 ± 1.0
93	323 ± 16	115 ± 5.6	17.8 ± 1.3

Table 2. Second-order rate constants for the reaction of DDT, DDD, and DDM with hydroxide ion (9.75×10^{-3}M) in the presence of CTAB at 25 °C

10^3[CTAB]/ M	$10^3k_{2\psi}$/l mol^{-1} s^{-1}		
	DDT	DDD	DDM
3.0	830 ± 32	98.7 ± 6.5	6.83 ± 0.45
4.0	876 ± 38	95.3 ± 6.3	7.09 ± 0.40
5.0	800 ± 29	84.4 ± 7.0	6.98 ± 0.42
6.0	787 ± 33	84.0 ± 6.2	6.85 ± 0.48
7.0	750 ± 30	78.2 ± 5.7	6.01 ± 0.35
8.0	738 ± 32	70.4 ± 5.8	5.52 ± 0.29
9.0	698 ± 28	68.7 ± 5.6	4.88 ± 0.29
10	621 ± 28	67.7 ± 4.1	4.58 ± 0.30
50	263 ± 16	25.7 ± 2.8	1.85 ± 0.18
100	155 ± 11	16.5 ± 1.4	0.98 ± 0.09

Table 3. Second-order rate constants for the reaction of DDT, DDD, and DDM with hydroxide ion (9.75×10^{-3}M) in the presence of CHEDAB at 25 °C

10^3[CHEDAB]/ M	$10^2k_{2\psi}$/l mol^{-1} s^{-1}		
	DDT	DDD	DDM
0.60	490 ± 24	104 ± 5	15.0 ± 1.0
0.80	550 ± 28	103 ± 6	12.8 ± 1.0
1.0	520 ± 29	99.4 ± 5.9	12.5 ± 0.8
2.0	325 ± 18	92.5 ± 6.3	9.33 ± 0.62
3.0	296 ± 17	75.8 ± 4.9	9.96 ± 0.73
4.0	301 ± 16	65.4 ± 4.8	8.42 ± 0.68
5.0	292 ± 17	63.9 ± 5.0	8.36 ± 0.64
6.0	280 ± 16	50.9 ± 4.9	6.50 ± 0.52
7.0	285 ± 16	53.5 ± 4.2	6.78 ± 0.50
8.0	271 ± 19	49.2 ± 3.9	6.58 ± 0.54
9.0	271 ± 17	46.4 ± 3.8	5.50 ± 0.49
10	263 ± 18	43.6 ± 3.7	5.59 ± 0.42

mental error up to 75% v/v ethanol content. This indicates that specific solvent effects for more dilute aqueous ethanol are absent in our reactions, which allows us to assume averages of the log k_2/f(OH) values in this range as reasonable values for the extrapolated rates of the reactions in pure water.

Addition of CTAB to aqueous hydroxide solutions of the pesticides resulted in (417 ± 77), (208 ± 40), and (70 ± 14)-fold increases of the second-order rate constants of DDT, DDD, and DDM in aqueous hydroxide respectively. Table 2 gives the second-order rate constants for the dehydrochlorination of DDT, DDD, and DDM at constant hydroxide concentration (9.75×10^{-3}M) and increasing concentrations of CTAB. At concentrations of surfactant below 3.0×10^{-3}M, the low solubility of the pesticides did not allow us to measure the rate constants. After the initial catalytic acceleration at low CTAB concentrations, the rate constants tend to decrease with increasing concentration of surfactant. These observations parallel other micellar catalytic processes where an excess of surfactant tends to reduce the reaction rate by dilution of the reagents in the micellar phase.

CHEDAB proved a better catalyst than CTAB in the basic dehydrochlorination of the pesticides. Second-order rate increases of (2 620 ± 504), (2 190 ± 404), and (1 470 ± 215)-fold were observed for DDT, DDD, and DDM, respectively. Table 3 gives the second-order rate constant values for the reactions at constant hydroxide concentration (9.75×10^{-3}M) and increasing CHEDAB. As in the case of CTAB, rates tend to decrease with increasing CHEDAB concentrations. Since CHEDAB has a lower c.m.c. than CTAB [17] the rate measurements could be carried out at lower surfactant concentration.

Table 4. Values of the second-order rate constants in water and in the micellar phase for CTAB and CHEDAB

	k_2^0/l mol^{-1} s^{-1}	k_{2m}/l mol^{-1} s^{-1}	
		CTAB [a]	CHEDAB [b]
DDT	(2.10 ± 0.25) × 10^{-3}	(6.9 ± 0.4) × 10^{-3}	(4.0 ± 0.4) × 10^{-2}
DDD	(4.74 ± 0.50) × 10^{-4}	(6.9 ± 0.5) × 10^{-4}	(6.6 ± 0.6) × 10^{-3}
DDM	(1.02 ± 0.13) × 10^{-4}	(4.1 ± 0.3) × 10^{-5}	(7.8 ± 0.7) × 10^{-4}

[a] Calculated following Berezin's treatment.[7] [b] Calculated following Bunton's treatment.[18]

Since the dehydrochlorination of DDT, DDD, and DDM can be considered as a bimolecular reaction between a hydrophobic substrate and an univalent ion of charge opposite to the surfactant, the theoretical treatment developed by Berezin *et al.*[7] can be applied to the experimental data. Berezin's assumption that the rate constant–surfactant concentration profile may be explained in terms of partitioning of substrate and reagent between the aqueous and micellar phases and of differential reactivities in both phases yields equation (2), when applied to our system.

$$k_{2\psi} = \frac{(k_{2m}/V).K_{DDT}.K_{OH}.C_D + k_2^0}{(1 + K_{DDT}.C_D)(1 + K_{OH}.C_D)} \quad (2)$$

The experimental second-order rate constant $k_{2\psi}$ is a function of the second-order rate constants in the micellar and in the aqueous phase, k_{2m} and k_2^0, respectively, of the molar volume of surfactant V, the binding constants K_{DDT} and K_{OH} of the pesticide and hydroxide ion respectively, and of the surfactant concentration in the micellar form, C_D.

Since rate constants were much larger in the presence of micelles than in the aqueous phase ($k_{2\psi} \gg k_2^0$), equation (2) can be written as (3) where $\alpha = V/k_{2m}.K_{DDT}.K_{OH}$,

$$C_D/k_{2\psi} = \alpha + \beta C_D + \gamma C_D^2 \quad (3)$$

$\beta = \alpha(K_{DDT} + K_{OH})$, and $\gamma = V/k_{2m}$.

Inspection of equation (3) shows that plots of $C_D/k_{2\psi}$ against C_D from the data in Tables 2 and 3 should extrapolate to values of α. In all cases negligible intercepts (α *ca.* 0) were obtained from our kinetic values (graphs not shown). Thus, equation (3) can be simplified to (4), which anticipates a linear dependence of the reciprocal of the experimental second-order rate constant $k_{2\psi}$ on the micelle concentration C_D.

$$1/k_{2\psi} = \beta + \gamma C_D \quad (4)$$

Plots of $1/k_{2\psi}$ *versus* C_D for DDT, DDD, and DDM are shown in Figures 1A—C, respectively. The good agreement obtained between the experimental data and the theoretical equation (4) derived from Berezin's model substantiates the simplifications and assumptions used in the derivation.

Since $\gamma = V/k_{2m}$ [equation (3)], values of the second-order rate constants in the micelle can be obtained from the slopes of the plots in Figures 1A—C, assuming a value for V of 0.37 l mol^{-1} for the molar volume of surfactant.[4]

The values of k_{2m} for CTAB together with the values of k_2^0 are given in Table 4. As can be seen from Table 4, the values of the ' true ' rate constant in the presence of CTAB are similar to those observed in water, the catalytic advantage

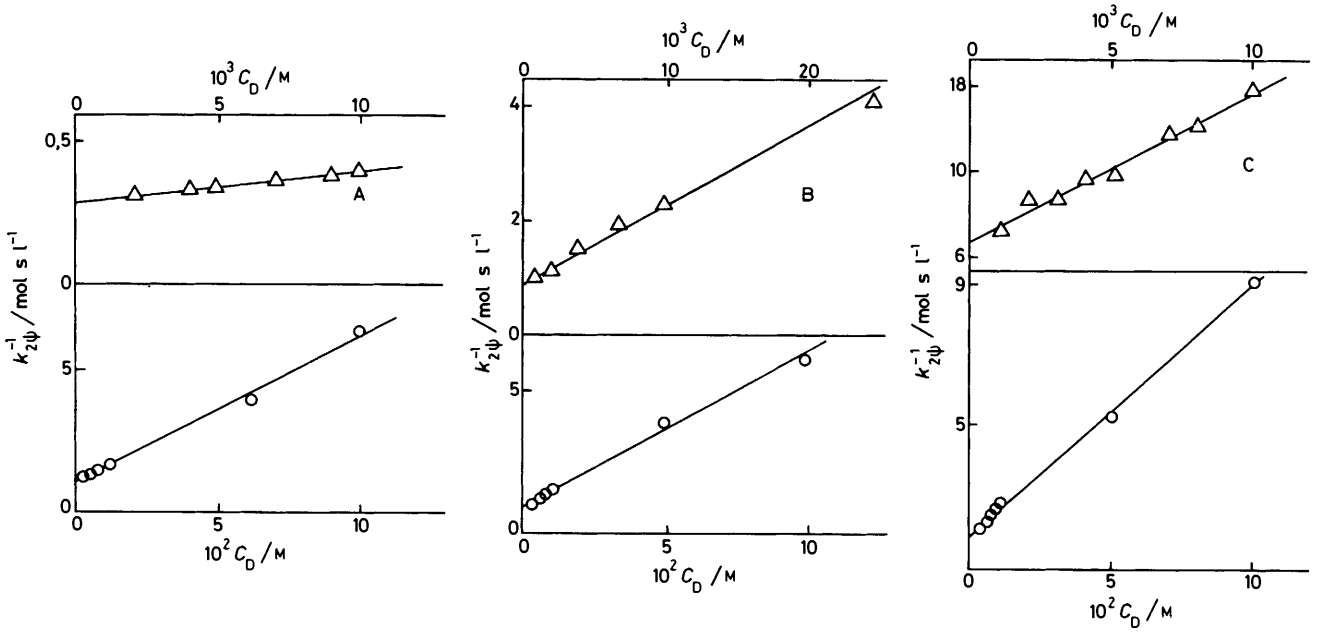
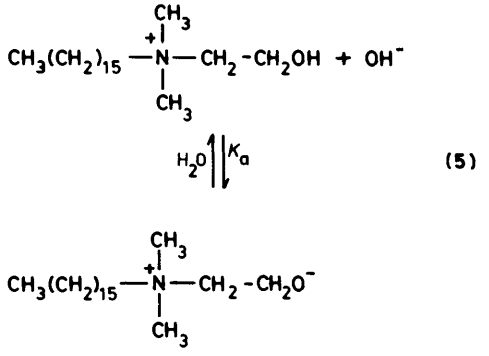


Figure 1. Treatment of the experimental data according to Berezin's theory. Dependence of the reciprocal of $k_{2\psi}$ on the surfactant concentration, C_D, for CTAB (○) and CHEDAB (△) for DDT (A), DDD (B), and DDM (C)



of micelles being the increase in the concentration of reagents in the micellar phase.

It is surprising that the experimental data for CHEDAB fit equation (4), since, considering the equilibrium described in equation (5), the application of Berezin's model to this functional surfactant is open to objection.

In fact, $k_{2\psi}$ is a composite term of the catalytic effect of two bases (hydroxide and alkoxide) and accordingly k_{2m} and K_{OH} do not have any physical meaning in the case of the functional micelle.

In order to determine the values of k_{2m} for the reactions with CHEDAB, the pseudo-first-order rate constants for the dehydrochlorination of DDT, DDD, and DDM at different hydroxide ion concentrations in the presence of 10^{-3}M-surfactant were measured. The results are shown in Figure 2; in all cases the pseudo-first-order rate constant increases with hydroxide ion concentration up to a constant value, a behaviour which reflects the gradual ionization of the 2-hydroxyethyl group with increasing concentration of base. Following the treatment described by Bunton *et al.*,[18] the experimentally determined pseudo-first-order rate constant (k_ψ) is given by equation (6), where K_a is the acid dissociation

$$k_\psi = \frac{k_m K_a [OH^-]/K_w}{1 + [OH^-]K_a/K_w} \qquad (6)$$

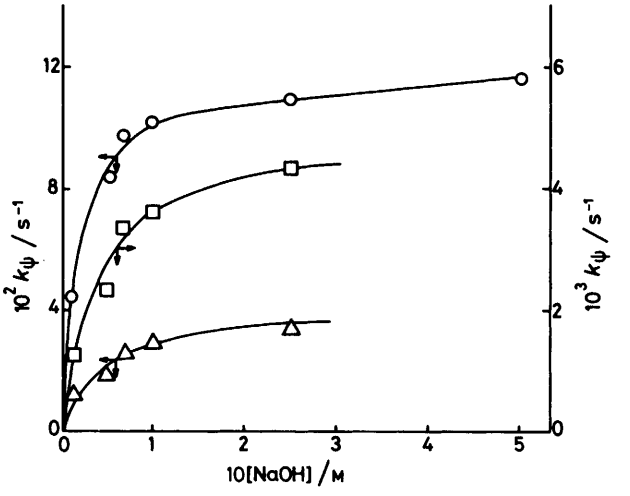


Figure 2. Variation of the experimental rate constant k_ψ with hydroxide ion concentration at [CHEDAB] 1.0×10^{-3}M, for DDT (○), DDD (△), and DDM (□)

constant of the micellized surfactant and k_m is the pseudo-first-order rate constant in the micellar phase, which is equal to k_ψ in the plateau region. Using the kinetic data obtained for DDT, DDD, and DDM (Figure 2) and assuming pK_w 14 in the presence of the surfactant, a value of 12.4 ± 0.1 was calculated for the pK_a of CHEDAB, which is identical to that reported by Bunton and Ionescu.[17] The values of k_m can be transformed into second-order k_{2m} values using the concentration of alkoxide in the Stern layer in order to obtain true second-order rate constants in the micellar phase, for the fully ionized surfactant. An estimate of the alkoxide concentration in the Stern layer of CHEDAB was obtained assuming a hexadecyl chain length of 22.1 Å [19] and a head group (^+N–CH_2–CH_2–O^-) length of 4.5 Å; [20] for a CHEDAB concentration near its c.m.c. one can further assume for the spherical micelle an aggregation number of 60, close to the

value of structurally similar CTAB.[21] These parameters yield [22] an alkoxide concentration of 3M in the Stern layer of fully ionized CHEDAB. The values of k_{2m} obtained for DDT, DDD, and DDM are given in Table 4. Comparison of these values with those calculated for CTAB, following Berezin's treatment, shows that CHEDAB is a more effective catalyst than CTAB for all the substrates studied. It might be argued that both CTAB and CHEDAB would not form spherical micelles with an aggregation number of 60 in the presence of 10^{-2}M-electrolyte. Instead, rod micelles with larger aggregation number would be expected. This would lead to a decrease in area per charge and to an increase in the concentration of alkoxide in the Stern layer, with the consequent decrease of the k_{2m} values for CHEDAB in Table 4. However correct this observation, it does not invalidate our results, since the decrease of k_{2m} values should not be large. Assuming a larger aggregation number, say 200, and a prolate spheroid micelle with axes of 22 and 40 Å, an area per head group of 40 Å^2, and the same head group length of 4.5 Å, results in only a 1.7-fold decrease of the k_{2m} values for CHEDAB. Thus our results support Bunton's observations [17,18] that micelles which contain an ionizable hydroxy-group are better catalysts than simple cationic micelles for reactions with hydroxide. This superior performance of the functional micelles has been rationalized in terms of a greater basicity or nucleophilicity of the generated alkoxide, as compared to the external hydroxide ion.[17,18]

The above results show that pesticides of the DDT family can be solubilized and dehydrochlorinated in the presence of cationic micelles, the highest catalytic activities being found when the surfactant contains an ionizable hydroxy-group (like CHEDAB). Since micelles have been used as models for processes normally occurring in biological membranes,[5] our results suggest that dehydrochlorination of the pesticides of the DDT family (a major degradation pathway *in vivo* [23,24]) may also take place in biological interfaces.

Experimental

1,1,1-Trichloro-2,2-bis-(*p*-chlorophenyl)ethane (DDT) and 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethane (DDD) were purchased from the Aldrich Chemical Co. (Golden Label). 1-Chloro-2,2-bis-(*p*-chlorophenyl)ethane (DDM) was prepared as previously described [2,14] and crystallized several times from ethanol, m.p. 51—51.5 °C (lit.,[25] 51—51.5 °C). Purification of hexadecyltrimethylammonium bromide (CTAB) and hexadecyldimethyl-(2-hydroxyethyl)ammonium bromide (CHEDAB) has been described.[17,26] All other materials used were the best available grade. Aqueous hydroxide solutions were prepared with distilled water. The concentrations of hydroxide ion were determined by titration with standard HCl solutions. Rates of dehydrochlorination of DDT, DDD, and DDM were determined by following (Shimadzu UV-210-A spectrophotometer) the appearance of 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethylene (DDE) at 260 nm, 1-chloro-2,2-bis-(*p*-chlorophenyl)ethylene (DDMU) at 257 nm, and 1,1-bis-(*p*-chlorophenyl)ethylene (DDNU) at 252 nm, respectively.

The temperature of the kinetic runs was maintained at 25.0 ± 0.1 °C by using a water-jacketted cell compartment. Individual pseudo-first-order rate constants were obtained from linear plots of $\ln(A_\infty - A_t)$ *versus* time. All plots were linear for at least 90% of the reaction, and the corresponding correlation coefficients were greater than 0.99.

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