compound 3. The product was recrystallized from ethanol: mp 143-145 °C; NMR ($CDCl_3$) δ 1.40 (6 H, s), 3.85 (6 H, s), 6.80 (1 H, s), 7.20 (5 H, m). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.09. Found: C, 80.15; H, 7.25.

2,3,6,7-Tetramethoxyfluorene (14). 6-Bromoveratraldehyde (2.45 g, 0.01 mol) was heated with copper powder (2.5 g) at 220 °C for 16 h. The chloroform solubles were purified by chromatography (hexane/ethyl acetate, 5:1). Minor amounts of tetramethoxy dialdehyde coupling product were eluted first followed by 2,3,6,7-tetramethoxyfluorenone as a red-orange solid: mp 206-207 °C (lit. mp 207-208.5,[8] 203 °C[10]). Reduction as before gave 2,3,6,7-tetramethoxyfluorene (14) (recrystallization from ethanol): mp 193-194 °C (lit.[11] mp 196 °C). Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.05; H, 6.21.

2,3,4,5,6,7-Hexamethoxyfluorene (15). 2,3,4,5,6,7-Hexamethoxyphenanthrene[12] (1.92 g, 5.4 mmol) in dioxane/water (9:1, 10 mL) was mixed with osmium tetraoxide in dioxane (2 mL of a 20 mg/mL standard solution). The reaction was heated at 50 °C for 1 h, and then sodium periodate (1.5 g) was added in portions over a period of 2 h. Heating at 50 °C was continued for 48 h. The cooled reaction mixture was extracted with ether and the extract washed with saturated sodium bicarbonate followed by 3% aqueous sodium sulfide. The washed extract was dried and concentrated to yield the hexamethoxy dialdehyde as an essentially pure oil (90%): NMR ($CDCl_3$) δ 3.54 (3 H, s), 3.90 (6 H, s), 7.32 (1 H, s), 9.44 (1 H, s). Without further purification the dialdehyde was treated with copper powder (2 g) at 220 °C overnight. 2,3,4,5,6,7-Hexamethoxyfluorenone was obtained as a red solid (33%): mp 143-145 °C; NMR ($CDCl_3$) δ 3.85 (6 H, s), 3.91 (3 H, s), 6.98 (1 H, s); IR ν (NaCl) 1695 cm^{-1} (C=O). Reduction with hydrogen as described afforded the desired 2,3,4,5,6,7-hexamethoxyfluorene (15) (recrystallization from ethanol): mp 132-133 °C; NMR ($CDCl_3$) δ 3.66 (1 H, s), 3.82 (3 H, s), 3.85 (3 H, s), 3.88 (3 H, s), 6.76 (1 H, s). Anal. Calcd for $C_{19}H_{22}O_6$: C, 65.69; H, 6.67. Found: C, 65.81; H, 6.82.

Registry No. 2, cation radical, 34539-20-3; 3, 42523-30-8; 3, cation radical, 51548-21-1; 4, 70278-85-2; 4, cation radical, 72442-87-6; 5, 525-64-4; 5, cation radical, 72442-88-7; 6, 18675-95-1; 7, 72442-89-8; 8, 244-99-5; 9, 26060-14-0; 10, 2523-46-8; 11, 26060-13-9; 12, 42523-12-6; 12, cation radical, 72442-90-1; 13, 72442-91-2; 13, cation radical, 72442-92-3; 14, 51487-65-1; 14, cation radical, 65989-21-1; 15, 70278-86-3; 15, cation radical, 72442-93-4; 2,7-dihydroxyfluorenone, 42523-29-5; 2-hydroxyfluorene, 2443-58-5; methyl iodide, 74-88-4; toluenesulfonanthranilic acid, 6311-23-5; veratrole, 91-16-7; dimethoxy-2'-(toluenesulfamido)benzophenone, 72453-52-2; 1,2-dimethoxyfluorenone, 42523-09-1; 3,4-dimethoxyfluorenone, 23346-81-8; 2,3-dimethoxyfluorenone, 2041-27-2; 6-bromoveratraldehyde, 5392-10-9; 2,3,6,7-tetramethoxyfluorenone, 58532-06-2; 2,3,4,5,6,7-hexamethoxyphenanthrene, 63557-97-1; 2,3,4,5,6,7-hexamethoxyphenanthrenequinone, 63557-99-3; 2,3,4,5,6,7-hexamethoxyfluorenone, 72442-94-5.

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Micellar Effects on the Base-Catalyzed Oxidative Cleavage of a Carbon-Carbon Bond in 1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethanol

Faruk Nome,* Erineu W. Schwingel, and Lavinel G. Ionescu

Departamento de Química, Universidade Federal de Santa Catarina, 88000-Florianópolis, SC, Brasil

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The base-catalyzed oxidative cleavage of 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol (Dicofol) results in the formation of chloroform and 4,4'-dichlorobenzophenone. The reaction was studied in the presence of hexadecyltrimethylammonium bromide (CTAB) and hexadecyldimethyl(2-hydroxyethyl)ammonium bromide (CHEDAB), and catalytic factors of 200- and 345-fold, respectively, were obtained. The experimental results are rationalized in terms of an increase of the concentration of the reagents in the micellar phase. Sodium dodecyl sulfate (NaLS) inhibits the reaction, and dodecylcarnitine chloride (LCC) essentially does not alter the rate. The catalysis by cationic surfactants (CTAB, CHEDAB) is inhibited by added salts. The effectiveness of the salts in decreasing the rate constant is NaCl < NaBr < $NaNO_3$ < Na_2SO_4 < NaOTs. The activation parameters for 4.0×10^{-3} M CTAB ($\Delta H^{\ddagger}$ = 27.7 kcal/mol, $\Delta G^{\ddagger}$ = 19.8 kcal/mol, $\Delta S^{\ddagger}$ = 25.9 eu) and for 1.0×10^{-1} M CTAB ($\Delta H^{\ddagger}$ = 26.7 kcal/mol, $\Delta G^{\ddagger}$ = 20.8 kcal/mol, $\Delta S^{\ddagger}$ = 19.6 eu) indicate that the rate decrease observed at high surfactant concentration is due to an entropic contribution to the free-energy term.

1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethanol, Kelthan or Dicofol, is a pesticide used on a commercial scale. It has also been identified as a metabolite in the enzymatic degradation of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)-ethane, DDT. Several other products have been confirmed in the enzymatic transformation of DDT. Scheme I presents a commonly accepted mechanism for this degradation.[1]

According to this scheme, the formation of 4,4'-dichlorobenzophenone (DBP) occurs through several steps, without participation of Dicofol. However, from a purely chemical point of view, it would be very plausible to postulate the formation of DBP upon treatment of Dicofol with base. Indeed, the presence of three chlorine atoms on C-2 should result in the stabilization of a developing carbanion. Thus, the ionization of Dicofol in the presence of base would result in the formation of an alkoxide ion which would later lead to an oxidative carbon-carbon bond cleavage and produce DBP and chloroform. This type of oxidative carbon-carbon bond cleavage reaction involving a tertiary alcohol is well documented and has been described extensively in the literature.[2-4]

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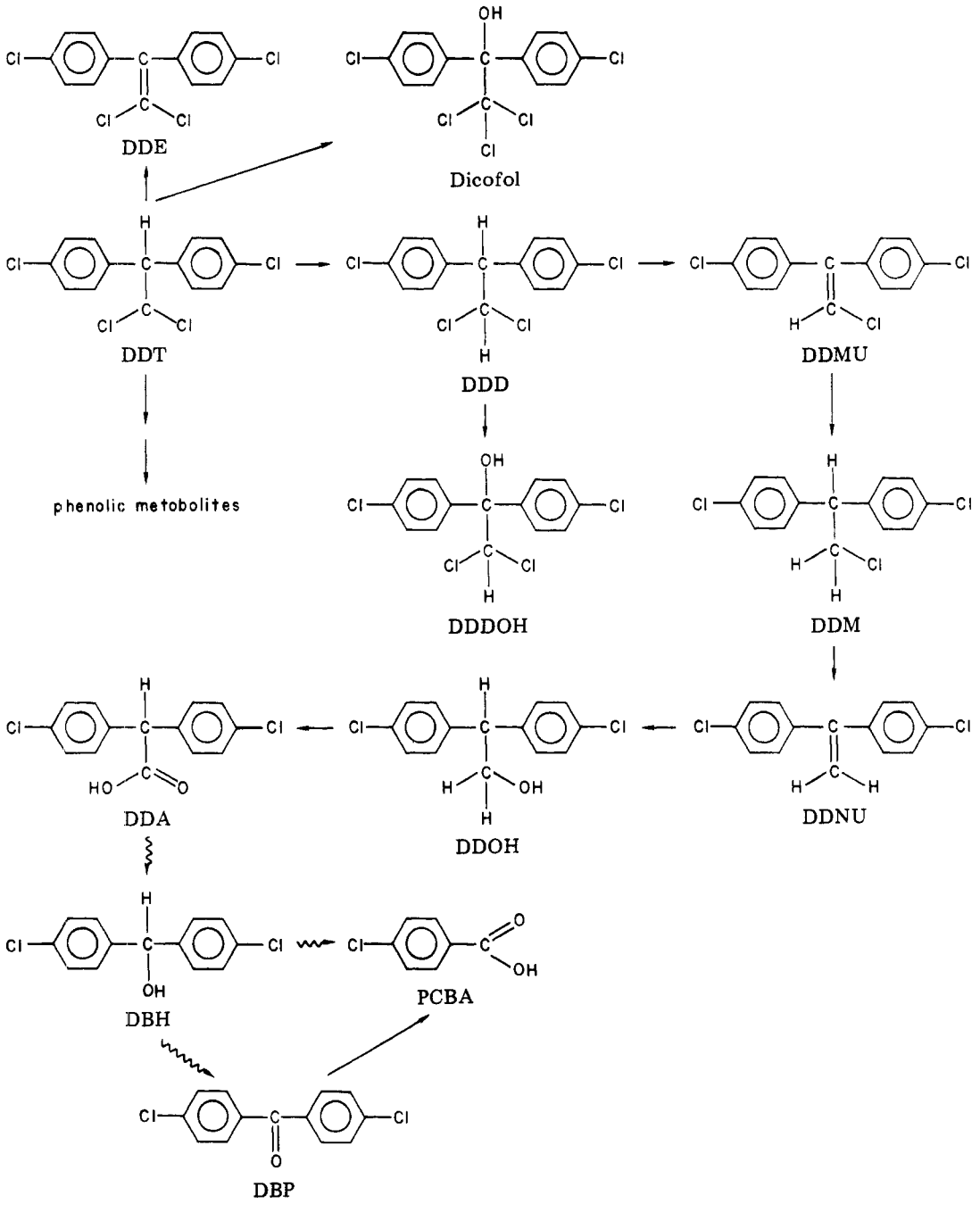
Scheme I



If the reaction of Dicofol with base is considered as a possible "metabolic pathway" for the formation of DBP, it should occur at a reasonably fast rate and at low base concentration.

The role of micelles in the enhancement of the rate of chemical reactions is well-known and has been thoroughly reviewed in the literature.[5-14] It is generally agreed that significant micellar catalytic effects are observed only when there is a favorable partition of the substrate and reactant between the aqueous and the micellar phases. Due to its hydrophobic nature, Dicofol should be readily incorporated into micelles. Therefore, the rate of its base-catalyzed oxidative cleavage should be significantly enhanced by micelles. Since micelles have also been used as simple membrane models,[15,16] it appeared of interest to study the decomposition of Dicofol, which has many biological implications, in a microenvironment which would mimic biomacromolecular ensembles and biological interfaces.

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Table I. Observed Pseudo-First-Order Rate Constants for the Reaction of Dicofol with Hydroxide Ion in Water[a]

pH	10^4k_ψ, s^{-1}	pH	10^4k_ψ, s^{-1}
8.5	1.86	10.1	36.1
9.0	4.32	10.4	77.0
9.5	7.91	10.7	178
9.8	28.0	11.0	289

[a] The temperature was 30.0 °C.

Experimental Section

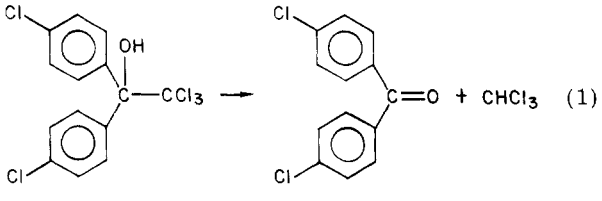
1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethanol, Dicofol, was purchased from Chem. Service, and its purity found to be satisfactory by thin layer chromatographic, UV, and IR analysis. Purification of sodium dodecyl sulfate (NaLS), hexadecyltrimethylammonium bromide (CTAB), hexadecyldimethyl(2-hydroxyethyl)ammonium bromide (CHEDAB), and dodecylcarnitine chloride (LCC) has been described.[5,17] All other materials used were the best available grade. Aqueous solutions were prepared in distilled water. The pH was determined by a Metrohm E-350-B pH meter.

Rates of oxidation of 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol were determined by following (Varian 634 spectrophotometer) the appearance of 4,4′-dichlorobenzophenone at 267.5 nm. The temperature for the kinetic runs was maintained within ±0.1 °C of the desired value by using a water-jacketed cell. Individual pseudo-first-order rate constants, k_ψ values, were obtained from linear plots of ln $(A_\infty - A_t)$ vs. time. All of these plots were linear for at least 90% of the reaction, and the correlation coefficients were greater than 0.99. The energy of activation was determined from linear plots of ln k_ψ vs. $1/T$ with experimental data from at least five different temperatures in the 25–40 °C range. The enthalpy of activation ($\Delta H^\ddagger$) was obtained by using the relation $\Delta H^\ddagger = E_a - RT$, the entropy of activation ($\Delta S^\ddagger$) from $\Delta S^\ddagger = 2.303R(\log k_\psi - \log ek/h - \log T + E_a/2.303RT)$, and the free energy of activation ($\Delta G^\ddagger$) from $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$.

Chloroform was identified with a Varian 2440-D gas chromatograph using a 2 m × 3.2 mm column packed with squalane. The temperatures of the column, detector, and injection block were 85, 120, and 125 °C, respectively. A retention time of 80 s was found.

Results and Discussion

The reaction of Dicofol with base was studied in water as a function of hydroxide ion concentration and of the four surfactants CTAB, CHEDAB, NaLS, and LCC. Equation 1 describes the reaction occurring in our system.



(1)

As the reaction proceeded, the fine structure in the 255–272-nm region (log ϵ 2.81) characteristic of the nonconjugated aromatic system of Dicofol disappeared and was replaced by a strong absorption band at 267.5 nm (log ϵ 4.39) due to the conjugated aromatic chromophore of the product. This approximately 40-fold increase in the molar absorptivity value was used to monitor the rate of appearance of 4,4′-dichlorobenzophenone at 267.5 nm.

Table I includes a summary of the experimental results obtained for the reaction in water alone as function of pH. The results clearly indicate that the reaction is first order in hydroxide ion. Accordingly, the observed pseudo-first-order rate constant is described by

$$k_\psi = k_2[OH] \quad (2)$$

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Table II. Observed Pseudo-First-Order Rate Constants for the Reaction of Dicofol with Hydroxide Ion in the Presence of CTAB[a]

	10^4k_ψ, s^{-1}		
10^3[CTAB], M	pH 8.5	pH 9.0	pH 9.5
0.00	1.86	4.32	7.91
0.50	7.80	26.0	38.5
1.00	23.9	53.7	126
2.00	96.3	208	413
3.00	214	721	1100
4.00	357	737	1320
5.00	340	707	1283
6.00	330	660	1150
7.00	304	624	1100
8.00	295	580	960
9.00	262	502	900
10.0	250	470	753
50.0	106	310	509
100	69.5	236	284

[a] The temperature was 30.0 °C.

Table III. Observed Pseudo-First-Order Rate Constants for the Reaction of Dicofol with Hydroxide Ion in the Presence of CHEDAB[a]

10^4 × [CHEDAB], M	10^4k_ψ, s^{-1}	10^4 × [CHEDAB], M	10^4k_ψ, s^{-1}
0.00	1.86	40.0	462
0.50	18.0	50.0	413
1.00	35.5	60.0	355
2.00	82.5	70.0	316
3.00	177	80.0	280
4.00	350	90.0	290
5.00	444	100	274
10.0	642	500	90.2
20.0	597	1000	47.0
30.0	520		

[a] At pH 8.5 and 30.0 °C.

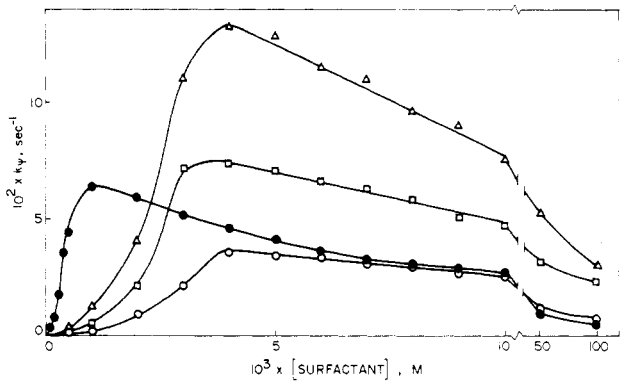

Figure 1. Plot of the pseudo-first-order rate constant for the decomposition of Dicofol, k_ψ, vs. surfactant concentration for CTAB at pH 8.5 (○), pH 9.0 (□), and pH 9.5 (△) and for CHEDAB at pH 8.5 (●) at 30.0 °C.

where a value of the second-order rate constant, k_2, of 2.0 × 10^1 M^{-1} s^{-1} was calculated.

Table II contains the experimental results obtained for the reaction of Dicofol with base as a function of pH and CTAB concentration. Table III shows the pseudo-first-order rate constants obtained for the same reaction in the presence of CHEDAB at pH 8.5. An analysis of the experimental data shows that a marked enhancement in the rate of formation of DBP takes place in the presence of both of the surfactants. It can be also observed that for CTAB the maximum rate enhancement takes place at a concentration of surfactant corresponding to 4.0 × 10^{-3} M, independently of the pH of the solution. Indeed, plots of the observed rate constant vs. CTAB concentration (Figure

Table IV. Observed Pseudo-First-Order Rate Constants for the Reaction of Dicofol with Hydroxide Ion in the Presence of CTAB[a]

pH	10^4k_ψ, s^{-1}	pH	10^4k_ψ, s^{-1}
6.5	3.38	7.6	47.5
6.8	3.50	8.5	357
7.1	10.7	9.0	737
7.1	15.2	9.5	1320

[a] [CTAB] = 4.0×10^{-3} M, T = 30.0 °C.

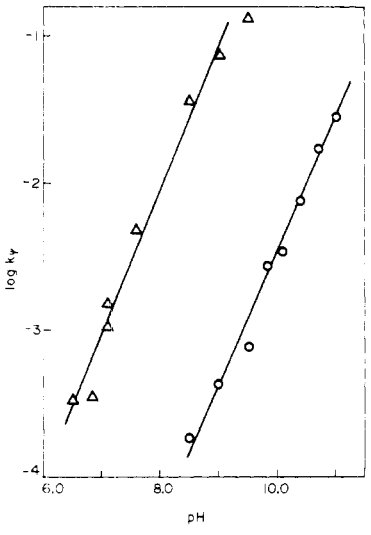

Figure 2. Plot of the logarithm of the observed rate constant for the decomposition of Dicofol, k_ψ, vs. pH in water (○) and in aqueous solutions of 4.0×10^{-3} M CTAB (△) at 30.0 °C.

1) for three different pH values had very similar shapes. Figure 1 also includes, for comparison purposes, a typical plot obtained for the same reaction in the presence of CHEDAB at pH 8.5. As can be seen, the rate maximum is shifted to lower concentration of this surfactant as compared to CTAB. Table IV describes the data obtained for the oxidative carbon–carbon bond cleavage of Dicofol at constant CTAB concentration (4.0×10^{-3} M) as a function of pH. Figure 2 illustrates a comparison of the experimentally observed rate constants for the reaction in water alone and in aqueous solutions of CTAB over a pH range. The slope of both straight lines is approximately unity. For the reaction in water, a slope of 1.0 indicates a reaction which is first order in hydroxide ion. In the case of the aqueous solution of CTAB, since the pH in the micellar phase can not be evaluated, the bulk pH was plotted. However, the fact that the lines are parallel suggests that the concentration of hydroxide ion in the micellar phase is linearly dependent on the concentration of hydroxide ion in the aqueous phase in the range of pH studied. The catalytic factor obtained from the difference between the two was about 200 and, since it represents an average value, is considered to be more accurate than the catalytic ratio obtained at a single pH value. For the reaction of CHEDAB a catalytic factor of about 345 was obtained at pH 8.5.

There are several relatively recent quantitative treatments that have been proposed for micellar "catalysis" and "inhibition" in aqueous solutions.[13,18,19] Berezin, Martinek, and Yatsimirskii have put forward a comprehensive kinetic theory[13] that explains micellar catalysis with a pseudophase model. This theory considers the partition of the

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Table V. Kinetic Parameters Obtained for the Reaction of Dicofol with Base in the Presence of Micelles

		10^4k, s^{-1}		
	$K_{OH}K_{Di}$, M^{-2}	pH 8.5	pH 9.0	pH 9.5
water		1.8[a]	4.32[a]	7.91[a]
CHEDAB	1.0×10^6	1.5[b]		
CTAB	6.3×10^4 [c]	2.4[b]	10.0[b]	11.0[b]

[a] $k = k_w$. [b] $k = k_m$. [c] $K_{OH}K_{Di}$ did not change with pH, as can be deduced from eq 5 and Figure 1.

reagents between the bulk and micellar phases and the simultaneous course of the reaction in both phases. Its advantage is that treatment of the kinetic data affords the calculation of partition coefficients of the reagents and, more importantly, a value for a "true" rate constant in the micellar phase.

Equation 3 represents a general form for the description

$$k = \frac{k_m P_{OH} P_{Di} CV + k_w(1 - CV)}{[1 + (P_{OH} - 1)CV][1 + (P_{Di} - 1)CV]} \quad (3)$$

of micellar effects on a bimolecular reaction, where k_m is the rate constant in the micellar phase, k_w is the rate constant in the aqueous phase, C is the total surfactant concentration (cmc_1), V is the molar volume of the surfactant, P_{OH} is the partition coefficient of OH^- between the micellar and aqueous phase, and P_{Di} is the partition coefficient of Dicofol between the micellar and aqueous phase.

Considering that P_{OH} and P_{Di} are both much greater than unity and that at low surfactant concentrations the term $(1 - CV) \approx 1$ and using the general relation $K = (P - 1)V$ for the binding K, eq 3 reduces to

$$k_\psi = \frac{(k_m/V)K_{OH}K_{Di}C + k_w}{(1 + K_{OH}C)(1 + K_{Di}C)} \quad (4)$$

where K_{OH} and K_{Di} represent binding constants for OH^- and Dicofol, respectively. When the contribution of the term $(k_m/V)K_{OH}K_{Di}C$ is much greater than k_w it follows that

$$C_{opt} = 1/(K_{OH}K_{Di})^{1/2} \quad (5)$$

where C_{opt} is the surfactant concentration at which a maximum micellar effect on the observed rate constant, k_ψ, is obtained.

On the other hand, a value for k_m/V can be obtained by using eq 6, where $\alpha = V/k_mK_{OH}K_{Di}$, $\beta = V(K_{OH} + K_{Di})/k_mK_{OH}K_{Di}$, and $\gamma = V/k_m$.

The value of α can be determined from a plot of $C/(k_\psi - k_w)$ vs. C, where α corresponds to the limiting case when C approaches zero. A plot of the left-hand side of eq 6 vs. C should yield the respective values for β and γ.

$$\frac{C/(k_\psi - k_w) - \alpha\left(1 - \frac{k_w}{k_\psi}\right)}{C} = \beta + \gamma C \quad (6)$$

Analysis of our experimental results with the use of eq 5 and 6 led to the values summarized in Table V.

The treatment of our experimental data resulted in the determination of $K_{OH}K_{Di}$ product without any difficulty. However, the determination of α, β, and γ from eq 6 is not straightforward. The main problem that appears in the application of eq 6 is that the analysis of the experimental points at low surfactant concentration (surfactant concentration smaller than C_{opt}) shows considerable scatter, and the value obtained for α is not very reliable. On the contrary, the determination of γ was much more precise (an error of about ±10% was estimated), the reason being

Table VI. Observed Pseudo-First-Order Rate Constants for the Reaction of Dicofol with Hydroxide Ion in the Presence of CTAB at Various Temperatures

	$10^4 k_\psi$, [a,b] s^{-1}	
T, °C	[CTAB] = 4.0×10^{-3} M	[CTAB] = 1.0×10^{-1} M
25.0	139	30.4
28.0	220	45.7
30.0	357	69.5
31.0		77.5
34.0	609	120
37.0	970	190
40.0	1305	263

[a] Each value represents the average of at least two different experimental determinations. [b] pH 8.5.

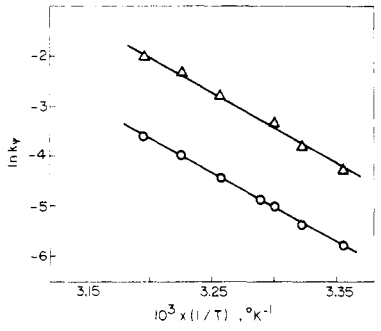

Figure 3. Dependence of the natural logarithm of the observed rate constant for the decomposition of Dicofol, k_ψ, on the temperature for 1.0×10^{-1} M (O) and 4.0×10^{-3} M (Δ) CTAB at pH 8.5.

that the value of the ratio $C/(k_\psi - k_w)$ at high surfactant concentration is much greater than α.

Thus, the left-hand side of eq 6 becomes insensitive to the error in the determination of α. Due to this fact γ was determined by using only the experimental data at "high" surfactant concentration ([CTAB] $\geq 4 \times 10^{-3}$ M and [CHEDAB] $\geq 5 \times 10^{-4}$ M).

As can be seen from Table V, the catalytic effectiveness of micelles, in our case, results from an increase in the binding constants of the reagents to the micellar phase, which in turn represents an increase in their concentration in the micelles. Indeed, values of the "true" rate constant in the micellar phase for CHEDAB (1.5×10^{-4} s^{-1}), for CTAB (2.4×10^{-4} s^{-1}), and for the reaction in water (1.86×10^{-4} s^{-1}) can be considered to be the same within experimental error. Thus, the higher "catalytic" ratio of CHEDAB (345) as compared to CTAB (200) can be attributed to the increase in the binding constants.

A basically identical conclusion, with respect to the value of the rate constant in the micellar phase, can be reached when the models of Romsted[18] or Chaimovich and Quina[19] are used. In the latter, the binding of hydroxide ion to the micellar surface is described in a fashion analogous to an ion-exchange resin.

It is generally agreed that the decrease in the observed rate constant at surfactant concentrations higher than C_{opt} is due to a dilution of the reactants. If such is the case, a consideration of the activation parameters for this reaction should give additional insight into the nature of the process. Table VI shows the data obtained for the reaction of Dicofol with base at 0.004 M and 0.1 M CTAB concentrations as function of temperature. A graphical representation of the experimental results is given in Figure 3. The values determined for the energy of activation, E_a, and enthalpy of activation, $\Delta H^\ddagger$, for the two different CTAB concentrations are identical within experimental error (E_a = 28.3 kcal/mol and $\Delta H^\ddagger$ = 27.7 kcal/mol for 0.004 M CTAB; E_a = 27.3 kcal/mol and $\Delta H^\ddagger$ = 26.7 kcal/mol for 0.1 M CTAB).

Table VII. Effect of Added Salt for the Reaction of Dicofol with Hydroxide Ion in the Presence of CTAB[a]

$10^3 \times$ [salt], M	$10^3 k_\psi$, s^{-1}				
	NaBr	NaCl	$NaNO_3$	Na_2SO_4	NaOTs
0.00	8.88	8.88	8.88	8.88	8.88
0.50					1.66
1.00					1.40
5.00	7.08	8.55	4.66	1.19	0.56
10.0	6.87		3.05	1.06	0.34
15.0	5.77	7.70	2.20	1.10	
20.0	5.13	7.00	2.03	1.48	
30.0	2.96	3.90	1.60	1.11	
40.0	2.59		1.48	1.30	
50.0	2.47	3.50	1.03	1.28	

[a] [CTAB] = 4.0×10^{-3} M, pH 8.0, T = 30.0 °C.

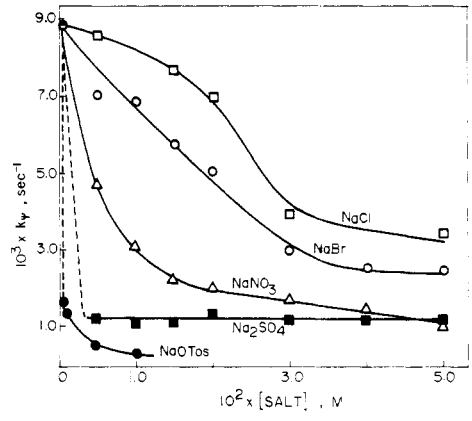

Figure 4. Effect of various salts upon the micellar-catalyzed decomposition of Dicofol at 4.0×10^{-3} M CTAB at pH 8.00 and 30.0 °C.

Since E_a and $\Delta H^\ddagger$ do not depend on the manner in which the rate constant is calculated but rather on the ratio of the rate constants at different temperatures, this result indicates that the rate decrease is not due to any enthalpic contribution to the free energy of activation, $\Delta G^\ddagger$. Obviously, then, the contribution must be entropic in nature. The values of $\Delta S^\ddagger$ at 0.004 and 0.1 M CTAB were found to be 25.9 and 19.6 eu and those of $\Delta G^\ddagger$ were 19.8 and 20.8 kcal/mol, respectively.

This decrease in entropy is consistent with the decrease in rate constant upon increasing surfactant concentration and with the idea that the biggest catalytic advantage of micelles is to concentrate the reagents in the micellar phase. As should be expected, all the concentration effect should be part of the entropic contribution to the free energy of activation.

This micellar-catalyzed reaction is inhibited by added salts. Some representative results obtained in the presence of 0.004 M CTAB are given in Table VII. In general, the effect of all the added salts was similar. An increase in their concentration resulted in a decrease of the experimentally observed rate constant (Figure 4). The effect of the added salts is generally attributed to both a change in micellar structure and exclusion of one of the reagents from the micelle.[20] The effectiveness of the salts in decreasing the rate constants is NaCl < NaBr < $NaNO_3$ < Na_2SO_4 < NaOTs. This ordering is similar to that normally observed for salt inhibition in micellar systems[20] and it appears to follow the Hofmeister series. The effect of salts, using the concept of selective ion binding,[18] is to

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Table VIII. Observed Pseudo-First-Order Rate Constants for the Reaction of Dicofol with Hydroxide Ion in the Presence of NaLS and LCC

10^3[NaLS], M	10^4k_ψ,[a] s^{-1}	10^3[NaLS], M	10^4k_ψ,[a] s^{-1}
	289	7.00	5.98
1.00	224	8.00	4.50
2.00	154	9.00	3.00
3.00	136	10.0	1.75
4.00	85.6	50.0	0.109
5.00	46.3	100	0.074
6.00	29.6		
10^3[LCC], M	10^4k_ψ,[b] s^{-1}	10^3[LCC], M	10^4k_ψ,[b] s^{-1}
	41.8	11.0	47.0
1.00	40.3	13.6	51.0
5.00	41.2	18.2	49.0
9.06	43.0		

[a] At pH 11.0, T = 30.0 °C. [b] At pH 10.34, T = 30.0 °C.

"wash out" hydroxide ion from the micellar surface.

As would be expected from consideration of Hartley's rules,[5] anionic and zwitterionic micelles do not catalyze the reaction of Dicofol with hydroxide ion. Table VIII shows experimental data obtained for various concentrations of NaLS and LCC. The inhibition produced by NaLS is relatively pronounced over the entire concentration range studied. LCC, which is in a zwitterionic form at the pH studied, does not affect the reaction rate to any significant extent. Indeed, the slight increase in the rate constant is in the range normally expected for a nonspecific salt effect.

Since micelles have often been used as elementary membrane models,[5,15,16] it would appear reasonable to suggest, in the light of the described results, that the decomposition of Dicofol leading to the formation of 4,4'-dichlorobenzophenone may proceed via a similar pathway in biological systems. Thus, in the presence of a positively charged biological interface, many of the steps outlined in Scheme I can be disregarded and the formation of DBP can be explained in terms of a process analogous to that reported for CTAB and CHEDAB.

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Registry No. Dicofol, 115-32-2; DBP, 90-98-2; chloroform, 67-66-3; CTAB, 57-09-0; CHEDAB, 20317-32-2; NaCl, 7647-14-5; NaBr, 7647-15-6; $NaNO_3$, 7631-99-4; Na_2SO_4, 15124-09-1; NaOTs, 657-84-1.

Carbon-13 Nuclear Magnetic Resonance Spectral Properties of Alkyl Disulfides, Thiolsulfinates, and Thiolsulfonates

S. Woody Bass and Slayton A. Evans, Jr.*

William Rand Kenan, Jr., Laboratories of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514

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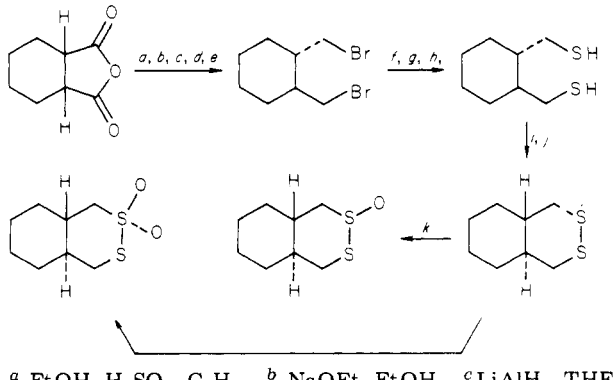
The ^{13}C nuclear magnetic resonance spectra, as well as substituent effects, of acyclic and some cyclic disulfides, thiolsulfinates, and thiolsulfonates are reported. β_{SO} effects are deshielding and range from 13.2 to 20.6 ppm. β_{SO_2} effects are also deshielding and slightly larger (+22.1 to +26.7 ppm) than the β_{SO} effects. The γ_{SO} values in the acyclic systems are shielding (-3.3 to -6.83) while the γ'_{SO} values reflect a gradual *decrease* in shielding (-8.30 to +2.3). Sulfur lone-pair electron back-donation into the C-S σ^* orbital and/or electron polarization has been proposed to account for this trend in the γ'_{SO} values. The γ'_{SO_2} values are about half the magnitude of the γ'_{SO} values and follow the same trend of decreasing shielding. Additional long-range substituent effects are in harmony with similar effects in other systems and these comparisons are mentioned briefly.

The disulfide bonds of various amino acid residues (e.g., L-cystine) play important roles in maintaining protein structure.[1] Detailed NMR studies designed to reveal conformational preferences about $RS(O)_nSR$ bonds in disulfides (n = 0), thiolsulfinates (n = 1), and thiolsulfonates (n = 2) are fundamentally important for understanding the factors which influence and ultimately control conformational mobility and stability of protein structure. Comparative ^1H and ^{13}C NMR chemical shift data would allow assignments of hydrogens and carbons proximal to the -SS-, -S(O)S-, and $-SO_2S-$ functional groups to be made with a high degree of certainty.[2]

Presently, there are few detailed ^{13}C NMR studies of simple acyclic disulfides and the corresponding oxide derivatives.[3,4] In this report, we have attempted to remedy this situation by describing some useful trends in ^{13}C NMR data obtained from a number of acyclic as well as cyclic

Scheme I



[a] EtOH, H_2SO_4, C_6H_6. [b] NaOEt, EtOH. [c] $LiAlH_4$, THF. [d] p-TsCl, Pyr. [e] LiBr, Me_2SO. [f] $(NH_2)_2C=S$, MeOH. [g] NaOH, reflux. [h] H_2SO_4. [i] $Pb(OAc)_2$, NaOAc. [j] S, C_6H_6. [k] MCPBA, $CHCl_3$. [l] KIO_4, Me_2CO-H_2O.

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