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The Two-phase Oxidation of Some Aromatic Compounds with Cerium Ammonium Nitrate in the Presence of Surfactants

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The two-phase oxidations of 3,6-dimethoxydurene and xylenes in cyclohexane solutions with the aqueous solution of cerium ammonium nitrate were carried out in the presence of cationic, nonionic, and anionic surfactants. Both cationic (ammonium salt) and nonionic (Dipodand) surfactants inhibited the reaction. The anionic surfactant (sodium dodecyl sulfate, SDS) catalyzed these oxidations. From the product distribution it was concluded that the catalytic action of SDS is due to the binding of aromatic compounds and the Ce(IV) ions to the surface of the SDS micelles. The micellar oxidant has the high oxidation potential which should allow to oxidize the comparatively nonreactive substrates.

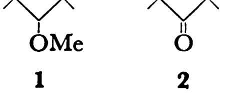
Although there have been many investigations of micellar effects on electron transfer reactions,[1] only very few studies have since appeared which consider a micellar catalysis in the oxidation of organic substrates by metal ions.[2] However, it seems obvious that the aggregates of amphiphilic molecules should help to bring together hydrophobic substrates and hydrophilic, highly charged metal ion oxidants. This is particularly important when the reaction is run under the two-phase conditions, so there is a gap of hydrophobic repulsions between the reagents.

Our interest in the oxidation of aromatic compounds by cerium ions[3] prompted us to examine the influence of the complexing surfactants on the two-phase oxidation reactions. In a previous paper we reported the catalytic effect of a lipophilic complexone **6** bringing the Ce(IV) species into an organic phase.[4] This report describes our study of the title reactions carried out in the presence of typical cationic, anionic, and nonionic surfactants.

Results and Discussion

In the case of the two-phase system with the micelle-forming catalyst the reaction can take place at the interface, or in the bulk aqueous, bulk organic or micellar phases. With the catalyst located in an aqueous layer, one can expect that the lipophilic substrate will be solubilized partially in the micellar phase and in this way will be brought to the oxidant. In an organic phase the reversed micelles can be formed thus takeing the oxidant to the substrate. The micelles can also affect the reactivity of both organic substrate and metal ion, changing their redox potentials by the electrostatic interactions. The high ionic strength of the oxidant solution should favour an increase of density of surface charge of the aqueous micelles as well as the higher solubility of organic substrate in this micellar phase.

With these general considerations in mind we examined the catalytic activity of surfactants by determining the extent of reactions 1 and 2 with and without catalyst.

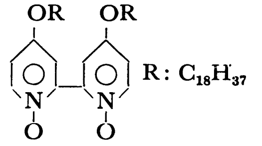


(1)

1 **2**

$$\underset{\mathbf{3}}{ArCH_3} \longrightarrow \underset{\mathbf{4}}{ArCH_2ONO_2} + \underset{\mathbf{5}}{ArCHO} \qquad (2)$$

Both reactions were carried out in cyclohexane–water system under mild, standard stirring at 20 °C and gave the same products as previously reported.[3–5] The following surfactants were tested: Dipodand **7**,[6] sodium dodecyl sulfate (SDS), and dodecyltriethylammonium nitrate (**8**). These compounds were compared with 4,4′ bis (octadecyloxy)-2,2′-bipyridine 1,1′-dioxide (**6**) which was used earlier.[4] The results are given in Table 1.



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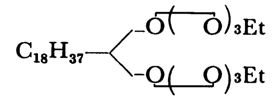


7

$C_{12}H_{25}\overset{+}{N}(C_2H_5)_3NO_3^-$

8

From Table 1 it can be seen that nonionic Podand **7** and cationic dodecyltriethylammonium nitrate (**8**) hinder the oxidation while lipophilic complexone **6** and SDS accelerate the reaction. The inhibitory effects are analogous to lowering of the rates of oxidation of phenothiazine by Fe^{3+} ions in the presence of both cationic (CTAB) and nonionic (Triton-X-100) surfactants reported by Pelizzetti and Pramauro.[2] They ascribed these effects to the difficulty of approach of the metal ion to the organic substrate in the micelle as well as to an increase of the apparent reduction potential of the substrate. The same effects can be responsible for the decrease of the reaction rate in our case. Additionally, the hampering effect of salt **8** on the oxidation in the presence of **6** (acting in the organic phase only[4]) suggests that some modification of the interface can take place as well. Such modification would prevent the reagents from reaching each other. In the presence of SDS, a remarkable increase of the oxidation rate was observed and this result was also in agreement with that of Pelizzetti and Pramauro.[2] In their case it was due to a concentration effect as well as to decrease of the reduction potential of substrate in the micelles.

Since only SDS showed the accelerating effect, this surfactant was used in all subsequent experiments. Thus,

TABLE 1. EFFECTS OF SURFACTANTS ON THE TWO-PHASE CAN OXIDATION OF 3,6-DIMETHOXYDURENE IN CYCLOHEXANE[a]

Catalyst (10×No. of mol)	Consumption of CAN(%)	
	After 6 min	After 40 min
None	19.1	57
6(1.30)	41.3	—
7(5.84)	8.0	—
8(10.0)	10.2	42
6 and **8**(1.30, 10.0)	22.2	74
SDS(6.00)	57.0	—

a) A solution of **1** in cyclohexane (0.10 M, 2 ml) was oxidized with aqueous CAN (1.0 M, 1 ml) in the presence of catalyst at 20 °C. The consumptions of CAN based on organic substrate were determined by oxidimetry.

consumption of cerium ammonium nitrate (CAN) in the two-phase oxidation of **1** *vs.* SDS concentration was determined and shown in Fig. 1. This plot demonstrates that the rate enhancement was strongly affected by the concentration of surfactant in its CMC-range. Figure 2 presents the time dependent effects of SDS and SDS with **6** on the oxidation of *p*-xylene. The catalytic effects of SDS were higher than those of **6** and the competitive inhibition was observed when both catalysts were used together. The second effect can be due to the association of weaker oxidant [**6**. Ce(IV)][4] with the micelles.[8]

In order to learn about the new oxidant, we studied the oxidation of *p*-xylene (1 M[†] solution in cyclohexane) with aqueous CAN solution in the presence of SDS in various concentrations and under standard stirring conditions (magnetic stirrer, ellipsoid-like mixing bar, >300 min^{-1}). As in all experiments, so far described, if the stirring rate dropped below *ca.* 100 min^{-1}, the yields were much lower and hardly reproducible. The resulting mixture was analyzed (Ce^{4+}-by oxidimetry, organic products-by GLPC) and the reaction advancements were determined from the consumption of CAN and from the yields of **4** and **5**, respectively (Fig. 3). The yields of organic products *vs.* concentration of SDS are presented in Fig. 4. The experiments run under nitrogen gave the same results as those under air atmosphere.

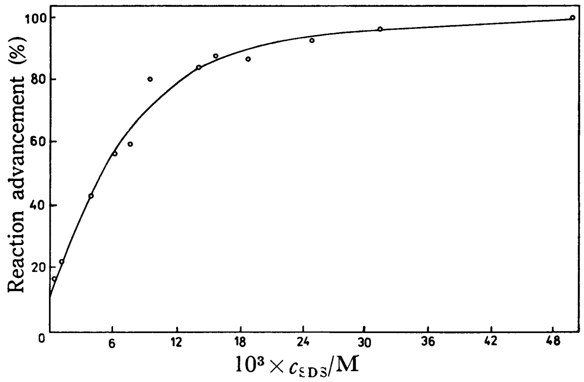


Fig. 1. Dependence of the yield of the two-phase oxidation on the concentration of SDS in water solution. Conditions: **1** (0.10 M in cyclohexane, 2 ml), CAN (1.00 M in an appropriate solution of SDS in water, 1 ml), 20 °C, 6 min.

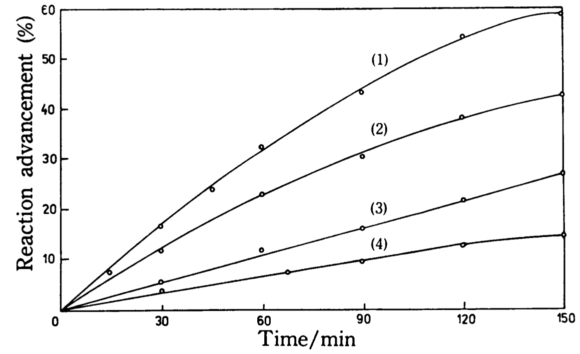


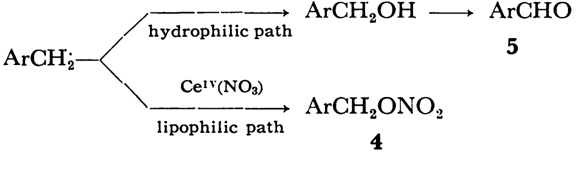
Fig. 2. Effects of SDS (6.0×10^{-5} M), **6** (6.0×10^{-5} M), and both catalysts on the oxidation of *p*-xylene (1.0 M) in cyclohexane with aqueous CAN (1.0 M) at 20 °C. (1): SDS, (2): SDS+**6**, (3): **6**, (4): none.

TABLE 2. OXIDATION OF *p*-TOLUALDEHYDE WITH AQUEOUS CAN[a]

c_{SDS}/M	Comsumption of CAN (%)
0.0	3.6
5.0×10^{-5}	5.0
5.0×10^{-4}	9.6
5.0×10^{-3}	39

a) A solution of *p*-tolualdehyde (freshly distilled) (0.10 M, 5 ml) in cyclohexane was stirred under N$_2$ with aqueous CAN (1.0 M, 10 ml) for 1 h at 25 °C.

From the results given in Fig. 3 it is apparent that the catalytic effect occurs at the concentration of surfactant which is much less (10^{-5} M) than the CMC value for diluted solution of SDS (8.1×10^{-3} M).[1] It seems to be caused by the extremelly high ionic strength of 1 M CAN solution (μ 12 M), thus "salting out" all the hydrophobic species and forming the micelles at very low concentration of surfactant. The discrepancy between CAN consumption and the yield of organic products observed for $c_{\mathrm{SDS}}\approx10^{-4}$ M led us to check the possibility of the consecutive oxidation of *p*-tolualdehyde (**5**). This was the case and as can be seen from Table 2, the rate of this reaction increases sharply at higher concentration of SDS. Analysis of the product distribution (Fig. 4) shows that the micellar oxidant increases a contribution of aldehyde in the reaction mixture. The true increase is even higher than this observed from the plot because of the consecutive oxidation of **5**. This result suggests that the catalyzed oxidation takes place in a hydrophilic medium (3).



(3)

It is well known that aromatic compounds are located at the surface of micelles.[9] On the other hand, the recently investigated association of metal ions to SDS

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† 1 M=1 mol dm^{-3}.

Table 3. Oxidation of xylenes with aqueous CAN[a)]

Substrate(IP/eV)[b)]	SDS (M)	Yield			
		Nitrate (mmol)	Aldehyde (mmol)	Total/%	Unchanged substrate/%
p-Xylene (8.44)	—	2.7	3.6	78	20
	5×10^{-4}	1.7	3.0	58	0
o-Xylene (8.56)	—	1.9	1.9	46	41
	5×10^{-4}	3.5	4.1	93	7
m-Xylene (8.59)	—	1.4	1.4	35	33
	5×10^{-4}	2.7	3.3	74	19

a) Xylene (1.00 ml) was oxidized with CAN (20 g, *ca.* 10% oxcess) in water or SDS solution (16 ml) when the two-phase system was stirred for 6 h at 25 °C. The resulting mixture was treated as described earlier.[4)] b) R. P. Blaunstein and L. G. Christophorou, *Radiat. Res. Rev.*, **3**, 69 (1971).

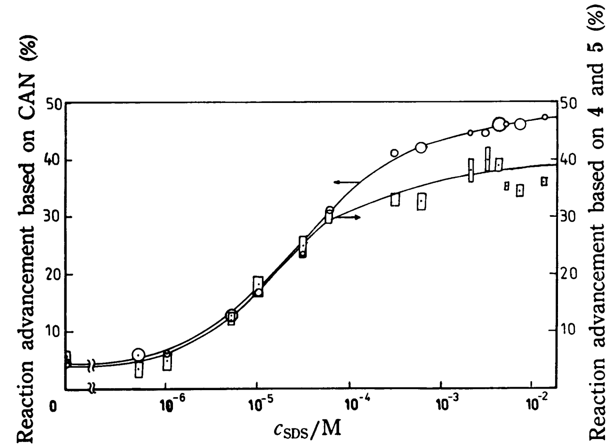

Fig. 3. The advancements of the oxidation (2) based on the consumption of CAN (⊙) and on the yields of **4** and **5** (⊡) *vs.* the concentrations of SDS.
Conditions: *p*-xylene (1.0 M in cyclohexane, 5 ml), CAN (1.00 M in the SDS solution), 25 °C, 1 h.

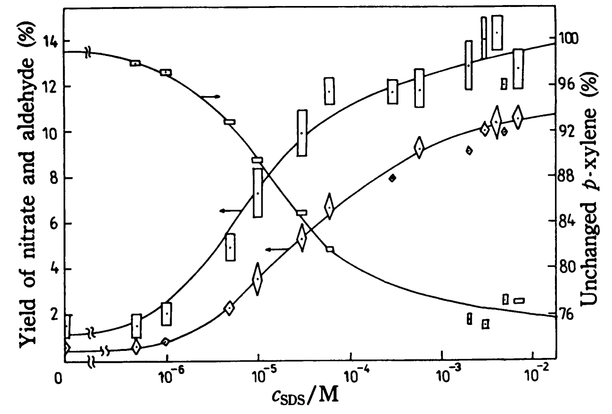

Fig. 4. The yields of nitrate and aldehyde formed in the oxidation (2) *vs.* the concentration of SDS.
⊡: Aldehyde, ◇: nitrate, ⊡: unchanged *p*-xylene.
Conditions: as for Fig. 3.

micelles has revealed that the metal ions were bound to the micellar surface. The association constant has been rationalized by considering the chemistry of the specific ion.[10)] The Ce(IV) ions associate more strongly to the sulface than to nitrate ions and the reduced metal ions form the weaker complexes.[11)] The above arguments suggest that the catalytic reaction site is located at the hydrophilic surface of micelles.

In order to gain insight into the properties of the new oxidizing system, we studied, as previously for **6**,[4)] the yields of benzylic nitrates (**4**) and aldehydes (**5**) obtained in the two-phase oxidation of xylenes without diluent in the presence and absence of SDS. The ionization potentials of these substrates differ slightly so the effectiveness of catalyst in each case can test the oxidation potential of the oxidant. The corresponding benzoic acids were formed as by-products and this fact was responsible for the lack of material balance (Table 3). The results in Table 3 indicate that catalyst has almost the same effectiveness for *o*- and *m*-xylene. For *p*-xylene there was the relatively high oxidation yield without SDS, so the addition of catalyst led to the consecutive oxidation of aldehyde. The observed lack of selectivity of the oxidant action implies its high oxidation potential, perhaps related to the potential of Ce(IV) in an equilibrium with the sulfate ions (1.44 V[12)]). All these facts support the evidence that the reaction takes place at the micellar surface.

Summarizing, we conclude that the two-phase oxidation of aromatic compounds with the aqueous CAN solution is inhibited by cationic and nonionic surfactants and catalyzed by the anionic one.

The catalytic action of SDS is due to the binding of aromatic compounds and the Ce(IV) ions to the surface of micelles. The micellar oxidant has the high oxidation potential which should allow to oxidize the comparatively nonreactive substrates. The catalyst is effective at the very low concentration level, so it does not disturb the phase separation process during the work up.

Experimental

Reagents. The following surfactants were prepared and purified as described in the literature: 4,4′-bis(octadecyloxy)-2,2′-bipyridine 1,1′-dioxide,[7)] Dipodand **7**,[6)] and dodecyltriethylammonium nitrate.[13)] Sodium dodecyl sulfate (Merck) was recrystallized twice from ethanol and dried in vacuum desiccator over P_2O_5. Cyclohexane was shaken with aqueous $KMnO_4$, concd. H_2SO_4, water, and $NaHCO_3$ soln, dried over $CaCl_2$ and distilled. 3,6-Dimethoxydurene was prepared and purified according to the literature.[14)] Xylenes (GLPC standard grades) were used as purchased. Cerium ammonium nitrate and other inorganic reagents were of highest available purity. Doubly distilled water was used.

Procedure. All the reactions were carried out in Erlenmeyer flasks (Quickfit, Ŧ 14/23) in sizes 5 and 10-ml with a Teflon-coated ellypsoidal stirring bar (5 mm × 15 mm) or in sizes 25 and 50-ml with the (7 mm × 21 mm) bar.

In a typical experiment, 5 ml of a solution of *p*-xylene (1.00 M) in cyclohexane, an appropriate quantity of SDS, and 10.0 ml of CAN solution (1.00 M) in water were introduced *via* pipette into a 25-ml flask. The flask was sealed with a ground joint stopper, placed in a water bath maintained at the desired temperature (20 or 25 °C), and stirring was started. After appropriate time the phases were separated in a small separatory funnel. Samples of CAN solution were quenched with an excess of a standardized iron(II) sulfate solution and then titrated with 0.1 M CAN. The organic phase was washed with the $FeSO_4$ solution, water, $NaHCO_3$ soln., water, dried over $MgSO_4$ and subjected to the GLPC analysis (GCHF-18.3.6, Gide apparatus, 20% Carbowax on Chromosorb W, 1 m -long column at 120 °C, FID-detector). The identified products were the same as observed earlier.[4]

In the reaction under nitrogen, the water solution was bubbled with a stream of N_2 and then organic substrate solution was injected, the flask was sealed and the reaction started. The work up was the same as described above. Cyclohexane itself was found not to undergo any changes under the conditions used.

The reproducibility of the results obtained was within a few per cent when the same flask and stirring bar were applied.

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8) A Referee has pointed out that the reversed micelles in the organic phase can be responsible for the catalysis. In order to check this possibility we extracted a 1 M CAN solution (5×10^{-3} M in SDS) with an equal volume of cyclohexane. After the saturation a sample of cyclohexane was treated with the same volume of ferroin (1×10^{-5} M) solution in water which, in turn, did not lose its extinction at 510 nm. This experiment demonstrated that under the conditions used no appreciable amount of Ce(IV) was transferred to the organic phase so we belive that the reaction was catalyzed by the aqueous micelles, even if some aggregates of the surfactant were present in cyclohexane. The results of product distribution study support this conclusion (see the text).

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