

even though the solvents have similar dielectric constants. The reactions of primary environmental interest occur in water. There are a number of solvent parameters ( $Y$ ,  $\Omega$ ,  $Z$ ,  $S$ ,  $E_T$ ,  $\delta$ )<sup>21</sup> which could be used to correlate reaction rates in various solvents. Kosower<sup>22</sup> has used  $Z$  to correlate the rates of SN2 reactions in a series of protic solvents. We can write  $\log k_2 = AZ + C$ , where  $A \approx 0.025$  in protic solvents and  $C$  is a constant which depends only on the nucleophile and substrate. Using our results for trimethylstibine and trimethylarsine reacting with methyl iodide in methanol ( $Z$  value 83.6), the  $C$ 's for the reactions are  $-5.5$  and  $-5.0$ , respectively. The  $Z$  value of water is 94.6. Thus, the rate constant for reaction of  $(\text{CH}_3)_3\text{Sb}$  and  $(\text{CH}_3)_3\text{As}$  with  $\text{CH}_3\text{I}$  in water can be estimated to be  $7 \times 10^{-4}$  and  $3 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ , respectively. A similar approach can be applied to the other reactions in Table I. The result is that the reactions are expected to be about twice as fast in water as in methanol.

### Experimental Section

Trimethylantimony dibromide was prepared by the method described by Doak et al.<sup>23</sup> It was recrystallized from acetone. Solutions of trimethylstibine for kinetic studies were prepared in a recirculating inert atmosphere ( $\text{N}_2$ ) box by refluxing  $(\text{CH}_3)_3\text{SbBr}_2$  with a twofold excess of 30-mesh zinc in the solvent of choice (methanol or acetonitrile) for 1 hr, followed by vacuum distillation of the solution. The solutions were standardized by adding an excess of methyl iodide to a weighed sample of each solution and weighing the tetramethylstibonium iodide isolated after removal of solvent.

Trimethylarsine was obtained from a commercial source. Solutions of trimethylarsine for kinetic studies were prepared by weight using conventional vacuum line techniques.

The reactions of trimethylstibine and trimethylarsine with alkyl halides were observed by an NMR technique using a commercial 60-MHz instrument. In an inert atmosphere box, approximately 1 ml of the typically 0.5 M stibine or arsine solution was transferred into a tared thin-wall NMR tube which was then stoppered with a rubber septum. The exact quantity of solution was determined by weight. After allowing the sample to equilibrate thermally in the NMR probe, about 0.15 ml of a mixture of the desired alkyl halide and hexamethyldisilane (prepared and stored under nitrogen; typical mole ratio 10:1) was injected through the septum to initiate the reaction. The exact amount of  $\text{RX}-(\text{CH}_3)_6\text{Si}_2$  solution added was determined by weight at the completion of the reaction. In most kinetic runs, only the signals for the stibine or arsine and the standard,  $(\text{CH}_3)_6\text{Si}_2$ , were observed using 50-Hz sweep width and changing the offset as necessary to put both signals in the scan. The areas of the two signals were measured ( $\pm 3\%$ ) with a planimeter and related to the moles of reactant and standard. Concentrations were calculated by relating the liquid level in the sample tube to the volume of the reacting solution. For the slow reactions which required days to reach a reasonable extent of reaction, the sample tubes were stored in a bath regulated to the probe temperature,  $29.5 \pm 1^\circ\text{C}$ . The concentration vs. time data was fitted by computer to a second-order rate equation by the method of least squares.

In the course of this study the chemical shifts of trimethylstibine ( $\delta$  0.73), trimethylarsine ( $\delta$  0.91), and tetramethylstibonium iodide ( $\delta$  1.58 low concentration,  $\delta$  1.66 saturated) were determined in methanol relative to internal hexamethyldisilane ( $\delta$  0.04).<sup>24</sup> The signal for tetramethylstibonium iodide is quite broad ( $W_{1/2} \approx 4.5$  Hz) owing to unresolved Sb-C-H coupling. The signal for trimethylstibine is not detectably broadened ( $W_{1/2} \approx 0.7$  Hz) because in an asymmetric electric field the antimony quadrupole successfully relaxes the Sb-C-H coupling. In addition, it was noted that the maximum solubility of  $(\text{CH}_3)_4\text{SbI}$  in methanol is 0.24 M and the maximum solubility of  $\text{CH}_3\text{CH}_2\text{Sb}(\text{CH}_3)_3\text{I}$  in acetonitrile is about 0.2 M.

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**Registry No.**—Tetramethylstibonium iodide, 2185-78-6; tetra-(methyl- $d_3$ )stibonium iodide, 56929-85-2; ethyltrimethylstibonium iodide, 56929-86-3; ethyltrimethylstibonium bromide, 56929-87-4; trimethylpropylstibonium iodide, 56929-88-5; tetramethylarsonium iodide, 5814-20-0; ethyltrimethylarsonium iodide, 56929-89-6;

trimethylpropylarsonium iodide, 56929-90-9; trimethylantimony dibromide, 5835-64-3.

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### Applications of Surfactants to Synthetic Organic Chemistry

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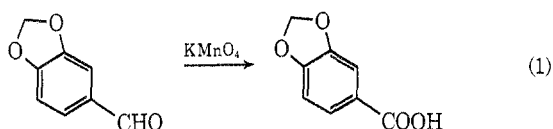
Synthetic chemists are frequently faced with the problem of reacting a water-insoluble organic compound with a water-soluble reagent (hydroxide, permanganate, formate, periodate, hypohalite, hydrogen peroxide, hydrobromic acid, hydrazine, etc.)<sup>2</sup>. Several methods are available for countering this difficulty. The organic phase can be stirred rapidly with the aqueous phase; agitation promotes interfacial contact between the two reactants. An alternative procedure utilizes a cosolvent such as dioxane or ethanol in the water. Although a water-cosolvent mixture does not usually dissolve all the organic reactant, the hope is that at least a small portion of the reactant will enter the watery solvent. As the compound is consumed, more of it is supplied from the organic layer. Dipolar aprotic solvents,<sup>3</sup> crown ethers,<sup>4</sup> and phase transfer catalysts<sup>5</sup> are also commonly used in synthesis; they function by dissolving or solubilizing ionic reagents in organic phases. In the present article we assess the value of surfactants in several two-phase reactions. Surfactants disperse organic liquids in water; this could conceivably generate higher yields and shorter reaction times. Surfactants also form micelles which are capable of catalyzing organic reactions.<sup>6</sup> Yet neither "emulsion catalysis" nor micellar catalysis by surfactants has been exploited to any degree in synthetic organic chemistry.<sup>7</sup>

Table I  
Percent Yields of Piperonylic Acid Produced  
from the Oxidation of Piperonal at 55° by  $\text{KMnO}_4$

Reaction mode	Reaction time, min		
	70	100	150
Magnetic stirring	37	33, 36	37
Mechanical stirring	39	37	38
Magnetic stirring (0.01 M surfactant) <sup>a</sup>	66, 74 <sup>b</sup>	64	65
Magnetic stirring (20% dioxane)	43		

<sup>a</sup> The initial concentration of surfactant (cetyltrimethylammonium bromide) was 0.01 M. When aqueous  $\text{KMnO}_4$  was added to the reaction mixture, the surfactant was diluted about twofold. <sup>b</sup> In this one run only the  $\text{KMnO}_4$  solution contained 0.01 M surfactant so that the surfactant concentration in the reaction vessel was maintained at 0.01 M throughout the addition of  $\text{KMnO}_4$ .

We first investigated the heterogeneous oxidation of piperonal to piperonylic acid (eq 1). Reactions were carried



out by stirring 1.0 g of aldehyde with 60 ml of aqueous  $\text{KMnO}_4$  in the presence or absence of a small quantity (0.11 g) of cetyltrimethylammonium bromide, a cationic surfactant. Yields of piperonylic acid are listed in Table I. A single person performed all the reactions, and no attempt was made to maximize yields by varying the conditions other than those shown in the table.<sup>8</sup> Although changing the mode of stirring had no effect, the presence of surfactant invariably elevated the yields from about 37% to about 65%. Even a 20% dioxane cosolvent did not improve the yield as much as 0.01 M surfactant.

Table II lists the yields of benzoic acid formed when 4.1 g of neat  $\alpha, \alpha, \alpha$ -trichlorotoluene was hydrolyzed with 30 ml of 20% NaOH at 80°. The reaction times were easily assessed from the disappearance of the organic phase. Hydrolysis of  $\alpha, \alpha, \alpha$ -trichlorotoluene in the presence of 0.01 M cetyltrimethylammonium bromide required 1.5 hr. By contrast, the reaction without surfactant took 60 hr. No product was isolated if the reaction without surfactant was allowed to proceed only for 1.5 hr. Brij 35 (a neutral surfactant,  $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{23}\text{OH}$ ) accelerated the hydrolysis but to a lesser extent than did the quaternary ammonium salt. The facility of the surfactant-induced hydrolyses may stem either from an "emulsion catalysis" or from a micellar catalysis.<sup>8</sup> Since micelles of cationic but not neutral surfactants are known catalysts for basic hydrolyses,<sup>9</sup> we suspect that cetyltrimethylammonium bromide operates by both emulsification and micellization whereas Brij 35 serves as a dispersing agent only.

Phase transfer catalysis is an alternative explanation for the data in Table II. Cetyltrimethylammonium ion might dissolve in the organic phase, dragging hydroxide counterions with it.<sup>10</sup> Hydroxide ion consumed by reaction in the organic phase would be replenished continuously by hydroxide in the water. Three considerations argue against phase transfer catalysis. (1) Cetyltrimethylammonium bromide and Brij 35 aid the hydrolysis of  $\alpha, \alpha, \alpha$ -trichlorotoluene far more effectively than does tetrabutylammonium bromide (Table II). This is true despite the fact that tetrabutylammonium ion is a 35-fold better phase transfer catalyst than our cationic surfactant in the reaction of thiophenoxide and 1-bromooctane.<sup>11</sup> Tetrabutylammonium ion

Table II  
Hydrolysis Yields of  $\alpha, \alpha, \alpha$ -Trichlorotoluene  
to Benzoic Acid in 20% NaOH at 80°

Additive	Reaction time, hr	% yield
0.01 M $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3^+\text{Br}^-$	1.5 <sup>a</sup>	98
None	1.5	0
None	60 <sup>a</sup>	97
0.006 M Brij 35 <sup>b</sup>	11 <sup>a</sup>	97
0.02 M $n\text{-Bu}_4\text{N}^+\text{Br}^-$	15 <sup>a</sup>	98
20% dioxane <sup>c</sup>	1.5	0

<sup>a</sup> This is roughly minimum time required for completion of the reaction. <sup>b</sup>  $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{23}\text{OH}$ . <sup>c</sup> Two phases.

and other short-chain quaternary salts are known to mediate several phase transfer reactions involving hydroxide ion.<sup>5,12,13</sup> (2) The concentration of surfactant used in our work (0.01 M) is much smaller than the concentration of quaternary salt generally used in phase transfer processes.<sup>14</sup> (3) Diluting the  $\alpha, \alpha, \alpha$ -trichlorotoluene with 10 ml of benzene increases the reaction time for the cationic surfactant-containing system by a factor of 11. These data suggest, but do not prove, the presence of an emulsion or micellar catalysis. Obviously Brij-35 must operate by one of these mechanisms.

Cetyltrimethylammonium bromide does not benefit the heterogeneous nitric acid oxidation of *o*-xylene to *o*-toluic acid.<sup>15</sup> However, the reaction time for hydrolysis of ethyl naphthoate in 5% NaOH at 80° decreases fourfold in the presence of 0.005 M cationic surfactant. Brij 35 also catalyzes the hydrolysis. Finally, we tested the effect of cetyltrimethylammonium bromide on a recently reported conversion of amides to acids using sodium peroxide.<sup>16</sup> It is stated that "only extremely water-insoluble amides failed to react and, although ethanol can be substituted as solvent for some of the reactions, it was of no value in these cases".<sup>16</sup> We treated *N,N*-diethylbenzamide, one of the water-insoluble amides which gave no product, with sodium peroxide at 90° in the presence and absence of 0.005 M surfactant. After a long reaction time (30 hr) we isolated 57 and 32% benzoic acid, respectively.

In summary, we have shown that cationic and neutral surfactants can in certain cases lead to higher yields and shorter reaction times. If the work-up of the product includes an extraction step, then the time saved by using a surfactant may not justify possible problems caused by emulsions.<sup>17</sup> On the other hand, emulsion-micellar catalysis may find utility in large-scale reactions or in reactions of sensitive water-insoluble liquids that require a minimum exposure to an aqueous solution.

### Experimental Section

**Oxidation of Piperonal.** Piperonal (1.00 g, 6.7 mmol) and 25 ml of water were placed into each of three 100-ml round-bottom flasks. After cetyltrimethylammonium bromide (0.11 g, 0.30 mmol) was added to one of the flasks, all of them were immersed in oil baths preheated to 55°. Magnetic stirring was initiated in two vessels including the one containing the surfactant (every effort being made to equalize the stirring rates). The third flask was stirred with a motor-driven shaft and propeller. Solutions of 1.50 g (9.5 mmol) of  $\text{KMnO}_4$  in 35 ml of water were added dropwise over a period of 30 min, and heating was continued for 70–150 min. Briefly stated, the work-up consisted of adding KOH, removing the  $\text{MnO}_2$  by filtration, combining the filtrate and  $\text{MnO}_2$  wash, removing the unreacted material with an ether extraction, acidifying the water, and filtering, washing, and drying the resulting piperonylic acid. When surfactant was present, 2 hr were allowed for phase separation during the ether extraction step. The product was a colorless powder melting at 227–228° (lit.<sup>8</sup> mp 227–228°). Product from reactions containing surfactant had a slightly sharper melting point than product from reactions without surfactant.

**Hydrolysis of  $\alpha,\alpha,\alpha$ -Trichlorotoluene.**  $\alpha,\alpha,\alpha$ -Trichlorotoluene (4.1 g, 21 mmol) was stirred magnetically with 30 ml of 20% aqueous NaOH at 80°. Runs catalyzed by surfactant contained either 0.11 g (0.30 mmol) of cetyltrimethylammonium bromide or 0.20 g (0.17 mmol) of Brij 35. All organic reagents were purchased from Aldrich. The work-up of product consisted of acidifying with HCl, cooling in ice, filtering, washing the collected solid with cold water, and drying the solid. The unpurified benzoic acid melted at 119–121°.

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**Registry No.**—Piperonal, 120-57-0; piperonylic acid, 94-53-1;  $\alpha,\alpha,\alpha$ -trichlorotoluene, 98-07-7; benzoic acid, 65-85-0; cetyltrimethylammonium bromide, 57-09-0; Brij 35, 9002-92-0; tetrabutylammonium bromide, 1643-19-2.

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- An ideal surfactant forms only unstable emulsions. Cetyltrimethylammonium bromide (although commercially available and cheap) leaves something to be desired in this regard. Further work is required to improve the technology.

### Anodic Acetoxylation of Dimethoxybenzenes

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Many of the electrochemical oxidations of aromatic compounds are considered to proceed via cation radical intermediates.<sup>1</sup> Dimethoxybenzenes produce the quinone diketals in methanolic potassium hydroxide<sup>2</sup> and form methoxybenzonitriles in acetonitrile solution of tetraethylammonium cyanide<sup>3</sup> or in methanol containing sodium cy-

anide.<sup>4</sup> These products arise from the attack of nucleophiles on the highest positive center of cation radical, a carbon atom bearing a methoxy substituent. When a bulky nucleophile such as pyridine or substrate itself is used, the attacking point changes; the anodic pyridination<sup>5</sup> and the anodic coupling<sup>6</sup> of *o*-dimethoxybenzene<sup>10</sup> occur on the carbon atom with an aromatic hydrogen.

On the other hand, the electron transfer reaction of dimethoxybenzenes by lead tetraacetate in acetic acid produces dimethoxyphenyl acetates.<sup>11</sup> In this case, the acetoxylation position is the carbon atom with an aromatic hydrogen. Data on anodic acetoxylation are indispensable to clarify which is the cause of an apparent contradiction of attacking points, the different oxidant or the nature of nucleophile. Anodic acetoxylation of dimethoxybenzenes has been described only in the case of the para isomer. The reported product is 2,5-dimethoxyphenyl acetate; however, details are not clear.<sup>12</sup>

### Results

Methoxybenzenes were electrolyzed in a one-compartment cell under a nitrogen atmosphere using platinum foil anode in glacial acetic acid containing sodium acetate with a constant current of 0.1 A. The results of these studies are summarized in Table I.

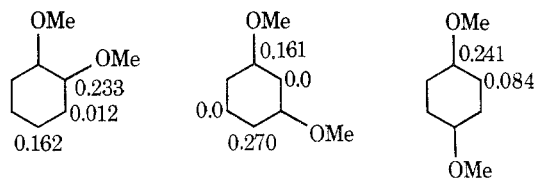
Anodic oxidation of *p*-dimethoxybenzene produced a 68% yield of 2,5-dimethoxyphenyl acetate as the sole organic product, except for a very small amount of a brownish substance.

The electrochemical oxidation of *m*-dimethoxybenzene gave a 2.5% yield of a 16:1 mixture of 2,4- and 2,6-dimethoxyphenyl acetate, respectively, together with a considerable amount of tarry product.

Under identical conditions, *o*-dimethoxybenzene produced a 8.9% yield of a mixture of 2,3- and 3,4-dimethoxyphenyl acetate in the proportions 1:90, along with a significant amount of tarry residue.

### Discussion

The primary step of anodic acetoxylation is attributed to a direct discharge of the aromatic at the anode to a cation radical intermediate.<sup>1,13</sup> The second stage is the combination reaction of the cation radical intermediate with nucleophile. Observed orientations in the aromatic cyanation of methoxybenzenes are in accord with the spin density distributions calculated from ESR spectra of the cation radicals.<sup>3,14,15</sup> In each case, the methoxyl displacement by



cyanide ion occurs at the position of highest spin density. This can also account for the position of attack by methoxide ion.<sup>2</sup> In contrast, the acetoxylation by a metal ion oxidant<sup>11</sup> and the present electrode process does not occur at these positions. This would be ascribable to the instability of an acylal type intermediate, because acetate ion is a better leaving group than methoxide ion.<sup>20</sup> Bonding between the oxygen atom of the cation radical and acetate ion, followed by rearrangement,<sup>21</sup> is also improbable, because *o*-dimethoxybenzene does not produce 2,3-dimethoxyphenyl acetate predominantly (see Table I). The mechanism shown in Scheme I would, therefore, be reasonable to account for the anodic acetoxylation of dimethoxybenzenes.