

## Micellar Catalysed Elimination Reactions of *p*-Substituted Phenethyl Bromides and Related Compounds in Alkaline Solutions

By Yumihiko Yano, Yasuhiro Yoshida, Akira Kurashima, Yoshiharu Tamura, and Waichiro Tagaki,\*  
Department of Chemistry, Faculty of Engineering, Gunma University, Gunma, Japan

The rates of dehydrobromination of *para*-substituted  $\beta$ -phenethyl bromides (3) were determined in alkaline solutions under micellar ( $k_\psi$ ) and non-micellar ( $k_0$ ) conditions by using hexadecyltrimethylammonium bromide (1) and dimethyl-(2-hydroxyethyl)octadecylammonium chloride (2) as the micellar surfactants. Large micellar effects ( $k_\psi/k_0$ ) were observed. Good Hammett relationships were obtained for both  $k_\psi$  and  $k_0$  with  $\sigma_p^-$  constants. Fairly large isotope effects ( $k_H/k_D = 8-9$ ) were also observed for both  $k_\psi$  and  $k_0$ . The results suggest that the transition states are more carbanion-like under the micellar conditions compared with the non-micellar conditions. However, H-D exchange of the starting bromides with solvent water, which would indicate carbanion formation prior to elimination, was not detected.

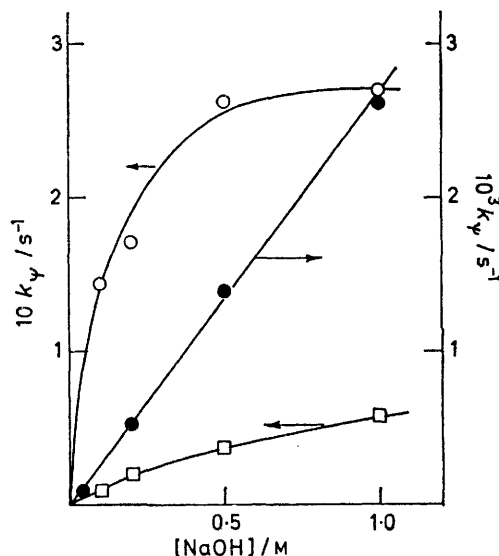
THE favoured formation of carbanions in cationic micelles has been reported in a number of micellar reactions<sup>1a,b</sup> and in related phase-transfer catalytic systems.<sup>1c</sup> For example, we have reported recently that in the hydroxide ion-catalysed hydrolysis of  $\alpha$ -substituted *p*-nitrophenyl acetate, the mechanism changes from an ordinary addition-elimination under non-micellar conditions to an E1cB mechanism with a large rate acceleration under micellar conditions with a cationic surfactant.<sup>2</sup> Similar large micellar effects are also known for other carbanion-forming reactions such as the H-D exchange reaction of sulphonium salts,<sup>3</sup> ionization of carbon acids,<sup>4</sup> and nucleophilic aromatic substitutions.<sup>5</sup> A cationic micelle of a choline analogue was reported to favour E2 elimination by inhibiting competitive S<sub>N</sub>1 process in the reactions of 1-bromo-2-phenylpropane<sup>6</sup> and 3-bromo-3-phenylpropionate ion.<sup>7</sup> The same micelle was also effective in the Hofmann elimination of 4-nitrophenethyltrimethylammonium iodide.<sup>8</sup> In these studies, however, the carbanionic character of the E2 transition state was not of major interest. This aspect was studied by Roblot and his co-workers in the micellar catalysed E2 elimination of substituted  $\beta$ -phenethyl halides,<sup>9</sup> although details are lacking.

In the present work,<sup>10</sup> we have compared the catalytic activities of the surfactants hexadecyltrimethylammonium bromide (1) and dimethyl-(2-hydroxyethyl)octadecylammonium chloride (2). The substrates examined are all uncharged neutral compounds: the *para*-substituted phenethyl bromides (3), 2-phenoxyethyl

phenyl sulphone (4), and the *S*-*t*-butyl 3-(*p*-substituted phenoxy)thiopropionates (5). These substrates were selected since their non-micellar eliminations have been well studied<sup>11-14</sup> so that any micellar modification of the mechanism would be easy to detect.

### RESULTS AND DISCUSSION

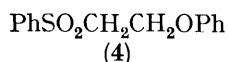
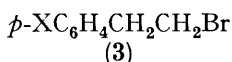
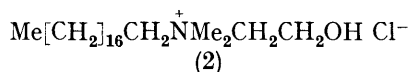
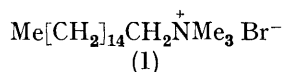
*Substituted Phenethyl Bromides (3).*—The pseudo-first-order rate constants ( $k_\psi$ ) were determined spectrophotometrically by following the formation of styrenes. In



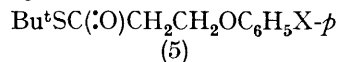
Effect of sodium hydroxide concentration on the rate of elimination of *p*-nitrophenethyl bromide (3; X = NO<sub>2</sub>) in the presence and absence of the surfactants (1) and (2) at 25 °C (see Table 1); ○, (2) (1 × 10<sup>-2</sup>M); ●, no surfactant; □, (1) (1 × 10<sup>-2</sup>M)

all cases, under both non-micellar and micellar conditions, the absorbance at  $t = \infty$  indicated a quantitative yield of olefin, which was also confirmed by g.l.c. analysis of the products.

*Effect of hydroxide ion on the rate of elimination of p-nitrophenethyl bromide (3; X = NO<sub>2</sub>).* The results at 25 °C are shown in Table 1 and the Figure. The concentration of surfactant ( $C_p = 1 \times 10^{-2}$ M) is enough to incorporate the substrate ( $5 \times 10^{-5}$ M) completely into



X = NO<sub>2</sub>, CN, Cl, H, or OMe



X = H or NO<sub>2</sub>

TABLE 1

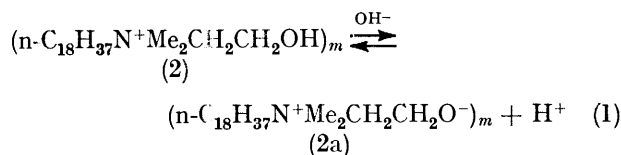
Effect of sodium hydroxide concentration on the rate of elimination of *p*-nitrophenethyl bromide (3; X = *p*-NO<sub>2</sub>)<sup>a</sup> at 25 °C

[NaOH]/ M	$k_{\psi}/s^{-1}$		
	No surfactant	(1) (1 × 10 <sup>-2</sup> M)	(2) (1 × 10 <sup>-2</sup> M)
0.04	0.92 × 10 <sup>-4</sup>		
0.1		0.85 × 10 <sup>-2</sup>	1.43 × 10 <sup>-1</sup>
0.2	5.16 × 10 <sup>-4</sup>	1.93 × 10 <sup>-2</sup>	1.71 × 10 <sup>-1</sup>
0.5	14.4 × 10 <sup>-4</sup>	3.47 × 10 <sup>-2</sup>	2.62 × 10 <sup>-1</sup>
1.0	26.1 × 10 <sup>-4</sup>	5.65 × 10 <sup>-2</sup>	2.70 × 10 <sup>-1</sup>

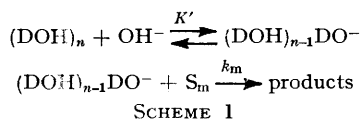
<sup>a</sup> [Bromide] = 5 × 10<sup>-5</sup>M.

the micellar phase as described later. The Figure indicates that in the absence of surfactant the rates ( $k_{\psi}$ ) are first order with respect to hydroxide ion concentration to give  $k_{OH} = 2.63 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . In the presence of (2), however, the rates apparently show a saturation with increasing hydroxide ion concentration, with much higher rates at low concentrations than those in the presence of (1) or in the absence of (1) and (2), indicating that (2) has a marked catalytic activity. The rate constants for (1) also tend to level off at higher hydroxide ion concentrations. This rate-saturation phenomenon has been observed in other cases.<sup>3a,5</sup>

According to Bunton,<sup>5</sup> (2) is converted into its zwitterion (2a) with increasing hydroxide ion concentration [reaction (1)]. If all the substrate is in the



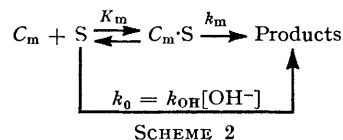
micelle, the variation of rate constant with hydroxide ion concentration can be treated using Scheme 1 and equation (2), where D = C<sub>18</sub>H<sub>37</sub>N<sup>+</sup>Me<sub>2</sub>C<sub>2</sub>H<sub>2</sub>CH<sub>2</sub>, S<sub>m</sub> is the micellized substrate, and  $K' = K_a/K_w$ . The rate constant  $k_m$  refers to the reaction with DO<sup>-</sup> in the micelle. The data for (2) in Table 1 were treated by equation (2) to give  $k_m = 0.298 \text{ s}^{-1}$  and  $\text{p}K_a = 13.1$ .<sup>\*</sup> Although these are approximate values owing to lack of data points, they may be useful for a rough estimate of the reactivity of (2). The  $k_m$  value can also be obtained by another approach, as described later.



$$\frac{1}{k_{\psi}} = \frac{1}{k_m} + \frac{1}{k_m(K_a/K_w)} \cdot \frac{1}{[\text{OH}^-]} \quad (2)$$

*Effect of surfactant concentration.* As already described the catalyst (2) is almost fully ionized into its zwitterionic form (2a) in 0.5M sodium hydroxide solution. Under these conditions, the variation of rates with surfactant concentration was examined for *para*-substituted phen-

ethyl bromides. The results are summarized in Tables 2 and 3. Values for the apparent micellar effect,  $k_{\psi}(C_D = 1 \times 10^{-2}\text{M})/k_0(C_D = 0)$ , are 182 (*p*-NO<sub>2</sub>), 144 (*p*-CN), 130 (*p*-Cl), 52 (H), and 35 (*p*-OMe), respectively. These values are dependent on the hydroxide ion concentration. For example,  $k_{\psi}/k_0 = 880$  for the *p*-NO<sub>2</sub> derivative at pH 12.4 (25 °C). The data for the *p*-NO<sub>2</sub> derivative in Table 2 were further analysed on the basis of the normal Scheme 2 and equation (3)<sup>1a,b</sup> for micellar



reactions, where  $C_m$ , S,  $C_m \cdot S$ ,  $K_m$ ,  $N$ ,  $C_D$ , and C.M.C. are the micellar concentration, substrate, micelle-substrate complex, its association constant, the micellar aggregation number, the surfactant monomer concentration, and the critical micellar concentration, respectively. The values obtained are  $k_m = 0.254 \text{ s}^{-1}$ ,  $K_m/N =$

TABLE 2

Rate constants for elimination from *p*-XC<sub>6</sub>H<sub>4</sub>CR<sub>2</sub>CH<sub>2</sub>Br (3) to form styrenes in the presence of different concentrations ( $C_D$ ) of (2) at 25 °C; [NaOH] = 0.5M; [(3)] = 5 × 10<sup>-5</sup>M

X	$C_D/\text{M}$	$k_{\psi}/s^{-1}$	
		R = H	R = D
NO <sub>2</sub>	0	1.44 ± 0.02 × 10 <sup>-3</sup>	1.88 × 10 <sup>-4</sup>
	5 × 10 <sup>-5</sup>	1.15 ± 0.01 × 10 <sup>-2</sup>	1.54 ± 0.01 × 10 <sup>-3</sup>
	2 × 10 <sup>-4</sup>	5.10 × 10 <sup>-2</sup>	
	5 × 10 <sup>-4</sup>	9.16 × 10 <sup>-2</sup>	
	1 × 10 <sup>-3</sup>	1.26 ± 0.02 × 10 <sup>-1</sup>	1.64 × 10 <sup>-2</sup>
	5 × 10 <sup>-3</sup>	2.43 ± 0.01 × 10 <sup>-1</sup>	2.72 ± 0.01 × 10 <sup>-2</sup>
CN	1 × 10 <sup>-2</sup>	2.62 ± 0.01 × 10 <sup>-1</sup>	2.89 ± 0.02 × 10 <sup>-2</sup>
	0	2.82 × 10 <sup>-4</sup>	
	5 × 10 <sup>-5</sup>	1.59 × 10 <sup>-3</sup>	
	1 × 10 <sup>-3</sup>	2.19 × 10 <sup>-2</sup>	
Cl	1 × 10 <sup>-2</sup>	4.07 × 10 <sup>-2</sup>	
	0	1.74 × 10 <sup>-5</sup>	
	5 × 10 <sup>-5</sup>	2.87 × 10 <sup>-4</sup>	
	1 × 10 <sup>-3</sup>	1.93 × 10 <sup>-3</sup>	
H	1 × 10 <sup>-2</sup>	2.26 × 10 <sup>-3</sup>	
	0	1.23 × 10 <sup>-5</sup>	
	5 × 10 <sup>-5</sup>	4.02 × 10 <sup>-5</sup>	
	1 × 10 <sup>-3</sup>	3.93 × 10 <sup>-4</sup>	
OMe	1 × 10 <sup>-2</sup>	6.35 × 10 <sup>-4</sup>	
	0	6.29 × 10 <sup>-6</sup>	
	5 × 10 <sup>-5</sup>	2.10 × 10 <sup>-5</sup>	
	1 × 10 <sup>-3</sup>	1.49 × 10 <sup>-4</sup>	
	1 × 10 <sup>-2</sup>	2.18 × 10 <sup>-4</sup>	

TABLE 3

Rate constants for elimination from *p*-XC<sub>6</sub>H<sub>4</sub>CR<sub>2</sub>CH<sub>2</sub>Br (3) to form styrenes in the presence of different concentrations ( $C_D$ ) of (1) at 25 °C; [NaOH] = 0.5M

X	$C_D/\text{M}$	$k_{\psi}/s^{-1}$
		R = H
NO <sub>2</sub>	1 × 10 <sup>-4</sup>	4.38 × 10 <sup>-3</sup>
	5 × 10 <sup>-4</sup>	2.09 × 10 <sup>-2</sup>
	1 × 10 <sup>-3</sup>	3.26 × 10 <sup>-2</sup>
	1 × 10 <sup>-2</sup>	3.59 ± 0.01 × 10 <sup>-2</sup> <sup>a</sup>
CN	1 × 10 <sup>-2</sup>	7.36 × 10 <sup>-3</sup>
	1 × 10 <sup>-2</sup>	3.24 × 10 <sup>-4</sup>
Cl	1 × 10 <sup>-2</sup>	1.16 × 10 <sup>-4</sup>
	1 × 10 <sup>-2</sup>	3.43 × 10 <sup>-5</sup>

<sup>\*</sup> The ionic product of water was assumed to be  $K_w = 10^{-14}$ .

<sup>a</sup> 4.06 ± 0.04 × 10<sup>-3</sup> for R = D.

$1.20 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ , and  $k_m K_m/N = 3.05 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively. The  $k_m$  values in equations (2) and (3) should be the same. In fact, the former value of  $0.298 \text{ s}^{-1}$  is in fair agreement with the latter,  $0.254 \text{ s}^{-1}$ . The value of association constant ( $K_m/N$ ) seems to be

$$\frac{1}{(k_\psi - k_0)} = \frac{1}{(k_m - k_0)} + \frac{1}{(k_m - k_0)} \cdot \frac{N}{K_m} \cdot \frac{1}{(C_D - \text{C.M.C.})} \quad (3)$$

reasonable for such a hydrophobic substrate.<sup>1a,b</sup> The  $k_m K_m/N$  value is the micellar second-order rate constant for the zwitterion (2a) which may be compared with the non-micellar second-order hydroxide ion rate constant,  $k_{\text{OH}}$ , of  $2.63 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The ratio,  $(k_m K_m/N)/k_{\text{OH}} = 10^5$ , is very large.

*Hammett relationship and  $\beta$ -hydrogen kinetic isotope effect.* The foregoing large micellar effect might result in a change of the mechanism from that of the non-micellar reaction. As is usual in studies of the transition states of E2 reactions of phenethyl halides, the substituent effects for the phenyl ring and the  $\beta$ -hydrogen kinetic isotope effect were then examined.\* Hammett  $\rho$  values and isotope effects for the data in Tables 2 and 3 are in Table 4.

TABLE 4

Micellar effect on Hammett  $\rho$  values and  $k_{\text{H}}/k_{\text{D}}$  values for (3; X = NO<sub>2</sub>) (see Tables 2 and 3)

	$C_D/M$	$\rho^a$	$\gamma^b$	$k_{\text{H}}/k_{\text{D}}$
	0	1.57	0.994	$7.66 \pm 0.11$
(1)	$1 \times 10^{-2}$	2.06	0.999	$8.34 \pm 0.06$
(2)	$1 \times 10^{-2}$	2.09	0.999	$9.07 \pm 0.10$

<sup>a</sup> For  $\sigma_p^-$  values. <sup>b</sup> Correlation coefficient.

In all cases, the rates are correlated better with the  $\sigma_p^-$  constants<sup>15</sup> than with the  $\sigma$  constants. The resulting  $\rho$  values are larger for the micellar than for the non-micellar reaction. The isotope effects ( $k_{\text{H}}/k_{\text{D}}$ ) are also larger for the former than for the latter case. These results may suggest that the transition state is more carbanion-like<sup>16,17</sup> in the micellar than in the non-micellar reaction. However, the possibility of equilibrium carbanion formation prior to elimination was ruled out because of the failure to detect H-D exchange for the substrate (3) (X = *p*-NO<sub>2</sub>) (see Experimental section). Thus the present micellar effect on rates, although large, does not seem to cause any drastic change in the mechanism, such as from E2 to E1cB, between the micellar and non-micellar elimination reactions of phenethyl bromides.

*2-Phenoxyethyl Phenyl Sulphone (4) and S-t-Butyl 3-(Phenoxy)thiopropionate (5).*—In order to obtain more information on micellar effects on these eliminations, the reactions of (4) and (5) were also examined. It has

\* Roblot, Meyer, and Viout (ref. 9) have also examined Hammett relationships and isotope effects by using essentially the same system as in the present work. However, they did not include  $\sigma_p^-$  substituents, and the reaction conditions seem to be widely different from the present conditions. Moreover, details are lacking for comparison.

been shown that the base-catalysed elimination reactions of (4) proceed through pre-equilibrium carbanion formation and rate-limiting departure of phenoxide ion.<sup>13</sup> Rate-limiting carbanion formation was suggested for the elimination reaction of (5), however, on the basis of the insensitivity of the rate to leaving group (phenoxide) properties.<sup>14</sup>

The results are summarized in Table 5. The apparent

TABLE 5

Rate constants for elimination reactions of (4) and (5) at pH 11.4<sup>a</sup> and 25 °C in the presence of different concentrations ( $C_D$ ) of (2)

$C_D/M$	$k_\psi/s^{-1}$		
	(4) <sup>b</sup>	(5; X = H) <sup>b</sup>	(5; X = NO <sub>2</sub> ) <sup>c</sup>
0	$7.14 \times 10^{-4}$	$4.46 \times 10^{-3}$	$5.54 \times 10^{-3}$
$1 \times 10^{-4}$	$3.55 \times 10^{-3}$	$4.05 \times 10^{-2}$	$1.64 \times 10^{-1}$
$5 \times 10^{-4}$	$2.15 \times 10^{-2}$	$1.89 \times 10^{-1}$	$6.74 \times 10^{-1}$
$1 \times 10^{-3}$	$3.54 \times 10^{-2}$	$3.86 \times 10^{-1}$	$7.02 \times 10^{-1}$
$1 \times 10^{-2}$	$3.53 \times 10^{-2}$	$2.95 \times 10^{-1}$	$6.92 \times 10^{-1}$

<sup>a</sup> 0.1M Borate buffer. <sup>b</sup> [Substrate] =  $2 \times 10^{-4} \text{ M}$ . <sup>c</sup> [Substrate] =  $5 \times 10^{-3} \text{ M}$ .

micellar effects,  $k_\psi/k_0$ , are 49, 66, and 125 for (4) (5; X = H), and (5; X = NO<sub>2</sub>), respectively. These are rather small compared to the value of 880 for (3; X = NO<sub>2</sub>; pH 12.4). In addition, the effect of substitution of the leaving phenoxy group in (5) (H vs. NO<sub>2</sub>) is very small. Here again, there is no indication of a change of mechanism for the micellar and non-micellar conditions; only the rates are affected.

*Micellar Effect and Substrate Structure.*—Lapinte *et al.*<sup>6</sup> observed a micellar effect,  $k_\psi/k_0 = 29$ , for the rate of E2 elimination of 1-bromo-2-phenylpropane catalysed by hexadecyl-(2-hydroxyethyl)dimethylammonium bromide. Using the same catalyst, Minch *et al.*<sup>8</sup> observed a small micellar effect, only a few fold rate acceleration, for 4-nitrophenethyltrimethylammonium iodide. These micellar effects are much smaller than those observed for (3). The  $\beta$ -Me substituent in the former substrate may destabilize the carbanion formed at the transition state through its electron-donating effect, whereas in the latter substrate the positive trimethylammonium group may lead to repulsion with the catalyst's positive head group or it may inactivate the nucleophilic hydroxy-anion by ion-pair stabilization. Micellar effects appear to become large when a substrate has a structure which can delocalize the developing negative charge on carbon at the transition state, such as in (3) (X = NO<sub>2</sub> or CN) and (5).

#### EXPERIMENTAL

*Materials.*—Commercial phenethyl bromide (Wako Chemicals, Co.) was purified by distillation, b.p. 105 °C at 14 mmHg.

*p*-Nitrophenethyl bromide was synthesized by direct nitration of phenethyl bromide; yield 30%, m.p. 69 °C (lit.,<sup>18</sup> 69–70 °C). *p*-Cyano-, *p*-chloro-, and *p*-methoxyphenethyl bromides were prepared from the corresponding alcohols by treatment with phosphorus tribromide according to the literature procedures.<sup>19</sup> *p*-Cyanophenethyl

alcohol was obtained from *p*-aminophenethyl alcohol by the Sandmeyer reaction.<sup>20</sup> *p*-Cyanophenethyl bromide, yield 30%, had m.p. 50 °C (from light petroleum) (lit.,<sup>19,21</sup> 50 °C); *p*-chlorophenethyl bromide, yield 60%, had b.p. 129–130 °C at 15 mmHg (lit.,<sup>12a</sup> 132–134 °C at 18 mmHg); *p*-methoxyphenethyl bromide, yield 55%, had b.p. 138–141 °C at 12 mmHg (lit.,<sup>12a</sup> 146–148 °C at 15 mmHg). *p*-Nitro[ $\beta$ -<sup>2</sup>H<sub>2</sub>]phenethyl bromide was prepared by direct nitration of [ $\beta$ -<sup>2</sup>H<sub>2</sub>]phenethyl bromide, which was itself prepared by the method of Saunders.<sup>16a</sup> The n.m.r. spectrum showed no detectable  $\beta$ -protons.

2-Phenoxyethyl phenyl sulphone (4) was prepared from 2-phenoxyethyl phenyl sulphide by oxidation with 30% hydrogen peroxide in acetic acid according to the literature,<sup>13</sup> yield 90%, m.p. 124 °C (from EtOH) (lit.,<sup>13</sup> 123–124.5 °C).

*S*-t-Butyl 3-(phenoxy)thiopropionate (5; X = H) was prepared from  $\beta$ -phenoxypropionyl chloride and *t*-butyl thiol in dry benzene. To a stirred solution of  $\beta$ -phenoxypropionic acid (4.5 g, 0.027 mol) in benzene (30 ml) was added thionyl chloride (13 ml). The mixture was refluxed for 24 h under a stream of nitrogen to remove hydrogen chloride and sulphur dioxide. The excess of thionyl chloride and benzene was evaporated off. *t*-Butyl thiol (35 ml) in benzene (30 ml) was added and the mixture was refluxed for 24 h under a stream of nitrogen. The excess of thiol and solvent was evaporated off, and the residue was passed through a silica gel (200 mesh) column with light petroleum (b.p. 40–60 °C) as eluant. The fraction which showed one spot on t.l.c. was collected. After removal of solvent, the product was obtained by distillation, yield 62%, b.p. 111–113 °C at 2 mmHg (lit.,<sup>14</sup> b.p. 95–97 °C at 0.07 mmHg);  $\delta$ (CCl<sub>4</sub>; Me<sub>4</sub>Si) 1.44 (9 H, s), 2.84 (2 H, t), 4.18 (2 H, t), and 6.70–7.30 (5 H, m).

*S*-t-Butyl 3-(*p*-nitrophenoxy)thiopropionate (5; X = NO<sub>2</sub>) was prepared similarly, from *p*-nitro- $\beta$ -phenoxypropionic acid, yield 66%, b.p. 173 °C at 1 mmHg (lit.,<sup>14</sup> 155–156 °C at 0.01 mmHg);  $\delta$ (CCl<sub>4</sub>; Me<sub>4</sub>Si) 1.49 (9 H, s), 2.94 (2 H, t), 4.33 (2 H, t), and 6.96 and 8.17 (4 H).

Hexadecyltrimethylammonium bromide (1) (Tokyo Kasei, Co.) was used without further purification. Dimethyl-(2-hydroxyethyl)octadecylammonium chloride (2) was prepared by the reaction of dimethyloctadecylamine and ethylene chlorohydrin in benzene under reflux. Solvent was removed, and the product was recrystallized from ethanol-ether, yield 56%, m.p. 204–207 °C (decomp.) (Found: C, 69.95; H, 12.8; N, 3.8. C<sub>22</sub>H<sub>48</sub>ClNO requires C, 70.1; H, 12.8; N, 3.7%).

*H-D Exchange*.—Two separate heterogeneous mixtures of the same composition of *p*-nitrophenethyl bromide (0.3 g) in benzene (0.7 ml), compound (2) (0.05 g), and potassium hydroxide (0.3 g) in D<sub>2</sub>O (5 ml) were stirred for 10 and 30 min, respectively. Both mixtures were extracted with ether. The ether layers were dried (MgSO<sub>4</sub>), and evaporated to dryness. The n.m.r. spectra of solutions of the residues in CDCl<sub>3</sub> showed the presence of *p*-nitrostyrene (48%) and recovered *p*-nitrophenethyl bromide (52%) after 10 min stirring, and *p*-nitrostyrene (80%) and *p*-nitrophenethyl bromide (20%) after 30 min stirring. The recovered *p*-nitrophenethyl bromide and the *p*-nitrostyrene formed showed no deuterium incorporation from the solvent. These results indicate that a reversible E1cB mechanism is not involved in this elimination.

*Kinetic Measurements*.—*para*-Substituted phenethyl bromides (3). 15  $\mu$ l of a stock solution of the substrate (3) (1  $\times$  10<sup>-2</sup>M in MeOH) was added by microsyringe to 3 ml of

a solution of sodium hydroxide containing a given concentration of surfactant in a thermostatted (25  $\pm$  0.1 °C) rubber-capped cell in a Shimadzu 200 u.v. spectrometer. The rate constants were determined by following the appearance of the *para*-substituted styrenes (*p*-NO<sub>2</sub>, 310; *p*-CN, 266; *p*-Cl, 253; H, 248; *p*-OMe, 258 nm). The absorbances at  $t = \infty$  for slower reactions were obtained by raising the temperature to 55 °C after 40–50% reaction. The pseudo-first-order kinetic plots showed good linearity up to >80% of reaction (40–50% for the slower reactions). The kinetics for the *p*-nitro-derivative at pH 12.4 (0.1M borate buffer) and at 25 °C were studied similarly using (2) as surfactant to give  $k_{\psi}$  ( $C_D = 1 \times 10^{-2}$ M) = 1.95  $\times$  10<sup>-2</sup> s<sup>-1</sup> and  $k_0 = 2.21 \times 10^{-5}$  s<sup>-1</sup>.

*Compounds (4) and (5)*. Essentially the same kinetic procedures as for the aforementioned compounds (3) were employed except that the formation of phenoxide was monitored at 290 nm for (4) and (5; X = H), and at 400 nm for (5; X = NO<sub>2</sub>). The buffer solution contained 10% of methanol (v/v) for the kinetic studies of (5).

This research was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Japan.

[8/1205 Received, 30th June, 1978]

#### REFERENCES

- (a) J. H. Fendler and E. J. Fendler, 'Catalysis in Micellar and Macromolecular Systems,' Academic Press, New York, 1975; (b) C. A. Bunton, in 'Application of Biochemical Systems in Organic Chemistry,' eds. J. B. Jones, C. J. Sih, and D. Perlman, Wiley, New York, 1976, ch. IV; (c) J. Dockx, *Synthesis*, 1973, 441.
- W. Tagaki, S. Kobayashi, K. Kurihara, A. Kurashima, Y. Yoshida, and Y. Yano, *J.C.S. Chem. Comm.*, 1976, 843.
- (a) Y. Yano, T. Okonogi, and W. Tagaki, *J. Org. Chem.*, 1973, **38**, 392; (b) T. Okonogi, T. Umezawa, and W. Tagaki, *J.C.S. Chem. Comm.*, 1974, 363.
- M. J. Minch, M. Giaccio, and R. Wolf, *J. Amer. Chem. Soc.*, 1975, **97**, 3766.
- C. A. Bunton and S. Diaz, *J. Amer. Chem. Soc.*, 1976, **98**, 5663.
- (a) C. Lapinte and P. Viout, *Tetrahedron Letters*, 1973, 1113; (b) V. Gani, C. Lapinte, and P. Viout, *Tetrahedron Letters*, 1973, 4435.
- C. A. Bunton, A. A. Kamego, and P. Ng, *J. Org. Chem.*, 1974, **39**, 3469.
- M. J. Minch, S.-S. Chen, and R. Peters, *J. Org. Chem.*, 1978, **43**, 31.
- G. Roblot, G. Meyer, and P. Viout, *Tetrahedron Letters*, 1975, 2331.
- Y. Yoshida, Y. Tamura, Y. Yano, and W. Tagaki, reported in part at the 36th Annual Meeting of the Japanese Chemical Society, Osaka, April 1977, Abstract II, p. 840.
- (a) J. F. Bunnett, *Angew. Chem. Internat. Edn.*, 1962, **1**, 225; (b) J. F. Bunnett, *Surveys Progr. Chem.*, 1969, **5**, 53; (c) F. G. Bordwell, *Accounts Chem. Res.*, 1972, **5**, 374; (d) W. T. Ford, *Accounts Chem. Res.*, 1973, **6**, 410; (e) D. J. McLennan, *Tetrahedron*, 1975, **31**, 2999; (f) W. H. Saunders, *Accounts Chem. Res.*, 1976, **9**, 19.
- (a) L. F. Blackwell, P. D. Buckley, K. W. Jolley, and A. K. MacGibbon, *J.C.S. Perkin II*, 1973, 169; (b) L. F. Blackwell and L. J. Woodhead, *J.C.S. Perkin II*, 1975, 234, 1218; (c) L. F. Blackwell, *J.C.S. Perkin II*, 1976, 488.
- J. Crosby and C. J. M. Stirling, *J. Amer. Chem. Soc.*, 1968, **90**, 6869; *J. Chem. Soc. (B)*, 1970, 671, 679.
- L. Fedor and R. C. Cavestri, *J. Org. Chem.*, 1976, **41**, 1369.
- C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323.
- (a) W. H. Saunders, jun., and D. H. Edison, *J. Amer. Chem. Soc.*, 1960, **82**, 138; (b) J. Banger, A. F. Cockerill, and G. L. O. Davis, *J. Chem. Soc. (B)*, 1978, 498.

- <sup>17</sup> (a) F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265; (b) R. A. More O'Ferrall and J. Kouba, *J. Chem. Soc.*, 1967, 985; (c) A. M. Katz and W. H. Saunders, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 138; *J.C.S. Perkin II*, 1976, 488.
- <sup>18</sup> E. L. Foreman and S. M. McElvain, *J. Amer. Chem. Soc.*, 1940, **62**, 1435.
- <sup>19</sup> W. H. Saunders, jun., and R. A. Williams, *J. Amer. Chem. Soc.*, 1957, **79**, 3712.
- <sup>20</sup> G. M. Bennett and M. M. Hafex, *J. Chem. Soc.*, 1941, 652.
- <sup>21</sup> F. F. Blicke and W. M. Lilienfeld, *J. Amer. Chem. Soc.*, 1944, **65**, 2282.