

that for carbon in the cyclopropyl ring as demonstrated by increased  $^1J_{CH}$ ,  $^1J_{CC}$ , and  $^{13}C$  chemical shielding.

Figure 1 illustrates the dependence on ring size of the  $^{15}N$  shifts and one-bond N-P couplings. The shift dependence is strikingly similar to that noted for carbocyclic systems<sup>12</sup> except that the four-membered ring is intermediate between the three and higher membered ring systems here. In both carbocyclic systems<sup>12</sup> and in these nitrogen analogues, the six- or seven-membered ring has the lowest shielding. The  $^{15}N$  shifts and N-P couplings have a very similar ring size dependence. As discussed above, N-P couplings are sensitive to the geometry at the nitrogen, i.e., large and negative in the trigonal geometry. These data seem to indicate substantially complete trigonal character at the five-membered ring stage.

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**Registry No.**—Trimethyl phosphite, 121-45-9; 1-azido-2-iodoethane, 42059-3-3; 2-azido-1-iodopropane, 69500-70-1; 2-azido-1-iodo-2-methylpropane, 16484-01-8; 2-azido-3-iodobutane, 69502-71-2; 2-azido-3-iodo-2-methylbutane, 25022-26-8; 2-azido-3-iodo-2,3-dimethylbutane, 58503-58-5.

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## Role of the Central Thiol in Determining Rates of the Thiol-Disulfide Interchange Reaction

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Ellman's reagent, 5,5'-dithiobis(2-nitrobenzoic acid) (1, ESSE) in dilute aqueous solution, reacts with excess 3-mercaptopropanol to form  $HOCH_2CH_2CH_2SSE$  followed by a slower second reaction giving the symmetrical disulfide and a second mole of  $ES^-$ . In this study, we report the rates of reaction of a variety of aliphatic and aromatic thiol anions with  $HOCH_2CH_2CH_2SSE$  which were measured by rapidly mixing the thiol with the mixed disulfide immediately after it was formed. The Brønsted type plot for this reaction shows a  $\beta_{nuc}$  of about 0.58 for either aromatic or aliphatic thiol anions. The aromatic thiol anions were more reactive for their basicity by a factor of about 6 than aliphatic thiols. Exactly the same behavior has been observed for ESSE and  $HOCH_2CH_2CH_2SSE$ , indicating that the cause of the split structure reactivity correlation cannot be a favorable aryl-aryl interaction between attacking and central thiols. The previously proposed explanation based on hard-soft acid-base theory is therefore supported. Inductively withdrawing groups on the central thiol increase the rate with  $\beta_{CT} \approx -0.3$ . The rates of reaction with  $ES^-$  as the central thiol are slower than predicted by extrapolation of data for aliphatic central thiols, probably because of the effect of the negative charge on  $ES^-$ .

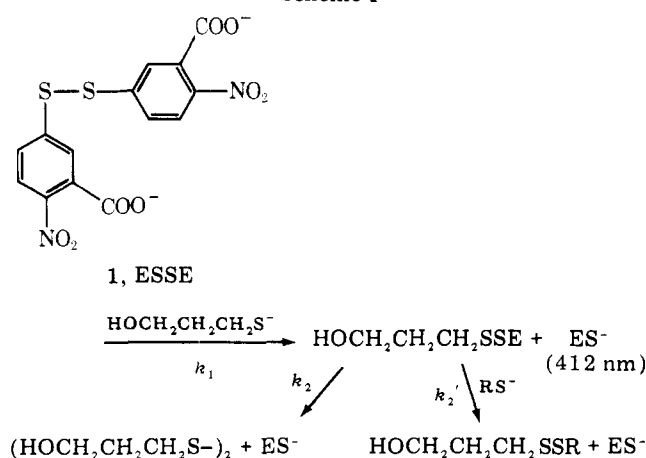
It has been shown previously<sup>1,2</sup> that Ellman's reagent,<sup>3</sup> 5,5'-dithiobis(2-nitrobenzoic acid) (1, ESSE), reacts in aqueous solution with thiols in a biphasic manner. When  $RS^-$  is a highly basic alkyl thiol anion, the first step is much faster than the second ( $k_1/k_2 \approx 50$ ) and this difference decreases as the basicity of attacking thiol decreases. By adding, for ex-

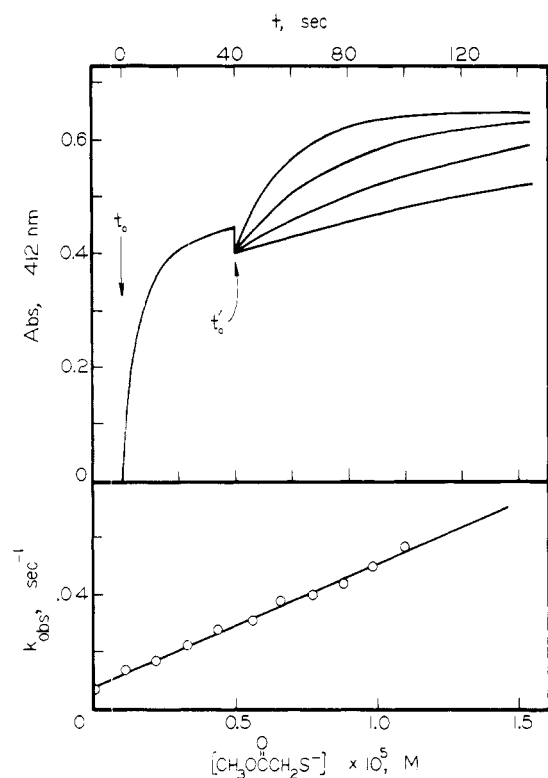
ample, excess mercaptopropanol to 1, a solution of the mixed disulfide  $HOCH_2CH_2CH_2SSE$  is generated in a few seconds and this is then more slowly converted to the symmetrical disulfide yielding a second mole of  $ES^-$ .

The rates of attack ( $k_1$ ) on ESSE by aryl and alkyl thiol anions were fit by separate correlation lines, each with a slope,  $\beta_{nuc}$ , of 0.5. The rates for the aromatic thiol anions were faster by a factor of about 6 than correspondingly basic alkyl thiol anions.<sup>1</sup> Two explanations seemed possible for this behavior. The greater reactivity of aryl thiol anions could have arisen because of a favorable aryl-aryl interaction between the attacking and central thiols in the transition state since such small hydrophobic enhancements are predated.<sup>1,4-6</sup> Alternatively, this split  $\beta_{nuc}$  plot may have reflected the fact that aromatic thiol anions are softer than correspondingly basic aliphatic thiol anions. With hard electrophiles, a single correlation line is found for aromatic and aliphatic thiol anions<sup>7,8</sup> whereas with suitably soft electrophiles aryl thiol anions react much more rapidly even though they are much less basic than the aliphatic thiol anions with which they are compared.<sup>9,10</sup>

In this study we present measurements of the rates of reaction of a series of aliphatic and aromatic thiol anions with the mixed disulfide of mercaptopropanol and  $ESH$ . These data should demonstrate whether an aryl central thiol is re-

Scheme I





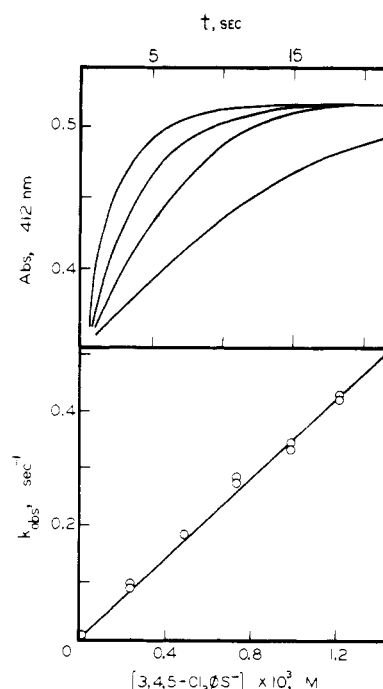
**Figure 1.** The upper graph shows a plot of absorbance at 412 nm vs. time obtained upon rapidly adding 0.2 mL of  $3.63 \times 10^{-4}$  M ESSE to 1.8 mL of  $3.03 \times 10^{-2}$  M 3-mercaptoacacetate solution buffered to pH 5.09 at  $t_0$ . At time  $t_0'$  (>99% ESSE reacted), 0.2 mL of a solution of methylmercaptoacetate was added rapidly. The typical curves shown were those obtained when the final concentration of methylmercaptoacetate was  $7.22 \times 10^{-3}$ ,  $2.89 \times 10^{-3}$ ,  $7.22 \times 10^{-4}$ , and 0 M. The lower graph shows a plot of a series of  $k_{\text{obs}}$  values measured at pH 5.09 plotted vs. the concentration of methylmercaptoacetate anion present. The slope is  $4.29 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  (correlation coefficient 0.992).

quired in order to observe the split in  $\beta_{\text{nuc}}$  values observed for ESSE. An estimation of the inductive effect of the central thiol on the rate of the reaction would also be obtained.

### Experimental Section

The rates of reaction of a series of alkyl thiol anions with the mixed disulfide of mercaptoacacetate and ESH were measured in a manner similar to the following typical procedure. The thiols were purified and solutions prepared using previously described<sup>1</sup> precautions and techniques. Solutions were generated wherein one contained  $3.03 \times 10^{-2}$  M 3-mercaptoacacetate, another  $3.63 \times 10^{-4}$  M ESSE, and another  $7.94 \times 10^{-2}$  M methylmercaptoacetate. Each was  $10^{-4}$  M in acetate buffer and adjusted to pH 5.09, and each had enough KCl present so that  $\mu = 1.0$ . A solution containing only buffer and KCl was also prepared. A sample of 1.800 mL of the 3-mercaptoacacetate solution was allowed to thermally equilibrate in a cuvette within a Cary 14 spectrophotometer while being rapidly mixed by a previously described<sup>1</sup> stirring device designed to fit into the cuvette. Using a spring loaded micrometer-type Hamilton injector syringe, exactly 0.200 mL of the ESSE solution was added and mixed, apparently within the pen response time. After exactly 40 s, a sample of 0.200 mL of methylmercaptoacetate solution was rapidly injected using a second Hamilton injector syringe and stirred. Lesser concentrations of methylmercaptoacetate were available by dilution with buffer. The pseudo-first-order curves generated after  $t_0'$  were converted into  $k_{\text{obs}}$  values as previously described<sup>1</sup> and as demonstrated in Figure 1.

The rates of reaction of aryl thiols with  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{SSE}$  were measured using a stopped-flow spectrophotometer in a modification of a procedure previously described<sup>1</sup> and as typified by the following example. A solution of  $4.65 \times 10^{-4}$  M  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{SH}$  was prepared and maintained at pH 7.5 with  $2 \times 10^{-4}$  M imidazole buffer. An  $8.21 \times 10^{-5}$  M solution of the dipotassium salt of Ellman's reagent was adjusted to pH 7.5. A solution of 3,4,5-trichlorothiophenol was made that also contained  $1 \times 10^{-4}$  M imidazole buffer at pH 7.4 and



**Figure 2.** The upper plot shows the traces of absorbance at 412 nm vs. time for the reaction of various concentrations ( $1.28 \times 10^{-3}$ – $2.45 \times 10^{-4}$  M) of  $3,4,5\text{-Cl}_3\text{PhS}^-$  with  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{SSE}$ . The mixed disulfide was prepared by allowing  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{SH}$  and ESSE to react in the drive syringe prior to mixing with the solution of aromatic thiol anion. The  $k_{\text{obs}}$  values obtained from these curves are plotted vs. the concentration of  $3,4,5\text{-Cl}_3\text{PhS}^-$  to obtain the second-order rate constant listed in Table II.

an identical buffer solution without thiol was prepared. All solutions had  $\mu = 1.0$ , maintained with KCl. At  $t = 0$ , equivalent amounts of  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{SH}$  solution and ESSE solution were added to the load syringe of the stopped-flow instrument, mixed by inverting the syringe several times, and the resulting solution was passed into one of the drive syringes. After 40 s (and after several initial mixes to clear the mixing chamber), this solution was mixed with an equal volume of the trichlorothiophenol solution. A range of concentrations of the thiophenol was available by dilution with buffer. All solutions, drive syringes, mixing block, and other equipment were maintained at 25 °C prior to the mixing. The resulting curves for the appearance of the second mole of  $\text{ES}^-$ , shown in Figure 2, gave  $k_{\text{obs}}$  values for the reaction. These were plotted versus the concentration of the thiophenoxide to give the rate constants listed in Table II.

The synthesis of 2,2,3,3,3-pentafluoropropyl thiolacetate was accomplished in the following manner. To a stirred suspension of lithium hydroxide monohydrate (2.9 g,  $7.0 \times 10^{-2}$  mol) in 2-methoxy ethyl ether (5 mL) was added thioacetic acid (5.3 g,  $7.0 \times 10^{-2}$  mol) followed by 2,2,3,3,3-pentafluoropropyl iodide (10.2 g,  $3.9 \times 10^{-2}$  mol). The mixture was stirred under  $\text{N}_2$  for 12 h at 25 °C and then slowly heated to 85 °C for another 2.5 h. A mixture of immiscible liquids was distilled off at 54 °C (20 mm Hg). The lower layer of the distillate was separated as a crude, yellow oil (7.6 g). A purified sample was obtained as a colorless liquid by using preparative VPC (Varian 90-P, Se 30 column (1/4 in.  $\times$  5 ft), 70 °C,  $R_f$  3.6 min). From the VPC trace, the yield of the 2,2,3,3,3-pentafluoropropyl thiolacetate was approximately 40%: IR (neat)  $1721 \text{ cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  2.40 (s, 3 H,  $\text{CH}_3\text{COS}$ ), 3.58 (t, 2 H,  $\text{CH}_2\text{COSCH}_2\text{C}_2\text{F}_5$ ,  $J = 9 \text{ Hz}$ ); MS  $m/e$  208; analysis satisfactory.

The 2,2,3,3,3-pentafluoropropanethiol stock solutions were prepared as follows. To a 25-mL volumetric flask flushed with Ar was added doubly distilled, freshly boiled water, buffered with  $1.0 \times 10^{-4}$  M imidazole and made alkaline (pH 12.0) with enough KCl to maintain (25.24 mg,  $1.335 \times 10^{-4}$  mol). The solution was stirred for 1 h at 25 °C. The pH was then readjusted to 6.0 and the solution was diluted to volume. The stock solution was stored under Ar and was frequently standardized using Ellman's reagent.

The  $\text{pK}_a$  value of 7.03 was measured spectrophotometrically as previously described.<sup>7</sup> The rate of the reaction of  $\text{F}_3\text{CCF}_2\text{CH}_2\text{S}^-$  with ESSE and the subsequent reaction with  $\text{F}_3\text{CCF}_2\text{CH}_2\text{SSE}$  were also measured as previously described.<sup>1</sup>

**Table I. Second-Order Rate Constants for the Reaction of Aliphatic Thiol Anions with HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SSE in Aqueous Solution at 25 °C ( $\mu = 1.0$ )**

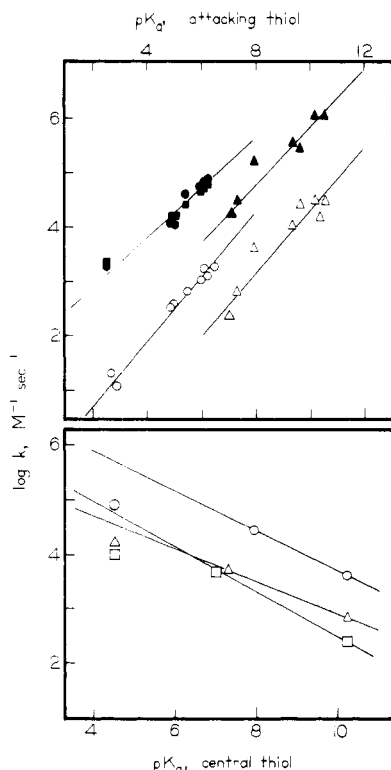
thiol	registry no.	pK <sub>a</sub> <sup>a</sup>	concn range, M	k, M <sup>-1</sup> s <sup>-1</sup>
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> SH	107-03-9	10.53	(0.19 -1.08) × 10 <sup>-3c</sup>	3.02 × 10 <sup>4</sup>
CH <sub>3</sub> CH <sub>2</sub> SH	75-08-1	10.35	(0.327-3.27) × 10 <sup>-3c</sup>	1.47 × 10 <sup>4</sup>
HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SH	19721-22-3	10.19		3.12 × 10 <sup>4a</sup>
HOCH <sub>2</sub> CH <sub>2</sub> SH	60-24-2	9.61	(0.721-7.21) × 10 <sup>-3b</sup>	2.55 × 10 <sup>4</sup>
CH <sub>3</sub> OOCCH <sub>2</sub> CH <sub>2</sub> SH	2935-90-2	9.33	(0.744-7.44) × 10 <sup>-3b</sup>	1.09 × 10 <sup>4</sup>
CH <sub>3</sub> OOCCH <sub>2</sub> SH	2365-48-2	7.91	(0.722-7.22) × 10 <sup>-3b</sup>	4.29 × 10 <sup>3</sup>
CF <sub>3</sub> CH <sub>2</sub> SH	1544-53-2	7.30	(0.269-2.69) × 10 <sup>-4c</sup>	6.84 × 10 <sup>2</sup>
CF <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> SH	677-57-6	7.03	(0.041-5.76) × 10 <sup>-5c</sup>	2.4 × 10 <sup>2</sup>

<sup>a</sup>Taken from ref 1. <sup>b</sup>Measured at pH 5.0. <sup>c</sup>Measured at pH 7.0.

**Table II. Second-Order Rate Constants for the Reaction of Aromatic Thiol Anions with HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SSE in Aqueous Solution at 25 °C ( $\mu = 1.0$ )**

thiol	registry no.	pK <sub>a</sub> <sup>a</sup>	concn range, M	k, M <sup>-1</sup> s <sup>-1</sup>
C <sub>6</sub> H <sub>5</sub> SH	108-98-5	6.43	(1.50 -7.50) × 10 <sup>-4</sup>	1.84 × 10 <sup>3</sup>
4-FC <sub>6</sub> H <sub>4</sub> SH	371-42-6	6.20	(0.201-1.01) × 10 <sup>-3</sup>	1.23 × 10 <sup>3</sup>
4-CH <sub>3</sub> CONHC <sub>6</sub> H <sub>4</sub> SH	1126-81-4	6.08	(0.232-1.16) × 10 <sup>-3</sup>	1.58 × 10 <sup>3</sup>
4-ClC <sub>6</sub> H <sub>4</sub> SH	106-54-7	5.97	(0.207-1.03) × 10 <sup>-3</sup>	1.04 × 10 <sup>3</sup>
3,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> SH	5858-17-3	5.48	(0.242-1.21) × 10 <sup>-3</sup>	6.52 × 10 <sup>2</sup>
3,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> SH	17231-94-6	4.94	(0.244-1.22) × 10 <sup>-3</sup>	3.64 × 10 <sup>2</sup>
3,4,5-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> SH	57730-96-8	4.89	(0.245-1.23) × 10 <sup>-3</sup>	3.32 × 10 <sup>2</sup>
2,3,5,6-F <sub>4</sub> C <sub>6</sub> HSH	769-40-4	2.75	(0.319-1.59) × 10 <sup>-2</sup>	7.14
F <sub>3</sub> C <sub>6</sub> SH	771-62-0	2.68	(0.435-2.17) × 10 <sup>-2</sup>	2.05 × 10 <sup>1</sup>

<sup>a</sup>Taken from ref 1.



**Figure 3.** In the upper graph the log of the rate constants for aromatic (●, ■) and aliphatic (▲) thiol anions with ESSE is plotted vs. the pK<sub>a</sub> of the attacking thiol (data from ref 1). The least-squares slopes are 0.53 (correlation coefficient 0.973) for alkyl thiol anions and 0.48 (correlation coefficient 0.964) for aryl thiol anions. Also plotted are the corresponding points for HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SSE which has a least-squares slope of 0.57 (correlation coefficient 0.929) for alkyl thiol anions (▲) and a slope of 0.59 (correlation coefficient 0.969) for aryl thiol anions (○). The lower plot shows the dependence of the second-order rate constants upon the pK<sub>a</sub> of the central thiol, as described in the text.

## Results

The second-order rate constants for the production of ES<sup>-</sup> from HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SSE with alkyl and aryl thiols are listed in Tables I and II. The  $\beta_{\text{nuc}}$  plot for these data is shown in Figure 3 along with the comparable data for the attack of alkyl and aryl thiol anions on ESSE under identical conditions.<sup>1</sup> Also plotted in this figure are the rate constants for the attack of F<sub>3</sub>CCF<sub>2</sub>CH<sub>2</sub>S<sup>-</sup> on ESSE (1.80 × 10<sup>4</sup> M<sup>-1</sup> s<sup>-1</sup>) and for the attack of F<sub>3</sub>CCF<sub>2</sub>CH<sub>2</sub>S<sup>-</sup> on F<sub>3</sub>CCF<sub>2</sub>CH<sub>2</sub>SSE (5.1 × 10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup>).

The  $\beta_{\text{nuc}}$  values were determined for alkyl thiol anions by ignoring the point for CH<sub>3</sub>COOCH<sub>2</sub>SH which consistently shows a positive deviation of about 0.3 log units in Brønsted plots for nucleophilic reactions.<sup>1,7</sup> The  $\beta$  values for HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SSE are slightly larger than those for ESSE, although the difference is small enough that it may not be significant. The aryl thiol anions are more reactive for their basicity than alkyl thiol anions with HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SSE by a factor of about 6. This is exactly the same behavior as was found with ESSE, as shown in Figure 3.

Plotted in the lower half of Figure 3 are the second-order rate constants for the attack of CH<sub>3</sub>OCOCH<sub>2</sub>S<sup>-</sup> (○), CF<sub>3</sub>CH<sub>2</sub>S<sup>-</sup> (△), and CF<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>S<sup>-</sup> (□) on mixed disulfides RSSE versus the pK<sub>a</sub> of RSH. The group RS was either HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S, ES, or the same as the attacking thiol. The two-point Brønsted plots for the case where the central thiol is an uncharged alkyl thiol show that the reaction is assisted by electron-withdrawing groups ( $-\beta_{\text{CT}} = 0.3-0.4$ ). The values of the rate constants for ESSE were divided by 2 to correct for symmetry<sup>17</sup> and these points fall well below the lines drawn through the other two points.

## Discussion

A thiol anion attacking HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SSE may displace either HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S<sup>-</sup> or ES<sup>-</sup>. Previous experiments have

shown that  $\beta_{\text{nuc}}$  (which, by symmetry, is equivalent to  $-\beta_{\text{leaving group}}$ )<sup>7</sup> for this reaction is  $\sim 0.5$ . Because  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{S}^-$  is roughly  $10^6$  more basic than  $\text{ES}^-$ , the latter should be a better leaving group in this process by a factor of about  $10^3$ . It was expected therefore that all measurable nucleophilic attack on the mixed disulfide would occur to give  $\text{ES}^-$ . The first-order curves generated as shown in Figures 1 and 2 confirm the validity of this assumption.

The greater reactivity of aryl thiol anions compared to alkyl thiol anions of a given basicity may be due to the greater softness of the aryl thiol anions, as discussed previously.<sup>1</sup> It is certainly not due to a favorable interaction between an aryl central thiol and an aryl attacking thiol since changing the central thiol from  $\text{ES}^-$  to  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{S}^-$  has no effect on the difference in reactivity of the two groups of nucleophiles, as shown in Figure 3.

Limited data exist which allow the inductive effect of the central thiol to be estimated. Shown in Figure 3 is a plot of rate constants for attack of  $\text{RS}^-$  on ESSE, RSSE, and  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{SSE}$  plotted as a function of the central thiol  $\text{p}K_{\text{a}}$ . Only low  $\text{p}K_{\text{a}}$  alkyl RSH data were used so that the difference in  $\text{p}K_{\text{a}}$  of RSH and  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{SH}$  would be maximized and the slope generated by the two points would be meaningful. A  $\beta_{\text{CT}}$  of approximately  $-0.3$  to  $-0.4$  is found for the inductive effect due to a change in the central thiol. Negative deviations from these lines drawn through the alkyl points were found for the reactions with  $\text{ES}^-$  as the central thiol. It has previously been demonstrated<sup>18</sup> that the negative charge on ES can cause a fivefold decrease in the rate constant which is consistent with the data in Figure 3.

**Acknowledgments.** We are indebted to Professor Charles Overberger for allowing us to use the stopped-flow spectrophotometer. Financial support was provided by Research Corporation and the National Science Foundation (Grant CHE-7808723). J.M.W. was an N.S.F. undergraduate research participant.

**Registry No.**—ESSE, 552-24-9; 5-[(3-hydroxypropyl)dithio]-2-nitrobenzoic acid, ion(1-), 69531-82-4; 2-nitro-5-[(2,2,3,3,3-pentafluoropropyl)dithio] benzoic acid, ion(1-), 69531-85-3; 2,2,3,3,3-pentafluoropropyl thiolacetate, 69531-84-6; thioacetic acid, 507-09-5; 2,2,3,3,3-pentafluoropropyl iodide, 354-69-8.

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## Application of Phase-Transfer Catalysis to the Chemical Modification of Cross-Linked Polystyrene Resins

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The application of phase-transfer catalysis to the introduction of new functionalities in several cross-linked polystyrene resins was studied. In general, the three-phase reactions gave excellent results and high functional yields. Nucleophilic displacements on chloromethylpolystyrene were used to prepare resins containing acetyl, hydroxymethyl, cyanomethyl, dinitrile, mononitrile monoester, diester, thiol, and various other functionalities. Addition of cyanide ion to a polystyrylcarboxaldehyde resin produced cyanohydrins which could be trapped by reaction with acetic anhydride or a reactive halide. Other phase-transfer reactions involving the use of thiol, hydroxyl, or cyanomethyl resins as nucleophiles were also studied. Reactions involving symmetrical difunctional molecules occurred mostly at one extremity only, indicating that in these phase-transfer reactions site-site interactions can be limited.

The preparation of polymers carrying various functional groups is a problem which has received much attention in recent years, as evidenced by the large body of literature devoted to this subject.<sup>1,2</sup> Functional polymers have been used in a large variety of applications in which they may serve as supports, reagents, or catalysts for various reactions.<sup>3</sup> The polymers which are used most often in these applications are cross-linked polystyrene resins. These are chosen mainly because the aromatic rings of the polymer can be functionalized relatively easily while the polymer itself has good mechanical and chemical resistance.<sup>1</sup> One of the most important reactions in the functionalization of cross-linked polystyrene is doubtless its chloromethylation<sup>4</sup> since the chloromethyl group provides a reactive handle on the polymer and can

subsequently be transformed into numerous other functional groups.<sup>1</sup> Two other important steps in the functionalization of cross-linked polystyrene, bromination and lithiation, have been described in a previous report from this laboratory,<sup>5</sup> and a number of functional polymers have been prepared from lithiated polystyrene.<sup>1,5,6</sup>

A large number of reactions can be used to effect the chemical modification of polymers but in a number of cases the reactions are accompanied by undesired side reactions and the functional yields are low. Since the functional polymers cannot be purified once they have been prepared, it is desirable to use very simple systems in the functionalization reactions to avoid all side reactions whenever possible.

For the past year we have been using phase-transfer catal-