Solid–Solid–Liquid Three Phase Transfer Catalysis of Polymer-Bound Acyclic Poly(oxyethylene) Derivatives. Applications to Organic Synthesis[1]

Shozo Yanagida,* Kazutomo Takahashi, and Mitsuo Okahara

*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Japan 565*

Phase-transfer catalysis of insoluble polystyrene-bound poly(oxyethylene) monomethyl ethers in the reactions of anhydrous inorganic salts with liquid substrates, which was previously developed for the iodide ion-exchange reactions, has been successfully applied to generation and reactions of dichlorocarbene, further displacement reactions, cocatalysis to fluoride ion catalysis, a Wittig reaction, and a reduction with NaBH$_4$. Mechanism of the catalysis was discussed in terms of anion activation by soft oxonium ion formation.

Since Starks[2a] introduced the concept of phase-transfer catalysis in organic chemistry, various types of phase-transfer catalysts[2b,3] and modified techniques have been developed. Success in the employment of insoluble polymer-bound phase-transfer catalysts[4-9] and in the use of anhydrous inorganic salts[10-15] is quite attractive from a practical standpoint. We demonstrated in the preceding paper[8] that acyclic poly(oxyethylene) (POE) monomethyl ethers insolubilized on chloromethylated cross-linked polystyrene beads catalyze the reaction of a benzene solution of *n*-octyl bromide (liquid phase) with powdered anhydrous metal iodide (solid phase), and that this triphasic catalysis is based on the metal–ion complexation of POE with the catalysts.

In this paper we report the applications of this triphasic technique to a variety of useful reactions. Further, on the basis of the results obtained, anion activation of POE on the polymer matrix is also discussed.

Results and Discussion

Generation of Dichlorocarbene and Its Related Reactions. The generation and reactions of dichlorocarbene have recently been improved by employment of polymer-bound quaternary ammonium salts[5c] or by use of powdered anhydrous NaOH with quaternary ammonium salts.[13] We have now found that employment of catalytic quantities of polystyrene-bound POE with anhydrous NaOH is quite effective in generation of dichlorocarbene. When cyclohexene was added to the reaction system, high yields of the dichlorocyclopropane derivative were formed (Table I). As expected, the catalytic activity was pronounced when the number of oxyethylene groups of the POE unit in the catalyst exceeded six.

CHCl$_3$ $\xrightarrow{\text{solid NaOH/cat.}}$ [:CCl$_2$] $\xrightarrow{\text{ROH}}$ RCl

[:CCl$_2$] $\xrightarrow{\text{RCONH}_2}$ RCN
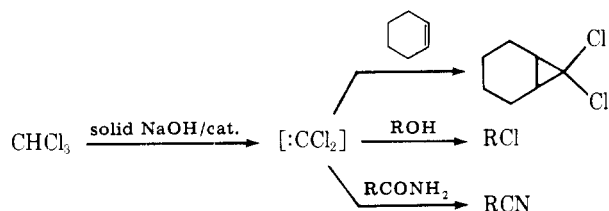
cat., PCH$_2$O(C$_2$H$_4$O)$_n$Me: P = ca. 100% chloromethylated cross-linked polystyrene (n = 3, AEO3Me; n = 6, AEO6Me; n = 8, AEO8Me); P = ca. 25% chloromethylated cross-linked poly(styrene) (n = 6, BEO6Me)

Even in the absence of any phase-transfer catalysts, a fair yield of the dichlorocyclopropane was obtained when freshly powdered anhydrous NaOH was employed (Table I, run no. 4). Similar reactivity of powdered alkali metal hydroxide was also noted previously in its reaction with tetrachloromethane.[16]

The uses of dichlorocarbene in the conversion of alcohols

to alkyl chlorides and in the dehydration of amides to nitriles were described by Tabushi[17] and by Saraie et al.[18] We have now also found that dichlorocarbene generated by the present technique is also capable of carrying out similar transformations (Table I). The conversion of alcohols to chlorides, however, is accompanied by the formation of dialkyl ethers and alkyl formates to a fair extent. Their formation is apparently due to the anhydrous conditions, i.e., the generation of reactive alkoxide anions and retardation of hydrolysis.
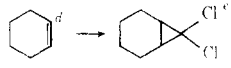
The technique using the catalyst AEO8Me with powdered anhydrous NaOH was also applicable to the Darzens reaction between benzophenone and chloroacetonitrile (Table I, run no. 9).

Enhancement of Catalysis of Potassium Fluoride. Striking catalysis of fluoride ion has recently been demonstrated by the use of quaternary ammonium fluoride[19-21] or by combination of KF with an aprotic polar solvent[22] or with 18-crown-6.[23] The cocatalytic activity was ascribed to the enhanced basicity of fluoride ion by the catalytic system. We have found that the resin AEO8Me can be used to advantage as a cocatalyst of KF in the Michael addition of nitroethane to acrylonitrile, and in the preparation of a phenacyl ester (Table II, runs no. 10 and 12). In the Michael reaction, however, no reaction occurred when KF was replaced by NaF. In the light of the insolubility of NaF even in water, no catalysis indicates the importance of transportation of fluoride ion into the solid catalyst through dissolution.[8] The observed cocatalysis of the insoluble POE resin is quite in conflict with the concept of solubilized "naked" fluoride ion catalysis.[11,23]

Anion Activation in Nucleophilic Substitution Reactions. The nucleophilic enhancement of fluoride ion in acetonitrile by soluble POE derivatives has been concurrently reported by Lehmkul et al.[24] and by Kitazume and Ishikawa.[25] Thus, polymer-bound POE-catalyzed fluoride displacement reactions have been effected by using reactive benzyl bromide as a halide, powdered anhydrous KF, and the resin AEO8Me as a catalyst, but with less satisfactory results than with the use of 18-crown-6 as a catalyst under comparable conditions (Table III, run no. 18). Further, no reaction was observed in benzene, or when benzyl bromide was replaced by *n*-octyl bromide. These facts, combined with the cocatalytic reactivity of the resin POE, have led to a conclusion that the insoluble POE resin is quite powerful in enhancement of fluoride ion basicity but is not so effective in increasing its nucleophilicity, especially compared with quaternary onium catalysts.[4b,26]

While the catalyst AEO8Me did not catalyze the chloride displacement reaction with *n*-octyl bromide in acetonitrile (Table III, run no. 19), its effective and powerful catalysis in the solid–solid–liquid three phase transfer process has been established for the synthesis of nitriles and acetates (Table III). Poor yields or no reaction were observed when a poor solvent or unactivated halides were chosen (Table III, run no.

Table I. Generation and Reactions of Dichlorocarbene and a Darzens Condensation

reaction scheme	run no.	catalyst (EOn unit mmol)	reagents and/or solvent, (mmol)	temp, °C	time, h	yield, %
(cyclohexene → dichloronorcarane)	1	AEO8Me (0.08)	cyclohexene (1.6), NaOH (16.0), chloroform (16)	rt	3.4	ca. 100
	2	AEO6Me (0.08)	cyclohexene (1.6), NaOH (16.0), chloroform (16)	rt	3.4	ca. 100
	3	AEO3Me (0.08)	cyclohexene (1.6), NaOH (16.0), chloroform (16)	rt	3.4	46
	4	no catalyst	cyclohexene (1.6), NaOH (16.0), chloroform (16)	rt	3.4	20–56
ROH → RCl	5	AEO8Me (0.08)	PhCH$_2$OH (3.04),[g] NaOH (16.4), chloroform (16.0)	rt	6.0	39[a]
	6	AEO8Me (0.08)	PhCH$_2$OH (1.60), NaOH (15.7), chloroform (16.5)	rt	3.5	56[b]
	7	AEO8Me (0.08)	1-octanol (1.65),[h] NaOH (19.6), chloroform (16.0)	rt	5.0	65[c]
RCONH$_2$ → RC≡N	8	AEO8Me (0.08)	PhCONH$_2$ (1.64),[i] NaOH (16.0), chloroform (16.3)	rt	24.0	ca. 100
PhCOPh → (epoxide)	9	AEO8Me (0.08)	PhCOPh (1.8),[j] NaOH (4.22), chloroacetonitrile (1.72)	rt	24.0	61

[a] Byproducts: 13% PhCH$_2$OCHO and 47% of a mixture of PhCH$_2$OCH$_2$Ph and PhCH$_2$OH (mol ratio, 1:3). [b] Byproducts: 12% PhCH$_2$OCHO and 32% of a mixture of PhCH$_2$OCH$_2$Ph and PhCH$_2$OH (mol ratio, 5:2). [c] Byproducts: 25% n-C$_8$H$_{17}$OCHO and 10% (n-C$_8$H$_{17}$)$_2$O. [d] Registry no. 110-83-8. [e] Registry no. 823-69-8. [f] Registry no. 21432-18-8. [g] Registry no. 100-51-6. [h] Registry no. 111-87-5. [i] Registry no. 55-21-0. [j] Registry no. 119-61-9.

Table II. Enhancement of Fluoride Ion Catalysis by Polymer-Bound POE

reaction schemes	run no.	catalysts (EOn unit mmol)	reagents (mmol) and solvent	temp, °C	time, h	yield,[a] %
C$_2$H$_5$NO$_2$[b] →(CH$_2$=CHCN[c]) CH$_3$C(C$_2$H$_4$CN)$_2$NO$_2$[d]	10	AEO8Me (0.08), KF (0.70)	C$_2$H$_5$NO$_2$ (1.59), CH$_2$=CHCN (3.37), benzene (1 mL)	rt	24	91
	11	AEO8Me (0.08), NaF (0.56)	C$_2$H$_5$NO$_2$ (1.87), CH$_2$=CHCN (2.80), benzene (1 mL)	rt	24	0
C$_2$H$_5$COOH[e] → C$_2$H$_5$COOCH$_2$CO—⟨⟩—Br[f]	12	AEO8Me (0.04), KF (2.05)	C$_2$H$_5$COOH (1.10), benzene (1 mL), p-bromophenacyl bromide (1.00)	80	1	96
	13	KF (2.00) only	C$_2$H$_5$COOH (1.23), benzene (1 mL), p-bromophenacyl bromide (1.00)	80	1	81
	14	KF (2.03) only	C$_2$H$_5$COOH (1.19), benzene (1 mL), p-bromophenacyl bromide (1.00)	80	17	ca. 100

[a] Determined by NMR. [b] Registry no. 79-24-3. [c] Registry no. 107-31-1. [d] Registry no. 19932-75-3. [e] Registry no. 79-09-4. [f] Registry no. 14041-01-1.

Table III. Catalysis of Polymer-Bound POE in Nucleophilic Substitution Reactions

reaction schemes	run no.	catalysts (EOn unit mmol)	reagents (mmol) and solvent	temp, °C	time, h	yield, %
RX $\xrightarrow{MY}$ RY	15	AEO8Me (0.08)	PhCH$_2$Br (1.60),[d] KF (8.00), acetonitrile (1 mL)	80	24	10[a]
	16	AEO8Me (0.08	PhCH$_2$Br (1.60), KF (8.00), benzene (1 mL)	80	24	trace[b]
	17	AEO8Me (0.08)	n-C$_8$H$_{17}$Br (1.64), KF (8.08), acetonitrile (1 mL)	80	24	0
	18	18-crown-6 (0.10)	PhCH$_2$Br (1.60), KF (8.10), acetonitrile (1 mL)	80	24	47[a]
	19	AE08Me (0.08)	n-C$_8$H$_{17}$Br (1.66), NaCl (5.22), acetonitrile (1 mL)	80	24	0
RX $\xrightarrow{KCN}$ RCN	20	BE06Me (0.08)	n-C$_8$H$_{17}$Br (1.61),[e] NaI (8.28), benzene (1 mL)	80	1.5	93[b]
	21	AEO8Me (0.08)	PhCH$_2$Br (1.60), KCN (8.00), acetonitrile (1 mL)	80	24	ca. 100[a]
	22	AEO8Me (0.08)	PhCH$_2$Cl (1.75), KCN (8.02), acetonitrile (1 mL)	80	24	ca. 100[c]
	23	AEO8Me (0.08)	n-C$_8$H$_{17}$Br (2.08), KCN (8.00), acetonitrile (1 mL)	80	20.5	87[a]
	24	AEO8Me (0.08)	n-C$_8$H$_{17}$Cl (1.60), KCN (8.02), acetonitrile (1 mL)	80	15.2	0
RBr $\xrightarrow{AcOK}$ ROAc	25	AEO8Me (0.08)	n-C$_8$H$_{17}$Br (1.64), AcOK (8.25), benzene (1 mL)	80	24	ca. 9.3[a]
	26	AEO8Me (0.08)	n-C$_8$H$_{17}$Br (1.65), AcOK (8.20), acetonitrile (1 mL)	80	24	89[a]

[a] Determined by NMR. [b] Determined by GLC. [c] Determined by GLC and IR. [d] Registry no. 100-39-0. [e] Registry no. 111-83-1.

23 and 24). It is apparent that solvent assistance does work in this process.

A recent patent[27] claimed the preparation of isocyanates from KOCN and organic halides by the phase-transfer technique. However, the organic halides which gave successful results are quite restricted because the isocyanates once formed are apt to trimerize readily giving triazine deriva-

tives.[28] It is also well known that the polymerization of isocyanates occurs easily in aprotic polar solvents.[29] Accordingly, the present technique using benzene as solvent was thought promising for the preparation of isocyanates from a wide range of organic halides. However, benzyl bromide in benzene did not react with anhydrous KOCN in the presence of the catalyst AE08Me. The reaction in acetonitrile resulted in the

formation of N,N',N''-tribenzyl cyanurate (78%) and N,N'-dibenzylurea (20%). These products were apparently produced from benzyl isocyanate, i.e., the former by trimerization and the latter by its reaction with the moisture in the reaction system, or during the workup.

The triphasic technique using the AE08Me resin was also successfully applied both to a Wittig reaction and to a reduction with aqueous sodium borohydride (see Experimental Section). The solvent effect which was observed when the Wittig reaction was conducted with 18-crown-6[30] was not recognized, i.e., trans alkenylation was exclusively observed both in tetrahydrofuran and in dichloromethane.

Mechanistic Rationalization. The present triphasic technique involves a reaction between the insoluble POE resin and seemingly insoluble anhydrous salts in organic solvents. In the iodide exchange reaction with octyl bromide, we proposed the transportation of metal iodides into the resin catalysts through dissolution in the liquid phase. In order to confirm this speculation, the solubility of NaI was examined in benzene because NaI is much more soluble in organic solvents than KI.[31] The iodide (0.8 mg) was completely dissolved in 20 mL of dry benzene in a sealed tube after heating overnight at 80 °C and, on cooling, the iodide precipitated in part.[32] In other applications of this process, we have observed that solvent also plays an important role, i.e., solubility of salts is another factor causing the remarkable difference in catalysis. These facts suggest that, when salts are once transported into the POE resin phase, counteranions should increase effectively either the nucleophilicity or the basicity.

Recently Fendler et al.[33] have characterized the catalysis of POE-type nonionic surfactants in nonaqueous solvents as a kind of reversed micellar catalysis owing to the presence of a trace amount of water. When the halogen-exchange reaction of n-octyl bromide with powdered anhydrous NaI using the catalyst BE06Me was reinvestigated under rigorously anhydrous conditions, however, the observed reaction rate increased slightly and no retardation was observed. Accordingly, it seems inappropriate to adopt the concept of reversed micellar catalysis to explain the presently developed POE resin catalysis.[34]

Evidence for the strong complexation of acyclic POE derivatives with metal cations in aprotic solvent has already been obtained by NMR studies and isolation of their complexes.[35,36] Catalysis by the POE resins is apparently related to that of the crown-type compounds.[8,37]

Catalysis of the crown-type compounds has been explained in terms of the solubilized or dissociated "naked" or "bared" anions formation, although no direct evidence has been obtained.[10,11] However, as was speculated by Ugelstad et al.,[38] the contribution of an ion pair as the reacting entity is not unlikely on the basis of the following observations: (1) Polymer-bound acyclic or cyclic POE show a striking enhancement of anion reactivity even in nonpolar solvents like benzene in spite of their clear insolubility.[8,9] (2) In benzene, which is energetically unfavorable for ion dissociation,[39] freshly pulverized anhydrous NaOH or KF showed considerable reactivity as a base even in the absence of POE catalysts. (3) As had been shown in the case of the iodide-exchange reactions by the use of KI,[8] polymer-bound POE serves as an efficient catalyst in the two-phase benzene–water system just as other soluble POE[24] and crown ethers.[40] If only dissociated anions were reactive nucleophiles, the reaction should have been retarded because water is more apt to solvate dissociated anions.

While phase-transfer catalysts have often been discussed by dividing them into two types of compounds, i.e., quaternary onium salts (charged catalysts) and crown-type compounds (uncharged catalysts),[2,3] the metal–ion complexation of the latter compounds can be regarded as the formation of oxonium
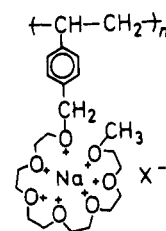
salts. Thus it is reasonable to presume that onium salts themselves or the substances which produce onium compounds may function as anion activators. Brändström[41] has recently described that in phase-transfer catalysis with quaternary onium salts, reactive nucleophiles are present as their ion pairs and not as dissociated free anions from them. The similarity in behavior in catalysis is now understood. Their ion-pair reactivity may possibly be explained due to the large size of the cation giving a relatively low cation–anion interaction energy in the ion pair,[38] i.e., looser ion pair[42] or ion-pair separation.[43]

Anion activation by combining with bulky onium cations would be more comprehensively rationalized by Pearson's Hard and Soft Acids and Bases Principle.[44] As is shown in the structure above, for example, the oxonium cation produced by the metal–ion complexation of POE is soft in the HSAB sense. As a result, the soft POE oxonium cations tend to pair with soft anions but not sufficiently to deactivate them by soft–soft interaction,[50] or to soften rather hard anions by the symbiosis effect. Moreover, it would appear that soft oxonium cations may produce those circumstances which are convenient for soft transition states thereby lowering the activation energy of the reactions. This rationale makes it easier to understand the striking feature in the generation and reactions of soft dichlorocarbene and in the activation not only of soft iodide, cyanide, and tetrahydroborate anions but also of hard hydroxide, carboxylate, and acetate anions. It is apparent from the present study that intrinsically hard fluoride anion, when paired with soft polymer-bound POE oxonium cations, indeed increases its basicity but not so much its nucleophilicity.

Conclusion. The solid–solid–liquid triphasic reactions using insoluble polymer-bound noncyclic POE with powdered anhydrous salts have now been proved to be a simple and effective technique for the activation of anions such as cyanide, iodide, acetate, and tetrahydroborate anions, and of the basicity of hydroxide and fluoride ions. Although the insoluble POE catalysts were somewhat less active than the soluble analogues,[51] the actual rates can be accelerated if desired by increasing the catalyst quantity.[8] The absence of water in the process minimizes side reactions such as hydrolysis. Quaternary onium salts are known to be much prone to decomposition or side reactions with soft nucleophiles.[52] Although similar decomposition is conceivable for the POE catalysts in view of the formation of soft oxonium salts through metal–ion complexation, no degradation was observed as far as the freshly prepared or carefully stored POE catalysts were concerned.[53] The present technique is characterized by easy preparation of the POE catalysts, their stability during reactions, the formation of clean products with generally good yields, and easy workup, suggesting that the procedures are especially valuable in small scale synthetic reactions.

Recently, Mckenzie and Sherrington[54] also reported the use of this technique for phenolate alkylations.

Experimental Section

GLC analyses were carried out on a Yanagimoto G-8 model instrument or a Shimadzu GC-4CPT instrument, equipped with a thermal conductivity detector. The columns were Silicon Gum SE-30 on a Diasolid L (60–80 mesh) (4 mm × 2 m) and Silicon OV-1 on a Umport KS (60–80 mesh) (4 mm × 2 m). The ¹H NMR spectra were obtained using a JEOL LMN-PS-100 spectrometer (100 MHz).

Materials. Benzene, tetrahydrofuran, dichloromethane, acetonitrile, chloroacetonitrile, benzyl alcohol, benzyl bromide, benzyl chloride, n-octyl alcohol, and n-octyl bromide were purified by distillation after appropriate drying. Chloroform was distilled with several water washes and drying with anhydrous MgSO₄. All other organic reagents were obtained commercially and were used without further purification. All metal salts were obtained commercially; they were used after being ground to a powder and dried in a vacuum oven at 100 °C. Triphenylethylphosphonium bromide was prepared from triphenyl phosphine and ethyl bromide.[56] The POE resin catalysts used in this study were identical with those in the preceding paper.[8] A series of catalysts were prepared from chloromethylated polystyrene (6.36 mmol of chlorine/g of the resin) cross-linked by 3% divinylbenzene (DVB) (Mitsubishi Chemical Co. Ltd.) and B series catalysts from chloromethylated polystyrene (2.07 mmol of chlorine/g of the resin) cross-linked by 2% DVB (Nakarai Chemical Ltd.).

General Procedure. Procedures similar to those previously[8] described for the iodide exchange reactions were followed for all of the reactions summarized in the tables. The quantity of reactants and reaction conditions are listed in the tables. Typical procedures are described:

Reactions of Dichlorocarbene. To a 75-mL-glass test tube (30 mm × 100 mm) with a ground glass stopper were added successively 0.0432 mg of the resin AE08Me (0.08 E08Me unit mmol), 0.0632 mg of powdered NaOH (16 mmol), 0.0138 mg (1.68 mmol) of cyclohexene, and 1.92 g (16 mmol) of chloroform. The slurried mixture was stirred with a magnetic stirrer at room temperature for 3.4 h. The solid materials were filtered and the filtrate was analyzed by IR, NMR, and GLC.

Procedures used for conversion of alcohols to chlorides, of benzamide to benzonitrile, and a Darzens reaction (Table I, run no. 9) were similar.

The Michael Addition Reaction of Nitroethane to Acrylonitrile. To 1 mL of acetonitrile, nitroethane (0.1195 g, 1.59 mmol), acrylonitrile (0.1787 g, 3.37 mmol), powered anhydrous KF (0.0409 g, 0.70 mmol), and the resin AE08Me (0.0438 g, 0.08 unit mmol) were added successively. The mixture was stirred at room temperature for 24 h. The solid material was filtered and after removal of acetonitrile and excess acrylonitrile, an oily residue was obtained. NMR analysis indicated that 91% of the nitroethane was converted to 1,2-bis(cyanoethyl)nitroethane.

The Reaction of n-Octyl Bromide with Anhydrous Potassium Acetate in Acetonitrile. To a 75 mL-glass tube containing 0.0438 g (0.08 mmol) of the resin AE08Me was added 0.7895 g (8.20 mmol) of potassium acetate followed by n-octyl bromide (0.3188 g, 1.65 mmol) and 1 mL of acetonitrile. The tube was stoppered and the mixture was stirred magnetically at 80 °C for 24 h. The solid material was filtered with suction. Analysis of the filtrate by GLC and NMR indicated an 89% yield of n-octyl acetate, based on starting bromide.

The Reaction of Benzyl Bromide with Anhydrous Potassium Cyanate. To a 75 mL-glass tube containing 0.044 g (0.08 unit mmol) of the resin AE08Me were added powdered anhydrous KOCN (0.6491 g, 8.00 mmol), benzyl bromide (0. 2770 g, 1.62 mmol), and 1 mL of acetonitrile, successively. The tube was stoppered and the mixture was stirred magnetically at 80 °C for 24 h. The solid materials were filtered with suction. The filtrate was concentrated by rotary vacuum evaporation, giving solid products which were separated into benzene-soluble and benzene-insoluble components. IR spectra indicated the former material to be N,N',N''-tribenzylcyanuric acid, and the latter N,N'-dibenzylurea. NMR analysis showed that the crude products consisted of 74% cyanuric acid, 20% urea, and 7% starting bromide.

Polymer-Bound POE-Catalyzed Wittig Reaction. To a 75-mL glass tube were added the resin AE08Me (0.0227 g, 0.04 unit mmol), triphenylethylphosphonium bromide (1.57 g, 4.23 mmol), powdered anhydrous K₂CO₃ (0.5825 g, 4.21 mmol), benzaldehyde (0.3818 g, 3.60 mmol), and 17 mL of THF, successively. The reaction mixture was refluxed with stirring for 24 h. The solid materials were filtered with suction and the filtrate was concentrated by rotary vacuum evaporation yielding a residue which was washed with petroleum ether. The ether washings were filtered to remove insoluble triphenylphosphine oxide. Evaporation of the solvent afforded a 56% yield of 1-phenylpropene (NMR) with a trans/cis ratio of 72/28. When THF was replaced by dichloromethane, a 47% yield of the olefin was obtained with a trans/cis ratio of 82/18.

Polymer-Bound POE-Catalyzed Reduction with Sodium Borohydride. To a 75-mL glass tube were added the catalyst AE08Me (0.0433 g, 0.08 unit mmol), NaBH₄ (0.0378 g, 1.00 mmol), acetophenone (0.2077 g, 1.73 mmol), and 1 mL of water, successively.

The mixture was stirred at room temperature for 24 h. The insoluble catalyst was removed by suction filtration and the filtrate was extracted with dichloromethane. The extract was dried with anhydrous sodium sulfate and removal of dichloromethane gave an oily product. NMR and IR analysis indicated a 61% yield of 1-phenylethanol.

Polymer-Bound POE-Catalyzed Reaction of n-Octyl Bromide with NaI under Careful Anhydrous Conditions. Benzene was dried by distillation from sodium and benzophenone under a nitrogen atmosphere. n-Octyl bromide was distilled and stored in the presence of activated molecular sieve 3A. Powdered NaI and the resin BE06Me were dried in a vacuum oven at 100 °C for 24 h. The mixture of NaI (1.2415 g, 8.28 mmol) and BE06Me (0.0615 g, 0.08 unit mmol) was placed in a 75-mL glass tube and dried again in a vacuum desiccator with P₂O₅ for 48 h. In a drybox, n-octyl bromide (0.3112 g, 1.61 mmol) and 1 mL of benzene were added to the above mixture. According to the procedure reported previously,[8] the pseudo-first-order rate constant at 80 °C was determined to be 4.9×10^{-4} s⁻¹. Duplicate runs in good agreement were obtained.

References and Notes

(1) Part 6 in the series of metal-ion complexation of noncyclic poly(oxyethylene) derivatives. This work was presented at the 37th National Meeting of the Chemical Society of Japan, Yokohama, April, 1978.
(2) (a) C. M. Starks, *J. Am. Chem. Soc.*, **93**, 195 (1971); (b) W. P. Weber and G. W. Gokel, "Phase Transfer Catalysis in Organic Synthesis", Springer-Verlag, New York, 1977.
(3) E. V. Dehmlow, *Angew. Chem., Int. Ed. Engl.*, **16**, 493 (1977).
(4) G. Cainelli and F. Manescalchi, *Synthesis*, 723 (1975); (b) G. Cainelli, F. Manescalchi, and M. Ranurzio, *ibid.*, 472 (1976).
(5) (a) S. L. Regen, *J. Am. Chem. Soc.*, **97**, 5956 (1975); (b) S. L. Regen, *ibid.*, **98**, 6270 (1976); (c) S. L. Regen, *J. Org. Chem.*, **42**, 875 (1977).
(6) G. Gelbard and S. Colonna, *Synthesis*, 113 (1977).
(7) S. L. Regen and L. Dulak, *J. Am. Chem. Soc.*, **99**, 623 (1977).
(8) S. Yanagida, K. Takahashi, and M. Okahara, *Yukagaku*, **28**, 14 (1979).
(9) (a) M. Cinquini, S. Colonna, H. Molinari, F. Montanari, and P. Tundo, *J. Chem. Soc., Chem. Commun.*, 394 (1976); (b) H. Molinari, F. Montanari, and P. Tundo, *ibid.*, 639 (1977); (c) P. Tundo, *ibid.*, 641 (1977).
(10) (a) D. J. Sam and H. E. Simmons, *J. Am. Chem. Soc.*, **94**, 4024 (1972); (b) D. J. Sam and H. E. Simmon, *ibid.*, **96**, 2252 (1974).
(11) C. L. Liotta and H. P. Harris, *J. Am. Chem. Soc.*, **96**, 2250 (1974).
(12) (a) H. D. Durst, *Tetrahedron Lett.*, 2421 (1974); (b) J. W. Zubrick, B. I. Dunbar, and H. D. Durst, *ibid.*, 71 (1975).
(13) S. Julia and A. Ginebreda, *Synthesis*, 682 (1977).
(14) A. Zwierzak and A. Sulewska, *Synthesis*, 835 (1976).
(15) S. Yanagida, Y. Noji, and M. Okahara, *Tetrahedron Lett.*, 2337 (1977).
(16) C. Y. Meyers, *Prepr., Div. Pet. Chem., Am. Chem. Soc.*, **19**, 199 (1974); *Chem. Abstr.*, **84**, 43231c (1976).
(17) I. Tabushi, Z. Yoshida, and N. Takahashi, *J. Am. Chem. Soc.*, **100**, 1820 (1978).
(18) T. Saraie, I. Ishiguro, K. Kawashima, and K. Morita, *Tetrahedron Lett.*, 2121 (1973).
(19) S. Holz, M. Albeck, and Z. Roppoport, *Synthesis*, 162 (1975).
(20) I. Kuwajima, T. Murofushi, and E. Nakamura, *Synthesis*, 602 (1976).
(21) J. H. Clark and J. M. Miller, *J. Chem. Soc., Perkin Trans. 1*, 1743 (1977).
(22) (a) J. H. Clark and J. M. Miller, *Tetrahedron Lett.*, 599 (1977); (b) J. H. Clark and J. M. Miller, *J. Chem. Soc., Perkin Trans. 1*, 2063 (1977).
(23) I. Belsky, *J. Chem. Soc., Chem. Commun.*, 237 (1977).
(24) H. Lehmkuhl, F. Rabet, and K. Hauschild, *Synthesis*, 184 (1977).
(25) T. Kitazume and N. Ishikawa, *Chem. Lett.*, 283 (1978).
(26) D. Landini, F. Montanari, and F. Rolla, *Synthesis*, 428 (1974).
(27) Y. Nadachi, Japan Kokai, 75-84529.
(28) P. A. Argabright, B. L. Phillips, and C. H. DePuy, *J. Org. Chem.*, **35**, 2253 (1970).
(29) S. Ozaki, *Chem. Rev.*, **72**, 457 (1972).
(30) R. M. Boden, *Synthesis*, 784 (1975).
(31) W. F. Linke, "Solubilities of Inorganic and Metal-organic Compounds", Vol. II, 4th ed., W. F. Linke, American Chemical Society, 1965.
(32) The solution became pale pink on standing at room temperature under room light illumination.
(33) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, 1975.
(34) The catalysis of POE type nonionic surfactants, designated reversed micellar catalysis, might be related to the metal–ion complexation of POE units when metal salts are involved in the reaction. For example, W. Hinze and J. H. Fendler, *J. Chem. Soc., Dalton Trans.*, 238 (1975).
(35) S. Yanagida, K. Takahashi, and M. Okahara, *Bull. Chem. Soc. Jpn.*, **51**, 1294

(1978).
(36) S. Yanagida, K. Takahashi, and M. Okahara, *Bull. Chem. Soc. Jpn.*, **51**, 3111 (1978).
(37) S. Yanagida, Y. Noji, and M. Okahara, *Tetrahedron Lett.*, 2893 (1977).
(38) J. Ugelstad, T. Ellingsen, and A. Berge, *Acta Chem. Scand.*, **20**, 10 (1966).
(39) M. H. Abraham and P. L. Grellier, *J. Chem. Soc., Perkin Trans. 2*, 1735 (1976).
(40) M. Makosza and M. Ludwikow, *Angew. Chem., Int. Ed. Engl.*, **13**, 665 (1974).
(41) A. Brändström, *Adv. Phys. Org. Chem.*, **15**, 267 (1977).
(42) A. W. Herriott and D. Picker, *J. Am. Chem. Soc.*, **97**, 2345 (1975).
(43) W. L. Dorn, A. Knochel, J. Oehler, and G. Rudolph, *Z. Naturforsch., B*, **32**, 776 (1977).
(44) T. Ho, "Hard and Soft Acid and Bases Principle in Organic Chemistry", Academic Press, New York, 1977.
(45) The HSAB theory has already been introduced to explain the characteristic catalysis of quaternary ammonium salts in micellar systems[46] and in phase-transfer systems,[2] respectively. Moreover, taking into account the fact[47,48] that most aprotic polar molecules strongly coordinate with metal cations, sometimes giving isolable complexes just as POE derivatives, it would appear that the enhancement in reactivity by polar molecules[49] might be similarly explained.

(46) C. A. Bunton, *Pure Appl. Chem.*, **49**, 969 (1977).
(47) M. R. Truter, *Struct. Bonding (Berlin)*, **16**, 71 (1973).
(48) S. Yanagida and M. Okahara, *Kagaku Zokan*, **73**, 149 (1978).
(49) (a) H. Normant, N. T. Cuvigny, and P. Savignac, *Synthesis*, 805 (1975); (b) M. Mikolajczyk, S. Grejszczak, and A. Zatotski, *Tetrahedron Lett.*, 3757 (1975); (c) M. Tomoi, T. Takubo, M. Ikeda, and H. Kakiuchi, *Chem. Lett.*, 473 (1976).
(50) The reduced nucleophilicity of quaternary ammonium iodide or LiI in acetone may be attributable to the strong soft–soft interaction.[10b]
(51) Probably because the reagents need to diffuse into the resins.
(52) (a) E. V. Dehmlow, M. Slopianka, and J. Heider, *Tetrahedron Lett.*, 2361 (1977); (b) H. J-M. Dou, R. Gallo, P. Hassanaly, and J. Metzger, *J. Org. Chem.*, **42**, 4275 (1977).
(53) The polymer-bound POE resins were found to undergo gradual decomposition on standing in the atmosphere, i.e., simply leaving pure POE resins in a desiccator for several months caused a carbonyl peak to develop at 1720 cm^{-1} in the IR spectrum, which was not present initially. Similar oxidation is known for POE-type nonionic surfactants.[55]
(54) W. M. McKenzie and D. C. Sherrington, *J. Chem. Soc., Chem. Commun.*, 541 (1978).
(55) J. M. Corkill, J. F. Goodman, and R. H. Ottowill, *Trans. Faraday Soc.*, **57**, 1627 (1961).
(56) G. Wittig and U. Schoellkopf, *Org. Synth.*, **40**, 66 (1960).

Photosensitized Anaerobic Oxidation of Dibutyl Sulfide

Marye Anne Fox,* Paul K. Miller, and Michael D. Reiner

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712

Upon photoexcitation, acetone can function as an oxidant for dibutyl sulfide by a low quantum yield route (ϕ = ~0.016). A complex mixture of photoproducts results. Solvent effects, kinetics, product distributions, and quenching studies indicate that a radical pathway is important. Unlike the analogous oxidation of methionine, both sulfoxide and sulfone are produced along with smaller quantities of sulfur-containing products produced from radical fragments. In addition to acting as an oxygen source, acetone undergoes normal solution-phase photoreactions and significant polymerization. A mechanism for the oxygen-transfer process is suggested, and experiments which examine the generality of this photoprocess are described.

Although the conversion of dialkyl sulfides to the corresponding sulfoxides is very easily achieved with a variety of oxidants,[1] one technique (the photosensitized transfer of carbonyl oxygen from a ketone to a sulfide) struck us as particularly novel and as worthy of mechanistic investigation. Gennari and Jori have shown that methionine can be cleanly oxidized to methionine sulfoxide (>95% yield) when a *deaerated* solution of methionine in acetone is irradiated at 311 nm.[2] They suggested that acetone acts both as a sensitizer and as an oxygen donor in this photooxidation. Subsequently, it was demonstrated,[3,4] *even in the absence of oxygen*, that biacetyl can similarly act as a photosensitizer and oxygen source. Since only amino acid photoproducts were analyzed in these studies, the fate of the sensitizer after oxygen transfer was unknown. Molecular oxygen was found to *inhibit* these photoreactions. This is a curious observation since in addition to interrupting a radical chain, oxygen itself could also function as an oxidant. Dye-sensitized photooxidation of sulfides proceeding with the participation of singlet oxygen are well-known.[1b,5] Although n,π* sensitizers apparently function in complex fashion with some substrates,[6] such sensitizers have been shown to generate singlet oxygen[7] and therefore, presumably, to function as a source of an effective oxidant.

Since the cleavage of the σ and π bonds of a carbonyl double bond requires ~180 kcal/mol,[8] the discovery of an efficient photoprocess for oxygen transfer from carbonyl groups is most interesting. Furthermore, the possibility of employing sulfides as a photochemical deoxygenation reagent with ketones would provide an intriguing synthetic reaction should such photolyses prove to be general and to be capable of producing useful quantities of deoxygenation product in a wide variety of ketones. With these thoughts in mind, we undertook a mechanistic study of the reaction of some photoexcited ketones with dialkyl sulfides, choosing the reaction of acetone with dibutyl sulfide (1) as a convenient model system.

Results

Photolysis of Acetone in the Presence of Dibutyl Sulfide (1). Irradiation for 6 h with RPR 3000-Å lamps of degassed Pyrex ampules containing a solution of 1 (0.025 M) in neat, dry acetone gives about 15% disappearance of 1 and a complex mixture of photoproducts. Identifiable products and typical yields (with respect to reacted dibutyl sulfide) from the analogous preparative scale irradiation are listed in Chart I. Significant polymer formation is also evident. Continued irradiation results in further conversion of sulfoxide 2 to sulfone 3 and to the disappearance of sulfur-containing product. The quantum yield for disappearance of 1 is ~1.6 × 10^{-2}.

If the photolysis is conducted in cyclohexane (0.025 M 1, 5 M acetone), the reaction is slower (about 6% conversion in 6 h) but somewhat cleaner: the major products are bicyclohexyl (81%),[9] 9 (28%), 2 (58%), 3 (25%), 11 (6%), and 4 (5%). Again, significant photopolymerization occurs.

The rate of sulfoxide production in the photolysis of 0.025 M dibutyl sulfide in a 50% acetone–50% solvent mixture was followed by gas chromatography. Table I summarizes the relative rates observed. The results of an analogous experiment in which the rate of sulfoxide formation was monitored as a function of the initial concentrations of each reactant are tabulated in Table II.

If the photolysis (0.025 M dibutyl sulfide in neat degassed acetone) is conducted in the presence of hydroquinone, nearly