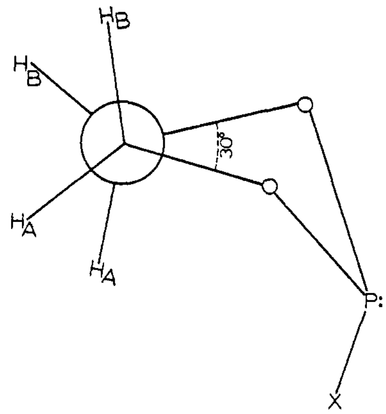

Figure 5. Twist–envelope conformation for ethylene phosphites; Newman projection down C–C bond.

we can then assign H_A (downfield, $J_{PH_A} \sim 2$ cps) as *cis* to X and H_B (upfield, $J_{PH_B} \sim 9$ cps) as *trans* to X. However, the uncertainty about the conformational size of S and P lone pairs makes this a tentative conclusion. If **14** were favored rather than **15**, the reverse assignment would be required.

Structure of Ethylene Phosphites. The vicinal hydrogen–hydrogen coupling constants are not in agreement with a simple envelope conformation (**15**). Instead, **14** and/or **15** must be twisted to yield an H–C–C–H dihedral angle of about 30°. Therefore, taking **15** to be the favored envelope form, *ethylene phosphites appear to prefer two equivalent twist–envelope forms*, one of which is approximately shown in Figure 5. A time average of other conformations yielding the same effect as H–C–C–H dihedral angles of about 30° and very different P–O–C–H dihedral angles would, of course, also satisfy the results found here. However, it seems quite reasonable that the nonbonded interactions in ethylene phosphites and ethylene sulfite should result in the twist–envelope conformation being favored.

This conformational result was obtainable because both H–C–C–H and P–O–C–H couplings could be observed. However, the twist–envelope conformation may well have applicability to other five-membered rings.

Acknowledgment. The 60-Mc spectra were taken on a Varian A-60 instrument purchased by an institutional grant from the National Science Foundation. The 100-Mc spectra were taken on a Varian HA-100 instrument at the University of California at Riverside through the courtesy of Professor Robert C. Neuman. We thank Professor H. Goldwhite for a P^{31}-decoupled spectrum of **10**. The machine calculations were done on an IBM 7094 at the UCLA Computing Facility. Valuable conversations with Drs. F. A. L. Anet, J. L. Sudmeier, and P. C. Turley are acknowledged.

A Kinetic Study of Double-Bond Migration in Allyloxy Polyether Alkoxides

Edwin C. Steiner and Roger O. Trucks

Contribution from The Dow Chemical Company, Edgar C. Britton Research Laboratory, Midland, Michigan 48640. Received September 1, 1967

Abstract: The rates of rearrangement of $CH_2{=}CHCH_2(OC_3H_6)_nO^-M^+$ to *cis*-$CH_3CH{=}CH(OC_3H_6)_nO^-M^+$ have been studied kinetically at 30° in tetrahydrofuran solution. The rates are cation dependent. The Cs^+ compounds react about 60 times as fast as the K^+ compounds; the Na^+ compounds do not rearrange under the conditions used. The rates depend on the value of n, being maximum when $n = 3$ in the K^+ series and when $n = 3$ or 4 in the Cs^+ series. Chelation of cation by the polyether chain is adduced as the cause of this dependence. Addition of fluorenylpotassium or potassium dodecylbenzenesulfonate greatly reduces the rearrangement rates, suggesting that mixed ion pair aggregation is occurring in these systems.

There has been considerable interest in the last few years in elucidating the details of the mechanism of base-catalyzed double-bond migration reactions. An excellent review of the subject is given by Cram,[1] who points out many of the subtleties of the reaction, including the effects of the solvent, the type of base catalyst, and the associated cation on the course of the reaction. During our study of the base-catalyzed polymerization of propylene oxide (PO),[2] we have had the occasion to study the rates of rearrangement of a series of allyl ethers to the corresponding propenyl ethers and have found some interesting results which we would like to report here.

The polymerization of propylene oxide is ordinarily carried out at elevated temperatures using basic catalysts and mono- or polyhydroxylic compounds as initiators. Price and St. Pierre,[3] however, found that the polymerization could be accomplished at room temperature with anhydrous KOH as the catalyst and with no added hydroxylic initiators. The products of the polymerization under the latter conditions comprised mainly compounds of the type

$$CH_2{=}CHCH_2O(C_3H_6O)_nH \qquad AO(PO)_nH$$

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(1) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965.

(2) E. C. Steiner, R. R. Pelletier, and R. O. Trucks, *J. Amer. Chem. Soc.*, **86**, 4678 (1964).

(3) L. E. St. Pierre and C. C. Price, *ibid.*, **78**, 2432 (1956).

and

$$cis\text{-}CH_3CH{=}CHO(C_3H_6O)_nH \qquad PO(PO)_nH$$

A detailed study of the polymerization in this laboratory revealed that the ratio of propenyl to allyl ethers remained almost constant throughout the reaction, a result which was shown to be caused by a marked dependence of the rate of rearrangement of the allyl ethers on the number of PO units in the chains.[2] It was also found that the polymerization conditions were such that the hydroxylic end groups were almost quantitatively in the form of potassium alkoxides. These results led us to study the rearrangement of the compounds $AO(PO)_n^-M^+$ where n = 1–7 in order to gain an understanding of the factors which cause the dependence of rate on chain length.

Experimental Section

Solvents. Tetrahydrofuran (THF) was distilled from potassium-naphthalene complex and stored under nitrogen at all times. The storage flask was equipped with a three-way Teflon stopcock, and the liquid was transferred *via* syringe through the stopcock while nitrogen was flowing through the side arm of the stopcock to prevent entrance of oxygen or moisture. The dimethyl ether of tetraethylene glycol (Ansul Ether 181) was fractionated before use and stored under nitrogen, bp 107° (1.5 torr).

Allyl Ethers of Propylene Oxide Oligomers, $AO(PO)_nH$. Allyl alcohol (212 g, 3.61 mol, <100 ppm of H_2O) was placed in a 2-l. iron bomb. After the bomb was flushed with nitrogen, small pieces of sodium (2.8 g, 0.12 g-atom) were added under nitrogen and allowed to dissolve. Propylene oxide (638 g, 11.0 mol) which had been dried to less than 1 ppm of H_2O by passing it over anhydrous potassium form of a sulfonic acid ion-exchange resin (Dowex 50W) was added portionwise to the bomb which was heated to about 110°. After reaction was complete the mixture was just neutralized with nonaqueous HCl, and the product was flash distilled. The distillate was stabilized to oxidation by addition of of a small amount of phenothiazine and fractionated through a 2 ft × 10 mm jacketed Vigreux column. Center cuts were taken for each adduct and were found to be essentially pure by gas–liquid partition chromatography. A second preparation was carried out similarly using 5 mol of propylene oxide per mole of allyl alcohol. The products were stabilized to autoxidation by excluding air during distillation and handling, adding a trace of phenothiazine to them, and storing them in dark bottles under nitrogen. Erratic rate data were obtained if these precautions were omitted. The apparent boiling points of the products are listed in Table I. These values when n = 3–7 are not true boiling points because the conditions were such that there was considerable back pressure between the thermocouple at the head of the column and the condenser. This was necessary in order to obtain practical distillation rates with these compounds having low vapor pressures.

Table I

$AO(PO)_nH$, n	Bp, °C (torr)
1	52–56 (10)
2	55–60 (0.1)
3	70 (0.01)
4	86 (0.005)
5	97–100 (0.005)
6	120 (0.004)
7	186 (0.7)

Anhydrous Metal Hydroxides. Reagent grade KOH (85%) was heated in a silver crucible over a flame until boiling ceased. The molten KOH was poured into a stainless steel pan and allowed to cool under nitrogen. It was pulverized in a Mikro Pulverizer (Pulverizing Machinery Division, Metal Disintegrating Co., Inc.) keeping contact with air at a minimum. The resultant powder was found on titration to contain 96% KOH and about 4% K_2CO_3. The latter was present in the starting material. CsOH was prepared in the same general way from an aqueous solution (The Dow Chemical Co.)

Alkali Metal Triphenylmethides. A slight modification of the method of Levine, Baumgarten, and Hauser[4] was used. Ammonia was distilled from a sodium solution into a reaction flask equipped with an equilibrated dropping funnel, magnetic stirrer, Dry Ice condenser, and a nitrogen blanket. A trace of ferric nitrate[5] was added and then the desired amount of Na or K was added in small pieces, allowing the blue color to disappear before the next addition. If all the metal was added at once, the reaction proceeded for a short time and then became extremely slow. Apparently, it is necessary to add traces of oxide or peroxide continuously to catalyze the reaction. Cesium metal was added as a liquid through the dropping funnel in the preparation of $CsNH_2$. When amide formation was complete a THF solution of triphenylmethane in slight excess was added slowly through the dropping funnel. The Dry Ice in the condenser was replaced with ice and the ammonia was allowed to distil off. Finally, the ice was removed and part of the THF was boiled off under enough vacuum to lower its boiling point to room temperature to ensure complete removal of ammonia. Saturated solutions of the methide salts contained approximately 0.35, 1.19, and 0.65 mmol/g of sodium, potassium and cesium triphenylmethides, respectively, as determined by titration with formanilide.[6] They typically contained about 0.4, 1.2, and 0.67 mmol/g of total base as titrated with aqueous acid to the phenolphthalein end point. Titration curves made with large samples of these solutions showed that the ammonia was completely removed by the procedure described.

Potassium Dodecylbenzenesulfonate. Dodecylbenzenesulfonic acid (97% assay, Pilot Chemical Co.) was dissolved in about two parts of water and neutralized with aqueous KOH. The water was evaporated overnight in a ventilated oven set at 130°, and then in a vacuum oven at 105° for 2 hr. About 138 g of the solids was dissolved in 1500 ml of THF, treated with activated charcoal (Darco), and filtered warm after addition of Filter-cel to facilitate filtration. The THF was removed under vacuum in a rotating evaporator, and the resultant solids were dried in a vacuum oven for 2.5 hr at 120°. To ensure removal of the last traces of water the solids were ground thoroughly and dried overnight at 110° *in vacuo*.

Kinetic Runs. a. Apparatus. Glass vessels were unsuitable for use in making kinetic determinations because the strongly basic solutions reacted with the glass and caused reaction rates to decrease to zero before reaction was complete. Monel vessels were therefore used. These consisted of approximately 1-in. i.d. cylindrical containers of 45-ml capacity capped with a lid to which was attached a three-way Teflon stopcock and which was sealed with a Viton O ring. The lid was designed so that metal-to-metal contact was made inside the O ring seal so that solvent would not be absorbed by the rubber. A nitrogen source was attached to the side opening of the stopcock so that materials could conveniently be added or withdrawn *via* hypodermic syringe under a stream of nitrogen, thereby preventing oxygen and moisture from entering the reaction vessel. A diagram of the vessels is shown in Figure 1.

b. Procedure Using Triphenylmethides. The desired amount of deoxygenated polyether alcohol was weighed from a syringe into a nitrogen-filled 25-ml volumetric flask containing a Teflon-covered magnet and topped with a three-way stopcock through which a slow stream of nitrogen was flowing. The flask was calibrated to contain an amount of THF at 0° equivalent to 30 ml at 30°. About 10 ml of anhydrous, oxygen-free THF was added, and the flask was placed in an ice bath mounted on a magnetic stirrer. A solution of metal triphenylmethide in THF was added slowly with stirring from a syringe and under a stream of nitrogen until the red color of the methide was just visible in the flask, or until a predetermined amount of the reagent had been added. The solution was brought to volume at 0° with more THF. It was then transferred *via* syringe to a nitrogen-filled Monel reaction vessel which was already mounted in a water bath maintained at 30°. The efficient heat transfer through Monel allowed the solution to come to temperature within 10 min. Temperature equilibrium could be hastened by stirring the contents with a magnetic stirrer if desired. As soon as transfer was complete, a 1-ml sample of the

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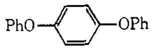
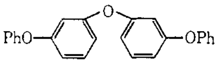
[4] R. Levine, E. Baumgarten, and C. R. Hauser, *J. Amer. Chem. Soc.*, **66**, 1230 (1944).

[5] K. W. Greenlee and A. L. Henne, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p 128.

[6] E. C. Steiner and J. M. Gilbert, *J. Amer. Chem. Soc.*, **85**, 3054 (1963).

Table II. Glpc Conditions for Analysis of Mixtures of $CH_2{=}CHCH_2(OC_3H_6)_nOH$ and $H(OC_3H_6)_nOH$

	Column			
n	Packing	Length, ft	Internal standard	Temp, °C
1	410 gum silicone rubber	10	$PhOCH_3$	125
2	410 gum silicone rubber	20		190
3	410 gum silicone rubber	20		215
4	410 gum silicone rubber	20		265
5	410 gum silicone rubber	10		275
6	410 gum silicone rubber	10		300

solution was removed with a syringe and added to a 1-dram vial containing either chlorohydrin or aqueous HCl, depending upon the analytical procedure to be used. Subsequently, more samples were withdrawn at timed intervals and analyzed.

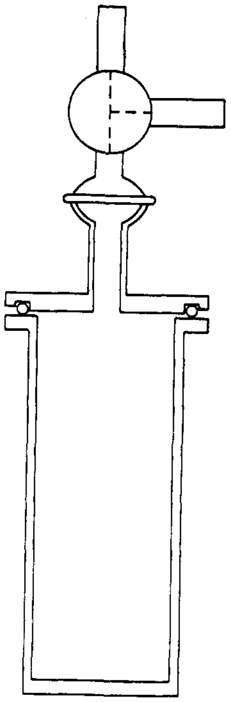


Figure 1. Reaction vessel for following reaction kinetics in strongly basic tetrahydrofuran solutions under nitrogen.

c. Procedure Using Metal Hydroxides. The desired amount of polyether alcohol was weighed from a syringe into a 50-ml volumetric flask which was sealed to a three-way stopcock and which was filled with nitrogen. The flask was placed in a 30° water bath, and THF was added to the mark at that temperature. The solution was then cooled in an ice bath. A Teflon-covered magnet and powdered anhydrous metal hydroxide (3 mol/mol of alcohol) were placed in a Monel reaction vessel under a nitrogen atmosphere. The vessel was capped and placed in an ice bath mounted on a magnetic stirrer. The cold alcohol solution was then transferred from the volumetric flask to the Monel vessel *via* syringe while nitrogen was flowing through the stopcocks to prevent entrance of oxygen and moisture. The mixture was stirred for 30 min at 0° to allow the alcohol to be converted to its alkoxide and then the vessel was transferred to a 30° water bath mounted above a magnetic stirrer. The solids were allowed to settle for a few minutes and a sample of the supernatant solution was withdrawn and added to aqueous HCl for analysis. The stirrer was started and allowed to run until a few minutes before the next sample was to be withdrawn.

d. Analytical Procedures. The most satisfactory method of following the rates of rearrangement of allyl to propenyl ethers was found to be as follows. A 1-ml sample of the reaction solution was withdrawn from the Monel vessel with a syringe and added to a 2.5M excess of 5 N aqueous HCl. After thorough mixing the sample was allowed to stand for 1 hr and anhydrous sodium carbonate was added to neutralize the acid and to absorb most of the water. The supernatant solution was analyzed by gas-liquid partition chromatography. The conditions for the glpc analyses are listed in Table II for the various reaction mixtures. The acid treatment was such that the propenyl ethers were quantitatively converted to the corresponding glycols, but the allyl ethers were unaffected. The glycol and allyl ether pairs were generally separable by glpc but the higher molecular weight compounds did not give completely resolved peaks. Nevertheless, the concentrations of allyl ether could be obtained very reproducibly using two methods of interpreting the glpc curves. If both the allyl ether and the glycol gave sharp peaks and were cleanly separable, the two peak heights were measured and compared with those obtained with a series of standard mixtures. When the glycol did not give a good peak, as was the case with propylene glycol, then an internal standard (anisole) was added to the reaction mixture and the peak height of the allyl ether was compared with that of the standard. When the ether and glycol were not cleanly separable, then suitable internal standards were again used and the concentrations of allyl ether determined by comparing peak heights with those obtained with standard mixtures of the three components in THF solution. The use of peak areas was found to be more time consuming and gave poorer results with these mixtures.

Infrared analysis was used initially in the study. It was found to be useful for determining, qualitatively, very small degrees of reaction, and it gave fairly good results over the first half of the reaction. However, since the C=C stretching frequency of the propenyl ether is very strong and quite close to that of the allyl ether, the latter could not be measured accurately. Consequently the allyl ether concentration had to be calculated by difference and the reactions had to be allowed to go to completion to obtain the infinite time absorbance of each propenyl ether. This process was both time consuming and imprecise and was abandoned in favor of the glpc method except in the cases described later. The other vibrational modes of the two groups could not be used since they were obscured by the polyether chains.

Results and Discussion

The original intent of the present investigation was to find an explanation for the relative amounts of allyl and propenyl ethers in the polymer obtained from the reaction of propylene oxide with anhydrous KOH. Since the polymerization conditions were such that alcohols were converted almost quantitatively to alkoxides, it was desirable to study the bond migration reaction under essentially alcohol-free conditions. This presented an experimental problem because the alcohol which was to be converted to alkoxide also contained the allyl ether group. This meant that the alkoxide had to be prepared quickly and quantitatively under mild conditions. Most methods of preparing alkoxides do not meet these requirements. For instance, the reaction of alcohols with alkali metals in the presence of inert solvents requires elevated temperatures and extended reaction periods to convert the last bit of alcohol to alkoxide. These conditions would lead to extensive rearrangement of the allyl ether and to some cleavage of the polyether chains. As an alternate method, titration of the alcohols with triphenylmethide salts was tried. This method worked very well with triphenylmethylsodium. The acid–base reaction is essentially instantaneous, the triphenylmethide reacts quantitatively with the alcohols to give alkoxide, and excess base can be avoided because the dark red color of the methide ion is easily seen when only a trace of it is present in solution. Price and Whiting reported that alcohols can also be titrated quantitatively with dimsylsodium (CH_3SOCH_2Na) in dimethyl sulfoxide (DMSO) solution using triphenylmethane as an indicator.[7] With the potassium and cesium methides, however, the method was unsatisfactory. As was reported earlier[6] stoichiometric end points cannot be obtained in either THF or DMSO solutions because of the unusual behavior of alcohols as weak acids. That is, the red color of methide ion persists before the calculated amount has been added. In the case of the potassium salt a visible amount of methide is present when about 85% of the calculated amount has been added; with the cesium salt, when about 50% has been added. A more detailed study of this phenomenon has been reported elsewhere.[8] In addition to giving nonstoichiometric end points, the use of triphenylmethylpotassium produced anomalous rate data which will be discussed later.

The most satisfactory reagents for converting alcohols to essentially alcohol-free potassium and cesium alkoxides were found to be the anhydrous metal hydroxides. It had been determined during the study of propylene oxide polymerization that excess KOH converts alcohols more than 90% to their alkoxides.[2] During the present work it was determined that 99–100% conversions are obtained with CsOH. However, the use of excess hydroxide presented the possibility that the inorganic base would also catalyze the bond migrations, thereby giving spurious rate data. The possibility was eliminated when it was found that KOH under the reaction conditions causes negligible rearrangement of a nonhydroxylic allyl ether, that nearly the same values of rate constants are obtained under comparable conditions using the methide and the KOH method, and that the solubility of the hydroxides is very low in THF solutions. Sodium hydroxide cannot be used to convert alcohols to sodium alkoxides because the acid–base reaction does not go to completion.[2]

In these essentially alcohol-free alkoxide solutions, it has been found that the sodium derivatives of the allyl ethers do not rearrange over extended periods at 30°. In some cases the reaction mixtures were allowed to stand for 2 weeks and showed no propenyl groups on analysis by infrared spectroscopy. This method of analysis is very sensitive to propenyl ethers because of their intense absorption peaks at 5.98 μ. The potassium derivatives rearrange readily, the rate depending upon the length of the polyether chain separating the allyl group from the alkoxide group. The cesium derivatives rearrange even faster and the rates also depend upon the polyether chain length. The experimental rates of bond migration for all compounds except $AO(PO)_2^-$ are first order in allyl ether group to better than 90% conversion. With $AO(PO)_2^-$ for some unknown reason, the rate decreases as reaction progresses. The first-order rate constants are shown in Table III and their average values, in Figure 2.

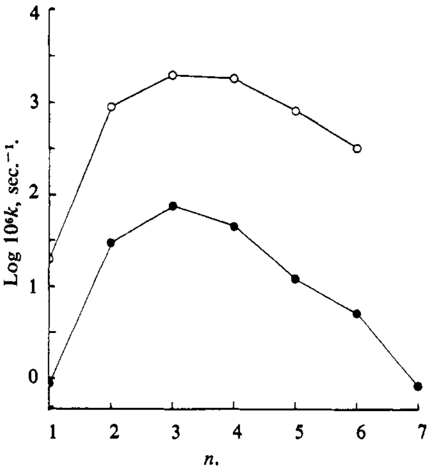


Figure 2. Average first-order rates of rearrangement of 0.28 M $CH_2{=}CHCH_2(OC_3H_6)_nO^-M^+$ in THF at 30°: ○, $M^+ = Cs^+$; ●, $M^+ = K^+$.

Table III. First-Order Rate Constants for the Rearrangement of $CH_2{=}CHCH_2(OCH_2CHCH_3)_nO^-M^+$ 0.28 M in THF, 30°

	10^6k_n, sec^{-1}		
n	$M^+ = Na^+$	$N^+ = K^+$	$M^+ = Cs^+$
1	0	0.78, 1.02	19.7
2	0	30.2, 30.2	880
3	0	75.1, 76.0	1930
4	0	45.5, 45.7	1780
5	0	12.3	766, 864
6	0	5.11	320
7	0	0.83	

The dependence of rate upon cation type is not unexpected. Ample data in the literature are in agreement with this. For instance, Snyder[9] found that the rate of reaction of alkali metal methoxides with propylene oxide increases drastically as the size of the cation increases. Lithium methoxide does not react significantly over a period of 2 years at room temperature whereas sodium methoxide reacts slowly and cesium methoxide reacts completely within a few hours. Or in another case, Cram, Kingsbury, and Rickborn[10] found that t-BuOK is 100 times as effective as t-BuONa as a catalyst for the racemization of 1-phenylethyl methyl ether. This phenomenon is due probably to the strength of the bond between the metal and the oxygen atoms. That there is a significant degree of covalent character to the bonds in the absence of ionizing solvents was suggested by Bains as a result of his measurements on the ease of sublimation of the metal alkoxides.[11] He reported a greater degree of covalency as the size of the cation diminished.

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(7) G. G. Price and M. C. Whiting, *Chem. Ind.* (London), 775 (1963).

(8) E. C. Steiner, J. D. Starkey, J. M. Tralmer, and R O. Trucks, 153rd National Meeting of the American Chemical Society, April 1967, Miami Beach, Fla., Abstracts, Q-33.

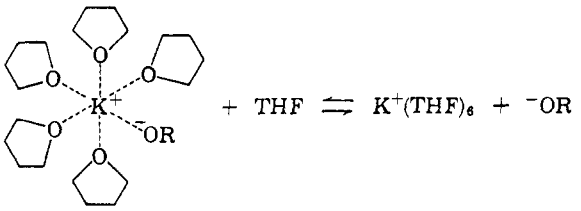
(9) W. H. Snyder, Ph.D. Thesis, University of Pennsylvania, 1961.

(10) D. J. Cram, C. A. Kingsbury, and B. Rickborn, *J. Amer. Chem. Soc.*, **83**, 3688 (1961).

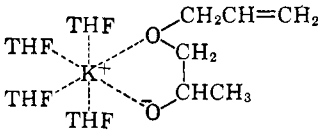
(11) M. S. Bains, *Can. J. Chem.*, **42**, 945 (1964).

The dependence of rate on chain length with a maximum rate for AO(PO)$_3^-$ is not suggested by reports in the literature. Most studies of this type of alkoxide have shown very little dependence of reactivity on chain length. For example, in the reaction of an alkoxide with ethylene oxide it has been found that the molecular weight distribution of the product, R(OC$_2$H$_4$)$_n$OH, is very close to that calculated on the assumption that the rate of attack of R(OC$_2$H$_4$)$_n$O$^-$ on ethylene oxide is essentially independent of n for $n \geqslant 1$.[12,13] Most of these studies, however, have been done on systems containing small concentrations of alkoxide in hydroxylic media where the alkoxide is probably largely dissociated into its ions. Under these conditions there is no apparent reason why the reactivity should depend strongly upon chain length. Other studies on the reactivity of alkoxides as a function of solvent composition have shown large effects, the most interesting in connection with the present results being the work of Ugelstad and his coworkers.[14] They found that the rate of bond migration in 4-phenyl-1-butene catalyzed by alcohol-free *t*-BuOK in the polyethers, CH$_3$(OC$_2$H$_4$)$_n$-OCH$_3$, increases markedly as the number, n, of ethylene oxide in units in the solvent molecule increases up to 6. They attributed this effect to the greater degree of ionization of *t*-BuOK in the higher polyethers caused by chelation of the K$^+$ ion. This appears to be a satisfactory explanation since it is known that K$^+$ forms both tetra- and hexacoordinate chelates.[15–17] A maximum rate, however, was not observed and would not be expected if the explanation is correct. In the compounds of the present study, a combination of factors makes the rate maximum reasonable and the results lend strong evidence for the type of chelate proposed by Ugelstad and Rokstad.[14]

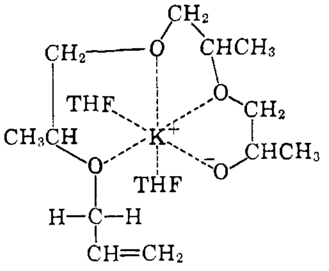
Very little work has been done on determining the state of aggregation of alkoxides in solution, but Bains[11] reports that potassium *t*-butoxide is a tetramer in benzene and a hexamer in cyclohexane. THF is a better coordinating solvent than the hydrocarbons and may cause lower states of aggregation but there is little doubt that the ions are at least paired. Assuming simple ion-pair formation in THF, one might draw the following structures for the solvated ion pair in equilibrium with dissociated ions, or more likely with the solvent-separated ion pair.



Clearly, in this equilibrium a multidentate solvent will favor dissociation because of the entropy effects involved in chelate formation.[18] However, if the alkoxide is attached to the polyether chain, ion-pair formation will be greatly enhanced and structures of the following type should predominate.

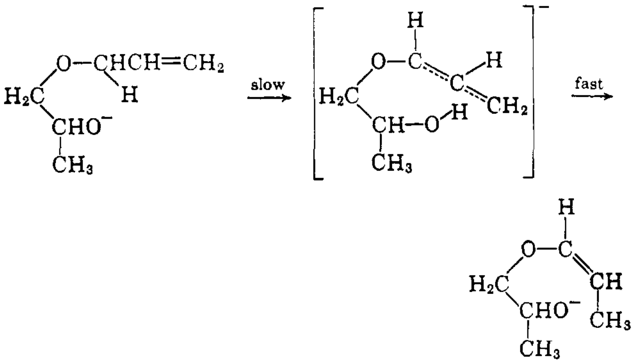


AO(PO)$_1^-$K$^+$



AO(PO)$_3^-$K$^+$

This would result in suppression of reactions which require free alkoxide as a catalyst but at the same time in the AO(PO)$_n$H alkoxides it would lead to the possibility of highly favored intramolecular catalysis. In turn intramolecular catalysis provides a good explanation of the rate data given in Table III. This may be seen in the above structures. In AO(PO)$_1^-$ the allyl group is actually held away from the alkoxide group and makes this compound rearrange very slowly. If free ions were the reactive entities one might expect this compound to rearrange much the fastest because of the favored six-membered cyclic transition state available for the proton abstraction reaction.



In AO(PO)$_{2-5}^-$ many of the possible chelate structures are such that the allyl group would be held in a favorable position for intramolecular proton abstraction. This is shown above for AO(PO)$_3^-$ where the bridged proton transition state proposed by Cram, *et al.*,[1] would be easily attained. The preferred way for the chain to coil around potassium is not known, but on a purely statistical basis there are higher proportions of favorable configurations for AO(PO)$_3^-$ and AO(PO)$_4^-$ than for the others. The fact that AO(PO)$_3^-$ rearranges faster than AO(PO)$_4^-$ when potassium is the cation but at about the same rate when cesium is the cation could be due to reduced crowding around the larger cesium ion.

Although the hypothesis rationalizes the data well and the dependence of rate upon chain length is difficult to explain without it, attempts to verify the hypothesis and to gain a satisfactory understanding of the reaction indicated that the reaction is more complex than the hypothesis implies. One of the requirements of the hypothesis which has been tested is the dependence of

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(12) B. Weilbull and B. Nycander, *Acta Chem. Scand.*, **8**, 847 (1954).

(13) G. J. Stockburger and J. D. Braudner, *J. Amer. Oil Chem. Soc.*, **40**, 590 (1963).

(14) J. Ugelstad and O. A. Rokstad, *Acta Chem. Scand.*, **18**, 474 (1964); J. Ugelstad, A. Berge, and H. Listou, *ibid.*, **19**, 208 (1965); A. Berge and J. Ugelstad, *ibid.*, **19**, 742 (1965).

(15) N. V. Sidgwick and S. G. P. Plant, *J. Chem. Soc.*, 209 (1925).

(16) N. V. Sidgwick and F. M. Brewer, *ibid.*, 2379 (1925).

(17) F. M. Brewer, *ibid.*, 361 (1931).

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bond migration rate upon the concentration of allyl ether alkoxide. Three situations could obtain: the reaction could be predominately intermolecular; it could be predominately intramolecular; or it could proceed by both routes. The three situations would lead to the kinetic expressions, $-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k_2[\mathrm{A}][\mathrm{A}_0]$, $-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k_1[\mathrm{A}]$, and $-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = (k_1[\mathrm{A}_0] + k_2)[\mathrm{A}]$, respectively, where A represents the allyl ether group and $[\mathrm{A}_0]$, the initial concentration of allyl ether alkoxide. In each case the rate within a kinetic run should be pseudo first order since the change from allyl to propenyl group at the end of the alkoxide molecule will have but little effect on the catalytic activity of the alkoxide. In the first case the rate should depend directly upon the initial concentration of the reactant; in the second, it should be independent of it. The dependence of rate upon concentration was studied with two of the compounds as shown in Table IV. It was found that the migration rates in $\mathrm{AO(PO)_1^-}$ are essentially independent of concentration (data were imprecise) and those in $\mathrm{AO(PO)_3^-}$, slightly dependent on concentration. The latter increased only by a factor of about 3 with a 36-fold increase in concentration with $\mathrm{K^+}$ as cation, and by about 2 with a tenfold increase in concentration with $\mathrm{Cs^+}$ as cation. These data best fit an intramolecular mechanism and lend support to the chelate hypothesis.

Table IV

	Initial concn, *M*	10^6k, sec^{-1} KOH	10^6k, sec^{-1} CsOH
$\mathrm{AO(PO)_1H}$	0.031	0.61, 0.85	
	0.29	0.78, 1.02	
	0.98	0.82	
$\mathrm{AO(PO)_3H}$	0.028	46.0, 44.2	925, 852
	0.28	75.1, 76.0	1930
	1.00	106.0, 102.0	

That the rate is not actually constant is disturbing. The change could be due to a number of factors such as disruption of the chelate, a certain degree of intermolecular reaction, salt effects, and so on. Several of these factors have been studied. If the chelate has low stability so that some dissociation occurs at lower concentrations, the reaction rate should diminish with dilution. The results of Ugelstad and Rokstad[14] suggest that under these conditions a polydentate solvent would readily displace the polyether chain of the alkoxide, thereby disrupting the reactive centers. This was tested by studying the rate of bond migration in 0.28 *M* $\mathrm{AO(PO)_3^-}$ in the dimethyl ether of tetraethylene glycol. The resultant rate constants were 49.0 and 53.6×10^{-6} sec^{-1} as compared to an average of 75.6×10^{-6} sec^{-1} in THF. The difference, though in the right direction, is too small to constitute good evidence for this effect. On the other hand, the lack of rate enhancement by the new solvent is good evidence that the $\mathrm{K^+}$ is already chelated and that Ugelstad and Rokstad's explanation is correct.

The possibility of intermolecular reaction was tested by adding a second alcohol of similar structure but without the terminal allyl group. The results are shown in Table V where it is seen that the second alkoxide does increase the rate constant of rearrangement, but not as much as a corresponding concentration increase in the rearranging alkoxide. These data are not compatible with either a simple intramolecular reaction or a simple bimolecular reaction.

Table V

Initial concn, *M* $\mathrm{AO(PO)_3^-}$	Initial concn, *M* $\mathrm{MeO(PO)_4^-}$	Initial concn, *M* Total	10^6k, sec^{-1}
0.028		0.028	45.1
0.028	0.251	0.281	57.0
0.28		0.28	75.6
0.28	0.73	1.01	87.0
1.00		1.00	104.0

Finally, the effect of added salts was studied. Most inorganic salts are not sufficiently soluble in THF to be useful for this purpose. Therefore, potassium dodecylbenzenesulfonate (DBSK) and fluorenylpotassium (FK) were used. Neither salt was expected to catalyze the rearrangement since the sulfonate is neutral and the fluorenyl ion is many times less basic than alcohol-free alkoxide ion.[8] The results are shown in Table VI. The marked decreases in reaction rates were completely unexpected and a satisfactory explanation for them has not been found. It is difficult to understand why these salts inhibit the reaction strongly whereas added alkoxide has very little effect. It might be that the alkoxides form simple ion pairs because of chelate formation, but that the other salts form ion aggregates including the alkoxides and disrupt their chelate structures. Brown and his coworkers[19] have recently reported such mixed aggregates of lithium alkyls and lithium alkoxides. On the other hand it is possible that the alkoxides form aggregates which enhance the rates for certain lengths and that these aggregates are disrupted by further aggregation with the organometallic compound. More work would have to be done to clarify this problem.

Table VI

Initial concn, *M* $\mathrm{AO(PO)_3K}$	Initial concn, *M* DBSK	Initial concn, *M* FK	Initial concn, *M* Total	10^6k, sec^{-1}
0.028			0.028	45.1
0.028	0.29		0.318	2.4
0.028		0.29	0.318	1.0
0.28			0.28	75.6
0.28	0.29		0.57	19.2
0.28		0.28	0.56	3.1

Another unexplained phenomenon was found during the attempts to use triphenylmethylpotassium to convert the alcohols to alkoxides. It was observed that the bond migration rate in $\mathrm{AO(PO)_3^-}$ was very dependent upon the amount of methide which was added. This is shown in Figure 3 where it may be seen that the rate increases by a factor of about 15 as the amount of methide increases from about 90% to 101% of the stoichiometric amount based on alcohol. Each of these reactions was cleanly first order (see Figure 4). Since there is an increasing amount of methide ion remaining in solution as the total amount added approaches 100%, there was the possibility of catalysis

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(19) L. M. Seitz and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 2174 (1966); T. L. Brown, J. A. Ladd, and G. N. Newman, *J. Organometal. Chem.* (Amsterdam), **3**, 1 (1965).

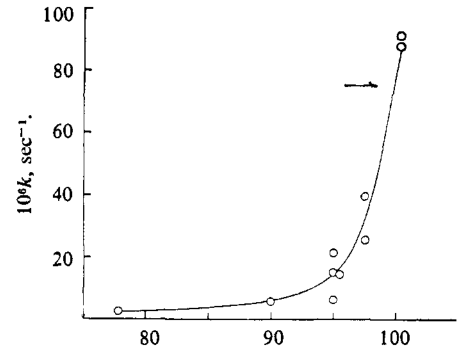

Figure 3. Dependence of first-order rate constant for rearrangement of $CH_2{=}CHCH_2(OC_3H_6)_3OH$ at 30° on amount of $Ph_3C^-K^+$ added. Arrow indicates rate obtained with KOH method.

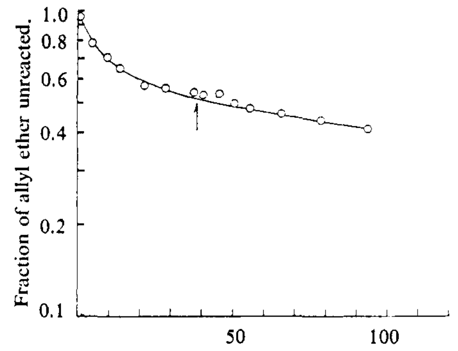

Figure 5. Rearrangement of $CH_2{=}CHCH_2(OC_3H_6)_3OH$ at 0° on addition of 110% $Ph_3C^-K^+$. Arrow indicates point of addition of 5% more $Ph_3C^-K^+$.

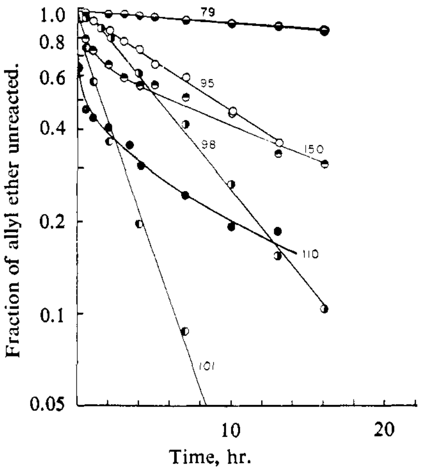

Figure 4. Dependence of rearrangement rate of $CH_2{=}CHCH_2(OC_3H_6)_3OH$ at 30° on amount of $Ph_3C^-K^+$ added. Figures indicate percentage of Ph_3C^- relative to alcohol.

by the methide itself. This possibility was examined by adding an excess of methide (10%). The unexpected result (Figure 4) was that the reaction went very fast at the beginning, almost 60% within 1 hr, but then slowed to a rate which was lower than when no excess methide was added. When a large excess (50%) of methide was added, even the initial reaction was not very high, giving about 30% propenyl ether in an hour. The initial part of the reaction was followed more closely at 0° using 10% excess methide and was found to proceed at a smoothly decreasing rate. When the reaction was about 50% complete, an additional 5% of methide was added, but this caused no significant effect on the rate (see Figure 5). The course of the reaction did not appear to be altered in any way other than kinetically since there were no irregularities in the gas–liquid partition chromatograms used for following the reaction, *i.e.*, no new peaks appeared nor were the shapes of the expected peaks altered. It seems probable that these effects and the inhibition observed with fluorenylpotassium and potassium dodecylbenzenesulfonate are closely related. It may be that with the methides there is a slow regrouping of the ions which tends to disrupt the chelate, thereby reducing the migration rate to the same order of magnitude as is obtained with $AO(PO)_1^-$ or $AO(PO)_7^-$ where the chelate structure does not enhance the reaction rate.

Several things about these rearrangements are clear. They undoubtedly involve chelation of the polyether chains about the cations. At the same time the anomalies in the kinetics and the effects of added alkoxide and other salts strongly suggest that the reactions involve species other than monomeric chelated ion pairs. It is felt that there are rather specific types of ion aggregates present in solution and that these aggregates and their interactions with added species account for the various experimental data obtained. It is probable that the proton transfer leading to the bond migration is quantitatively intramolecular, since external proton sources are lacking.

The combination of the varying chelating ability of the polyether chain, the intramolecularity of the reaction, the convenience of the bond migration reaction as a probe, and the strong effects of cation type and added salts make this system potentially very useful for studying the nature of alkoxides in aprotic media.