© 1998 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 71, 915—926 (1998)

Dimensiosolvatic Effects. IV.
Topomerization in Alkyl α-Chlorobenzyl Ethers and Insights into Mechanisms of Their Thermolyses[1)]

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(Received November 7, 1997)

Rates of topomerization in α-chlorobenzyl ethyl ether and its *p*-methyl as well as *p*-methoxy derivatives were determined in various solvents by the dynamic NMR method. The topomerization process was deduced to be ionic because the rates are enhanced in polar solvents as well as by electron-donating substituents. Concentration dependence study of the topomerization in carbon tetrachloride revealed that the observed process is unimolecular; the rates are not affected by concentration of the substrate if the concentration is lower than 0.2 $\mathrm{mol\,L^{-1}}$. The rates of topomerization are smaller for solutions in bulky solvents than in small solvents, the effects being clear for compounds with electron-donating substituents. The key feature of the kinetic parameters is that the entropy of activation is large and negative for all the solvents examined. The reaction mechanisms are discussed on the basis of these data. The effects of the molecular size of the solvent, dimensiosolvatic effects, are attributed to the effectiveness of the solvation in the formation of ion pairs. The results show that thermolyses of alkyl α-chlorobenzyl ethers are much slower reactions than the ionization. The nature of the reaction is discussed.

The solvent molecular size exhibits a remarkable effect on the rates of dissociation of the N–H bond in ammonium salts derived from tertiary amines.[2)] The key feature of the kinetic parameters for the process is large and positive entropy of activation. In addition, the rates of dissociation are greatly enhanced in solvents of bulky molecules (referred to bulky solvents hereafter) with respect to solvents of small molecules (small solvents). It is postulated that the solvation shell is formed by a smaller number of bulky molecules and thus the shell can be looser than in the cases of small molecules, rendering the solvation energy small for bulky solvents as well as affecting the entropy of activation.

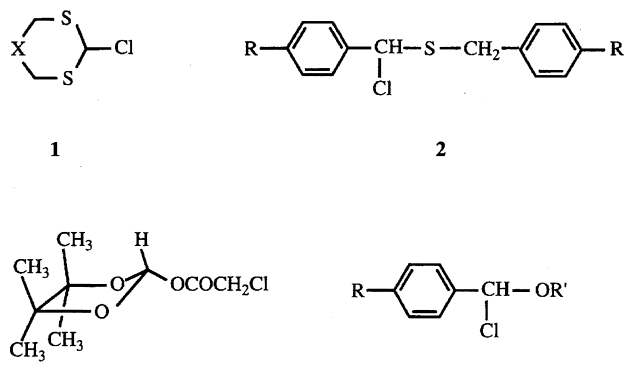
We have also reported on the effects of solvent molecular size on topomerization of organolithium compounds.[3)] The key feature of the results was that the bulky solvents tend to retard the reactions. It was postulated that the solvent intervention to solvent separated ion pairs (SSIP) is the rate-limiting step, by taking various observations including UV-vis spectra, which showed the presence of both contact ion pairs (CIP) and the SSIP, into consideration. The intervention of a bulky solvent molecule into the ion pair should be slow relative to that of a small solvent molecule because the bulkiness separates the positive and negative ends of the ion pair more by its intervention.

These are the cases where the initial states are composed of ionic species. It is expected that, if the initial state is a covalent species and the process is the ionizing one, then the effects of the bulky molecules should appear in a different manner. Though we have reported that solvent intervention into CIP, which is produced by ionization of an organic halide, is also affected by the molecular size,[4)] an example of the dimensiosolvatic effects on the ionization of organic halides has been lacking.

We have had three experiences of ionic dissociation studied by the dynamic NMR method. The first is dissociation of 2-chloro-1,3-dithiane or 2-chloro-1,3,5-trithiane (**1**),[5)] in which a developing carbocation is stabilized by two sulfur atoms. The second is dissociation of α-chlorodibenzyl sulfide and its *p*-substituted derivatives (**2**), a carbocation derived from which is stabilized by the presence of a phenyl group and a sulfur atom.[6)] The third is a carboxylate ester (**3**), a carbocation derived from which is stabilized by two neighboring oxygen atoms (Scheme 1).[7)] C.-Y. Kim, who visited our laboratory in Tokyo to carry out his work on dissociation of α-chlorobenzyl ethyl ether (**4b**), has published another paper on dissociation of the compound in organic solvents.[8)] In this case the produced carbocation is stabilized by the presence of an oxygen atom and a benzene ring.

We decided to reexamine the case of α-chlorobenzyl ethyl ether in the light of a new aspect of solvent effects, dimensiosolvatic effects, because this compound is more easily prepared than other cases: Also, the dissociation of compound **4b** must be an example of $\mathrm{S_N1}$ type reactions, which have attracted interests of many investigators, though no product is formed in this process but an enantiomeric compound turns back to its enantiomer.

Our choice was to use very bulky molecules to clearly demonstrate the bulkiness effects of solvent molecules. Thus molecules that carry *t*-butyl group(s) were selected. Molecules with *t*-butyl group(s) were either commercially



4a: R = H, R' = CH_3
4b: R = H, R' = C_2H_5
4c: R = H, R' = $CH(CH_3)_2$
4d: R = CH_3, R' = C_2H_5
4e: R = CH_3O, R' = C_2H_5

Scheme 1.

available or could easily be made according to the literature except di-*t*-butyl ether, of which the preparation posed some difficulties. Although there are several papers that report syntheses of this compound,[9—11] our choice is the classical method,[12] the reaction of silver carbonate with *t*-butyl chloride, as other authors explain.[13]

Our starting hypothesis was that the solvents of bulky molecules should retard the ionization because stabilization of the ionic transition state due to solvation is less effective. This paper presents results of such investigation and discusses the effects of the bulkiness of solvent molecules on solvation. Thermolyses of the compounds will be discussed also in conjunction with the ionization.

Results and Discussion

General Considerations. The method of measuring the rates is the dynamic NMR technique that utilizes the lineshape analysis of signals due to diastereotopic protons. The methylene protons of the ethyl group in compound **4b** are diastereotopic due to the presence of a chiral center in the molecule. The protons exchange their sites on enantiomerization at the chiral center, causing the lineshape change in a temperature range suitable for the dynamic NMR method.

Our measurement was carried out on a Varian EM-360L NMR spectrometer, which is a CW machine, at the outset, because the measurement was easily carried out for the solvent molecules which carry undeuterated methyl groups. Because of the D-lock technique for the modern FT-NMR spectrometers, we must use a deuterated compound for the measurement on an FT-NMR machine. A deuterated compound, which is sealed in a capillary for the D-lock in order to avoid contamination of the solvent, must be used. In the later work, the conditions of the 60 MHz machine forced us to use a 400 MHz machine and this technique of inserting a capillary posed various difficulties. In addition, the measurement at a high field necessarily enlarges the chemical shift differences of the diastereotopic protons and the operation at high temperatures becomes necessary. This is again inconvenient in the present work because the compounds tended to decompose at high temperatures. Our choice is thus to use a CW machine if it is available. Therefore, the results reported in this paper contain both those obtained at 60 MHz and those at 400 MHz. The agreement of the data obtained by the two machines were checked for two solvents (THF-d_8 and *t*-butyl methyl-d_3 ketone) and was found to be satisfactory.

Repeating Kim's experiments,[8] we found that his results were not reproducible under our conditions. We suspected that Kim's works were carried out with concentrations much higher than the standard we used, though the concentration had not been reported. We decided to see the concentration effects of the solute with use of carbon tetrachloride. The results are given in Table 1.

The results clearly show that, if the concentration is higher than 0.5 mol L^{-1}, the rates of topomerization are much larger than those obtained for solutions of lower concentrations. From the results shown in Table 1, we judge that, if the concentration is 0.2 mol L^{-1}, we obtain the intrinsic topomerization rates. This is in conformity with the results we had obtained earlier with another compound (**2**: R = H).[14] At the same time, the results show that Kim's data were obtained for solutions of much higher concentrations than 1.0 mol L^{-1}.

From the data in Table 1, we clearly see that we observe unimolecular topomerization, because the rates are not affected by concentration if the concentration is 0.2 mol L^{-1} or lower, although the concentration itself is two orders of magnitude higher than the case of classical kinetics. This must be the result of the amount of the solute ionizing being of negligible amount, as evidenced by the fact that we observe only covalent species by ^{1}H NMR spectra, and of negligible effects of the solute that are given to the solvent. If a solute is dissolved in a solvent in high concentration, it should affect the polarity of the solvent, especially when the solvent is nonpolar and the solute is highly polar. Thus the concentration of 0.2 mol L^{-1} is used throughout this work

Table 1. Concentration Dependence of Ionic Dissociation of α-Chlorobenzyl Ethyl Ether in Carbon Tetrachloride (60 MHz Data)[a]

Concn/mol L^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{290}$/kcal mol^{-1}	k_{290}/s^{-1}
2.0	5.8±0.5	−33.3±1.6	15.5	12
1.0	8.0±0.3	−29.0±0.9	16.4	2.7
0.50	8.1±0.4	−29.7±2.0	16.7	1.6
0.20	8.2±1.4	−30.0±4.1	16.9	1.1
0.10	8.4±0.5	−29.2±1.4	16.9	1.2

a) 1 cal = 4.184 J.

unless otherwise mentioned.

The next problem we must tackle is the nature of the reaction. It may be argued that the reaction can be of radical type. To establish the reaction mechanisms, we carried out the measurements of rates of dissociation in various solvents of different polarities. The results, compiled in Table 2, clearly show that the rates of dissociation are enhanced in polar solvents, whose polarities are shown by $E_T(30)$ values.[15] The reaction must be ionic in nature. This conclusion agrees with that derived by the substituent effects described later in this paper.

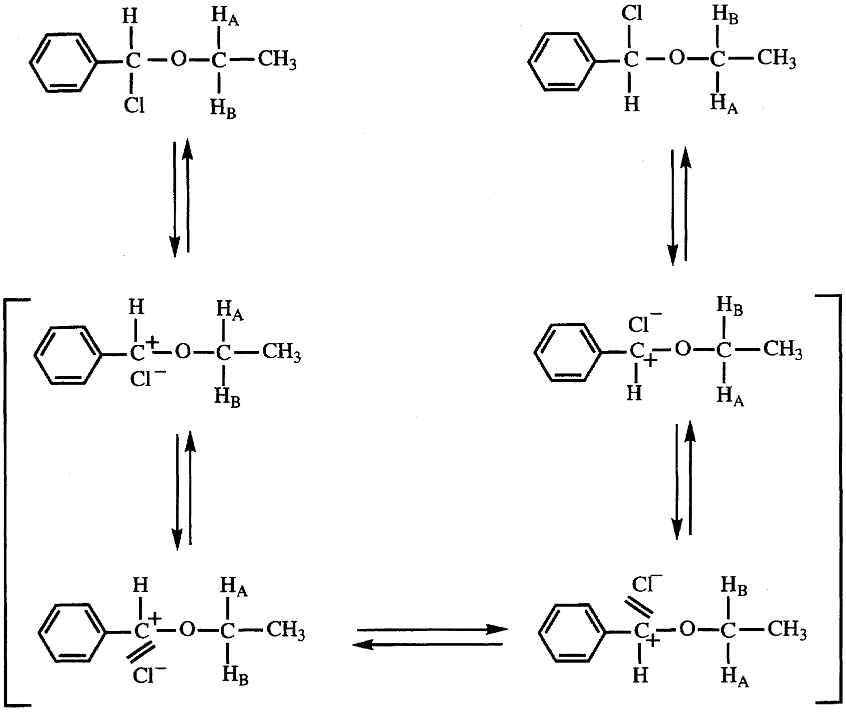
Having established that we observe a unimolecular ionic reaction, though we do not obtain any products except an enantiomer which we neglect, we may write the reaction mechanisms as shown in Scheme 2. Here we assume the followings. 1) The S_N1 mechanism proposed by Winstein et al.[16] is valid. 2) Enantiomerization will not occur at the stage of the CIP, because "contact" implies that positive and negative ion pairs behave as a pair and tumbling of the ion pair takes place without affecting the contact of the positive and the negative ions. 3) Then enantiomerization will occur at the stage of solvent-intervened ion pairs (SSIP), either solvent-shared[17] or solvent separated. This assumption is also made when ^{18}O scrambling and racemization rates were measured on a single, optically active, ^{18}O-labeled ester.[18] Thus we are observing an S_N1 process that does not proceed to the formation of substituted products.

In principle, there are three steps involved in the topomerization, formation of CIP, formation of SSIP, and independent tumbling of the ionic species (Scheme 2). If we take into account the fact that solvent intervention can be slow as was discussed in a preceding paper,[3] we must consider the second solvent-intervention into SSIP: There are four steps to be considered then. Of these, the independent tumbling step may be ruled out from the rate-limiting step, because this is usually very fast relative to the ionization of a covalent bond. This time we do not observe SSIP, differing from the case of the organolithium compounds. Therefore the second solvent-intervention step may be neglected as rate-limiting. Then the whole process is the topomerization with a pre-equilibrium, in which the formation of CIP is normally very slow, the collapse of the CIP to form the original state is fast, and solvent intervention should also be fast relative to the ionization step.

Table 2. Solvent Polarity Effects on the Kinetic Parameters of Topomerization of α-Chlorobenzyl Ethyl Ether (60 MHz Data)

Solvent	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{290}$/kcal mol^{-1}	k_{290}/s^{-1}	$E_T(30)$
CCl_4	8.2 ± 0.8	-29.9 ± 2.3	16.9	1.1	32.4
C_7D_8[a]	6.4 ± 0.4	-32.4 ± 1.3	15.8	7.2	33.9
ClC_6H_5	1.7 ± 0.3	-44.8 ± 0.8	14.8	46	36.8
$CDCl_3$	Too fast to be measured by this method				39.1

a) Toluene-d_8.



Scheme 2.

We postulate that the first step, the formation of CIP, is the rate-limiting step. Although the solvent intervention can be a rate-limiting step, if we start from ion pairs, either CIP or SSIP,[3)] the barrier to solvent intervention must be low. Calculations of solvent intervention also show that the barrier to solvent intervention to CIP is much lower than that for the formation of CIP.[19)] We consider that the barrier heights observed in these reactions are unusually high for solvent intervention. Rather the barriers seem to be appropriate for ionization of the covalent species, which is unusually easy for organic chlorides in this case. These are the reasons why we assume that the ionization to form CIP is the rate-limiting step.

Solvent Polarity Measures. Since the reactions discussed here are ionizing ones, solvent polarity should be taken into account, in addition to the dimensiosolvatic effects which are the main topic of this paper. $E_T(30)$ values of solvents are our choice as the measure of solvent polarity. Although dielectric constants are still used as a measure of the solvent polarity, this measure has been proved unsatisfactory in many cases because dielectric constant is a bulk property and the microscopic dielectric constant value can differ from the bulk value.[15)] Of the empirical parameters proposed to cover this drawback of dielectric constants, $E_T(30)$ values are most widely used. As a corollary, the $E_T(30)$ values of many solvents are known. In addition, the $E_T(30)$ values can be measured easily, if the dye is available, for a given solvent.[20)]

Rates of Dissociation. ***α*-Chlorobenzyl Ethyl Ether.** Table 3 shows the rates of dissociation of compound **4b** in a solvent of the ketone series and the ether series. This arrangement of data was made because it is the microscopic view of solvation rather than a macroscopic view and comparison in this manner was more promising in other cases.[3)]

Unfortunately, acetone, the smallest ketone, could not be used as a solvent for determination of rates of topomerization in compound **4** because the solute decomposes in that solvent. However, we still can compare the rates in solvents of different bulkiness in the ketone series. As is seen in Table 3, *t*-butyl methyl ketone and *t*-butyl methyl-d_3 ketone give almost the same rate constants with each other, whereas the rate constants for the di-*t*-butyl ketone solution are significantly smaller than those for the foregoing ketones. Because of the smallness of the effects, we feel that the polarity effects are important in these cases.

When we compare the rates obtained for the *t*-butyl methyl ketone solution with those for the chloroform solution (Table 2), the rates for the latter are definitely larger than the former, though their $E_T(30)$ values are the same. However, chloroform is a special solvent because it can form a hydrogen bonding with an electron-donor and is known to enhance ionization relative to its apparent polarity.

We have established in our previous works that entropy of activation is large and negative if a covalent molecule ionizes in solution, because of the decrease in the freedom of motion of solvent molecules, whereas it is large positive if an ionic species changes to a covalent species because of the increase in freedom of motion of solvent molecules.[21)] The general tendency seen in Tables 1, 2, and 3 conforms to this idea.

The data for the series of ether solvents reveal a similar tendency. The rate of dissociation is the largest in tetrahydrofuran-d_8 and values become smaller when the solvent molecules become bulkier: In diisopropyl ether, the dissociation is not observed at the highest temperature (342 K) we have studied at 60 MHz. In di-*t*-butyl ether also, no lineshape change was observed up to 50 °C, where decomposition of the solvent was noticed. A part of the cause for the slow dissociation should again be low polarities of the solvent which assists ionization less effectively but we believe that the cases of diisopropyl ether and di-*t*-butyl ether imply the importance of the bulkiness of the solvent molecules.

It is interesting to note that, irrespective of their identical $E_T(30)$ values, di-*t*-butyl ketone and tetrahydrofuran solutions give different kinetic data: Dissociation in di-*t*-butyl ketone is about 3 times faster than in tetrahydrofuran-d_8. We believe that this is because the oxygen atom of the ketone carbonyl group is more exposed to the environment than the ether-oxygen, when we compare ketones and ethers which carry the same alkyl groups. This supports our postulation that the comparison of the solvent effects should be made by the same functionalities rather than by $E_T(30)$ values only, if possible: We must take into account the differences in the steric effects on the main solvation sites of molecules.

In general, we conclude that the dimensiosolvatic effects on ionization of compound **4b** is very small, if any.

***α*-Chloro-*p*-methylbenzyl Ethyl Ether.** The difficulty in the work with compound **4b** is that its ionization rates are rather small; this forces us to use high temperatures and the solvent like di-*t*-butyl ether could not be used because of decomposition at the higher temperatures under the conditions.

Table 3. Dimensiosolvatic Effects on the Kinetic Parameters of Ionization of α-Chlorobenzyl Ethyl Ether (60 MHz Data)

Solvent	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal K^{-1} mol^{-1}	$\Delta G^‡_{290}$/kcal mol^{-1}	k_{290}/s^{-1}	$E_T(30)$
$CH_3COC(CH_3)_3$	9.5±0.9	−21.2±0.9	15.6	10	39.1
$CD_3COC(CH_3)_3$	9.8±0.4	−20.5±1.4	15.8	7.8	39.0
$[(CH_3)_3C]_2CO$	8.7±0.4	−26.1±1.1	16.3	3.2	37.4
C_4D_8O[a)]	14.4±1.3	−9.0±4.1	17.0	0.94	37.4
$(CH_3)_3COCD_3$	12.7±0.5	−14.8±1.6	17.0	0.80	36.0
$[(CH_3)_2CH]_2O$	Too slow to be measured by this method				34.3

a) Tetrahydrofuran-d_8.

We thought that, if we used a more easily ionizable substrate, we might be able to see ionization even in solvents of bulky molecules. Thus we decided to use α-chloro-*p*-methylbenzyl ethyl ether (**4d**) as a substrate. Unfortunately, however, di-*t*-butyl ether is too unstable under the conditions, probably due to induced decomposition of the ether by the cation, to obtain reliable data at 400 MHz. Even at 60 MHz the apparent rates of topomerization were unexpectedly large. Thus the data for di-*t*-butyl ether solutions are not included in Table 4, because the temperature range where measurements were made is quite different. Extrapolation to a temperature outside of the observation range may induce errors (For data for di-*t*-butyl ether solutions at 60 MHz, see Experimental).

The effects of the methyl group are clearly noted for the tetrahydrofuran-d_8 solutions. The topomerization rates of compound **4d** are ca. 5 times larger than those of compound **4b**. This is the normal effect of the methyl group on cation-forming reactions at the benzylic position. This is further evidence that the reaction studied here is an ionic reaction, in which a cation is produced at the benzylic position.

Apparently the bulkier the solvent molecule, the slower the topomerization in the solvents. This tendency is observed both in the ketone series and in the ether series. It is possible that the polarity effects of the solvent are operating in the observed rates, but we believe that the steric effects on solvation are also important. Solvation of a substrate in the original state should be less effective due to the steric effects, if a solvent molecule is bulky, than small molecules with the same polarity. This tendency should be enhanced in the transition state, because the molecular attraction becomes strong due to the enhancement of the appearance of the electric charge in the substrate relative to the original state. This should appear as the difference in free energy of activation for ionization and is clearly seen if one compares the data in the series of solvents.

The tendency that the topomerization of compound **4d** is faster in di-*t*-butyl ketone than in THF is reproduced, although their $E_T(30)$ values are the same. There must be a factor that affects the rates of dissociation of a covalent species into CIP. The reason must include the steric effects.

Generally, dimensiosolvatic effects are observed in ionization of compound **4d** but their extent is rather small. We thought that the effects could be larger than the case of **4d**, when a more easily ionizing compound is used. Thus ionization of **4e** was studied.

α-Chloro-*p*-methoxybenzyl Ethyl Ether. As expected, the ionic dissociation of **4e** was very fast. It was too fast to observe slow exchange limit of the methylene protons in the ketonic solvents even on a 600 MHz machine because the solvents tended to freeze at low temperatures: *t*-butyl methyl-d_3 ketone at −66 °C and di-*t*-butyl ketone at −39 °C. Thus the free energies of activation, which were obtained by the coalescence method, are listed in Table 5. If we assume −20 cal K^{-1} mol^{-1} entropy of activation, as for other known cases, the free energies of activation at 254 K for the two solvents are different by 0.5 kcal mol^{-1}. The difference is larger than that for compound **4d**, but is rather small.

By contrast, in the ether solvents, the dimensiosolvatic effects are apparent. There is a definite decrease in the rates of ionization when one goes from tetrahydrofuran to diethyl ether or *t*-butyl methyl ether. This difference exceeds the degree that is expected from the polarity effects. We expected that the tendency would be enhanced when we observe topomerization in di-*t*-butyl ether. Unfortunately, however, the spectra at low temperatures, which were necessary for observation of lineshape changes, exhibited considerable line-broadening; this prevents obtaining reliable data for the topomerization.

We have assumed, in the previous paper,[3] that *t*-butyl methyl ether was a slightly bulkier solvent than diethyl ether.

Table 4. Dimensiosolvatic Effects on the Kinetic Parameters of Ionization of α-Chloro-*p*-methylbenzyl Ethyl Ether (400 MHz Data)

Solvent	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{343}$/kcal mol^{-1}	k_{343}/s^{-1}	$E_T(30)$
$CD_3COC(CH_3)_3$	8.5±0.2	−21.8±0.6	15.9	505	39.0
$[(CH_3)_3C]_2CO$	6.8±0.1	−27.0±0.4	16.1	406	37.4
C_4D_8O[a)]	12.0±0.4	−14.3±1.3	16.9	120	37.4
$(C_2D_5)_2O$	11.7±0.5	−17.9±1.3	17.9	30	34.5
$(CH_3)_3COCH_3$	11.2±0.4	−21.3±1.0	18.5	12	36.0

a) Tetrahydrofuran-d_8.

Table 5. Dimensiosolvatic Effects on the Kinetic Parameters of Ionization of α-Chloro-*p*-methoxybenzyl Ethyl Ether (400 MHz Data)

Solvent	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{253}$/kcal mol^{-1}	k_{253}/s^{-1}	$E_T(30)$
$CD_3COC(CH_3)_3$			10.9[a)]	520[a)]	39.0
$[(CH_3)_3C]_2CO$			11.7[b)]	430[b)]	37.4
C_4D_8O[c)]	7.0±0.1	−17.7±0.6	11.6	570	37.4
$(C_2D_5)_2O$	7.8±0.1	−21.7±0.4	13.3	17	34.5
$(CH_3)_3COCH_3$	7.0±0.2	−23.1±0.8	12.8	41	36.0

a) The values obtained at 238 K. b) The values at 254 K. c) Tetrahydrofuran-d_8.

However, the present results indicate that these two solvents should be considered to exhibit almost the same bulkiness. This is probably due to the fact that the substrate and the forming cation are bulky in the present case. It is also possible that the higher polarity of *t*-butyl methyl ether than diethyl ether is playing a role here. By contrast, solvent intervention was the issue when topomerization of the lithium compounds was discussed.[3]

Comparison of the Dimensiosolvatic Effects on Dissociation of α-Chlorobenzyl Ethyl Ethers. Surveying the data (Table 6), we notice that the dimensiosolvatic effects are dependent on the ease of ionization. The most easily ionizable *p*-methoxy compound **4e** suffers from the strongest dimensiosolvatic effects, whereas the unsubstituted compound **4b** is little affected by the bulkiness of solvent molecules. This trend is worthy of discussion.

In the easily ionizable **4e**, the transition state for ionization should be early, if the Hammond postulate[22] is applicable. This means that the transition state of ionization for compound **4e** is less ionic than the case of **4b** and it will imply that the solvent effects should be less important for the **4e** case than the **4b** case. However, the results shown in Table 6 indicate that the solvent effects become more important for the **4e** case than for the **4b** case. It is tempting to consider that the second step, solvent intervention, is playing some roles in determining the rates, but the examples are limited. Further discussion is deferred until more data become available. The assumption that the CIP formation is rate-limiting is put forward for the time being.

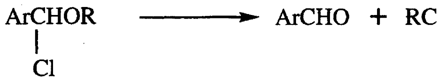
The rates of topomerization of **4d** in *t*-butyl methyl-d_3 ether are nearly equal to or a little smaller than those of **4b** in the same solvent. This is an interesting example where the *p*-methyl group does not enhance the ionization rates. We wish to attribute this to the dimensiosolvatic effects. Indeed, by comparing the rate constants of ionization, we note that the relative rates in tetrahydrofuran-d_8 for compounds **4b**, **4d**, and **4e** are similar to those of solvolyses of *p*-substituted 2-phenyl-2-chloropropanes in aqueous acetone,[23] but differences in those in the bulky solvents are diminished. Dimensiosolvatic effects reduce the effects of the substituents, because the stabilization by solvation of ion pairs becomes less effective with respect to small solvents.

Finally we wish to mention the relatively small dimensiosolvatic effects on the ionization of the halides studied in this paper. Probably it is the effects of the bulkiness of the substrate. It is a well-known fact that solvation of alcohols by hydrogen-bonding renders high solubility of small alcohols in water, but, as the alkyl part of alcohols become large, the solubility of an alcohol in water decreases. In the bulky substrate, even at the transition state for ionization, the solvation plays less significant roles than the case of small substrates, because the portion of the ionic nature in the molecule is rather small in the bulky substrates.

Significance of Dimensiosolvatic Effects in S_N1 Type Reactions. In the light of above presentation, some results reported in the literature deserve mention. In the past, the solvent effects were mainly interpreted in terms of polar–nonpolar and protic–aprotic nature of solvent molecules.[15] The results presented here indicate that there is a third factor that should be considered when we discuss the solvent effect. Although the cases presented in this paper are rather extreme, they clearly show that the solvent molecular size effect cannot be neglected in certain cases.

In the literature we find a few papers that report comparison of reaction rates in a series of alcohols; methanol, ethanol, isopropyl alcohol, and *t*-butyl alcohol. Isomerization of *cis*- and *trans*-chloro(*m*-tolyl)bis(triethylphosphine)platinum(II) is very slow in *t*-butyl alcohol.[24] Solvolysis of *t*-butyl chloride in *t*-butyl alcohol is very slow with respect to that in methanol.[25,26] The rate retardation in *t*-butyl alcohol should be the result of both the decrease in polarity and the increase in the molecular size of *t*-butyl alcohol compared to methanol. We urge that the results reported in the literature be reexamined on the light of this third aspect of the solvent effects.

Comparison of Topomerization with Thermolyses of Alkyl α-Chlorobenzyl Ethers. Since alkyl α-chlorobenzyl ethers are known to be thermolyzed rather easily to produce benzaldehyde and alkyl chloride (Scheme 3),[28,29] comparison of the topomerization data with those of thermolyses is interesting.



$$\underset{\displaystyle \mathrm{Cl}}{\mathrm{ArCHOR}} \longrightarrow \mathrm{ArCHO} + \mathrm{RCl}$$

Scheme 3.

Table 6. Comparison of Kinetic Parameters of Ionization of *p*-Substituted α-Chlorobenzyl Ethyl Ethers in Various Solvents

Substituent	Solvent	$\Delta G^{\ddagger}_{300}$/kcal mol^{-1}	k_{300}/s^{-1}	Relative rates
H	C_4D_8O[a]	17.1	2.2	1
	$(CH_3)_3COCD_3$	17.2	1.9	0.86
CH_3	C_4D_8O[a]	16.3	8.4	1
	$(C_2D_5)_2O$	17.1	2.2	0.26
	$(CH_3)_3COCH_3$	17.6	0.96	0.11
CH_3O	C_4D_8O[a]	12.3	6600	1
	$(C_2D_5)_2O$	14.3	230	0.035
	$(CH_3)_3COCH_3$	14.0	430	0.065

a) Tetrahydrofuran-d_8.

Kwart and Silver[29] measured the rates of thermolyses of these compounds and studied the stereochemical outcome of the reaction of α-chlorobenzyl (R)-1-methylheptyl ether. The stereochemistry in 2-chlorooctane was inverted from the starting material. The entropy of activation was large and negative and the Hammett correlation produced a large negative ρ value. From these experimental results, Kwart and Silver concluded that the nature of the reaction must be the back side attack of the chloride ion, which was produced in the system, on α-alkoxybenzyl cation in the system, the ionization being the rate-limiting step.

We reexamined the thermolyses of α-chlorobenzyl ethyl ether (**4b**) in several solvents as well as the effects of an alkyl group on the thermolyses of alkyl α-chlorobenzyl ethers. The results are compiled in Tables 7 and 8. The results of the methyl ether **4a** in chloroform are essentially the same as those reported by Kwart and Silver. The reaction rates were not affected to a significant extent by concentration within the range examined, providing evidence for a unimolecular reaction, and the rates are large in polar solvents, as was reported. We also examined the thermolyses in a bulky solvent. The dimensiosolvatic effects seemed little, but the rates in di-t-butyl ketone are almost the same as those in carbon tetrachloride, irrespective of the polarity of the former, being higher than that of the latter. The entropy of activation is large and negative throughout, except for α-chlorobenzyl isopropyl ether.

The isopropyl ether **4c** is a little more easily thermolyzed than the ethyl ether **4b** or the methyl ether **4a**. Although Kwart and Silver reported that the secondary alkyl ethers of type **4** are more sluggishly decomposed than primary alkyl compounds, they compared the rates at 298 K, which is well outside the temperature range of the reactions. We believe that, because of errors involved in values obtained by extrapolation with use of enthalpies and entropies of activation, the comparison should be made at a temperature which is close to or within the range of actual measurements. Indeed, calculations of free energy of activation at 393 K with use of enthalpy and entropy of activation, which are reported by Kwart and Silver, indicate that **4a** is more reluctantly decomposed than s-butyl α-chlorobenzyl ether.

Apparently, thermolysis rates are much smaller than topomerization. This means that there is a very efficient internal return in the ion pairs, CIP and SSIP, in this case. We therefore consider that the mechanisms developed by Kwart and Silver should be modified: That is, the rate-limiting step is the attack by chloride ion in the system on α-alkoxybenzyl cation rather than ionization of the substrate. We propose that the chloride ion within the SSIP must move to the back side of the C_{alkyl}–O bond (**5**) from the original position for formation of benzaldehyde and alkyl chloride and that this attack of the chloride ion on **5** is rate-limiting. For compound **4c**, this C_{alkyl}–O bond is partially ionic because the alkyl group is secondary, and the intermediate is close to an alkyl ion coordinated with incipient benzaldehyde (**6**) (Scheme 4). This picture can accommodate the easier thermolysis of **4c** than that of the methyl or the ethyl ether.

The large negative ρ values in the Hammett plot of the reaction, reported by Kwart and Silver, must be attributed to the effect of the ionization step. Because the whole process is a combination of pre-equilibriums of ionization/solvent intervention and an attack by a chloride ion on the complex (**5**) of benzaldehyde and alkyl cation, the observed activation parameters are affected by the pre-equilibrium.

The large negative entropy of activation must be attributed to the ionization of the compounds, which restricts freedom of solvent molecules. It could be argued that the S_N2 type reaction can also exhibit large negative entropy of activation, but we believe this effect is small, because the reaction is taking place within the ion pair, as the unimolecularity of the reaction suggests. The required activation energy of the reaction is then the energy which is necessary to bring the chloride ion to the back side of the C–O bond within the interacting range with the cation as well as to deform the alkyl part of the intermediate **5**.

Thermolyses of alkyl α-chloroethyl ether in the gas phase is known to afford alkyl vinyl ether and hydrogen chloride.[30]

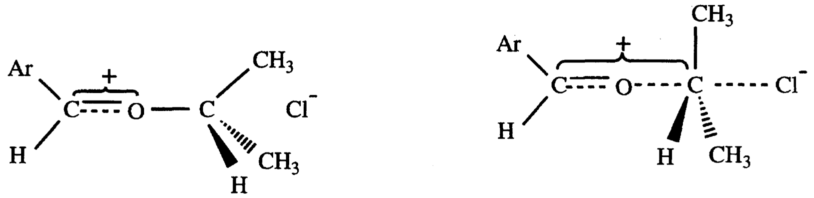
Table 7. Rates and Kinetic Parameters of Decomposition of α-Chlorobenzyl Ethyl Ether in Various Solvents[a)]

Solvent	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{373}$/kcal mol^{-1}	k_{373}/s^{-1}	$E_T(30)$
CCl_4	12.2 ± 2.8	-52.3 ± 7.2	31.7	2.0×10^{-6}	32.4
CCl_4[b)]	11.3 ± 6.7	-54.0 ± 17	31.5	2.8×10^{-6}	32.4
$[(CH_3)_3C]_2CO$	24.0 ± 5.3	-21.3 ± 14	32.0	1.5×10^{-6}	37.4
$CDCl_3$	19.7 ± 3.7	-26.7 ± 10	29.7	3.3×10^{-5}	39.1

a) Concentrations are 0.20 mol L^{-1} unless otherwise described. b) Concentration 0.50 mol L^{-1}.

Table 8. Rates and Kinetic Parameters of Decomposition of Alkyl α-Chlorobenzyl Ether in Chloroform-d

Alkyl	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{373}$/kcal mol^{-1}	k_{373}/s^{-1}
CH_3	18 ± 2	-31 ± 5	30	3.7×10^{-5}
C_2H_5	20 ± 4	-27 ± 10	30	3.3×10^{-5}
$(CH_3)_2CH$	27 ± 5	-5 ± 14	29	8.7×10^{-5}



5 6

Scheme 4.

This different behavior of the compound in the gas phase from that in the liquid phase has remained as a question. Now we can shed light on the differences and discuss the reason in some details. In the gas phase, the compound will ionize at the wall surface or might do so even in the gas phase, judged from the facile ionization in nonpolar solvents, but the chloride ion cannot leave from the counter ion in the ion pair. Thus the chloride has to abstract a proton which is located close to it, forming an enolic ether and hydrogen chloride in the aliphatic system. By contrast, in the liquid phase, the chloride ion can "swim" to the site of the S_N2 type reaction because ions are stabilized by solvation and can change their relative sites due to the fluid nature. We believe this difference, attributable to the difference in phase, should be a critical factor to the quite different reactivities exhibited by the similar compounds.

Experimental

Boiling points are not corrected. Elemental analysis of chlorine was carried out by decomposing the materials with water; the concentration of chloride ion was titrated by the Mohr method. ^{1}H NMR spectra were measured on a Varian Gemini-300 spectrometer which operated at 300.1 MHz. Dynamic ^{1}H NMR data were collected on a Varian EM-360L or on a Bruker AMX-R400 spectrometer unless otherwise mentioned.

Solvents. Since the solute was sensitive to moisture, solvents were dried with utmost care. Commercially available solvents were dried over calcium hydride, if applicable, and distilled. They were stored over Molecular Sieves 4A. *t*-Butyl methyl-d_3 ketone,[31] *t*-butyl methyl-d_3 ether,[32] di-*t*-butyl ketone,[33] and di-*t*-butyl ether[12] were prepared according to the established method and stored as above.

Measurement of $E_T(30)$ Values. For the most solvents, 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate[34] was used as the dye for determination of $E_T(30)$ values. Since these values agreed with literature data within the error limits, the literature values were used. Since this dye was not soluble enough for the measurement in di-*t*-butyl ketone and in di-*t*-butyl ether, 2,6-bis-(4-*t*-butylphenyl)-4-[2,4,6-tris(4-*t*-butylphenyl)-1-pyridinio]phenolate[35] was used for these solvents and calculated to afford the $E_T(30)$ values as reported. The absorption curve for di-*t*-butyl ether is very flat and determination of the maximum absorption may contain some errors. The following absorption maxima and $E_T(30)$ values were determined: di-*t*-butyl ether, λ_{max} 875.5 nm, $E_T(30)$ 32.0 kcal mol^{-1}; di-*t*-butyl ketone, λ_{max} 760.4 nm, $E_T(30)$ 37.4 kcal mol^{-1}.

α-Chlorobenzyl Methyl Ether (4a). This compound was prepared according to the method described.[27] bp 55 °C/0.9 mmHg (lit, 50 °C/0.1 mmHg) (1 mmHg = 133.322 Pa). ^{1}H NMR ($CDCl_3$) $\delta = 3.71$ (3H, s), 6.48 (1H, s), 7.37—7.41 (3H, m), 7.49—7.53 (2H, m).

α-Chlorobenzyl Ethyl Ether (4b). This compound was prepared from benzaldehyde diethyl acetal and acetyl chloride in the presence of thionyl chloride, as described in the literature.[28] It was found that rather rapid distillation of the product was necessary for purification of the compound, because it tended to decompose when heated for a long time. bp 60 °C/0.1 mmHg. The ^{1}H NMR spectrum showed the following signals ($CDCl_3$) $\delta = 1.36$ (3H, t, $J = 7.1$ Hz), 3.80—4.20 (2H, m), 6.60 (1H, s), 7.35—7.41 (3H, m), 7.51—7.55 (2H, m).

α-Chlorobenzyl Isopropyl Ether (4c). A mixture of 10.0 g (48 mmol) of benzaldehyde diisopropyl acetal,[36] 3.3 mL (47 mmol) of acetyl chloride, and 0.3 mL (4.7 mmol) of thionyl chloride was heated at 60 °C for 1 h, when further 3.3 mL (47 mmol) of acetyl chloride and 0.3 mL (4.7 mmol) of thionyl chloride were added and the mixture was heated for another hour at the temperature to complete the reaction. Excess of acetyl chloride and thionyl chloride was removed below 80 °C and the residue was distilled under reduced pressure. The distillation was best accomplished when the flask was immersed into an oil bath preheated at 80 °C and the distillate collected rather rapidly. Redistillation gave the pure sample. bp 55 °C/0.4 mmHg. Yield 63%. Found: Cl, 19.51%. Calcd for $C_{10}H_{13}ClO$: Cl, 19.20%. ^{1}H NMR ($CDCl_3$) $\delta = 1.33$ (6H, d, $J = 6.2$ Hz), 4.24—4.38 (1H, m), 6.72 (1H, s), 7.33—7.44 (3H, m), 7.48—7.59 (2H, m).

α-Chloro-*p*-methylbenzyl Ethyl Ether (4d). A mixture of 36.6 g (0.19 mol) of *p*-methylbenzaldehyde diethyl acetal,[37] 26 mL (0.37 mol) of thionyl chloride, and 2.7 mL (0.037 mol) of acetyl chloride was heated at 60—65 °C for 1 h and distilled to remove as much unreacted thionyl chloride and acetyl chloride as possible, keeping the bath temperature at 60—65 °C. Then the flask was immersed into a bath at 105 °C to distill the product rapidly. The product was purified by redistillation, bp 72 °C/0.8 mmHg. The yield was 86%. Found: Cl, 19.09%. Calcd for $C_{10}H_{13}ClO$: Cl, 19.20%. ^{1}H NMR ($CDCl_3$) $\delta = 1.35$ (3H, t, $J = 7.1$ Hz), 2.36 (3H, s), 3.90—4.02 (2H, m), 6.59 (1H, s), 7.19 and 7.42 (4H, ABq, $J = 8.1$ Hz).

α-Chloro-*p*-methoxybenzyl Ethyl Ether (4e). A mixture of 3.1 g (14.7 mmol) of *p*-methoxybenzaldehyde diethyl acetal[38] and 3.1 g (39.5 mmol) of acetyl chloride was stirred at room temperature for 16 h. Any volatile materials were removed in vacuo first by applying 25 mmHg pressure for 1 h and then 0.6 mmHg pressure for 2 h, both being done at 0 °C. The product thus obtained was practically pure, the main contaminant being *p*-methoxybenzaldehyde, which amounted to a few per cent. Found: Cl, 17.61%. Calcd for $C_{10}H_{13}ClO_2$: Cl, 17.67%. ^{1}H NMR ($CDCl_3$) $\delta = 1.31$ (3H, t, $J = 7.0$ Hz), 3.81 (3H, s), 3.84 (2H, br m), 6.45 (1H, s), 6.91 and 7.46 (4H, ABq, $J = 8.8$ Hz).

Dynamic NMR. The ^{1}H NMR spectra were obtained on the Varian EM-360L machine to meet the demand that spectra had to

Table 9. Correlation of Chemical Shift Differences with Temperature, T_2, and Coupling Constants of AB Protons in α-Chlorobenzyl Ethyl Ether (60 MHz Data)

Solvent	Concn/mol L^{-1}	T_2/s	$\Delta\nu_{AB}$/Hz[a)]	J_{AB}/Hz	J_{AX}/Hz	J_{BX}/Hz
CCl_4	2.0	0.13	$-0.12\,t+32.1$	−9.2	7.0	7.0
	1.0	0.20	$-0.08\,t+31.4$	−9.0	7.0	7.0
	0.50	0.20	$-0.07\,t+31.1$	−9.0	7.0	7.0
	0.20	0.30	$-0.07\,t+30.3$	−9.2	7.0	7.0
	0.10	0.25	$-0.06\,t+29.6$	−9.0	7.0	7.0
C_7D_8[b)]	0.20	0.25	$-0.15\,t+44.7$	−9.5	7.0	7.0
ClC_6H_5	0.20	0.23	$-0.15\,t+37.7$	−9.0	7.0	7.0
$(CH_3)_3CCOCH_3$	0.20	0.18	$-0.06\,t+21.7$	−9.0	7.0	7.0
$(CH_3)_3CCOCD_3$	0.20	0.23	$-0.05\,t+21.6$	−9.0	7.0	7.0
$[(CH_3)_3C]_2CO$	0.20	0.20	$-0.04\,t+24.1$	−9.5	7.0	7.0
C_4D_8O[c)]	0.20	0.28	$-0.05\,t+24.8$	−9.0	7.0	7.0
$(CH_3)_3COCD_3$	0.20	0.30	$-0.04\,t+26.5$	−9.0	7.0	7.0

a) t is given in °C. b) Toluene-d_8. c) Tetrahydrofuran-d_8.

Table 10. Rate Constants of Dissociation of α-Chlorobenzyl Ethyl Ether (60 MHz Data)

Solvent	Concn/mol L^{-1}	k/s^{-1} (Temp/°C)
CCl_4	2.0	11.6 (14.4), 17.2 (24.8), 24.0 (35.3), 34.0 (45.8), 51.0 (56.3), 64.0 (66.8)
	1.0	7.2 (37.3), 9.0 (42.2), 11.2 (47.2), 13.8 (52.1), 16.8 (57.0), 20.0 (62.0)
	0.50	4.4 (37.3), 5.4 (42.2), 6.4 (47.2), 8.0 (52.1), 10.2 (57.0), 12.2 (62.0), 15.0 (66.9), 17.6 (71.9)
	0.20	5.8 (51.1), 6.8 (56.3), 8.4 (61.6), 10.6 (66.8), 13.0 (72.1), 16.0 (77.3)
	0.10	5.8 (49.7), 7.0 (54.4), 8.8 (59.1), 10.4 (63.9), 12.8 (68.6), 15.0 (73.3)
C_7D_8[a)]	0.20	10.0 (24.8), 13.2 (35.3), 21.0 (45.8), 31.0 (56.3), 44.0 (66.8), 84.0 (87.8), 108.0 (98.3)
ClC_6H_5	0.20	26.0 (−21.3), 30.2 (−10.2), 44.0 (14.3), 52.0 (24.8), 60.0 (35.5)
$(CH_3)_3CCOCH_3$	0.20	8.6 (14.3), 11.2 (18.5), 14.4 (22.7), 18.4 (26.9), 22.4 (31.1), 28.8 (35.3), 36.0 (39.5)
$(CH_3)_3CCOCD_3$	0.20	6.6 (14.3), 9.2 (19.6), 12.4 (24.8), 17.2 (30.1), 22.2 (35.3), 31.0 (40.6)
$[(CH_3)_3C]_2CO$	0.20	5.0 (24.8), 8.6 (35.3), 13.4 (45.8), 22.0 (56.3), 34.8 (66.8), 54.0 (77.3)
C_4D_8O[b)]	0.20	4.6 (35.3), 7.0 (40.6), 8.0 (43.7), 10.0 (46.9), 13.0 (50.0), 16.2 (53.2), 22.2 (56.3), 27.4 (59.5)
$(CH_3)_3COCD_3$	0.20	5.0 (40.6), 6.0 (43.7), 7.6 (46.9), 9.4 (50.0), 11.6 (53.2), 13.8 (56.3), 16.6 (59.5)

a) Toluene-d_8. b) Tetrahydofuran-d_8.

be measured for solutions of undeuterated molecules. The spectra were also measured on a Bruker AMX-R400 machine, when acetone-d_6, which was sealed in a capillary, was used for the D-lock. NMR tubes (Aldrich) which were equipped with an adaptor for a capillary at the center of the bottom were used. Temperatures were calibrated with use of ethylene glycol for high temperatures and methanol for low temperatures. Reproducibility of the low temperature spectra was confirmed by lowering the temperature after observing the lineshape changes. Lineshapes were observed at least at six temperatures.

The lineshapes were simulated with use of the DNMR3K program[39)] and the best fit spectra were determined by visual fitting. The lineshapes were analyzed by assuming the exchange between ABX_3 and BAX_3 for the 60 MHz spectra. For the 400 MHz spec-

Table 11. Chemical Shift Differences, T_2, and Coupling Constants of AB Protons in α-Chloro-p-methylbenzyl Ethyl Ether at 0.20 mol L^{-1} Concentration (400 MHz Data)

Solvent	$\Delta\nu_{AB}$/Hz[a)]	T_2/s	J_{AB}/Hz
$(CH_3)_3CCOCD_3$	$-0.169t+146.5$	0.087	−9.4
$[(CH_3)_3C]_2CO$	$-0.163t+160.0$	0.075	−9.3
C_4D_8O[b)]	$-0.239t+164.0$	0.080	−9.5
$(C_2D_5)_2O$	$-0.349t+188.7$	0.085	−9.6
$(CH_3)_3COCH_3$	$-0.355t+190.0$	0.090	−9.6

a) t is expressed in °C. b) Tetrahydrofuran-d_8.

Table 12. Rate Constants of Dissociation of α-Chloro-*p*-methylbenzyl Ethyl Ether at 0.20 mol L^{-1} Concentration (400 MHz Data)

Solvent	k/s^{-1} (Temp/°C)
$(CH_3)_3CCOCD_3$	6.0 (−14.6), 10.0 (−8.6), 14.0 (−2.7), 28.0 (9.1), 44.0 (15.0), 58.0 (20.9), 80.0 (26.8), 100 (32.7), 126 (38.6), 170 (44.5), 226 (50.4), 276 (56.3), 350 (62.2), 460 (68.2), 600 (74.2), 760 (80.0)
$[(CH_3)_3C]_2CO$	28.0 (2.2), 38.0 (8.3), 50.0 (14.4), 62.0 (20.5), 80.0 (26.7), 110 (32.8), 136 (38.9), 180 (45.0), 210 (51.1), 260 (57.2), 320 (63.4), 400 (69.5), 500 (75.6), 580 (81.7)
C_4D_8O[a]	8.0 (26.5), 12.0 (32.4), 18.0 (38.3), 26.0 (43.1), 56.0 (56.0), 80.0 (61.9), 106 (67.9), 140 (73.8)
$(C_2D_5)_2O$	52.0 (81.2), 66.0 (85.5), 82.0 (89.8), 100 (94.0), 120 (98.3), 144 (102.6), 174 (106.9)
$(CH_3)_3COCH_3$	22.0 (82.8), 26.0 (87.3), 32.0 (90.7), 36.0 (94.0), 42.0 (97.4), 48.0 (100.7), 56.0 (104.1), 74.0 (110.8), 86.0 (114.2)

a) Tetrahydrofuran-d_8.

tra, the methyl protons were irradiated to simplify the spectra of the methylene protons to the AB system. Then the process was treated as the site exchange of AB to BA. The chemical shift differences drifted as temperature was varied. The differences were determined at several temperatures in the slow exchange limit and were found to be best correlated linearly. Chemical shift differences extrapolated by these lines were used for the temperature range where lineshapes changed. T_2's were obtained from lines which did not exchange and slightly adjusted to get the best fit, when necessary. Coupling constants between the A and B protons and those between the A or B proton and the methyl protons were constant throughout the ranges examined. These values together with equations that represent the drift of chemical shift changes are compiled in Tables 9, 11, and 13 for compounds **4b**, **4d**, and **4e**, respectively. Rate constants at various temperatures thus obtained are shown in Tables 10, 12, and

Table 13. Chemical Shift Differences, T_2, and Coupling Constants of AB Protons in α-Chloro-*p*-methoxybenzyl Ethyl Ether at 0.20 mol L^{-1} Concentration (400 MHz Data)

Solvent	$\Delta\nu_{AB}$/Hz[a]	J_{AB}/Hz	T_2/s
C_4D_8O[b]	$-0.123t+169.7$	−9.3	0.090
$(C_2D_5)_2O$	$-0.256t+184.8$	−9.3	0.093
$(CH_3)_3COCH_3$	$-0.297t+186.2$	−9.3	0.088

a) t is expressed in °C. b) Tetrahydrofuran-d_8.

Table 14. Rate Constants of Dissociation of α-Chloro-*p*-methoxybenzyl Ethyl Ether at 0.20 mol L^{-1} Concentration (400 MHz Data)

Solvent	k/s^{-1} (Temp/°C)
C_4D_8O[a]	6.0 (−80.8), 10.0 (−75.4), 16.0 (−70.1), 26.0 (−64.8), 40.0 (−59.5), 60.0 (−54.1), 92.0 (−48.8), 150 (−43.5), 200 (−38.2), 280 (−32.8), 400 (−27.5)
$(C_2D_5)_2O$	12.0 (−25.4), 16.0 (−21.1), 20.0 (−16.9), 28.0 (−12.6), 36.0 (−8.4), 44.0 (−4.1), 56.0 (0.2), 74.0 (4.4), 100 (9.7), 130 (15.1), 170 (20.4), 220 (25.7), 280 (31.0), 340 (36.4)
$(CH_3)_3COCH_3$	24.0 (−27.5), 36.0 (−22.2), 48.0 (−16.9), 70.0 (−11.6), 94.0 (−6.2), 120 (−0.9), 148 (4.4), 200 (9.7), 250 (15.1), 320 (20.4), 400 (25.7), 500 (31.0)

a) Tetrahydrofuran-d_8.

Table 15. Rates of Decomposition of Alkyl α-Chlorobenzyl Ethers in Various Solvents at 0.20 mol L^{-1} Concentration

Alkyl	Solvent	($k\times10^6$)/s^{-1} (Temp/°C)
C_2H_5	CCl_4	1.9 (100), 5.2 (120), 7.8 (130), 10.0 (140)
C_2H_5[a]	CCl_4	6.2 (120), 10.0 (130), 19.0 (150)
C_2H_5	$CDCl_3$	6.6 (80), 17.7 (90), 31.7 (100), 68 (110)
C_2H_5	$[(CH_3)_3C]_2CO$	0.62 (90), 6.8 (119), 81.0 (150)
CH_3	$CDCl_3$	18.6 (90), 37.8 (100), 52.1 (105)
$(CH_3)_2CH$	$CDCl_3$	18.6 (85), 30.4 (90), 88.1 (100)

a) Concentration is 0.50 mol L^{-1}.

14. These rate constants were put into the Eyring equation and the kinetic parameters shown in Tables 1, 2, 3, 4, and 5 were obtained. Correlation coefficients in the statistical treatment were better than 0.995 for all the data presented in the Tables.

For topomerization of **4d** in di-*t*-butyl ether, the following data are reported for reference, the data being obtained at 60 MHz. Rate constants (s^{-1}) (temperature in °C in parentheses): 7.0 (−32.2), 8.6 (−26.8), 10.0 (−22.5), 13.8 (−11.0), 16.6 (−4.6), 19.4 (0.9). These data produced the following activation parameters: $\Delta H^{\ddagger}$ $9.2\pm0.5\ \mathrm{kcal\,mol^{-1}}$, $\Delta S^{\ddagger}$ $-24.0\pm1.7\ \mathrm{cal\,K^{-1}\,mol^{-1}}$. The chemical shift differences ($\Delta\nu$) drifted as temperature (t/°C) changed. The correlation between them was $\Delta\nu=-0.02t+23.1$ Hz at 60 MHz.

Because compound **4e** ionizes easily and the solvents with *t*-butyl group(s) tend to crystallize at fairly high temperatures, the slow exchange limit was not obtained in *t*-butyl methyl ketone and di-*t*-butyl ketone at 400 MHz. The ^{1}H NMR spectra were recorded on a Varian Unity-600 machine which operated at 599.97 MHz. Even with this machine, we were not able to observe clear quartet signals at the lowest temperature where the solvent remained fluid. Thus the chemical shifts of the broad signals were recorded and the free energy of activation values were obtained by the coalescence method as the merging of two signals. The chemical shift differences for the broad signals were 236 and 194 Hz, respectively, in *t*-butyl methyl-d_3 ketone and di-*t*-butyl ketone. T_c's and k's at T_c are given in Table 5.

Thermolyses. The sample was dissolved in a given solvent to make up a 0.2 $\mathrm{mol\,L^{-1}}$ solution in an NMR tube and the tube was sealed. The sample tube was immersed in a thermostatted oil bath at a given temperature and the decrease in the signal intensity due to the methine proton of the substrate and the increase in the signal intensity due to the formyl proton of benzaldehyde were checked in appropriate intervals. Signals due to alkyl chlorides were also detected as the thermolyses proceeded. The rates of decomposition are given in Table 15 and kinetic parameters in Tables 7 and 8.

This work was supported by a Special Grant for Cooperative Research administered by Private School Promotion Foundation. We also wish to thank Professor C. Reichardt of Marburg University for providing the penta-*t*-butyl betaine dye for the solvent polarity measurement and to Professor S. Ito and his staff members of Tokushima Bunri University for the measurement of the spectra at 600 MHz.

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