Dimensiosolvatic Effects. VI. Rates of Ionization of 2-Fluoro-4,4,5,5-tetramethyl-1,3-dioxolane: Dimensiosolvatic vs. Hydrogen-Bond Effects[1,2]

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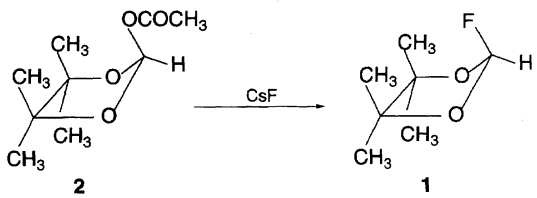
The title compound was prepared by treating 4,4,5,5-tetramethyl-1,3-dioxolan-2-yl acetate with cesium fluoride. Rates of ionization of this compound were determined in various solvents by the dynamic NMR technique. While effects due to polarity as well as solvent molecular size were observed in many solvents examined, the rates in solutions of which the solvent is capable of being an acceptor in hydrogen-bond formation with the substrate were unusually small, and this effect is diminished in bulky solvents. Such results are attributed to stabilization of the original state due to hydrogen-bond formation with the acidic C(2) – H group of the substrate in those solvents. The hydrogen-bond formation is hindered by the steric effects in bulkier solvents than in smaller solvents. The rates of contact ion pair and solvent-separated ion pair formations should be independently determined in 2-fluoro-4,4,5,5-tetramethyl-1,3-dioxolane, but so far no clear example which shows that the rate-limiting step is the solvent intervention has been found, even though various bulky solvents were examined.

Dimensiosolvatic effects, the effects of the molecular size of solvents on solvation, have been demonstrated in solvent intervention to contact ion pairs,[3,4] ionization of organic halides,[5] and dissociation of ammonium salts.[6] While the rates of dissociation of the ammonium salts were smaller in small solvents relative to those in bulky solvents, the rates of topomerization in organic halides were smaller for solutions in bulky solvents than in small solvents. The solvent intervention into the contact ion pairs (CIP) or solvent-separated ion pairs (SSIP) is also an example which shows slow intervention for bulky solvents. The slow intervention of bulky solvent molecules with respect to small molecules to contact ion pairs is a straightforwardly understandable phenomenon, while the other results were interpreted in terms of relative effectiveness of solvation in the transition states as well as original states. Namely, in the case of ionic species, the original state is less effectively stabilized by solvation with bulky solvents relative to small solvents with similar polarity, whereas the solvation of the transition state for ionization of a covalent species is less effectively stabilized by solvation with bulky solvents relative to small ones.

We have designed a compound, 2-fluoro-4,4,5,5-tetramethyl-1,3-dioxolane (**1**), which potentially shows CIP formation and SSIP formation independently. The reasons for designing this compound have been discussed in some detail in a previous paper.[2] It is rather a stable compound because of the steric effects due to four methyl groups, which prevent an intramolecular S_N2 type reaction between the ionic species formed on ionization,[7] differing from compounds in which such reactions are facile.[8]

This compound was prepared by treating 4,4,5,5-tetramethyl-1,3-dioxolan-2-yl acetate (**2**)[9] with dry cesium fluoride in vacuo (Scheme 1). Although its purification was difficult, it was obtained in a satisfactorily pure form by this method. The main impurities were the starting material and an open-chain compound, 2-fluoro-1,1,2-trimethylpropyl formate, which was formed by the S_N2 type reaction within the ion pairs. The method of obtaining the rate constants is the total lineshape analysis of ^1H or ^{19}F NMR spectra. The loss of coupling at the H–C(2)–F site is the probe for formation of CIP and the site exchange of the methyl groups is that for SSIP. This is an analogy of the work by Goering et al. who used ^{18}O-labeled optically active esters in which ^{18}O scrambling is the probe for CIP formation and the loss of optical activity is that of SSIP.[10]

Ionic dissociation of this compound was expected to be similar to α-chlorobenzyl ethyl ether,[5] because of its nature as an organic halide. However, on examining the rates of ionization, we found various anomalies which cannot be explained by simple consideration of solvent polarities and/or bulkiness of solvent molecules. This paper is to report and discuss those anomalies together with dimensiosolvatic effects.



2 **1**

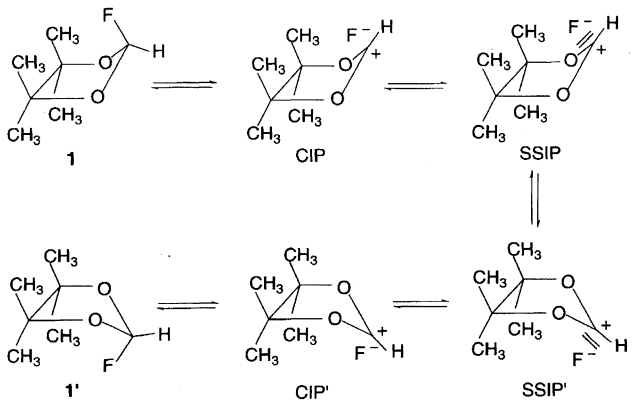
Scheme 1.

Results and Discussion

General Considerations. The results obtained for various solutions are summarized in Table 1. Solvents are arranged in the increasing order of polarity which is expressed by $E_T(30)$ values.[11] To facilitate comparison, the rate constants of ionization are shown at 270 K, although extrapolation from the observed data was necessary for some solvents. This extrapolation may cause some errors because the lineshapes are not directly observed at the specified temperature. However, since we discuss in the following parts large differences only, the rates at a particular temperature are useful to get a general idea.

The process that we observe is ionic in nature. Although there is no linear correlation of the rates of dissociation with solvent polarity, clearly the rates are enhanced in highly polar solvents. The seemingly anomalous results can be attributed to various factors which are discussed later in this paper, but the general tendency is as follows: The more polar the solvent, the larger the rates of ionization. This conclusion is also supported by the fact that generally the entropy of activation is large negative. It is established that when a covalent species ionizes, large negative entropy of activation is observed.[12]

As mechanisms of ionization of the substrate, the scheme proposed by Winstein et al.[13] may be used. That is, the reaction proceeds via CIP and then SSIP (Scheme 2): We assume that independent tumbling of ion pairs is possible in SSIP but is not possible in CIP.[14] If the barrier to solvent intervention to CIP is high enough and that to CIP formation is low enough, the solvent intervention step can be rate-limiting. Indeed, existence of a barrier to solvent intervention to CIP has been suggested by calculations.[15] Our compound should show the following behaviors in determining the rates of formations of CIP and SSIP: loss of coupling between ^1H



Scheme 2.

Table 1. Solvent Effects on the Kinetic Parameters of Ionization of 2-Fluoro-4,4,5,5-tetramethyl-1,3-dioxolane [a]

Solvent	Probe	$\Delta H^{\ddagger}$ /kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{270}$/kcal mol^{-1}	k_{270} /s^{-1}	$E_T(30)$/kcal mol^{-1}
C_7D_8 [b]	4,5-Me	9.0 ± 0.3	−18.2 ± 1.3	13.9	30	33.9
	2-H	8.9 ± 1.1	−17.8 ± 4.1	13.7	47	
	2-F	8.9 ± 0.9	−17.7 ± 3.3	13.7	48	
CH_3CCl_3	4,5-Me	12.4 ± 0.4	−9.3 ± 1.5	14.9	4.8	36.2
	2-H	11.5 ± 0.5	−11.7 ± 1.7	14.6	8.1	
	2-F	10.9 ± 1.2	−12.9 ± 4.2	14.4	12	
$C_5H_{10}O$ [c]	4,5-Me	13.9 ± 0.8	−8.8 ± 2.4	16.2	0.41	36.6
	2-H	13.9 ± 0.6	−8.9 ± 1.7	16.3	0.36	
	2-F	13.9 ± 1.3	−8.8 ± 4.0	16.2	0.42	
C_4D_8O [d]	4,5-Me	15.4 ± 0.8	−6.3 ± 2.3	17.1	0.086	37.4
	2-H	16.2 ± 0.6	−3.9 ± 1.9	17.3	0.062	
	2-F	16.5 ± 0.4	−2.9 ± 1.3	17.3	0.056	
$[(CH_3)_3C]_2CO$	2-H	14.3 ± 0.9	−4.9 ± 2.9	15.7	1.2	37.4
	2-F	13.1 ± 1.9	−8.6 ± 6.0	15.4	1.9	
$CD_3COC(CH_3)_3$	4,5-Me	17.3 ± 0.7	−2.1 ± 2.1	17.9	0.018	39.0
	2-H	16.8 ± 0.7	−2.8 ± 1.9	17.5	0.037	
	2-F	17.0 ± 0.7	−2.2 ± 2.0	17.6	0.032	
$CDCl_3$	4,5-Me	7.1 ± 0.2	−18.7 ± 0.9	12.2	800	39.1
	2-H	7.8 ± 0.4	−16.5 ± 1.9	12.2	700	
	2-F	7.9 ± 1.0	−15.9 ± 4.2	12.2	770	
$(CDCl_2)_2$	4,5-Me	7.5 ± 0.4	−19.3 ± 1.5	12.8	270	39.4
	2-H	8.2 ± 0.4	−17.2 ± 1.7	12.9	230	
	2-F	7.9 ± 0.3	−18.4 ± 1.1	12.8	230	
$CH_3CH_2NO_2$	4,5-Me	8.4 ± 0.6	−12.0 ± 2.6	11.7	2100	43.6
	2-H	7.7 ± 1.2	−14.9 ± 5.4	11.7	1900	
	2-F	8.1 ± 0.6	−13.6 ± 2.6	11.8	1700	

a) 1 cal = 4.184 J. b) Toluene-d_8. c) Tetrahydropyran. d) Tetrahydrofuran-d_8.

and ^{19}F at the 2-position and the exchange between methyl-protons *cis* to the fluorine atom and those *trans* to the fluorine.

The loss of coupling between ^{1}H and ^{19}F at position 2 should give kinetic data concerning the formation of the CIP. The discussion supporting this assumption is given below. According to the theory of collapse of spin–spin coupling,[16] the spin of a nucleus should be relaxed by 1) fields due to the magnetic moments of other nuclei, 2) fields due to the spins of unpaired electrons, or 3) fields due to the variable electronic screening of the static field. The most-often encountered is the case of exchange of an NMR active nucleus between molecular species. Line broadening of ethanol[17] and exchange of protons between ammonium ions in water[18] are examples of this sort. Such phenomena are observed when the concentrations of the solute is rather high. Our observation of collapse of coupling of the ammonium proton in ammonium halides and in sulfonates in organic solvents[19] is based on relaxation of nuclear spins due to quadrupole moments and/or spins of unpaired electrons, because there is a proton-accepting anion in the system and the concentration was low enough to exclude intermolecular exchange.[20] On ionization of compound **1**, a carbocation and a fluoride ion are formed. Then the relaxation of the spin due to unpaired electrons sets in. We assume this because fluoride anion carries four pairs of electrons, whereas there is neither cation-accepting anion nor anion-accepting cation in the system and the concentration is low enough to exclude the possibility of intermolecular exchange.[5,21]

On the other hand, the sites of the methyl groups are not exchanged as far as the ion pair remains in contact, because tumbling of the cation independent from the anion is impossible. If solvent molecule(s) intervene(s) to CIP to form SSIP, then the possibility of independent tumbling of the cation from the anion arises and this independent tumbling causes averaging the signals due to methyl groups through topomerization between SSIP and SSIP′ in Scheme 2. Thus the signals due to the methyl protons are the independent probe for formation of SSIP. If the solvent intervention is the rate-limiting step as was the case of organolithium compounds,[7] the rates obtained from the methyl signals should be smaller than those obtained from the loss of coupling between the ^{1}H and the ^{19}F nuclei.

Because we observe the same phenomenon, loss of coupling between ^{1}H and ^{19}F, which gives rates of ionization to CIP, the data obtained from loss of coupling of ^{1}H and ^{19}F signals should be identical. Therefore, comparison of the data indicates reliability of the data obtained. As can be seen in Table 1, they are in very good agreement, thus showing that the data are reliable.

It seems that there is no regularity in the kinetic data, at the first glance of Table 1. Because there are various factors which govern the results, it will be more convenient to discuss by dividing the data into clusters. We will discuss the results obtained for chlorinated hydrocarbons first and then the toluene solution, the nitroethane solution being discussed after these examples. Finally we will proceed to the problems observed for ether and ketone solutions.

Chloroalkanes, Toluene, and Nitroethane. When one compares the data of chlorinated hydrocarbons, one notices that the rates of dissociation in chloroform are the highest. This must be attributed to the hydrogen-bond forming ability of chloroform,[22] which should stabilize the transition state for ionization where an incipient anion is formed. 1,1,2,2-Tetrachloroethane should have the similar property, although weaker than chloroform, to facilitate ionization of the substrate. Thus relatively large rate constants for ionization are observed for these two solvents.

The results for 1,1,1-trichloroethane solution may be interpreted on the same basis. The solvent molecule is not capable of forming a hydrogen-bond and thus the rates of ionization are the smallest among the chlorinated hydrocarbons examined. The rate constants obtained from topomerization, which are derived by the lineshape analysis of the methyl-proton signals, seem to be a little off from the other two for this solvent. However, the relatively large errors involved in obtaining the rate data from methyl-proton signals preclude any meaningful discussion of the data. The large errors are derived by the presence of impurities which give rise to signals due to various methyl groups. We tentatively conclude that the rates are the same within the error limits. Although this solvent might be taken as a bulky solvent, its bulkiness is not very far from that of 1,1,2,2-tetrachloroethane. Therefore, the dimensiosolvatic effects will be small, if any. The large negative entropy of activation for chloroform and 1,1,2,2-tetrachloroethane solutions compared to that in 1,1,1-trichloroethane implies that hydrogen-bond formation in the transition states in the former two solvents is important, whereas that is less important in 1,1,1-trichloroethane.

Comparing the results obtained for toluene solutions with those for chlorinated hydrocarbon solutions, one is surprised to find that the dissociation in toluene is faster than that in 1,1,1-trichloroethane, irrespective of the fact that the $E_T(30)$ value of the former is smaller than that of the latter. We wish to attribute these apparently anomalous results to the solvation in the original state. One often discusses the rates of reactions by referring to the energy of the transition state only, but actually the rates of the reaction are affected by the energy difference between the original state and the transition state. Because toluene solvates poorly a very polar substrate such as compound **1**, the energy of the original state in toluene solution must be higher than that in 1,1,1-trichloroethane, which is more polar than toluene. The large negative entropy of activation in toluene, with respect to that for the 1,1,1-trichloroethane solution, can be cited as support for such an interpretation. The solvation due to toluene is loose in the original state, whereas that in the transition state restricts freedom of translation of solvent molecules more effectively because partial charge separation takes place in the transition state.

The ionic dissociation of **1** in nitroethane is very fast. The enthalpy of activation is comparable with those in chloroform and 1,1,2,2-tetrachloroethane solutions. Therefore the small free energy for ionization for nitroethane solutions is derived by relatively small negative entropy of activation. Probably,

the solvation in the original state in nitroethane is stronger than in chlorinated hydrocarbons because the substrate is very polar, rendering the restriction of freedom of motion of solvent molecules less important in the transition state. The data for this solution may also involve the effects of hydrogen-bond formation as discussed below, because the nitro group is known to behave as an acceptor in hydrogen-bond formation.[23]

Hydrogen-Bond Effects. We were surprised to find that the dissociation of the substrate was the slowest in tetrahydrofuran, irrespective of its more polar nature than toluene. The dissociation in toluene is about 500 times faster than in tetrahydrofuran. In order to see the generality of the phenomenon, we measured the rates of dissociation of **1** in tetrahydropyran. The rates for the tetrahydropyran solutions were a little enhanced with respect to those for tetrahydrofuran solutions, but were still smaller than those in toluene by a factor of ca. 100.

We wish to attribute such results to the stabilization of the original state by forming a hydrogen bond between the solute and the solvent, where the solvent molecule is the acceptor of the hydrogen bond and the substrate is the donor. By formation of such a hydrogen bond, the original state is more stabilized in these solvents than in toluene. Evidence follows.

Trisubstituted methanes, that carry electronegative substituents such as chloroform,[22] trifluoromethane,[24] and trimethoxymethane,[25] are known to form hydrogen bonds with appropriate hydrogen acceptors. These known facts suggest that there will be a hydrogen bond between fluorodimethoxymethane, a model compound for compound **1**, and electron donors. This interpretation is also supported by the relatively small negative entropy of activation for these solutions. If the translation of the solvent molecules in the original state is limited, the effects of limiting the freedom of solvent molecules in the transition state become relatively small, rendering the entropy of activation relatively small negative. Furthermore, the relatively large enthalpy of activation for ether solutions supports stabilization of the original state.

The reason why the dissociation in tetrahydropyran is faster than that in tetrahydrofuran becomes understandable when one sees the results for the ketone solutions. Ketones used as solvents exhibited the same tendencies with ethers: Slow dissociation, large enthalpy of activation, and relatively small negative entropy of activation. We attribute the relatively large rates of dissociation in di-*t*-butyl ketone with respect to those in *t*-butyl methyl ketone to the steric effects on hydrogen-bond formation. Because the C(2)H hydrogen, which forms the hydrogen bond, is attached to a bulky group, the hydrogen-bond formation is subject to the steric effects. Thus in di-*t*-butyl ketone, the hydrogen bond must be weaker than that in *t*-butyl methyl ketone. This is again reflected in enthalpies of activation and entropies of activation.

The relatively large rates of dissociation in tetrahydropyran compared with those in tetrahydrofuran may also be attributed to the steric effects on formation of the hydrogen bond. Tetrahydropyran is known to be puckered more strongly[26] than tetrahydrofuran.[27] This will necessarily cause stronger steric effects on the hydrogen-bond formation in tetrahydropyran than on that in tetrahydrofuran. The enthalpy of activation and the entropy of activation, though within error limits, show the tendency that tetrahydropyran gives larger values and more negative values than tetrahydrofuran, respectively. That is, the hydrogen bond in the original state is less effective in tetrahydropyran than in tetrahydrofuran.

Both infrared spectra[28] and the pK_{BH^+} measurements[29] indicate that ethers are more basic than ketones. The relatively strong basicity of ethers with respect to ketones suggests that the rates of dissociation of **1** should be smaller in ethers than in ketones when the polarity and the bulkiness of the solvent molecules are nearly the same. This situation is manifested in one case (the rates of dissociation are larger in di-*t*-butyl ketone than in ethers) but contradictory results (the rates are smaller in *t*-butyl methyl ketone than ethers) are obtained in another case. Discussion on these points follow. We postulate that in di-*t*-butyl ketone the steric hindrance to the hydrogen-bond formation is important and in *t*-butyl methyl ketone the dimensiosolvatic effects as well as steric effects on hydrogen-bond formation are important.

Dimensiosolvatic Effects. We believe dimensiosolvatic effects are operative in these cases as well as for the other halogen compounds.[5] That is, the bulkiness of the solvent molecules decelerates the ionization of compound **1**. However, differing from the simple organic halides,[5] the present substrate is capable of forming a hydrogen bond with the solvent molecules. We must take these into consideration in interpreting the results.

Apparently, bulky ketones give much smaller rates of dissociation than expected from the consideration of polarity only (compare data for tetrahydrofuran solutions with those for di-*t*-butyl ketone solutions). Therefore, the general tendency that the bulky solvents retard ionic dissociation is applicable in this case as well. The apparently very small rates of dissociation in *t*-butyl methyl ketone should include this effect also. However, the effects of hydrogen-bond formation are also important, while the effects are subject to the steric effects. Ketone oxygens are more exposed than ether oxygens, when two alkyl groups are the same, and thus the steric effects are more important in ethers than in ketones. When the hydrogen-bond effects are more important than the dimensiosolvatic effects, the rates of dissociation are diminished, and vice versa. The present situation is complicated by the fact that the steric effects affect both the original state by hydrogen bond formation and the transition state by poor solvation.

Possible Dimensiosolvatic Effects on Solvent-Intervention. As discussed earlier, compound **1** carries two independent probes for formation of CIP and SSIP. If a bulky solvent gives rise to a large barrier to solvent intervention to CIP, this process must be observed independently. We have checked various solvents in this direction, but so far we have not been successful in finding such a solvent.

Unfortunately, there are signals due to impurities in the range of the chemical shifts where the signals due to the methyl protons appear, thus making the data for topomerization less reliable than those obtained from the loss of coupling between the fluorine nucleus and the proton at the 2-position. We have wished to find an example where the rate-limiting step is the formation of SSIP by using di-*t*-butyl ketone. However, the signal due to the *t*-butyl protons masked the signals due to the methyl protons in **1** completely to make observation of the lineshape change impossible. Therefore, though there are a few cases where the rates of topomerization are smaller than those of CIP formations, we wish to summarize that the examples examined in this paper all show identical rates for the CIP formation with the SSIP formation. The rate-limiting step must be the formation of CIP, because the kinetic parameters are similar with other cases of ionization of organic halides[5,21] and an ester.[30]

Experimental

^{1}H and ^{13}C NMR spectra were measured on a Varian Gemini-300 spectrometer operating at 300.1 and 75.0 MHz, respectively. Dynamic ^{1}H and ^{19}F NMR data were collected on a Bruker AMX-R400 spectrometer, operating at 400.1 and 375.0 MHz, respectively. Mass spectra were recorded on a JEOL MStation JMS-700 Spectrometer.

Solvents and Reagents. 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. Cesium fluoride was dried under vacuum at 180 °C for over 6 h.

2-Fluoro-4,4,5,5-tetramethyl-1,3-dioxolane (1). A mixture of 2.00 g (10.6 mmol) of 4,4,5,5-tetramethyl-1,3-dioxolan-2-yl acetate (**2**)[9] and 2.00 g (13.2 mmol) of thoroughly-dried cesium fluoride was stirred at room temperature for a few minutes. Then the flask was immersed into a bath preheated at 65—70 °C to distill the product rapidly. The volatile material was trapped at −78 °C under 0.6 mmHg (1 mmHg = 133.322 Pa) pressure for 1.5 h. The product thus obtained was practically pure, the main contaminants being unreacted **2** and 2-fluoro-1,1,2-trimethylpropyl formate, which amounted to less than 10 per cent. The following ^{1}H NMR spectrum was observed at −63 °C ($CDCl_3$): δ = 1.22 (6H, s), 1.35 (6H, s), 6.20 (1H, d, J = 101.3 Hz). ^{19}F NMR ($CDCl_3$ at −63 °C/Ref. C_6F_6) δ = −63.5 (1F, d, J = 101.7 Hz). ^{13}C NMR ($CDCl_3$ at −65 °C) δ = 23.0, 84.5, 116.5 (1C, d, J = 249.5 Hz). The carbon signal due to *cis* and *trans* methyls to the fluoro group fortuitously overlapped in the spectrum. LRMS(EI) *m/z* 148 (M^+); HRMS Found: *m/z* 148.0899. Calcd for $C_7H_{13}FO_2$: M, 148.0907.

Dynamic NMR. The ^{1}H NMR spectra were obtained with an external D-lock, acetone-d_6 or toluene-d_8, which was sealed in a capillary. NMR tubes (Wilmad) which were equipped with an adapter (Shigemi) 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 six temperatures at least.

The lineshapes were simulated with use of the DNMR3K program[31] and the best fit spectra were determined by visual fitting. The lineshapes were analyzed by assuming the exchange of the uncoupled AB and BA system for the methyl protons. Similar treatment was made for the H–F coupled signals of the 2-methine proton and those of the fluorine nucleus. The chemical shift differences of the methyl signals 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. Extrapolated chemical shift differences by these lines were used for the temperature range where lineshapes changed. The ^{19}F–^{1}H coupling constant was constant throughout the temperature range examined, though it exhibited slight solvent dependence. T_2's were obtained from lines which did not exchange in the temperature range and slightly adjusted to get the best fit, when necessary. The equations that represent the drift of chemical shift changes together with T_2's are compiled in Table 2 for compound **1**. The coupling constants (J_{H-F}) and T_2's of the methine proton and those of the fluorine are shown in Table 3. Rate constants at various temperatures thus obtained are shown in Table 4. These rate constants were put into the Eyring equation and the kinetic parameters shown in Table 1 were obtained. Correlation coefficients in the statistical treatment were better than 0.995 for all the data presented in the Tables.

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Table 2. Temperature Dependence of Chemical Shift Differences and T_2's of Diastereotopic Methyl Protons in 2-Fluoro-4,4,5,5-tetramethyl-1,3-dioxolane at 0.20 mol dm^{-3} Concentration

Solvent	$\Delta\nu_{AB}$/Hz[a]	T_2/s
$CDCl_3$	$-0.441t+24.8$	0.040
CH_3CCl_3	$-0.058t+51.4$	0.085
$(CDCl_2)_2$	$-0.022t+49.5$	0.040
C_7D_8[b]	$-0.395t+90.4$	0.060
$CH_3CH_2NO_2$	$-0.025t+43.5$	0.045
C_4D_8O[c]	$-0.120t+55.6$	0.100
$C_5H_{10}O$[d]	$-0.130t+55.3$	0.045
$CD_3COC(CH_3)_3$	$-0.011t+49.0$	0.120

a) t is expressed in °C. b) Toluene-d_8. c) Tetrahydrofuran-d_8. d) Tetrahydropyran.

Table 3. Coupling Constants and T_2's of the Methine Proton and Those of the Fluorine in 2-Fluoro-4,4,5,5-tetramethyl-1,3-dioxolane at 0.20 mol dm^{-3} Concentration

	^{1}H		^{19}F	
Solvent	J_{H-F}/Hz	T_2/s	J_{F-H}/Hz	T_2/s
$CDCl_3$	101.3	0.060	102.0	0.035
CH_3CCl_3	100.1	0.060	100.0	0.030
$(CDCl_2)_2$	101.1	0.055	102.0	0.035
C_7D_8[a]	100.6	0.045	100.0	0.040
$CH_3CH_2NO_2$	101.5	0.050	102.0	0.040
C_4D_8O[b]	100.0	0.095	100.0	0.100
$C_5H_{10}O$[c]	99.7	0.045	100.0	0.035
$CD_3COC(CH_3)_3$	100.1	0.100	100.0	0.070
$[(CH_3)_3C]_2CO$	99.8	0.050	100.0	0.040

a) Toluene-d_8. b) Tetrahydrofuran-d_8. c) Tetrahydropyran.

Table 4. Rate Constants of Dissociation of 2-Fluoro-4,4,5,5-tetramethyl-1,3-dioxolane at 0.20 mol dm^{-3} Concentration

Solvent	Probe	k/s^{-1} (temp/°C)
$CDCl_3$	4,5-Me	20.0 (−58.8), 27.0 (−54.5), 43.0 (−50.2), 57.0 (−45.9), 75.0 (−41.5), 100 (−37.2), 140 (−32.9), 180 (−28.5), 240 (−24.2), 300 (−19.9), 440 (−14.5)
	2-H	12.0 (−58.8), 18.0 (−54.5), 27.0 (−50.2), 59.0 (−41.5), 80.0 (−37.2), 110 (−32.9), 140 (−28.5), 180 (−24.2), 230 (−19.9)
	2-F	18.0 (−54.5), 27.0 (−50.2), 40.0 (−45.9), 60.0 (−41.5), 90.0 (−37.2), 120 (−32.9), 150 (−28.5), 170 (−24.2)
CH_3CCl_3	4,5-Me	7.0 (0.5), 10.0 (5.7), 15.0 (10.8), 22.0 (16.0), 34.0 (21.2), 52.0 (26.3), 75.0 (31.5), 110 (36.7), 150 (41.8)
	2-H	7.0 (−4.7), 11.0 (0.5), 16.0 (5.7), 24.0 (10.8), 36.0 (16.0), 54.0 (21.2) 70.0 (26.3)
	2-F	10.0 (−4.7), 16.0 (0.5), 25.0 (5.7), 36.0 (10.8), 50.0 (16.0), 66.0 (21.2)
$(CDCl_2)_2$	4,5-Me	24.0 (−39.9), 34.0 (−35.8), 47.0 (−31.6), 63.0 (−27.5), 80.0 (−23.4), 100 (−19.3), 130 (−15.1), 180 (−10.0)
	2-H	12.0 (−44.0), 17.0 (−39.9), 25.0 (−35.8), 34.0 (−31.6), 47.0 (−27.5), 60.0 (−23.4), 80.0 (−19.3), 100 (−15.1)
	2-F	14.0 (−44.0), 20.0 (−39.9), 28.0 (−35.8), 36.0 (−31.6), 50.0 (−27.5), 67.0 (−23.4), 85.0 (−19.3), 110 (−15.1)
C_7D_8[a)]	4,5-Me	12.0 (−16.4), 16.0 (−12.1), 22.0 (−7.7), 30.0 (−3.4), 40.0 (0.9), 52.0 (5.3), 65.0 (9.6)
	2-H	18.0 (−16.4), 24.0 (−12.1), 36.0 (−7.7), 50.0 (−3.4), 63.0 (0.9), 78.0 (5.3), 95.0 (9.6)
	2-F	18.0 (−16.4), 26.0 (−12.1), 36.0 (−7.7), 50.0 (−3.4), 64.0 (0.9), 80.0 (5.3), 98.0 (9.6)
$CH_3CH_2NO_2$	4,5-Me	12.0 (−66.7), 22.0 (−61.5), 36.0 (−56.3), 50.0 (−52.2), 70.0 (−48.1), 100 (−43.9), 160 (−39.8)
	2-H	16.0 (−66.7), 32.0 (−61.5), 48.0 (−56.3), 68.0 (−52.2), 90.0 (−48.1), 120 (−43.9)
	2-F	13.0 (−66.7), 32.0 (−56.3), 50.0 (−52.2), 74.0 (−48.1),102 (−43.9), 136 (−39.8)
C_4D_8O[b)]	4,5-Me1	18.0 (52.8), 19.0 (57.2), 27.0 (61.5), 36.0 (65.8), 50.0 (70.1), 64.0 (74.5)
	2-H	6.0 (43.1), 9.0 (48.5), 13.0 (52.8), 18.0 (57.2), 27.0 (61.5), 36.0 (65.8), 50.0 (70.1), 64.0 (74.5)
	2-F	6.0 (43.1), 9.0 (48.5), 13.0 (52.8), 19.0 (57.2), 26.0 (61.5), 36.0 (65.8), 70.0 (74.5)
$C_5H_{10}O$[c)]	4,5-Me	24.0 (45.9), 34.0 (50.0), 47.0 (54.1), 64.0 (58.2), 80 (62.4), 100 (66.5), 124 (70.6), 160 (74.7), 240 (79.9)
	2-H	16.0 (41.8), 22.0 (45.9), 30.0 (50.0), 42.0 (54.1), 56.0 (58.2), 74.0 (62.4), 90.0 (66.5), 120 (70.6), 145 (74.7), 200 (79.9)
	2-F	18.0 (41.8), 24.0 (45.9), 35.0 (50.0), 48.0 (54.1), 66.0 (58.2), 85 (62.4), 110 (66.5), 130 (70.6), 150 (74.7)
$CD_3COC(CH_3)_3$	4,5-Me	10.0 (59.9), 14.0 (64.1), 20.0 (68.3), 28.0 (72.5), 37.0 (76.7), 50.0 (80.9)
	2-H	16.0 (59.9), 24.0 (64.1), 33.0 (68.3), 43.0 (72.5), 60.0 (76.7), 80.0 (80.9), 100 (84.0), 120 (87.1)
	2-F	10.0 (54.7), 16.0 (59.9), 22.0 (64.1), 30.0 (68.3), 40.0 (72.5), 55.0 (76.7), 78.0 (80.9)
$[(CH_3)_3C]_2CO$	2-H	38.0 (35.6), 70.0 (42.5), 100 (47.5), 130 (51.4), 170 (55.3), 220 (59.3)
	2-F	42.0 (35.6), 78.0 (42.5), 108 (47.5), 142 (51.4), 170 (55.3), 210 (59.3)

a) Toluene-d_8. b) Tetrahydrofuran-d_8. c) Tetrahydropyran.

References

1) For Part V of this series, see Ref. 6b.

2) M. Ōki, H. Ikeda, and S. Toyota, *Tetrahedron Lett.*, **39**, 7729 (1998).

3) M. Ōki, H. Ikeda, K. Kodama, and S. Toyota, *Bull. Chem. Soc. Jpn.*, **70**, 2791 (1997).

4) M. Ōki, H. Ikeda, and S. Toyota, *Bull. Chem. Soc. Jpn.*, **71**, 749 (1998).

5) M. Ōki, H. Ikeda, H. Miyake, H. Mishima, and S. Toyota, *Bull. Chem. Soc. Jpn.*, **71**, 915 (1998).

6) a) M. Ōki, M. Matsusaka, H. Mishima, and S. Toyota, *Chem. Lett.*, **1993**, 1249; b) M. Ōki, T. Ozaki, H. Ikeda, M. Matsusaka, H. Mishima, M. Koumura, and S. Toyota, *Zh. Org. Khim.*, **34**, 1608 (1998).

7) B. Capon and D. McL. A. Grieve, *J. Chem. Soc., Perkin Trans. 2*, **1980**, 300.

8) J. W. Scheeren, *Tetrahedron Lett.*, **1968**, 5613; J. W. Scheeren, R. J. F. M. Staps, and R. J. F. Nivard, *Recl. Trav. Chim. Pays-Bas*, **92**, 11 (1973).

9) J. W. Scheeren, A. P. M. Van der Veek, and W. Stevens, *Recl. Trav. Chim. Pays-Bas*, **88**, 195 (1969).

10) H. L. Goering, R. G. Briody, and J. F. Levy, *J. Am. Chem. Soc.*, **85**, 3059 (1963); H. L. Goering and J. F. Levy, *J. Am. Chem. Soc.*, **86**, 120 (1964).

11) C. Reichardt, "Solvents and Solvent Effects in Organic Chemistry," VCH, Weinheim (1988).

12) T. Morita and M. Ōki, *Bull. Chem. Soc. Jpn.*, **59**, 3605 (1986).

13) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Am. Chem. Soc.*, **78**, 328 (1956).

14) A referee argues that the stage where independent tumbling of the ion pairs takes place is not clear. We assume, by definition, that CIP means that the independent tumbling of each of the component ions cannot take place in it. Probably, intervention of only one molecule of a solvent is not sufficient to cause the independent tumbling of the ion pairs, as the case of lithium fluorenide derivatives, which showed that the independent tumbling of the ions did not take place in SSIP which is observed by UV spectra.[3)] The number of intervening solvent molecules which are necessary to cause independent tumbling of the ions in the ion-pairs is not known at the present time.

15) W. L. Jorgensen, J. K. Buckner, S. E. Huston, and P. J. Rossky, *J. Am. Chem. Soc.*, **109**, 1891 (1987); J. K. Buckner and W. L. Jorgensen, *J. Am. Chem. Soc.*, **111**, 2507 (1989); W. L. Jorgensen, *Acc. Chem. Res.*, **22**, 184 (1989).

16) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York (1959), p. 199.

17) J. T. Arnold, *Phys. Rev.*, **102**, 136 (1956).

18) E. Grunwald, A. Loewenstein, and S. Meiboom, *J. Chem. Phys.*, **27**, 630 (1957).

19) T. Morita and M. Ōki, *Bull. Chem. Soc. Jpn.*, **61**, 1185 (1988).

20) M. Ōki, M. Ohira, Y. Yoshioka, T. Morita, H. Kihara, and N. Nakamura, *Bull. Chem. Soc. Jpn.*, **57**, 2224 (1984).

21) A. Shimizu, Y. Sakamaki, K. Azuma, H. Kihara, N. Nakamura, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **54**, 2774 (1981).

22) A. Allerhand and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **85**, 1715 (1963); E. G. Paterson and D. M. Cameron, *Can. J. Chem.*, **41**, 198 (1963).

23) T. Urbanski, "On Hydrogen Bonds between Nitro and Hydroxy or Amino Groups," in "Hydrogen Bonding," ed by D. Hadzi, Pergamon Press, London (1959), p. 143.

24) C. J. Creswell and A. L. Alfred, *J. Am. Chem. Soc.*, **85**, 1723 (1963); N. S. Golubev, *Tezisy Dokl. Permsk. Obl. Nauchno-Tekh. Konf. Spektrosk., 15th 1975*, **1976**, 32; *Chem. Abstr.*, **89**, 33515n (1978); G. T. Fraser, F. J. Lovas, R. D. Suenram, D. D. Nelson, Jr., and J. Kempler, *J. Chem. Phys.*, **84**, 5893 (1988); See also: M. L. Chabinyc and J. I. Brauman, *J. Am. Chem. Soc.*, **120**, 10863 (1998).

25) R. Ehama, M. Tsushima, T. Yuzuri, H. Suezawa, K. Sakakibara, and M. Hirota, *Bull. Chem. Soc. Jpn.*, **66**, 814 (1993).

26) R. V. Muralidhara and R. Kewley, *Can. J. Chem.*, **47**, 1289 (1969); H. E. Breed, G. Gundersen, and R. Seip, *Acta Chem. Scand., Ser. A*, **A33**, 225 (1979).

27) A. Almenningen, H. M. Seip, and T. Williadsen, *Acta Chem. Scand.*, **23**, 2748 (1969); K. S. R. Murty, *Proc. Int. Conf. Spectrosc., 1st, Bombay, 1967*, **2**, 396; *Chem. Abstr.*, **69**, 2439p (1968); E. Díez, A. L. Esteban, F. J. Bermejo, and M. Rico, *J. Phys. Chem.*, **84**, 3191 (1980).

28) S. Searles and M. Tamres, *J. Am. Chem. Soc.*, **73**, 3704 (1951); M. Tamres and S. Searles, Jr., *J. Am. Chem. Soc.*, **81**, 2100 (1959).

29) A. Bagno and G. Scorrano, *J. Am. Chem. Soc.*, **110**, 4577 (1988). See also: A. Bagno, V. Lucchini, and G. Scorrano, *J. Phys. Chem.*, **95**, 345 (1991).

30) M. Ōki and S. Ito, *Chem. Lett.*, **1984**, 985.

31) DNMR3 program[32)] written for the use for NEC 98 series personal computers by Prof. H. Kihara, Hyogo University of Teacher Education.

32) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).