Solvent Effects on the Rate of Heterolysis of *t*-Butyl Chloride, Bromide, Iodide, and 2,4-Dinitrophenolate

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Rates of heterolytic decompositions of *t*-butyl chloride, bromide, iodide, and 2,4-dinitrophenolate have been measured by an NMR method in eight deuterated or undeuterated polar solvents; methanol-d_4, ethanol-d_6, dimethyl-d_6 sulfoxide, *N*,*N*-dimethylformamide-d_7, acetonitrile-d_3, pyridine, nitrobenzene, and acetone-d_6. The observed solvent effect is discussed on the basis of cation and anion solvation. With *t*-butyl halides, the anion solvation due to hydrogen bonding by protic solvents drastically decreases on increasing the radius of halide ions, and thus the differential solvation transferred from anion-solvating methanol to cation-solvating dimethyl sulfoxide is dramatically reversed on going from the chloride to the iodide ($k_{\mathrm{Me_2SO}\text{-}d_6}/k_{\mathrm{methanol}\text{-}d_4}$ at 60 °C: *t*-BuCl, 5×10^{-2}; *t*-BuBr, 6×10^{-1}; *t*-BuI, 7). The 2,4-dinitrophenolate behaves like the iodide. Complicated products are obtained in the decomposition of *t*-butyl bromide in dimethyl sulfoxide; however, a mechanism involving a bimolecular decomposition process of the bromide is ruled out. During the decomposition of *t*-butyl iodide in dimethyl sulfoxide, an intermediate salt *t*-butoxydimethylsulfonium iodide has been detected. The salt decomposes to isobutene, but the process is much slower than the heterolytic decomposition of *t*-butyl iodide itself at ambient temperature.

Heterolysis reactions of uncharged compounds provide useful information about solvation of ion pair-like species. Above all, *t*-butyl halides are among the best substrates for probing the difference in solvation on changing the size of leaving group anions, since negative charge is uniformly distributed in spherical halide ions and the size of the ions Cl^-, Br^-, and I^- is significantly different from one another. We have previously pointed out that the relative rate of a reaction in strongly anion-solvating methanol and that in strongly cation-solvating dimethyl sulfoxide (DMSO) can serve as a useful measure for examining the hydrogen bonding ability or charge-dispersed nature of leaving group anions in the decomposition of a series of substrates which possess a common alkyl group.[1)]

Solvolysis reactions (S_N1-E1) of *t*-butyl chloride have been studied kinetically in protic[2—6)] and aprotic[7)] solvents. The kinetic data in protic solvents for *t*-butyl bromide and iodide are also available.[2,6,8)] However, the data in aprotic solvents are very rare:[9)] Especially there is none in DMSO. That is to say, we know less about the effect of solvation than we should.

As has been reported,[1)] an NMR method is convenient for following a first-order rate process occurring at a moderate rate, because it tells how a reaction goes on by showing successive changes in the quantity of a substrate, reaction products, and occasionally reaction intermediates. These merits in rate measurement enabled us to determine the rate of decomposition of *t*-butyl halides and 2,4-dinitrophenolate in various protic and aprotic solvents. Dependence of the rates on both leaving group anions and solvents revealed important features of the heterolysis of these *t*-butyl derivatives. During the investigation, we observed the curious behavior of *t*-butyl bromide and iodide in DMSO. Mechanistic considerations of these reactions will be described as well.

Experimental

Material. *t*-Butyl halides and chemicals used as solvents were obtained commercially. *t*-Butyl 2,4-dinitrophenolate, 1,2-dibromo-2-methylpropane, and 1-bromo-2-methyl-2-propanol were prepared according to the literature procedure.

Product Analyses. The ^{1}H NMR and ^{13}C NMR spectra of decomposition mixtures of *t*-butyl bromide in DMSO-d_6 at 60 °C were obtained on a Bruker AM-500 spectrometer operating at 500 MHz in the FT mode. The formation of 1-bromo-2-methyl-2-propanol, 1,2-dibromo-2-methylpropane, and 2-methyl-2-propanol was confirmed by comparing the spectra with those of the authentic samples and finally with the spectra of the reaction mixtures involving the authentic samples. The product yields were determined by integrated intensities of the product proton signals as compared with the intensity of the *t*-butyl proton signal in the substrate before heating.

Kinetic Experiments. Rates of decompositions of *t*-butyl chloride, bromide, iodide, and 2,4-dinitrophenolate were determined by monitoring the decrease in the intensity of the *t*-butyl proton signal of a substrate relative to that of the methyl signal of anisole added as an internal reference. Eight protic and aprotic solvents, i.e., methanol-d_4, ethanol-d_6, DMSO-d_6, dimethylformamide-d_7 (DMF-d_7), acetonitrile-d_3, pyridine, nitrobenzene, and acetone-d_6, were chosen as representative polar solvents. Initial concentrations were about 0.08 M (1 M=1 mol dm^{-3}). One and a half molar amounts of pyridine were added to solutions other than those in DMSO and DMF to avoid accelerating effect of acids produced. The ^{1}H NMR spectra were obtained on a Varian EM-390 spectrometer operating at 90 MHz in the CW mode. A sample solution in a sealed NMR tube was heated in a thermostated bath (±0.01 °C for temperatures below 100 °C and ±0.02 °C for those above 100 °C) and was subjected to NMR measurement at appropriate intervals. Generally excellent first-order rate constants were obtained for the data points up to more than 80% reaction. In some cases [*t*-BuCl in MeCN and in pyridine, *t*-BuBr in nitrobenzene, in pyridine, and in acetone, and *t*-BuOC$_6$H$_3$(NO$_2$)$_2$-2,4 in nitrobenzene], a slight acceleration was observed after about 50% reaction, so that data points showing a good correlation (R>0.9997) were used for calculation of rate constants.

With decomposition reactions of *t*-BuI and the intermediate salt *t*-BuOSMe$_2$$^+I^-$ in DMSO, the spectra were obtained at 500 MHz, in which samples were directly heated in the NMR probe at the temperature range from 26 to 56 °C, in which the constancy of temperature was confirmed by a comparison of temperatures before and after kinetic measurements. In the most rapid reaction so far measured, i.e., the decomposition of *t*-BuI at 48 °C, sixteen one-scan spectra obtained every eight seconds were used for kinetic analysis. These spectra were measured after a considerable amount of *t*-BuI had decomposed. Heterolysis reactions in DMSO so far examined have not shown any deviation from a first-order rate plot, as the reaction proceeds.

The rate constants determined in the present work, which are reliable to ±3%, are summarized in Table 1.

Results and Discussion

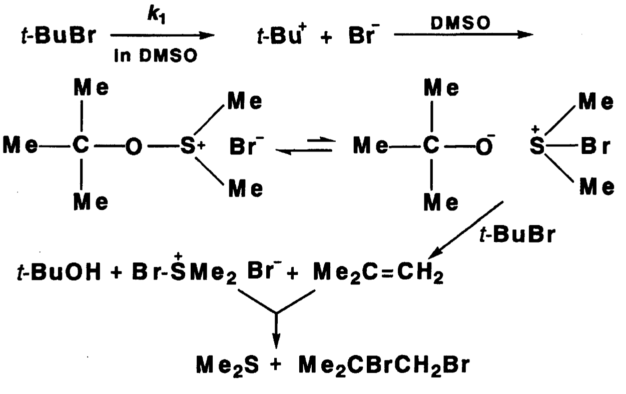
Reaction Products. Formation of reaction products was observed in ^{1}H NMR spectra during kinetic measurements. As has been evidenced, reactions of all the *t*-butyl derivatives in methanol and in ethanol gave the corresponding *t*-butyl ethers as the major product along with a small amount of isobutene. The major product in aprotic solvents was isobutene in most cases, and the reactions in pyridine gave in addition a small amount of *N*-*t*-butylpyridinium salts. Exceptional was the decomposition of *t*-butyl bromide in DMSO, which gave complicated products as will be shown below. The salt *t*-Bu-OSMe$_2$$^+I^-$ was detected by ^{1}H NMR as a long-lived intermediate during the decomposition of *t*-butyl iodide in DMSO. Hence we would like to discuss these two reactions in advance.

Mechanism of Decomposition of *t*-Butyl Bromide in DMSO. The decomposition of *t*-butyl bromide in DMSO at 60 °C gave isobutene in the yield of 9% only. This observation seemed quite strange, because *t*-butyl chloride, iodide, and 2,4-dinitrophenolate yielded isobutene almost quantitatively under the same conditions. Instead we detected, in addition, 1-bromo-2-methyl-2-propanol (75%), 1,2-dibromo-2-methylpropane (13%), and 2-methyl-2-propanol (3%). These compounds were identified by ^{1}H NMR and ^{13}C NMR spectroscopy using authentic samples.

The fact that *t*-butyl bromide in DMSO yields complicated products has already been reported by Marchelli and his co-workers.[10] However, they failed to detect the major product 1-bromo-2-methyl-2-propanol. The products they found were 1,2-dibromo-2-methylpropane, 2-methyl-2-propanol, and dimethyl sulfide. Although we made no effort to detect dimethyl sulfide in the reaction mixture, it is conceivable that the sulfide is formed in good yield, since they examined the decomposition of *t*-butyl bromide in dipropyl and dibutyl sulfoxides and found that the sulfoxides are reduced to the corresponding dialkyl sulfides in more than 90% yield. According to their mechanism (Scheme 1), *t*-butyl bromide undergoes heterolysis to give *t*-butoxydimethylsulfonium bromide, which again undergoes reversible heterolytic cleavage at the S–O bond to give bromodimethylsulfonium *t*-butoxide. The resulting *t*-butoxide ion acts as a base for the elimination of *t*-butyl bromide, and thus the reaction affords isobutene, 2-methyl-2-propanol, and bromodimethylsulfonium bromide, which then brominates isobutene to yield 1,2-dibromo-2-methylpropane and dimethyl sulfide. Olah and his co-workers supported the intermediacy of bromodimethylsulfonium bromide by the fact that the reaction mixture of *t*-butyl bromide in DMSO effects facile cleavage of dithioacetals.[11]

The mechanism proposed by Marchelli et al. involves a bimolecular process for the decomposition of *t*-butyl bromide in addition to a common unimolecular process. We confirmed that the decomposition at 60 °C obeys the excellent first-order rate law up to more than 80% reaction (k, 112×10^{-5} s^{-1}; R, 0.9997). The result is therefore in conflict with their mechanism. Further, we have found that the addition of two mols of pyridine per mol of *t*-butyl bromide results in quantitative formation of isobutene without change in rate (k, 111×10^{-5} s^{-1}; R, 0.9996).

We would like to propose a novel mechanism on the basis of our observation (Scheme 2). The kinetic result clearly indicates that *t*-butyl bromide decomposes solely via a rate-determining heterolytic process. It is most likely that the ion pair *t*-Bu$^+$Br$^-$ in DMSO forms *t*-butoxydimethylsulfonium bromide, which then quickly decomposes to isobutene and hydrogen bromide. The important feature of our mechanism is that alkoxydimethylsulfonium bromides oxidize hydrogen bromide existing in the form of dimethylhydroxysulfonium bromide to yield a bromination reagent bromodimethylsulfonium bromide. The oxidation of hydrogen bromide with *t*-butoxydimethylsulfonium bromide gives 2-

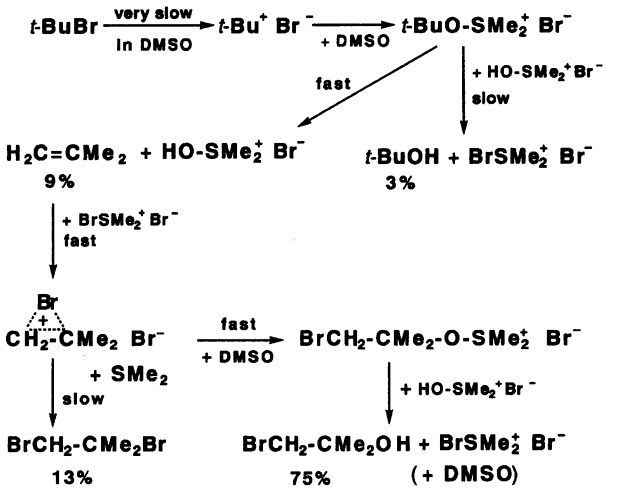


Scheme 1.

Table 1. Rate Constants of Decompositions of *t*-Butyl Halides and 2,4-Dinitrophenolate in Protic and Aprotic Solvents[a)]

Solvent	10^5k (s^{-1}) *t*-BuCl 120 °C	 *t*-BuBr 60 °C	 *t*-BuI 60 °C	 *t*-BuO$C_6H_3(NO_2)_2$-2,4 90 °C
Methanol-d_4	1260[b)] (1360)[f,j)] (1430)[g,j)]	195 (256)[f,j)] (242)[g,j)]	612[d)] (672)[f,j)] (753)[g,j)]	6.23
Ethanol-d_6	328 (429)[h,j)]	33.8	139	2.96
DMSO-d_6	74.6[c)] (43.7)[i,j)]	112	4200[e)]	26.6
DMF-d_7	12.3 (8.71)[i,j)]	12.9	643	8.30
MeCN-d_3	8.30 (6.92)[i,j)]	6.51	209	1.87
Pyridine	1.05	0.99	49.4	1.24
Nitrobenzene	1.56	0.89	29.0	0.817
Acetone-d_6	0.531 (0.60)[i,j)]	0.437	30.4	0.930

a) In parentheses are literature values in undeuterated solvents. b) Calculated from data at other temperatures: 10^5k (s^{-1}) 148 (95 °C), 79.4 (87 °C), 41.5 (80 °C), 21.5 (73 °C), 8.39 (65 °C), 5.10 (60 °C). $\Delta H^‡$, 23.1±1.1 kcal mol^{-1}; $\Delta S^‡$, −9±3 eu. c) Rates at other temperatures: 10^5k (s^{-1}) 2.07 (80 °C), 0.259 (60 °C). $\Delta H^‡$, 23.9±0.6 kcal mol^{-1}; $\Delta S^‡$, −12.7±1.7 eu. d) Rates at other temperatures: 10^5k (s^{-1}) 280 (52 °C), 1260 (68 °C). $\Delta H^‡$, 20.1±1.2 kcal mol^{-1}; $\Delta S^‡$, −8.0±3.7 eu. e) Calculated from data at other temperatures: see Table 2. f) From Ref. 2. g) From Ref. 6. h) From Ref. 3. i) From Ref. 7. j) Calculated from data at other temperatures.



Scheme 2.

methyl-2-propanol and the bromination reagent which attacks isobutene to give a bromonium bromide and dimethyl sulfide. Although a part of the bromonium ion yields 1,2-dibromo-2-methylpropane, the major process is formation of (2-bromo-1,1-dimethylethoxy)dimethylsulfonium bromide, which is reduced by hydrogen bromide to yield the major product 1-bromo-2-methyl-2-propanol and the bromination reagent that converts again isobutene to the bromonium ion. The presence of pyridine makes hydrogen bromide inactive so that the initially formed sulfonium bromide decomposes exclusively via a common process leading to isobutene.

It is noteworthy that the oxidation process appears in the decomposition of *t*-butyl bromide only. Considering the stability of halide ions in DMSO, the most reactive oxidant would be RO-$SMe_2^+Cl^-$. On the other hand, the salt HO-$SMe_2^+I^-$ would be oxidized most easily, as hydriodic acid serves as a good reductant. Those salts which are involved in the *t*-butyl bromide system therefore possess intermediate ability as an oxidant and a reductant.

Mechanism of Decomposition of *t*-Butyl Iodide in DMSO. The decomposition of *t*-butyl iodide in DMSO is so rapid that the half-life is about six minutes at room temperature. During NMR measurements in DMSO-d_6, we detected the intermediate *t*-butoxydimethylsulfonium iodide that is much more stable than *t*-butyl iodide itself. Figure 1 shows spectral change with the lapse of time. Chart 1 is a spectrum of the starting point measured at 26 °C, which already shows the presence of a certain amount of the sulfonium iodide produced during preparation of the solution. After six minutes, a half amount of *t*-butyl iodide disappears and instead the sulfonium iodide accumulates along with a small amount of isobutene (Chart 2). After thirty minutes, only a trace amount of *t*-butyl iodide is alive and the major species is the sulfonium iodide at this point (Chart 3). Chart 4 is a spectrum after heating the reaction mixture in Chart 3 at 55 °C for ten minutes, where none of the sulfonium iodide is alive and isobutene is the sole product while a very small peak due to an unidentified species appears at higher field.

The result obviously indicates that the decomposition proceeds simply via a common process.

$$t\text{-BuI} \rightarrow t\text{-Bu}^+\text{I}^- \ (+\text{Me}_2\text{SO}) \rightarrow t\text{-BuO-SMe}_2{}^+\text{I}^- \rightarrow \text{CH}_2\text{=CMe}_2 + \text{HO-SMe}_2{}^+\text{I}^- \qquad (1)$$

This is the first example of long-lived *t*-butoxysulfonium ions. Two reasons can be assumed as to why the salt is alive so long: One is rapid formation at room temperature, and the other is that the counter ion I^- is stable without specific solvation such as hydrogen bonding be-

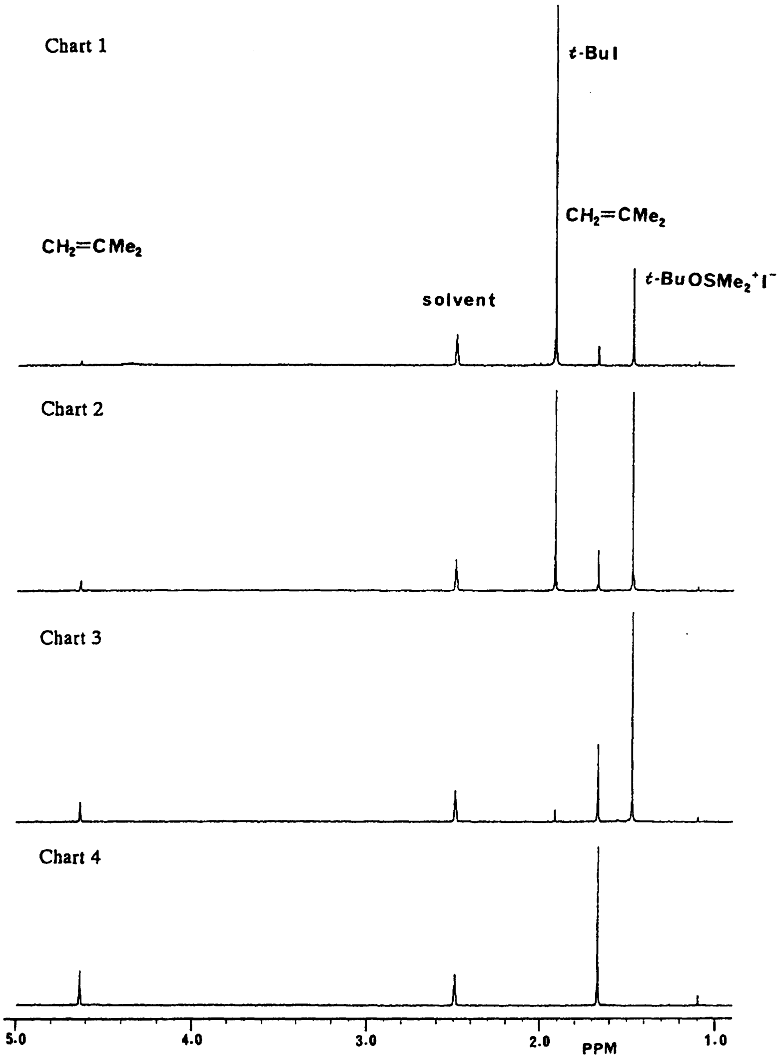


Fig. 1. ^{1}H NMR spectra of the products from decomposition of *t*-butyl iodide in DMSO-d_6 measured on a 500 MHz spectrometer. Chart 1, $t=0$ min at 26 °C (3.5 min after preparation of the solution); Chart 2, $t=6$ min; Chart 3, $t=30$ min; Chart 4, after heating the solution in Chart 3 at 55 °C for 10 min.

cause of the high degree of charge dispersion.

Table 2 shows the decomposition rates of *t*-butyl iodide and the sulfonium iodide measured at several temperatures. The value of $\Delta H^{\ddagger}$ for the heterolysis is much smaller than that for the elimination, reflecting high stability of the salt. The value of $\Delta S^{\ddagger}$ for the heterolysis is negatively large. In sharp contrast, the value of $\Delta S^{\ddagger}$ for the elimination is positively large. This observation is attributed to the difference in the degree of freedom due to the solvation of charged species: The heterolysis process is a conversion of the uncharged substrate to the solvated ion pair, whereas both reactant and product sides involve charged species in the elimination process. The major factor affecting the entropy of activation in the elimination process is therefore the intrinsic nature of unimolecular cleavage reactions leading to two fragments. The situation that both the enthalpy and entropy of activation for the elimination process have larger values leads to the suggestion that the relative magnitudes of reaction rates might be reversed at higher temperatures, probably above 78 °C (Fig. 2).

Comparison of Rates of Decomposition of *t*-Butyl Halides. Kinetic data for decompositions of *t*-butyl chloride, bromide, and iodide in methanol-d_4 and in DMSO-d_6 at 60 °C are compiled in Table 3. As has been reported,[2,6] the decomposition rate in methanol increases in the order *t*-BuCl<*t*-BuBr<*t*-BuI. The same order holds for the decomposition rate in DMSO, but with extraordinarily large rate ratios. Although no data had been reported as to the decomposition rate in DMSO itself, detailed kinetic studies of decompositions of the three *t*-butyl halides in methanol–DMSO binary mixtures have been made by Sakong and his coworkers.[6] They determined rates by a conductometric method in a range of solvent mixtures from methanol to DMSO–methanol (7 : 3 v/v) at three temperatures 35, 45, and 55 °C, and reported that the rate decreases with an increase in the composition of DMSO for *t*-butyl chlo-

Table 2. Decomposition Rates of *t*-Butyl Iodide and *t*-Butoxydimethylsulfonium Iodide in Dimethyl-d_6 Sulfoxide at Several Temperatures

	10^5k (s^{-1})					$\Delta H^\ddagger$	$\Delta S^\ddagger$
Temperature (°C)	26	33	40	48	56	kcal mol^{-1}	eu
t-BuI	193	383	725	1540		17.3±0.6	−13±2
t-Bu-OSMe$_2$$^+I^-$	14.1		120	391	1100	27.9±0.7	17±2

Table 3. Rates and Relative Rates for *t*-Butyl Halides at 60 °C

	10^5k (s^{-1})		k_{rel}		$k_{\text{DMSO}}/k_{\text{methanol}}$
	Methanol-d_4	DMSO-d_6	Methanol	DMSO	
t-BuCl	5.10	0.259	1	1	0.051
t-BuBr	195	112	38	432	0.57
t-BuI	612	4200	120	16200	6.9

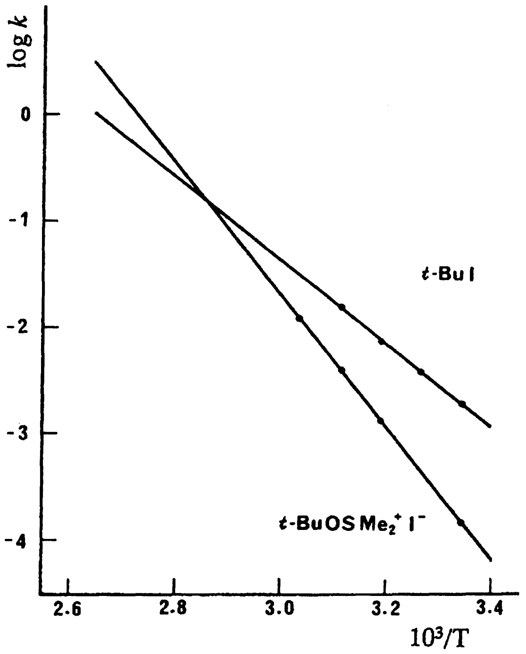


Fig. 2. Temperature dependence of the rate of decompositions of *t*-butyl iodide and *t*-butoxydimethylsulfonium iodide in DMSO-d_6.

ride, slightly decreases for *t*-butyl bromide but increases for *t*-butyl iodide. Further, they pointed out that apparently a good linear correlation holds in a plot of the free energy of activation against solvent composition. From their data, we can therefore calculate the rate constants in DMSO which are rather close to ours. The calculated rate constants and the relative rates ($k_{\text{calc}}/k_{\text{obs}}$) at 60 °C: *t*-BuCl, 0.38×10^{-5} s^{-1} (1.5); *t*-BuBr, 98×10^{-5} s^{-1} (0.88); *t*-BuI, 3140×10^{-5} s^{-1} (0.75).

As far as the rates for *t*-butyl halides are compared in a single solvent, we cannot obtain any information other than the order of reactivity (*t*-BuCl < *t*-BuBr < *t*-BuI). As has been reported previously,[1] the important mode of solvation can be estimated from the rate ratio $k_{\text{DMSO}}/k_{\text{methanol}}$, since DMSO is a solvent of strongly cation-solvating ability and methanol is that of strongly anion-solvating ability due to hydrogen bonding. We defined the type of reactions as follows: $k_{\text{DMSO}}/k_{\text{methanol}} < 1$, hydrogen bond-susceptible; $k_{\text{DMSO}}/k_{\text{methanol}} > 1$, hydrogen bond-insusceptible. The relative rates given in the last column of Table 3 clearly point to the hydrogen bond-insusceptible nature of decomposition of *t*-butyl iodide, in contrast to the hydrogen bond-susceptible nature of that of *t*-butyl chloride. *t*-Butyl 2,4-dinitrophenolate that produces a charge-dispersed anion behaves like *t*-butyl iodide ($k_{\text{DMSO}}/k_{\text{methanol}}$, 4.3 at 90 °C). It has been demonstrated that the ability of anions to hydrogen bond with protic solvents decreases with a decrease in the density of charge.[12] The volume of iodide ion is about twice that of chloride ion: Br$^-$/Cl$^-$, 1.3; I$^-$/Cl$^-$, 1.9 (as calculated by using the following ionic radius: Cl$^-$, 1.67; Br$^-$, 1.82; I$^-$, 2.06 Å).[13] Such a difference in the extent of charge dispersal makes iodide ion more stable without solvation and less susceptible to hydrogen bonding. We therefore conclude that the decomposition of *t*-butyl iodide is strongly affected by cation solvation, contrary to the decomposition of *t*-butyl chloride in which the transition state is highly stabilized by anion solvation.

Kosower's Z scale, which is a popular measure of solvent polarity based on the solvation of *N*-ethylpyridinium iodides, indicates that the solute salts are solvated much more strongly in methanol than in DMSO.[14] The discrepancy in solvation between the two systems involving iodide ion can readily be explained in terms of the *relative importance of cation and anion solvation.* The pyridinium ions are much more stable than the *t*-butyl cation so that its cation solvation is less important, even though the counter ion is a charge-dispersed anion. The Z scale should therefore be regarded not as a general measure but as a limited measure applicable only to hydrogen bond-susceptible systems in which anion solvation is more important. It is to be emphasized that hydrogen bond-insusceptible systems are no longer uncommon, since *t*-butyl halides are among the most popular substrates in heterolysis reactions, and the decomposition of the most reactive halide, i.e., *t*-butyl iodide, belongs to this type of reaction.

Effects of Eight Solvents on Rates. Figure 3 shows plots of the free energy of activation for decomposition reactions of *t*-butyl bromide, iodide, and 2,4-dinitrophenolate against that of *t*-butyl chloride in eight representative polar solvents. As far as the data points of four solvents DMSO, DMF, pyridine, and acetone are concerned, excellent linear free energy relationships are observed irrespective of the extent of charge dispersal of the leaving group anions. This clearly suggests that the order of the ionizing power among these solvents results from cation solvation and the contribution of specific anion solvation is small. On the other hand, downward shifts appear considerably in methanol and ethanol points, and slightly but significantly in acetonitrile and nitrobenzene points.

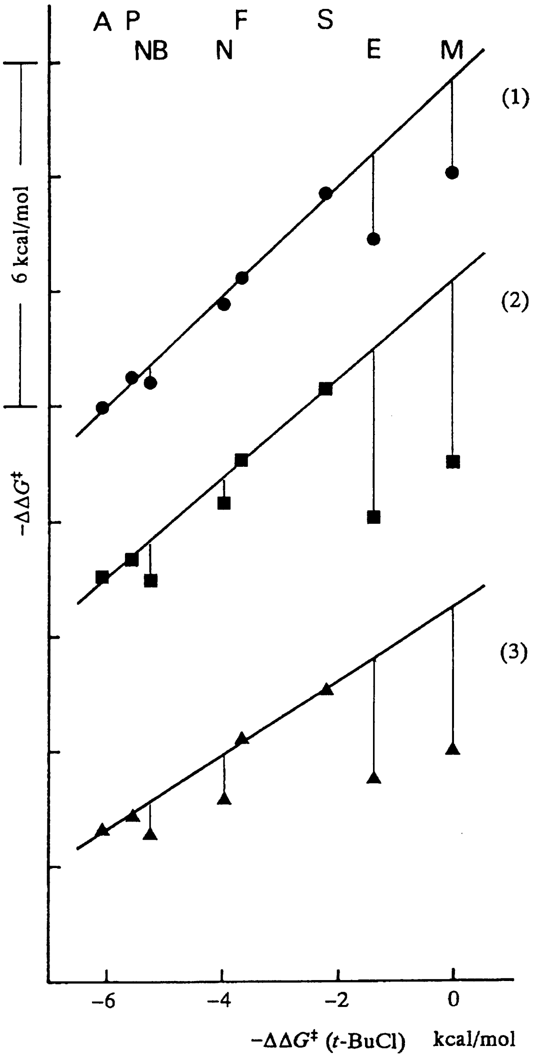


Fig. 3. Plots of $-\Delta\Delta G^{\ddagger}$ for decompositions of *t*-BuBr (1), *t*-BuI (2), and *t*-$BuOC_6H_3(NO_2)_2$-2,4 (3) vs. that for decomposition of *t*-BuCl. Solvents: A=acetone; P=pyridine; NB=nitrobenzene; F=DMF; N=MeCN; S=DMSO; E=ethanol; M=methanol. (1), slope=0.94 (R=0.999, the correlation coefficient of the APFS line); (2), slope=0.86 (R=0.999); (3), slope=0.65 (R=0.998).

We have already observed a similar phenomenon in the study of other hydrogen bond-insusceptible reactions.[1] The anionic portion is strongly stabilized by protic solvents through hydrogen bonding, and slightly by acetonitrile and nitrobenzene presumably through charge-transfer or Lewis acid-base interactions that would be reminiscent of a very early stage of the nucleophilic attack by anionic reagents. Such anion solvation decreases on changing the leaving group anion from chloride ion to an anion of more charge-dispersed type. In light of the structure of solvent molecules, it is likely that all the polar solvents used here have the ability to stabilize a cationic portion at the transition state, in which the mode of interaction would again be charge-transfer or Lewis acid-base type.

Two-parameter equations using π^* and α scales have been reported by Abraham, Taft, and Kamlet.[9] They present the following equations on the decomposition of *t*-butyl halides at 25 °C in fifteen protic and aprotic solvents: However, a number of rates for aprotic solvents used in their work are those assumed based on some linear free energy relationships.

$$\begin{aligned} -\log k(t\text{-BuCl}) &= 15.06 - 6.94\pi^* - 5.25\alpha \quad (R, 0.995) \\ -\log k(t\text{-BuBr}) &= 12.41 - 7.21\pi^* - 3.95\alpha \quad (R, 0.995) \\ -\log k(t\text{-BuI}) &= 10.52 - 6.86\pi^* - 2.71\alpha \quad (R, 0.993) \end{aligned} \tag{2}$$

The α scale is a measure of anion solvation due to hydrogen bonding, and by comparison of the coefficients of this term, it has been concluded that the decomposition of *t*-butyl iodide is the least susceptible to hydrogen bonding.

No effort has been devoted to examine the effect of DMSO which is the most important dipolar aprotic solvent to assess the validity of their equations in a sense that π^* values are defined as $\pi^*_{\text{DMSO}}=1.00$. Since $\alpha=0$ for DMSO, the rate constants in DMSO can easily be calculated from the above equations. However, the calculated rates are far smaller than our data. The calculated rate constants at 25 °C are as follows: *t*-BuCl, k_{calc}(DMSO) 7.6×10^{-9} s^{-1} [k_{obs}(DMSO-d_6) 3.34×10^{-8} s^{-1}]; *t*-BuI, k_{calc}(DMSO) 22×10^{-5} s^{-1} [k_{obs}(DMSO-d_6) 173×10^{-5} s^{-1}]. Another serious discrepancy is seen in the data for nitrobenzene which has almost the same parameters as DMSO: $\pi^*=1.01$ and $\alpha=0$. Their treatment therefore predicts that the decomposition in nitrobenzene proceeds as rapid as that in DMSO irrespective of reaction temperature. The data in Table 1 indicate that the reaction in DMSO is much faster: $k_{\text{DMSO}}/k_{\text{nitrobenzene}}$ *t*-BuCl at 120 °C, 49; *t*-BuBr at 60 °C, 126; *t*-BuI at 60 °C, 145. The π^* scale is a measure of solvent polarity based on the solvation of uncharged and very weakly polarized compounds such as *p*-nitroanisole in which there is no real distinction between positive and negative sites. In this case, a dominant mode of solvation may be that of electrostatic interaction capable of stabilizing the whole body of a solute molecule. Solvation of an actually charge-separated solute is expected to involve much stronger interactions in which solvent molecules are oriented to cationic and anionic portions. Although the π^* scale is a useful measure for the solvation of uncharged polar solutes, it seems unlikely that the major mode of solvation remains unchanged in the wide range of uncharged to charge-separated solutes. In the following paper,$^{15)}$ we will discuss our two-parameter treatment derived on the basis of cation and anion solvation.

Conclusions

The solvent order of the ability to stabilize ion pair species depends on the relative importance of cation and anion solvation. Ion pair-like solutes or heterolysis reactions are classified into two types as a rough expression: One is hydrogen bond-susceptible, in which anion solvation is more important, and the other is hydrogen bond-insusceptible, in which cation solvation is more important.

t-Butyl halides serve as the best substrates in understanding solvent effects on the rate of heterolysis reactions, because all kinds of heterolysis reactions are involved with regard to the type of solvation; hydrogen bond-susceptible for *t*-butyl chloride, hydrogen bond-insusceptible for *t*-butyl iodide, and further an intermediate type for *t*-butyl bromide.

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