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Quantitative Analysis of Solvent Effects on the Rate of Heterolysis Reactions: Relative Importance of Cation and Anion Solvation

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A number of heterolysis reactions which are insusceptible or less susceptible to hydrogen bonding by protic solvents are exemplified. It is emphasized that reactions of this type are as important as those of the hydrogen bond-susceptible type that are prone to be taken as a common feature of heterolysis reactions. Evidence that a primary factor in determining the type of reaction is the relative importance of cation and anion solvation is given by introducing a two-parameter equation for solvent effects on the rate: $\Delta G^{\ddagger}=\Delta G^{\ddagger}{}_{\mathrm{DMSO}}-a(\chi^{+}+b\chi^{-}-1)$ in which χ^{+} and χ^{-} are scales for cation and anion solvation for a particular solvent, respectively. These scales have been derived from purely kinetic data for eight solvents; methanol, ethanol, dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide, acetonitrile, pyridine, nitrobenzene, and acetone. The equation applies satisfactorily to twelve typical heterolysis reactions. The coefficients a and b represent the sensitivity to solvent change and the relative importance of cation and anion solvation, respectively. When $b=1$, the rate in DMSO is equal to that in methanol, and thus heterolysis reactions can be classified: $b>1$, hydrogen bond-susceptible; $b<1$, hydrogen bond-insusceptible.

The first convincing concept of the role of solvents in nucleophilic substitution reactions seems to have been introduced in the studies of $\mathrm{S_N2}$ mechanisms rather than those of $\mathrm{S_N1}$. A clear-cut interpretation has been given for the enormous rate enhancement of $\mathrm{S_N2}$ reactions involving anionic nucleophiles in dipolar aprotic solvents relative to those in protic solvents.[1] The most important factor is solvation of the anionic nucleophile and its counter ion in the initial state. Protic solvents stabilize anionic nucleophiles through hydrogen bonding and reduce their reactivity. On the other hand, dipolar aprotic solvents having strong affinities for cations but not for anions make the nucleophiles bare and thus highly reactive due to desolvation of the reactant anions as well as separation of them far apart from the counter ions surrounded with strong solvation shells. Although the solvation at the transition state should be considered for the discussion of more detailed reactivities,[2] this concept has found general acceptance.

Since $\mathrm{S_N1}$ or heterolysis reactions involve ion pair-like transition states, cation and anion solvation at the transition state should be discussed separately like that of a nucleophile salt in $\mathrm{S_N2}$ reactions. Although the importance of the anion solvation due to hydrogen bonding by protic solvents has been established in heterolysis reactions as well, many influential theories hitherto proposed are those based on the electrostatic properties of the bulk of solvent such as dielectric constants and dipole moments that have been claimed to stabilize the whole body of ion pair-like solute molecules.[3] Recognition of hydrogen bonding as a highly specific mode of solvation would have offered a good opportunity to explore a possibility that the ability of a solvent to stabilize the transition state for heterolysis reactions may depend on the nature of leaving group anions. The typical dipolar aprotic solvent, dimethyl sulfoxide (DMSO), is known to excel the protic solvent methanol in the ability to stabilize cations as well as in the electrostatic force (ε 48.9, μ 3.9 for DMSO; ε 32.65, μ 1.7 for methanol). It is therefore expected that a reaction in which anion solvation due to hydrogen bonding is less important may proceed faster in DMSO than in methanol no matter what kind of solvation works in DMSO.

Winstein's scale based on the rate of heterolytic decomposition of *p*-methoxyneophyl tosylate is the first measure of solvent ionizing power that was determined kinetically in a wide range of protic to aprotic solvents.[4] This scale judges methanol much more efficient than DMSO. Such a trend has been obtained not only in other heterolysis reactions, e.g., decompositions of *t*-butyl and α-cumyl chloride (1-methyl-1-phenylethyl chloride), but also in the spectroscopic measurements of solvation of stable ion pairs such as pyridinium iodides (Z scale)[5] and betaines consisting of a pyridinium ion and a phenolate ion (E_T scale).[6] A central feature common to these systems is that protic solvents other than bulky alcohols such as 2-methyl-2-propanol possess much stronger ionizing power than any kind of dipolar aprotic solvents. Such a coincidence of the order of solvent ionizing power had forced us to have the view that ion pair-like solutes are inherently stabilized more strongly in protic solvents than in dipolar aprotic solvents.

In the previous papers,[7—9] we demonstrated the reverse cases in which heterolysis reactions involving uncommon leaving groups proceed faster in DMSO than in methanol, and in the preceding paper,[10] analogous reactions using popular leaving groups such as iodo and 2,4-dinitrophenoxyl groups. In this article, further examples of this type of reaction are presented. We take the position that whether DMSO is more efficient than methanol is determined by the relative importance of cation and anion solvation during heterolytic bond cleavage,[7,10] and a two-parameter equation is derived from this point of view. The long-standing view not only favors the solvation by protic solvents but also overestimates electrostatic force as a factor determining the order of solvent ionizing power. Our conclusion is that such a view was a misleading guide in understanding the whole picture of solvent effects on the stability of ion pairs or charge-separated species.

Experimental

Material. The compounds subjected to rate measurements were prepared according to usual procedures.

1: mp 96 °C. Anal. Calcd for $C_{16}H_{14}N_2O_6$: C, 58.18; H, 4.27; N, 8.48%. Found: C, 57.94; H, 4.32; N, 8.45%.

15: mp 117 °C. Anal. Calcd for $C_{14}H_{10}ClN_3O_7$: C, 45.73; H, 2.74; N, 11.43%. Found: C, 45.57; H, 2.81; N, 11.52%.

The following two compounds are known but show mp's different from those reported.

3: mp 81 °C (lit, 95.5 °C).[11] Anal. Calcd for $C_{15}H_{14}N_2O_5$: C, 59.60; H, 4.67; N, 9.27%. Found: C, 59.66; H, 4.83; N, 9.18%.

9: 165 °C (lit, 150.5 °C).[12] Anal. Calcd for $C_{16}H_{17}N_3O_7$; C, 52.89; H, 4.72; N, 11.57%. Found: C, 52.60; H, 4.71; N, 11.52%.

Kinetics. Rate measurements were carried out as described in the previous papers.[7,10] Anisole was used as an internal reference but *p*-dibromobenzene was used for the picrates **9**, **19**, and **20**. Kinetic data are summarized in Tables 2 and 5, and they are reliable to ±3%. Kinetic data for compound **15** are as follows: 408×10^{-5} s^{-1} in DMSO-d_6; 59.4×10^{-5} s^{-1} in methanol-d_4 (34 °C).

Results and Discussion

Rate Ratios $k_{DMSO}/k_{methanol}$. We examined the solvent effects on the rate of heterolysis reactions generating a wide variety of carbocations and leaving group anions by an NMR method as previously described,[7] and particular attention was paid to the rate ratio $k_{DMSO}/k_{methanol}$, because it corresponds to the differential solvation transferred from a solvent of strongly anion-solvating ability to that of strongly cation-solvating ability. The rate ratios $k_{DMSO\text{-}d_6}/k_{methanol\text{-}d_4}$ obtained by our previous and present measurements are summarized in Table 1. Reactions producing chloride, bromide, tosylate, and 2,4-dinitrobenzoate ions exhibit rate ratios of less than unity. On the other hand, rate ratios of more than unity are achieved by substrates which form charge-dispersed leaving group anions, i.e., iodide, 2,4-dinitrophenolate, picrate, dicyanomethanone *p*-nitrophenylhydrazonide, dicyanonitromethanide, and tricyanomethanide ions. The first three are popular leaving group anions while the other three are those developed by the present authors.[7—9]

We previously termed reactions showing a rate ratio of less than unity "hydrogen bond-susceptible type" and those showing a rate ratio of more than unity "hydrogen bond-insusceptible type".[7] An intermediate type, however, should be allocated for *t*-butyl bromide and α-cumyl 2,4-dinitrophenolate, since the rate ratios are close to unity. These findings indicate that there is a continuous spectrum in the type of reaction and any type can be realized by a proper choice of a carbocation and a leaving group anion. In fact, only hydrogen bond-susceptible reactions have so far attracted much attention simply because chlorides and sulfonates have most frequently been used as favorite substrates for kinetic studies.

We examined a total of twenty reactions, eleven of which were found to possess the rate ratio of more than unity. In consequence, it is evident that hydrogen bond-insusceptible reactions are obtainable quite commonly by a combination of an unstable or charge-localized carbocation and a stable or charge-dispersed leaving group anion. Since the carbocations generated from heterolysis reactions are much more unstable than any cations involved in stable ion pairs, e.g., *N*-alkylpyridinium ions, the hydrogen bond-insusceptible behavior is more like a property intrinsic to heterolysis reactions.

Methanolysis of secondary alkyl compounds may involve in part an S_N2 process which would result in an apparent rate higher than that of S_N1 proper.[13] Accordingly, the rate ratios $k_{DMSO}/k_{methanol}$ for 1-(*m*-chlorophenyl)ethyl picrate and 2-*endo*-norbornyl derivatives may represent minimum values, although decompositions of 2-*exo*-norbornyl derivatives were confirmed to proceed via an S_N1 mechanism giving methyl 2-*exo*-norbornyl ether only.

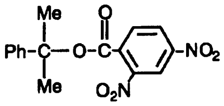
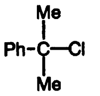
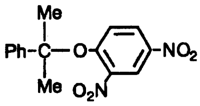
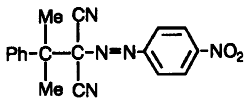
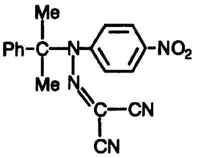
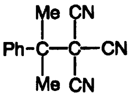
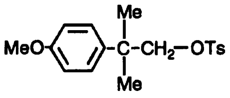
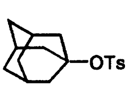
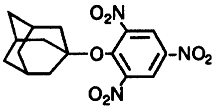
Quantitative Treatment of Solvent Effects. The quantitative treatment of solvent effects on reaction rates requires experimental data as many as possible. We have already reported kinetic data for the heterolysis reactions of four *t*-butyl derivatives in the preceding paper.[10] Table 2 lists the data for five α-cumyl derivatives along with *p*-methoxyneophyl tosylate and two 1-adamantyl derivatives. Eight protic and aprotic solvents were used, but in some cases, rate measurements in all the solvents were technically impossible. These data provide us with a quantitative basis for analyzing the effect of solvation.

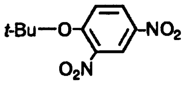
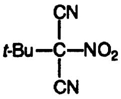
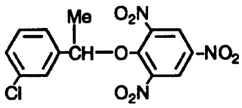
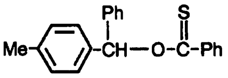
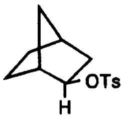
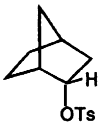
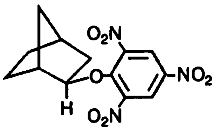
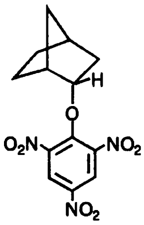
Figure 1 shows plots of a change in free energy of activation transferred from a solvent to methanol for five α-cumyl derivatives against Winstein's W_{ion} scale derived from the heterolysis reaction of *p*-methoxyneophyl tosylate (**7**).[4,7] Figure 1 reveals three important features described below.

1. As far as the four data points for DMSO, *N*,*N*-dimethylformamide (DMF), pyridine, and acetone are concerned, an excellent linear free energy relationship holds irrespective of the nature of leaving group anions. As has previously been pointed out,[7,10] the result suggests that the differential solvation among the four aprotic solvents arises mainly from cation solvation due to charge-transfer or Lewis acid–base interactions.

2. An apparent straight line throughout all the sol-

Table 1. Differential Solvation Transferred from Methanol to Dimethyl Sulfoxide in Heterolysis Reactions

		k (DMSO-d_6)/k (methanol-d_4)
(1)		0.052 (80 °C)
(2)		0.012 (50 °C)
(3)		1.3 (60 °C)
(4)		7.9 (60 °C)[7]
(5)		3.4 (60 °C)[7]
(6)		5.4 (33.5 °C)[8]
(7)		0.13 (75 °C)[7]
(8)		0.013 (60 °C)
(9)		2.1 (60 °C)

		k (DMSO-d_6)/k (methanol-d_4)
(10)	*t*-Bu–Cl	0.051 (60 °C)[10]
(11)	*t*-Bu–Br	0.57 (60 °C)[10]
(12)	*t*-Bu–I	6.9 (60 °C)[10]
(13)		4.3 (90 °C)[10]
(14)		ca. 50 (80 °C)[9]
(15)		6.9 (34 °C)
(16)		0.12 (85 °C)[14]
(17)		0.082 (90 °C)
(18)		0.46 (90 °C)
(19)		4.1 (90 °C)
(20)		3.0 (90 °C)

vents appears in the plot for α-cumyl chloride, which however should be taken as an incidental coincidence. With other α-cumyl derivatives, data points for the protic solvents methanol and ethanol show an upward or downward deviation depending on the nature of leaving group anions. The deviations are considered to arise from the difference in hydrogen-bonding ability.

3. The data points for acetonitrile and nitrobenzene exhibit analogous deviations to some extent. Probably anion solvation due to charge-transfer or Lewis acid–base interactions may be responsible for such deviations.

The present work deals with the differential solvation among polar solvents only, and it seems likely that electrostatic force, if it works, may exert most strongly through the solvent molecules located nearest to the cationic or anionic portion of an ion pair-like solute molecule, since the solvent molecules at such a posi-

Table 2. Kinetic Data for α-Cumyl and 1-Adamantyl Compounds and *p*-Methoxyneophyl Tosylate

	10^5k (s^{-1})							
Solvent	**1** (80 °C)	**2** (50 °C)	**3** (60 °C)	**4** (60 °C)[b]	**5** (60 °C)[b]	**7** (75 °C)[b]	**8** (60 °C)	**9** (60 °C)
DMSO-d_6	17.7	61.5	166	772	8.66	17.2	30.5	396
Methanol-d_4	343	5370[a]	133	97.2	2.53	132(160)[d]	2260	192
Ethanol-d_6	84.7	436	38.1	37.2[c]	1.56[c]	54.5[c](62.5)[d]	318	88.4
DMF-d_7	4.90	4.52	38.4	245	5.11	5.57	4.47	186
Acetone-d_6	1.17	0.166[b]	3.75	29.6	1.36	0.944	0.398	41.6
Pyridine	1.92	0.512[b]	9.20	76.8	2.94	2.36	0.394[e]	40.6[e]
MeCN-d_3	6.62	6.95	10.6	57.6	2.04	6.65	4.6	192
Nitrobenzene	2.39	0.92	4.33	16.3[c]	1.07[c]	2.54[c]	—	—

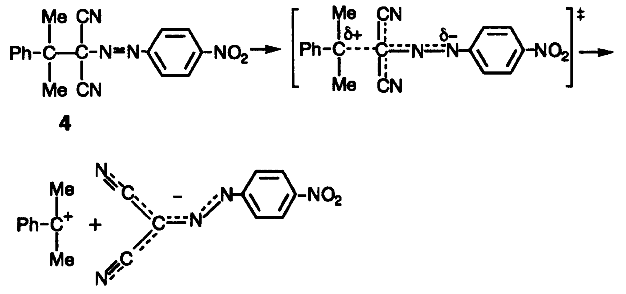
a) Calculated from data at other temperatures. 10^5k (s^{-1}): 37.3 (6 °C), 419 (26 °C), 742 (31 °C), 1880 (39.5 °C); $\Delta H^\ddagger = 19.7 \pm 0.3$ kcal mol^{-1}, $\Delta S^\ddagger = -3.6 \pm 1.0$ eu. b) Ref. 7 otherwise noted. c) This work. d) In undeuterated solvents (Ref. 4). e) Measured in pyridine-d_5.

tion would be highly polarized and oriented as a result of the specific interactions with the cationic or anionic portion. Our assumption is that the electrostatic solvation by polar solvents might stabilize each ionic portion rather than the whole body of an ion pair solute molecule and thus should be involved in cation or anion solvation.

These three features are common to all the heterolysis reactions examined. However, we found that the data point for pyridine shows a slight deviation from a straight line consisting of the data points for DMSO, DMF, and acetone, when the data for the α-cumyl series are compared with those for *t*-butyl and 1-adamantyl series. The effect of pyridine will be discussed later by taking into consideration the type of carbocations produced.

We therefore choose the three solvents DMSO, DMF, and acetone as the selected aprotic solvents for the quantitative treatment of cation solvation. Modes of cation solvation of the three solvents are expected to resemble one another, since they have an oxygen atom as an electron-donor site protruding out of the molecule and an electron-deficient site are hidden inside. Such a structural resemblance would be responsible for the good linear relationship that holds independent of the nature of carbocations.

Methanol and ethanol are adopted as the selected protic solvents. The alcohols can stabilize the cationic portion at the transition state through the interaction with the lone pair of a hydroxylic oxygen atom in addition to anion solvation due to hydrogen bonding. A difficult problem in the quantitative treatment is how to separate cation solvation from anion solvation in protic solvents. Fortunately, we have the kinetic data for decompositions of the azo compound **4** and the hydrazone **5** that generate an extensively charge-delocalized leaving group anion, i.e., the dicyanomethanone *p*-nitrophenylhydrazonide ion[7,14—17] and show the lowest reactivity in protic solvents among the heterolysis reactions so far examined.[18] The transition state and the leaving group anion for the decomposition of **4** are illustrated in Scheme 1. We therefore consider that, to a good approximation, the decomposition of **4** can serve as a reference reaction not involving anion solvation.



Scheme 1.

The following two-parameter equation is proposed to pursue the quantitative examination of solvent effects on the rate, in which χ^+ and χ^- are scales for cation and anion solvation for a particular solvent, respectively, and the coefficients *a* and *b* are appropriate constants for a particular reaction. The χ^+ values are determined on the basis of the free energy of activation

$$\Delta G^\ddagger = \Delta G^\ddagger{}_{\mathrm{DMSO}} - a\left(\chi^+ + b\chi^- - 1\right) \qquad (1)$$

for the decomposition of the azo compound **4**, in which DMSO and methanol are taken as the reference solvents. The χ^+ values are defined as 1.00 for DMSO and 0.50 for methanol in order to facilitate the classification of the type of reaction, as will be described below. Not only protic solvents but also acetonitrile and nitrobenzene are able to stabilize the anionic portion at the transition state. The χ^- values for these solvents are evaluated from the extent of deviations in the plot of the free energy of activation for Winstein's reaction[4] against χ^+ values, in which a straight line is drawn with respect to the data points for the three solvents DMSO, DMF, and acetone. Here, the χ^- value for methanol is adjusted so that the sum of parameters, i.e., $\chi^+ + \chi^-$, is unity: thus $\chi^- = 0.50$ for methanol. Accordingly, when $b = 1$, the rate of a reaction in DMSO is equal to that in methanol, and thus the type of reaction can be classified as follows: hydrogen bond-susceptible for $b > 1$; hydro-

Table 3. Solvent Parameters for Cation and Anion Solvation[a)]

	DMSO	DMF	Acetone	Pyridine	MeCN	Nitrobenzene	Methanol	Ethanol
χ^+	**1.00**	**0.70**	**0.22**	0.44[b)]	0.38	0.08	**0.50**	**0.27**
χ^-	**0**	**0**	**0**	0	0.16	0.18	**0.50**[c)]	**0.49**[c)]

a) Parameters written in bold letters are of the selected solvents. b) 0.31 for *t*-butyl derivatives and 0.23 for 1-adamantyl derivatives. c) **0.47** for methanol-d_4; **0.47** for ethanol-d_6.

Table 4. Coefficients *a* and *b* in Pure Heterolysis Reactions

Compound[a)]	Reaction Temp (°C)	*a*	*b*	$\Delta G^{\ddagger}{}_{\mathrm{DMSO}}$ (kcal mol^{-1}) Calcd	Obsd	*R*
$PhCMe_2O_2CAr$ (**1**)	80	2.56	2.64	26.87	26.85	0.995
$PhCMe_2Cl$ (**2**)	50	5.00	2.20	23.74	23.72	0.997
$PhCMe_2OAr$ (**3**)	60	3.25	0.94	23.80	23.81	0.999
$PhCMe_2$-Azo (**4**)	60	2.79	0	22.77	22.80	0.999[b)]
$PhCMe_2$-Hyd (**5**)	60	1.61	0	25.73	25.77	0.994
		(1.58	−0.06	25.72		0.995)[c)]
$ArCMe_2CH_2OTs$ (**7**)	75	4.90	1.81	26.50	26.45	0.999[b)]
1-Ad-OTs (**8**)	60	3.81	2.55	24.95	24.94	0.997
1-Ad-OPic (**9**)	60	1.95	0.46	23.20	23.24	0.997
t-BuCl (**10**)	120	4.94	2.02	28.84	28.86	0.999
t-BuBr (**11**)	60	4.73	1.21	24.07	24.07	0.999
t-BuI (**12**)	60	4.19	0.41	21.67	21.67	0.999
t-BuOAr (**13**)	90	3.06	0.38	27.33	27.34	0.996

a) For precise structures, see Table 1. b) Reference reactions. c) Two-parameter expression.

gen bond-insusceptible for $b<1$. Generally, heterolysis reactions in undeuterated protic solvents are slightly but significantly faster than those in the deuterated solvents (k_H/k_D, around 1.2), presumably because of the isotope effect on hydrogen bonding. This effect should be taken into consideration in the determination of χ^- values. Reliable kinetic data for undeuterated solvents are provided by Winstein's reaction (the decomposition of **7**, see Table 2).[4)] To set up the term $\Delta G^{\ddagger}{}_{\mathrm{DMSO}}$ in the equation, unity is taken away from a combination of solvent parameters $(\chi^+ + b\chi^- - 1)$. The parameters obtained are listed in Table 3, in which those for the selected solvents are written in bold letters (three aprotic solvents DMSO, DMF, and acetone, and two protic solvents methanol and ethanol).

The coefficient *a* represents the sensitivity to solvent change. This value is affected by the extent of both charge separation and charge dispersal at the transition state. In other words, it is dependent on the nature of the bond cleaved as well as on that of the ions formed. This value may be temperature-dependent. The coefficient *b* represents the relative importance of cation and anion solvation, and serves as a quantitative index of evaluation of the susceptibility of reaction to hydrogen bonding. To obtain reliable coefficients *a* and *b*, it is preferred to use a set of selected solvents. In Table 4, the coefficients *a* and *b* thus obtained are shown for twelve reactions that are considered to proceed via purely unimolecular mechanisms.

Table 5. Kinetic Data for 2-Norbornyl Compounds at 90 °C

Solvent	10^5k (s^{-1}) Tosylates *exo* (**17**)	*endo* (**18**)	Picrates *exo* (**19**)	*endo* (**20**)
DMSO-d_6	202	9.56	1450	30.2
Methanol-d_4	2460	20.9	356	9.94

The validity of this treatment is justified by the result of decompositions of the azo compound **4** and its isomeric hydrazone **5** that generate the same carbocation and leaving group anion. In Fig. 1, the downward deviation of the methanol point from the straight line is larger in the decomposition of **4** than in that of **5**. However, the sensitivity to solvent change, i.e., the slope of the straight line, is also larger in the decomposition of **4**, and thus the difference in the magnitude of deviation is canceled out in the above equation to give almost the same *b* value ($b=0$ for both **4** and **5**). The rate ratio $k_{\mathrm{DMSO}}/k_{\mathrm{methanol}}$ is a convenient index to classify the type of reaction. However, the ratio cannot give quantitative information about the relative importance of cation and anion solvation, because it is not a quantity free from the factor of the sensitivity to solvent change.

Solvent–solute interactions of charge-transfer or Lewis acid–base-type are considered to be a kind of specific mode. Pyridine is rather different from the selected aprotic solvents in the electronic structure as well as in the nature of the electron-donating group. This may not

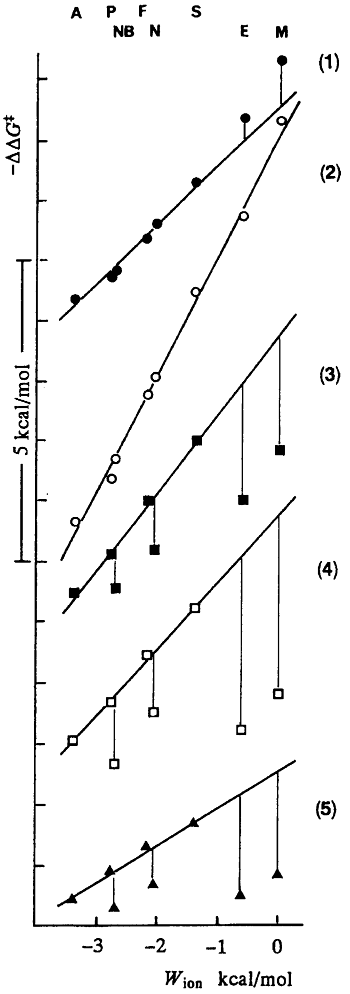


Fig. 1. Plots of $-\Delta\Delta G^{\ddagger}$ for decompositions of α-cumyl derivatives vs. W_{ion} ($\equiv RT\ln k/k_{\text{methanol}}$ for decomposition of **7**). Solvents; A=acetone; P=pyridine; NB=nitrobenzene; F=DMF; N=MeCN; S=DMSO; E=ethanol; M=methanol. **1**, slope=0.97 (R=0.989, the correlation coefficient of the APFS line); **2**, slope=1.94 (R=0.991); **3**, slope=1.28 (R=0.996); **4**, slope=1.09 (R=0.999); **5**, slope=0.61 (R=0.991).

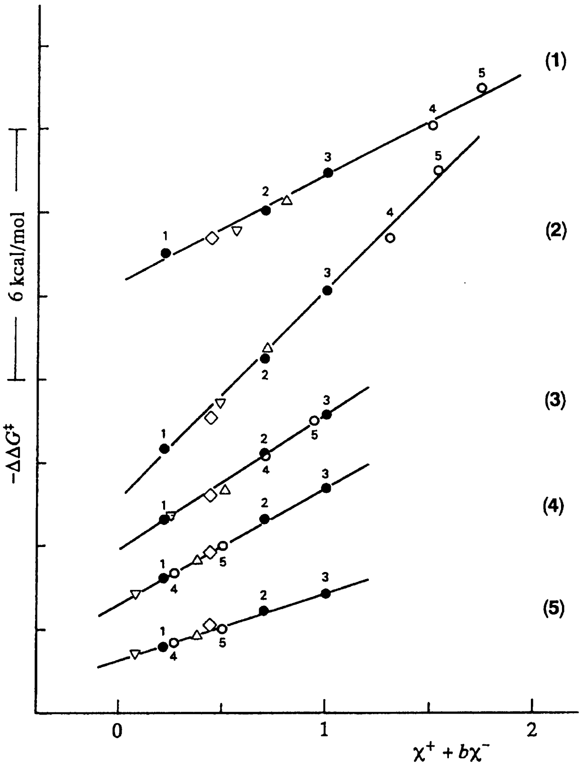


Fig. 2. Plots of $-\Delta\Delta G^{\ddagger}$ for decompositions of α-cumyl derivatives (**1**—**5**) vs. $\chi^{+}+b\chi^{-}$. ● 1, acetone; 2, DMF; 3, DMSO. ○ 4, ethanol; 5, methanol. ▽, nitrobenzene; ◇, pyridine; △, MeCN.

be a situation to determine the sole χ^{+} value required for obtaining a good linear free energy relationship. It was found that the χ^{+} value for pyridine depends on the type of carbocations formed. The χ^{+} value of 0.44 in Table 3 is satisfactorily applicable to the reactions generating the α-cumyl cation and a phenonium ion in Winstein's reaction. In cases of the reactions generating the *t*-butyl cation, much better correlations are obtained by using a smaller χ^{+} value of 0.31. The smallest χ^{+} value of 0.23 is well suited for the reactions generating the 1-adamantyl cation.

Correlations of the free energy of activation against a combination of solvent parameters ($\chi^{+}+b\chi^{-}$) are illustrated in Fig. 2 for α-cumyl derivatives, in Fig. 3 for *t*-butyl derivatives, and in Fig. 4 for 1-adamantyl derivatives together with Winstein's reaction. The straight lines are drawn based on the data points for the five selected solvents. In the Figures, three closed circles are aprotic solvent points, that is, acetone, DMF, and DMSO, and two open circles are protic solvent points, ethanol and methanol. There is a dramatic change in the relative position between the closed and open circles when the two extreme plots are compared in a given alkyl series. It is noteworthy that protic solvents are unexpectedly inefficient in the absence of solvation due to hydrogen bonding.

Acetonitrile and nitrobenzene can stabilize both cationic and anionic portions at the transition state. Since modes of cation and anion solvation by these solvents are dissimilar to those of the selected solvents, the χ^{+} and χ^{-} values for the two solvents may have some uncertainties. However, the data points are located close to the straight line, though certainly involving some deviations, indicating that the parameters for these solvents are reasonable.

A smaller b value in the reaction producing a given carbocation implies that the leaving group is less sensitive to hydrogen bonding during heterolytic cleavage. We can make such a comparison in α-cumyl and *t*-butyl series. The decomposition of 1-adamantyl picrate (**9**) has a significant b value in spite of the fact that it produces a much more charge-localized carbocation than the azo compound **4**. This affords an information

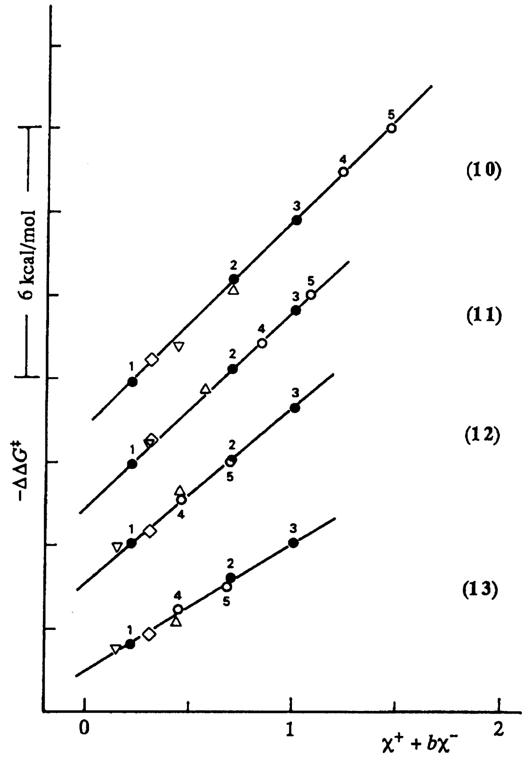


Fig. 3. Plots of $-\Delta\Delta G^{\ddagger}$ for decompositions of *t*-butyl derivatives (**10**—**13**) vs. $\chi^{+}+b\chi^{-}$. ● 1, acetone; 2, DMF; 3, DMSO. ○ 4, ethanol; 5, methanol. ▽, nitrobenzene; ◇, pyridine; △, MeCN.

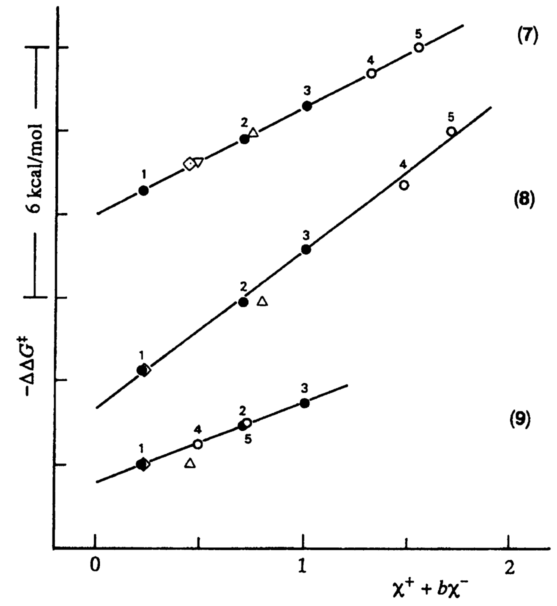


Fig. 4. Plots of $-\Delta\Delta G^{\ddagger}$ for decompositions of the tosylate (**7**) and 1-adamantyl derivatives (**8** and **9**) vs. $\chi^{+}+b\chi^{-}$. ● 1, acetone; 2, DMF; 3, DMSO. ○ 4, ethanol; 5, methanol. ▽, nitrobenzene; ◇, pyridine; △, MeCN.

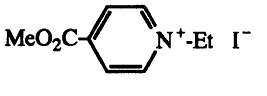
about the sensitivity of a 2,4,6-trinitrophenoxy group to hydrogen bonding. On this basis, we conclude that the ability of leaving groups to accept hydrogen bonding during heterolytic cleavage decreases in the order:

$$\begin{aligned}&\text{-O}_2\text{CC}_6\text{H}_3(\text{NO}_2)_2\text{-2,4} > \text{-Cl} > \text{-Br} > \text{-I}\\ &\approx \text{-OC}_6\text{H}_3(\text{NO}_2)_2\text{-2,4} > \text{-OC}_6\text{H}_2(\text{NO}_2)_3\text{-2,4,6}\\ &> \text{-(NC)}_2\text{CN=NC}_6\text{H}_4\text{NO}_2\text{-}p\\ &\approx \text{-N}\,[\text{N=C(CN)}_2]\,\text{C}_6\text{H}_4\text{NO}_2\text{-}p\end{aligned}$$

A comparison of *b* values for α-cumyl chloride (**2**) and *t*-butyl chloride (**10**) indicates that the anion solvation is more important in a reaction producing a more charge-dispersed carbocation. This trend is enhanced by using a more charge-dispersed leaving group anion, as can be seen in decompositions of 2,4-dinitrophenolates **3** and **13**. As has been pointed out in the preceding paper,[10] a drastic shift in the type of solvation appears when the *b* value for the decomposition of *t*-butyl iodide is compared with that for the solvation of 1-ethyl-4-methoxycarbonylpyridinium iodide as represented by the *Z* scale. According to the definition of the scale,[5] the energy difference in the solvation of the salt is expressed by the difference in a half of the *Z* value and the following equation holds among the selected solvents:

$$\frac{1}{2}Z(\text{kcal mol}^{-1}) = 35.6 + 3.90\left(\chi^{+} + 3.96\chi^{-} - 1\right), \quad R = 0.995. \qquad (2)$$

Whereas the reaction generating a very unstable carbocation *t*-Bu$^+$ and a rather stable anion I$^-$ is hydrogen bond-insusceptible ($b<1$), a combination of a very stable *N*-alkylpyridinium ion and the iodide ion behaves like a typical hydrogen bond-susceptible reaction ($b>1$). Nevertheless, the pyridinium ion in the system is significantly stabilized by solvation ($a=3.9$), simply because the salt is a real ion pair in which the extent of charge separation is much greater than in the transition state for heterolysis reactions.

	b
$t\text{-BuCl} \rightarrow [t\text{-Bu}^{\delta+}\cdots\text{Cl}^{\delta-}]^{\ddagger}$	2.02
$\text{PhCMe}_2\text{Cl} \rightarrow [\text{PhCMe}_2{}^{\delta+}\cdots\text{Cl}^{\delta-}]^{\ddagger}$	2.20
$t\text{-BuOC}_6\text{H}_3(\text{NO}_2)_2\text{-2,4} \rightarrow$ $[t\text{-Bu}^{\delta+}\cdots{}^{\delta-}\text{OC}_6\text{H}_3(\text{NO}_2)_2\text{-2,4}]^{\ddagger}$	0.38
$\text{PhCMe}_2\text{OC}_6\text{H}_3(\text{NO}_2)_2\text{-2,4} \rightarrow$ $[\text{PhCMe}_2{}^{\delta+}\cdots{}^{\delta-}\text{OC}_6\text{H}_3(\text{NO}_2)_2\text{-2,4}]^{\ddagger}$	0.94
$t\text{-BuI} \rightarrow [t\text{-Bu}^{\delta+}\cdots\text{I}^{\delta-}]^{\ddagger}$	0.41
	3.96

The b value for p-methoxyneophyl tosylate (**7**) is smaller than that for 1-adamantyl tosylate (**8**). The transition state for **7** has a charge-dispersed cationic portion in the form of a phenonium ion. However, it is likely that the cationic portion is accompanied by the instability inherent in a primary alkyl cation and thus the importance of cation solvation as compared with anion solvation is still larger in **7** than in **8** which produces a charge-localized tertiary alkyl cation (Table 4 and Fig. 4).

Finally, we would like to mention an interesting feature of the kinetic data for picrates. In both 1-adamantyl and 2-norbornyl derivatives, decompositions of the picrates **9**, **19**, and **20** are much faster in DMSO than those of the corresponding tosylates **8**, **17**, and **18**, while they are much slower in methanol (Tables 2 and 5). The picrate **9** has a smaller a value than the tosylate **8**, suggesting that the decomposition of the picrate proceeds via a more reactant-like transition state than that of the tosylate (Table 4 and Fig. 4).

Heterolysis reactions so far examined can be dealt with by our two-parameter equation without exception so that we can obtain significant information regarding the extent of charge dispersal and charge separation in the transition state for the reactions. However, it should be specified that the application of the solvent parameters introduced here is restricted to the system involving charge-separated species. Different modes of solvation are naturally operative for uncharged dipolar solutes.[10)] We have some kinetic data for the Cope rearrangements that proceed via polar transition states,[14,19)] in which the solvent effects cannot strictly be explained by the present treatment.

Conclusions

Heterolysis reactions can be classified into two types with respect to the differential solvation: One is hydrogen bond-susceptible and the other hydrogen bond-insusceptible.[7,10)] Both of them are equally ubiquitous. The fundamental principle as to heterolysis reactions is that charged species are inherently unstable. Facile bond heterolysis therefore requires charge dispersion, because infinite charge dispersion is equivalent to loss of charge or neutralization. There are two approaches to neutralization. One involves an intermolecular interaction in which charge is shared with solvent molecules, i.e., solvation. The other is intramolecular charge dispersal. The effect of solvation decreases with increasing intramolecular charge dispersal, and vice versa. Protic solvents are able to stabilize anions through hydrogen bonding, while dipolar aprotic solvents such as DMSO and DMF are well suited for cation solvation. In any heterolysis reaction, there exist cationic and anionic portions at the transition state, and the extent of charge dispersal in each portion is dependent on the nature of compounds. These complicated factors are all responsible for the differential solvation that has been discussed. The two-parameter treatment developed in the present work consistently describes this diversity.

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