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Linear Solvation Energy Relationships. 15. Heterolytic Decomposition of the *tert*-Butyl Halides

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The solvatochromic comparison method is used to analyze solvent effects on the unimolecular heterolytic decompositions of *tert*-butyl chloride, bromide, and iodide. It is shown that reaction rates depend on solvent dipolarity/polarizability (π^*) and on solvent hydrogen bond donor acidity (α), but that effects of solvent hydrogen bond acceptor basicity (β) are essentially *nil*. The dependence on α is believed to be a consequence of hydrogen bonding by protonic solvents to the leaving halide ion, the effect being strongest for *t*-BuCl and weakest for *t*-BuI.

In the field of linear solvation energy relationships (LSER's) multiple solvent effects are unravelled and rationalized in terms of linear combinations of dependences on three indices of solvent properties (the solvatochromic parameters). The π^* scale is an index of solvent dipolarity/polarizability, which measures the ability of the medium to stabilize a charge or a dipole by virtue of its dielectric effect;[1-4] the α scale of solvent hydrogen bond donor (HBD) acidities measures the solvent's ability to donate a proton in a solvent to solute hydrogen bond;[1,5-7] the β scale of solvent hydrogen bond acceptor (HBA) basicities describes the solvent's ability to accept a proton (donate an electron pair) in a solute to solvent hydrogen bond.[1,8-11]

Rather than being based on solvent effects on single indicators, as has been the case for most earlier solvent property scales,[12] the solvatochromic parameters were arrived at by averaging normalized solvent effects on diverse properties of many types of indicators. Values of π^* and β for most HBA solvents are now fairly well fixed (i.e., the averages have "settled down", and further correlations are unlikely to change them materially), but α, β, and π^* values of several amphiprotic solvents (most HBD solvents are amphiprotic) are still somewhat uncertain and remain subject to change. Thus, the π^* and α values used in the present paper for several protonic solvents differ somewhat from values used earlier.[13]

The solvatochromic parameters are intended for use in solvatochromic equations of the general form of eq 1, where

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + s(\pi^* + d\delta) + a\alpha + b\beta \qquad (1)$$

δ is a "polarizability correction term" equal to 0.0 for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents. Numerous kinds of relatively precise correlations have been reported wherein the XYZ term in eq 1 has been the logarithm of a rate or equilibrium constant, a fluorescence lifetime, a GLC partition coefficient, the position or intensity of maximal absorption in an NMR, ESR, IR, or UV/visible spectrum, an NMR coupling constant, or a free energy or enthalpy of solution or of transfer between solvents.

In practice we have found it quite difficult to disentangle the multiple solvent effects when all four solvatochromic parameters influence the XYZ (primarily because of complications by type AB hydrogen bonding when both solute and solvent are amphiprotic).[14] By judicious choice of solvents and/or reactants or indicators, however, it has been possible to exclude one or more of the terms in eq 1 and reduce it to a more manageable form.[15]

Thus, if XYZ is $\nu_{\max}$ or E_T of a $\pi \rightarrow \pi^*$ electronic spectral transition, the d term is zero; for other properties, if consideration is restricted to nonchlorinated aliphatic solvents (as in the correlations discussed here), the δ parameter is zero; in either case the $d\delta$ term drops out. If the indicators or reactants are nonprotonic (and non-Lewis acids),[11] b equals zero and the $b\beta$ term drops out. With protonic (or Lewis acid) reactants or indicators, correlations have usually been restricted to nonprotonic solvents for which the α parameter equals zero, so that the $a\alpha$ term drops out. Most of the correlations reported so far have been with π^* alone (with or without the $d\delta$ correction),[2-4,16] with β alone,[10] with π^* and α,[5,6,11b] and with π^* and β.[9,11b]

In the present paper we describe solvent effects on the unimolecular heterolytic decompositions of the *tert*-butyl halides,[17] key kinetic processes, important both in terms of the number of reported investigations and as model reactions in which weakly dipolar initial states are transformed into strongly dipolar transition states. Recent work has focused on the calculation of solvent cavity terms for

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(11) We have recently also shown that effects of HBA base solvents on properties of Lewis acid indicators are also linear with β: (a) Taft, R. W.; Pienta, N. J.; Kamlet, M. J.; Arnett, E. M. *J. Org. Chem.* **1981**, *46*, 661; (b) Taft, R. W.; Kamlet, M. J. *Org. Magn. Reson.* **1980**, *14*, 485.

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(13) In part 4 of this series,[6] we have discussed the difficulties (mainly from solvent self-association effects) encountered in determining the π^* and α values of protonic solvents.

(14) In type AB hydrogen bonding the solute acts as both donor and acceptor at the same site in a probably cyclic complex with two molecules of ROH solvent.

(15) However, correlations with π^*, α, and β are described in: (a) Kamlet, M. J.; Dickinson, C.; Taft, R. W. *Chem. Phys. Lett.* **1981**, *77*, 69; (b) Kamlet, M. J.; Dickinson, C.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1981**, 353.

(16) Kamlet, M. J.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1979**, 337.

(17) In this report we consider together the solvolysis reaction in hydroxylic solvents and the elimination reaction in aprotic solvents. We do not imply that the transition states for reaction in these two sets of solvents are the same or similar, and, indeed, our analysis indicates the contrary.

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Table I. Values of log k (s^{-1}) for the Decomposition of the *tert*-Butyl Halides in Aliphatic Aprotic and Hydroxylic Solvents at 298 K

solvent	π^*	α	β	$-\log k$, s^{-1} [a]		
				t-BuCl	*t*-BuBr	*t*-BuI
water	1.09	1.10	0.18	1.54	0.12	−0.19[f]
methanol	0.60	0.98	0.62	6.10	4.46	3.90[f]
ethanol	0.54	0.85	0.77	7.07	5.35	4.76[b]
2-propanol	0.47	0.77	0.95	7.74	6.00	5.36[b]
tert-butyl alcohol	0.40	0.66	1.01	8.27	6.50	5.84[b]
N-methylpyrrolidone	0.92	0	0.77	8.97	6.00	4.55[c]
dimethylformamide	0.88	0	0.69	8.55[d]	5.62	4.20[c]
dimethylacetamide	0.88	0	0.76	9.31[35]	6.50[c]	5.0[c]
acetonitrile	0.76	0.22	0.31	8.68[e]	5.90[30]	4.28[30]
acetone	0.68	0.10	0.48	9.90	7.13	5.21[33]
tetrahydrofuran	0.58	0	0.55	11.00[c]	8.30[c]	6.57[30]
dioxane	0.55	0	0.37	10.81	8.30	6.78[30]
ethyl acetate	0.55	0	0.45	11.50[c]	8.70[c]	7.02[30]
diethyl ether	0.27	0	0.47	12.74	10.00	8.2[c]
pentane	−0.08	0	0	16.0	13.3[c]	11.2[c]
gas phase				19.3[g]	16.7[g]	14.3[g]

[a] From previous compilations[20,21,37] unless shown otherwise. [b] Calculated from m values and the Grunwald–Winstein mY equation. [c] Calculated from the excellent linear relationships found between −log k values for the three halides in aprotic solvents and the gas phase. [d] From ref 20 and 35. [e] Average value from ref 20 and 30. [f] Moelwyn-Hughes, E. A.; Biordi, J. *J. Chem. Soc.* **1962**, 4291. Moelwyn-Hughes, E. A. **1962**, 4301. [g] Macoll, A. *Chem. Rev.* **1969**, *69*, 33.

Table II. Correlation Coefficients for the Regression Equations

parameter	no.[a]	*t*-BuCl	*t*-BuBr	*t*-BuI
π^*	15	0.727 (0.738)[b]	0.813 (0.730)[b]	0.879 (0.936)[b]
π^*, α	15	0.995 (0.994)[b]	0.995 (0.995)[b]	0.993 (0.997)[b]
π^*, α, β	15	0.995	0.995	0.993
E	14	0.888	0.839	0.780
E, f(ϵ)	14	0.964	0.949	0.921
E, f(ϵ), f(n)	14	0.975	0.963	0.934

[a] The 15 solvents of Table I. In the case of the parameters E, f(ϵ), and f(n), the solvent *N*-methylpyrrolidone was left out because a value of E was not available. [b] Values in parentheses are for correlation equations based on primary solvents only.

the transition states[18] and on the possibility of unusual effects in solvents such as trifluoroethanol (TFE),[19] but previous workers have described in some detail solvent effects on values of log k (or $\Delta G^{\ddagger}$).[18,20-29] In principle, this work on solvent effects may be divided into attempts to correlate the log k or $\Delta G^{\ddagger}$ values with free energies of transfer of model solutes[18,20,21] and correlations of log k or $\Delta G^{\ddagger}$ with either more-or-less empirical solvent parameters or solvent parameters that have some theoretical justification (such as functions of the solvent dielectric constant in reaction field theories).[22,23]

Results and Discussion

Due largely to the work of Ponomareva et al.,[30-34] as well as others,[35,36] rate constants for the *tert*-butyl halide reactions are now available for more aprotic solvents than have hitherto been documented.[20,21,37] In Table I we have assembled log k values for the *tert*-butyl chloride, bromide, and iodide reactions in 15 aliphatic aprotic and hydroxylic solvents (since all the solvents are nonchlorinated aliphatics, $\delta = 0$ and the $d\delta$ term in eq 1 drops out). In order that the correlations for the three *tert*-butyl halides be for the same solvent sets, we have included a number of secondary log k values which were not determined experimentally but rather were estimated from the excellent linear relationships found between log k values for the three halides in nonprotonic solvents and the gas phase.[38]

Correlations of the log k values with π^*, α, and β, both single and multiple, show that the influence of the term in β is statistically insignificant, which indicates that effects of nucleophilic solvation on the *tert*-butyl halide solvolysis reactions are correspondingly unimportant (as will be discussed further below). The correlation coefficients, r,

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(38) We have included the secondary values in the correlations in order that the results in protonic and nonprotonic solvents should have equal relative influences on the regression equations in all three cases.

for the various correlations involving the three solvatochromic parameters are given in Table II for the complete data sets and for the data sets excluding the secondary log k values. It is seen that inclusion of these latter results does not materially change the r values.[38]

Statistical tests indicate that the two-parameter equations (in π^* and α) are very satisfactory, with levels of significance >99.999% for both π^* and α. For the 15 solvents, the two-parameter regression equations are given by eq 2-4 in which there is significant variation in the ratio

$$-\log k(t\text{-BuCl}) = 15.06 - 6.94\pi^* - 5.25\alpha \qquad (2)$$

$$-\log k(t\text{-BuBr}) = 12.41 - 7.21\pi^* - 3.95\alpha \qquad (3)$$

$$-\log k(t\text{-BuI}) = 10.52 - 6.86\pi^* - 2.71\alpha \qquad (4)$$

of the coefficients of α/π^* from 0.76 (t-BuCl) to 0.56 (t-BuBr) to 0.39 (t-BuI). Since the solvents with appreciable α values are the alcohols and water, these results may be interpreted to indicate that, by comparison with the results in the aprotic solvents, the transition states in the hydroxylic solvents are stabilized by electrophilic solvation in the order $[t\text{-BuCl}]^\ddagger > [t\text{-BuBr}]^\ddagger > [t\text{-BuI}]^\ddagger$.

Two factors may lead to this order. Firstly, the transition state for the chloride reaction in hydroxylic solvents is "later" than for the bromide and for the iodide; indicators of the "lateness" of the transition states are Abraham's Z values[21] of 0.84 (t-BuCl), 0.82 (t-BuBr), and 0.77 (t-BuI). The later the transition state, the more ion-pair-like it will be and the more electrophilically solvated will be the departing halide. Secondly, even for the same degree of charge development, the leaving chloride will be more solvated by (form a stronger hydrogen bond with) hydroxylic solvents than will the leaving bromide or iodide. Free energies of transfer of the halide ions from a typical aprotic solvent, dimethylformamide, to methanol are as follows, in kilocalories/mole relative to $\Delta G_t°(\text{Br}^-) = 0$: Cl^- (-2.3), Br^- (0.0), I^- (+2.9).[39] In a similar vein, free energies of hydration for the gas phase reactions, $\text{X}^- + 4\text{H}_2\text{O} \rightarrow \text{X(H}_2\text{O)}_4^-$ are as follows, in kilocalories/mole: Cl^- (-22.9), Br^- (-19.3), I^- (-14.7).[40]

The regression in eq 2 can be used to predict k values in solvents other than those listed in Table I. Values of π^* and α and calculated and observed log k are as follows: for ethylene glycol (0.85, 0.92, -4.4, -4.6);[37] for formamide (0.98, 0.69, -4.8, -4.4);[41] for trifluoroethanol (0.73, 1.35,[42] -2.9, -4.0).[43] It is noteworthy that in TFE the observed log k value is 1.1 unit more negative than calculated; i.e., the observed rate constant is about 12 times smaller than called for by eq 2. Perhaps, as previously suggested,[19] there is some unusual factor in TFE, such as ion-pair return. This might be because TFE is relatively poorly self-associated compared with other alcohols or H_2O,[44] which could lead to increased stabilization of the reactant state by t-BuCl···TFE hydrogen bonding.[45] Such reactant-state solvation would slow the forward rate and/or increase the fraction of internal return.

Equations 2-4 also appear to correlate the gas-phase values in Table I. Applying the equations in reverse leads to gas phase π^* estimates of -0.61 (t-BuCl), -0.60 (t-BuBr), and -0.55 (t-BuI), which agree quite well with an estimate of -0.51 to -0.58 by Bekarek,[46] based on an analysis of electronic spectral data.

Correlations with the Koppel-Palm Parameters. We have also carried out regression analyses on the data of Table I, using the method of Koppel and Palm,[27,28] who advocated the four parameter equation (eq 5), where $f(\epsilon)$,

$$\log k = \log k_0 + y\cdot f(\epsilon) + p\cdot f(n) + e\cdot E + b\cdot B \qquad (5)$$

a measure of solvent polarity, is the dielectric constant function $(\epsilon - 1)/(\epsilon + 2)$ or sometimes $(\epsilon - 1)/(2\epsilon + 1)$;[47] $f(n)$, a measure of solvent polarizability, is the refractive index function $(n^2 - 1)/(n^2 + 2)$, and E and B are measures of electrophilic solvation ability and nucleophilic solvation ability of the solvent, respectively. When applied to the log k values in the 15 solvents (Table I), not only is the solvent nucleophilic power (B) insignificant[48] but the influence of the solvent polarizability function, $f(n)$, is also relatively small; this reduces the four-parameter equation, eq 5, to a two- or three-parameter equation containing the exploratory variables E and $f(\epsilon)$ or E, $f(\epsilon)$, and $f(n)$. Relevent correlation constants are collected in Table II, it being clear that the two-parameter equation in π^* and α reproduces the data very much better than the corresponding equation in E, $f(\epsilon)$, and $f(n)$.

Not only does the regression analysis using π^* and α reproduce the log k values better than do previous similar analyses but the relevant equations (eq 2-4) also provide a simple explanation of the effect of solvents on the log k values in terms of a parameter (π^*) that reflects general solute (transition state)/solvent interactions of the dipole/dipole or dipole/induced-dipole-type and a parameter (α) that reflects the stabilization of the transition state through solvent hydrogen bonding, no doubt to the incipient halide ion in the transition state.

Based on the above correlations with both the solvatochromic parameters and the Koppel-Palm parameters, we have concluded that, in the solvolysis reactions of the *tert*-butyl halides, electrophilic assistance by protonic solvents is important and nucleophilic assistance relatively unimportant. It should be recognized that these conclusions do not accord with recent papers on the subject,[26,49] which have suggested that the dominant solvation effect of alcohol solvents is to nucleophilically stabilize the forming carbonium ion, the latter species behaving in effect as a Lewis acid (such solvation being similar in concept to association effects between HBA bases and Lewis acids such as we have reported earlier).[11] We will discuss this subject further in a future paper, where we will suggest that "ethanol-trifluoroethanol" plots, which have been interpreted as demonstrating enhanced nucleophilic solvation by ethanol,[26,49] can be interpreted with equal validity as demonstrating enhanced electrophilic solvation by trifluoroethanol.

Conclusions similar to the above have been reported by Parker et al.[50] These workers have correlated $\Delta G_t°(\text{Tr})$, the free energy of transfer of the *tert*-butyl chloride transition state, with $\Delta G_t°$ values for K^+ and Cl^- and have

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[48] B values are not known for some solvents, and therefore we have used the solvatochromic parameter β instead. The relationship between B and β has been described in an earlier paper.[10]

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Table III. Values of ΔG_t° (from MeOH, kcal/mol) at 298 K for Me_4N^+ and Cl^- [a]

solvent	π^*	α	β	ΔG_t° (Me_4N^+)	ΔG_t° (Cl^-)
acetone	0.68	0.10	0.48	−2.5	9.9
acetonitrile	0.76	0.22	0.31	−1.4	6.1
tert-butyl alcohol	0.40	0.66	1.01	1.9	7.0
2-propanol	0.47	0.77	0.95	0.5	2.6
methanol	0.60	0.98	0.62	0.0	0.0

[a] From ref 21, 39, and: Abraham, M. H.; Danil de Namor, A. F. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 955; *Ibid.* **1978**, *74*, 2101; Kolthoff, I. M.; Chantooni, M. K. *J. Phys. Chem.* **1979**, *83*, 473; *Anal. Chem.* **1979**, *51*, 133.

shown that the term in Cl^- is dominant, suggesting that anion (nucleophilic) solvation is important. For the 11 aliphatic aprotic and hydroxylic solvents for which Parker et al.[50] list available data (based on the Ph_4As^+/Ph_4B^- assumption), we find the regression equation to be eq 6,

$$\Delta G_t^\circ(\mathrm{Tr}) = 0.03 + 0.53\Delta G_t^\circ(\mathrm{Cl^-}) + 0.21\Delta G_t^\circ(\mathrm{K^+})\ \mathrm{kJ/mol} \quad (6)$$

with $r = 0.991$; this represents a good correlation, only slightly poorer than the π^*/α correlation, for which $r = 0.995$ for 15 similar solvents.

For the *tert*-butyl bromide reaction, again using the data of Parker and co-workers, we find eq 7, with $r = 0.990$ for

$$\Delta G_t^\circ(\mathrm{Tr}) = 0.73 + 0.37\Delta G_t^\circ(\mathrm{Br^-}) + 0.18\Delta G_t^\circ(\mathrm{K^+})\ \mathrm{kJ/mol} \quad (7)$$

7 solvents (c.f. $r = 0.995$ for the π^*/α correlation over 15 solvents). Again, electrophilic solvation seems more important than nucleophilic solvation, although it is by no means clear how good a model is K^+ for the positive pole in the transition state.

In further support of these conclusions, if the free energies of the ions Me_4N^+ and Cl^- are examined in some moderately dipolar solvents (Table III), it is clear that hydroxylic solvents stabilize Cl^- through electrophilic solvation but do not stabilize Me_4N^+ through nucleophilic solvation [the $\Delta G_t^\circ(Me_4N^+)$ terms becoming more exogenic with increasing solvent dipolarity, but not with increasing solvent HBA basicity]. But if the free ion Me_4N^+ is not nucleophilically solvated, neither will be the Me_4N^+ moiety in the $Me_4N^+Cl^-$ ion pair. Since this ion pair has been shown to be a very good model for the *tert*-butyl chloride transition state,[18,20-22] by implication the latter will also not be nucleophilically solvated by the hydroxylic solvents but will (c.f. Cl^-) be subject to electrophilic solvation.

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Registry No. *t*-BuCl, 507-20-0; *t*-BuBr, 507-19-7; *t*-BuI, 558-17-8.

Nitrations and Oxidations with Inorganic Nitrate Salts in Trifluoroacetic Anhydride

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Metal nitrates in trifluoroacetic anhydride nitrate many aromatic compounds in high yields at room temperature, including polymers with aromatic groups. However, this system oxidizes phenols to quinoid products.

Inorganic nitrate salts have been used in the presence of strong mineral acids to nitrate organic compounds. Numerous examples of their use may be found primarily in the patent literature. Olah has recently reviewed the field of organic nitration reactions employing a variety of inorganic nitrate salts as nitrating agents.[1] Menke has shown that transition-metal nitrate salts, particularly copper nitrate, in acetic anhydride can be used to nitrate certain reactive, aromatic compounds such as phenol.[2] The yields appear to vary widely, and alkali and alkaline earth metal nitrates gave either very poor yields or did not react at all. Trifluoroacetic anhydride[3] (TFAA) and trifluoroacetic acid[4] (TFA) have also been used to a limited extent with nitric acid and form very effective nitrating agents. However, the use of nitrate salts in TFAA has not been investigated as a nitrating agent.

During the course of studies involving transition-metal-catalyzed oxidations of aromatic compounds, it was found that ammonium nitrate and TFAA react with aromatic substrates at 25 °C to produce aromatic nitro compounds in very good yields. Later it was found that it is possible to use any inorganic nitrate salt in TFAA.[5,6] It was decided to pursue this investigation further to determine the optimum reaction conditions and to broaden the scope of this reaction.

Results and Discussion

The general reaction shown in eq 1 may be written to describe the nitration of organic compounds with inorganic nitrate salts in TFAA.

$$\mathrm{ArH} + \mathrm{MNO_3} + (\mathrm{CF_3CO})_2\mathrm{O} \rightarrow \mathrm{ArNO_2} + \mathrm{CF_3CO_2M} + \mathrm{CF_3CO_2H} \quad (1)$$

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