Aromatic Protodealkylation. Evidence for an A-1 Reaction Mechanism

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Abstract: The transition-state activity coefficient approach has been applied to the protodealkylation reactions of some derivatives of phenol and anisole in perchloric acid. Two distinct types of medium dependence of log $f^*_{\pm}$ are observed for protodetritylation and protode-tert-butylation reactions. The former shows a pronounced salting-out or destabilization of $S^{\pm}$ over the whole region of acidity, similar to that found for aromatic hydrogen–deuterium exchange. This is associated with a typical A-SE2 reaction mechanism in which proton transfer is rate determining. For the *tert*-butyl derivatives, log $f^*_{\pm}$ shows much lower sensitivity to changes in medium composition, which is interpreted in terms of an A-1 mechanism, in which formation of the *tert*-butyl carbonium ion takes place in the rate-determining step. These mechanistic conclusions are supported by the solvent kinetic isotope effects for these reactions. For detritylation, the expected "normal" effect is found ($k_H/k_D > 1$); de-tert-butylation shows an inverse isotope effect ($k_H/k_D < 1$), indicating rate-determining cleavage of the substrate conjugate acid (or Wheland intermediate) in an A-1 process.

A recent review[1] of aromatic reactivity classifies all substitutions involving an acid (or a proton) as the effective electrophile, as A-SE2 reactions, where proton transfer to the aromatic takes place in the rate-determining step. According to this review, the alternative A-1 or A-2 mechanisms ". . . have been eliminated for all of the reactions so far investigated. . .". For numerous reactions of this type, the A-SE2 mechanism has been firmly established by solvent isotope effect studies and substituent effects on reaction rates. However, since this type of electrophilic substitution extends over a large variety of groups being replaced by hydrogen, it seems reasonable to expect that in some systems the rate of the second step (removal of a leaving group from the Wheland intermediate) could become, at least partially, rate determining, and that a mechanism change from A-SE2 to A-1 might take place.

The A-SE2 mechanism has been demonstrated for the protodesilylation and protodegermylation reactions (where SiR_3 or GeR_3 groups are displaced by hydrogen) under acid-catalyzed conditions, intensively studied by Eaborn and his co-workers.[2] Closely related to these reactions is the protodealkylation reaction, frequently observed for alkyl-substituted aromatic compounds in the presence of strong acids.[3] Only a few kinetic studies of this reaction have been reported. Rates of protode-tert-butylation of *tert*-butylbenzene were measured in aqueous H_2SO_4.[4] The reaction was considerably slower than hydrogen–deuterium exchange in C_6H_5D in the same medium;[5] such a result does not suggest a common A-SE2 mechanism, where the basicity of the aromatic C(1) carbon should determine the reaction rate. The initial rates of the acid-catalyzed cleavage of hydroxy- and methoxy-substituted tetraphenylmethane were measured in mixed aqueous-organic media.[6] The mechanistic conclusions, based solely on the log $k_{obsd} - H_0$ dependence and suggesting rate-determining $\pi - \sigma$ complex isomerization, seem rather unconvincing.

In a previous report[7] we have demonstrated that for the acid-catalyzed hydrolysis of esters, useful mechanistic information can be obtained by examining the behavior of the transition-state activity coefficient as a function of the reaction medium. This activity coefficient, $f^*_{\pm}$, expressed relative to the standard (tetraethylammonium) ion can be calculated from rate (k_ψ), substrate activity coefficient (f_S), and substrate basicity (K_{SH^+}) data, together with recently available[8] values of the proton activity ($a^*_{H^+}$), according to the equation:

$$\log (f^*_{\pm}/k_0) = -\log k_\psi - \log K_{SH^+} + \log f_S + \log a^*_{H^+} \quad (1)$$

where k_0 is the rate constant of the slow step. The medium variation of the left side of eq 1 was shown[7] to be very sensitive to mechanistic changes, due to changes in the hydration requirements of different transition states.

We now report the application of this approach to the protode-tert-butylation of four derivatives of *tert*-butylbenzene, XC_6H_4-*t*-Bu (X = *p*-OH, **1**; *o*-OH, **2**; *p*-OMe, **3**; *o*-OMe, **4**), and to the protodetritylation of *p*-triphenylmethylphenol, *p*-$HOC_6H_4CPh_3$ (**5**). It was hoped that comparison of log $f^*_{\pm}$ behavior for these systems with those where the A-SE2 mechanism has been established could provide valuable mechanistic conclusions with respect to the possibility of the alternative A-1 reaction path.

Results and Discussion

In Table I are listed pseudo-first-order rate constants for reactions of compounds **1–5** as a function of perchloric acid[9] concentration. For the *tert*-butyl derivatives, the decrease of the uv absorption due to the change from substrate to phenol (or anisole) was measured; for the trityl derivative **5**, the increase of the absorption due to the formation of the triphenylmethyl carbonium ion was recorded.[10] Because of the very low solubility of **5** in aqueous $HClO_4$, rates were measured in aqueous $HClO_4$/trifluoroacetic acid mixtures of various contents of TFA and were extrapolated to pure aqueous $HClO_4$ solution. For all compounds, good linearity of log k_ψ vs. molarity of $HClO_4$ was found ($r > 0.99$ for compounds **1–4** and $r > 0.98$ for **5**). This indicates that competitive O-protonation of the substituent is negligible over this acidity range, otherwise the rates would not have continued to increase monotonically with acidity.[12] The reactivity data show that the protode-tert-butylation differs markedly from the related protodesilylation and protodegermylation reactions. In the latter systems[13] the hydroxy derivatives are more reactive than the methoxy ones (by a factor of 5–7), and no steric acceleration was observed for the ortho-substituted compounds, which are in fact less reactive than the corresponding para isomers. Both features are consistent with an A-SE2 mechanism; for the methoxy substituent, the log f_o/log f_p ratios in numerous electrophilic reactions, including protodesilylation, are remarkably similar (0.8–0.9) and have been quantitatively correlated[14] with the charge distribution between the ortho and para positions in the benzenonium ion—an intermediate formed in a rate-determining step. However, for protode-tert-butylation, the reactivities of hydroxy and methoxy derivatives are almost identical within each pair, and the ortho

Table I. Protodealkylation Rates in Perchloric Acid at 25.0 °C

	$10^4 k_\psi$[a,b]				
M $HClO_4$	**1**	**2**	**3**	**4**	**5**[c]
7.58		0.150			
7.90		0.464			
8.23		1.73		0.678	
9.02	0.122	6.59		5.99	
9.42	0.366	24.95	0.464	15.36	
9.70			1.05		
10.21	2.92	126.7	2.58	159.3	0.478
10.65	12.34		19.57		1.91
11.47	112.5		142.2		5.03
12.07					15.85

[a] Pseudo-first-order rate constants, s^{-1}. [b] ±5%. [c] Extrapolated from data obtained in aqueous $HClO_4$/TFA mixtures.

Table II. Activity Coefficients of Substituted *tert*-Butyl- and Tritylbenzenes at 25.0 °C

	Log f_S				
M $HClO_4$	**1**[a]	**2**[a]	**3**[a]	**4**[b]	**5**[a]
1.03				−0.09	−0.30
1.73			−0.07		
2.24	−0.01	0.11	−0.07	−0.19	−0.35
3.56	0.00	0.15	−0.05	−0.26	−0.44
5.08	0.05	0.20	0.00	−0.28	−0.43
7.00	0.21	0.42	0.09	−0.27	
7.90	0.21		0.12		
8.23				−0.28	−0.43
9.02		0.52	0.14		
9.42	0.25	0.50	0.13		
10.21	0.29	0.47	0.11		
10.65			0.04		

[a] Obtained by distribution method. [b] Obtained by solubility method.

isomers are significantly more reactive (by a factor of at least 30) than para compounds, indicating considerable strain relief in the rate-determining step. The kinetic data show also that the reactivity of the *p*-hydroxytrityl derivative **5** is essentially different from that of its *tert*-butyl analogue **1**.

Activity coefficients for aromatic substrates **1**–**5** were determined by the usual distribution or solubility methods[15] and are listed in Table II. Values of the transition-state activity coefficient, log $f^*_\pm$ were then calculated according to eq 1[16] for different $HClO_4$ concentrations, and the variations obtained are presented in the Figure 1. The corresponding plots for a typical A-SE2 reaction, namely the protodedeuteration of *p*-cresol-*2-d* (**6**) and anisole-*4-d* (**7**) in aqueous H_2SO_4 were determined from the available kinetic[18] and activity coefficient[15] data and are included in Figure 1 for comparison. Transition-state activity coefficients of the discussed compounds exhibit two distinct patterns of behavior. For both dedeuteration reactions, a continual salting-out (or destabilization of the transition state) is observed with increasing acidity, which is in agreement with the hydration requirements of A-SE2 transition state, in which a proton is being only partially transferred from the hydronium ion or acid molecule. The more pronounced effect on $f^*_\pm$ for the cresol derivative can be explained in terms of the additional hydration requirements (by means of the $-OH\cdots OH_2$ hydrogen bonding) of the phenolic group involved in the electron-releasing stabilization of the transition state. The protodetritylation reaction falls into the same category of behavior, showing a strong

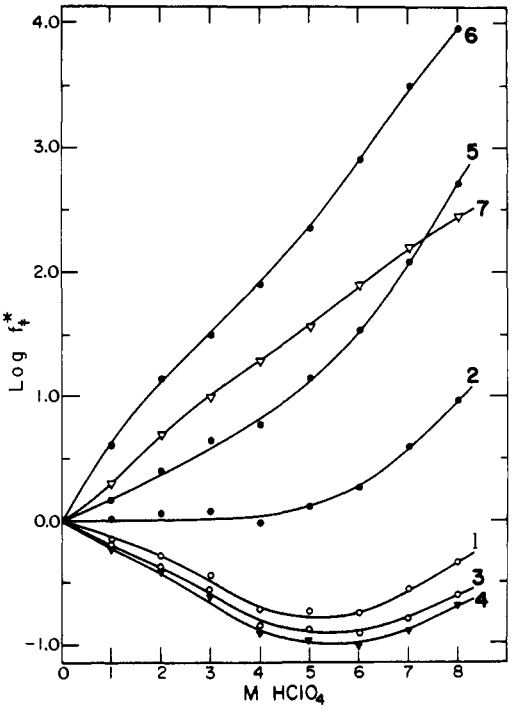
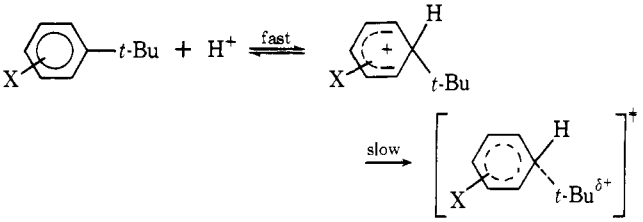
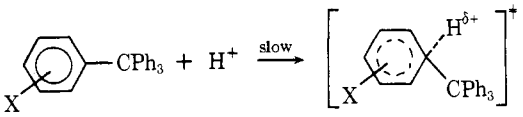


Figure 1. Transition-state activity coefficient (relative to TEA^+) for: Protodealkylation in aqueous $HClO_4$, **1**, *p-tert*-butylphenol; **2**, *o-tert*-butylphenol; **3**, *p-tert*-butylanisole; **4**, *o-tert*-butylanisole; **5**, *p*-triphenylmethylphenol. Protodedeuteration in aqueous H_2SO_4, **6**, *p*-cresol-*2-d*; **7**, anisole-*4-d*.

salting-out effect on log $f^*_\pm$ with an increase of $HClO_4$ concentration. This indicates that the trityl derivative **5** reacts according to the "normal" A-SE2 mechanism, and the low reactivity of this substrate results most probably from steric hindrance in the rate-determining proton transfer to the sterically crowded C(1) aromatic carbon. For the protode-tert-butylations, a completely different type of dependence was obtained; the log $f^*_\pm$ values show low sensitivity to changes in medium composition over a wide range of acidities and, in fact, even show a weak salting-in effect for substrates **1**, **3**, and **4**. This type of behavior is what would be expected if carbon–carbon bond cleavage occurs at the transition state and the formation of the *tert*-butyl carbonium ion is highly advanced, i.e., if the A-1 mechanism operates for this substitution reaction. Similarly, low sensitivity of log $f^*_\pm$ to changes in acidity was observed previously[7] for A_{Al}-1 ester hydrolysis and was



interpreted in terms of a high degree of a carbonium ion character of the transition state. In the case of the trityl derivative, the formation of the particularly stable triphenylmethyl carbonium ion is fast relative to the formation of the Wheland intermediate, and the reaction follows the A-SE2 mechanism:



According to the above interpretation, the essential difference between the protode-tert-butylation and protodetrityla-

Table III. Solvent Kinetic Isotope Effect in Aromatic Dealkylation at 25.0 °C

Compd	$LClO_4$ in L_2O, % (w/w)[a]	k_H/k_D[b]
1	59.56	0.10
	59.97	0.11
	63.02	0.10
2	51.25	0.12
	54.56	0.26
	59.97	0.36
5	68.32	4.3

[a] Concentrations of aqueous $HClO_4$ solutions were determined from their densities and concentrations of $DClO_4/D_2O$ solutions by titration. However, excellent agreement ($\Delta < 0.05\%$) between results obtained from densities and titration was found for aqueous solutions of $HClO_4$. [b] ±10%.

tion reactions lies in the fact that, for the former reaction, proton transfer occurs before and, for the latter, during the rate-determining step. If this is true, both reactions should respond differently to an isotopic change in the acidic medium. For the A-SE2 process, the usual kinetic solvent isotope effect ($k_{D_2O}/k_{H_2O} < 1$) should be observed, whereas for the A-1 reaction an inverse effect is expected, due to the higher concentration of the substrate conjugate acid in the deuterated medium. Rates of deuterodealkylations have been measured for compounds **1**, **2**, and **5** in $DClO_4/D_2O$ systems, and the observed solvent isotope effects are collected in Table III. For *p*-triphenylmethylphenol (**5**), the low solubility and low reactivity of the substrate limited measurements to the most concentrated $DClO_4$ solution. The observed k_H/k_D value remains, however, in excellent agreement with those reported for analogous reactions of aromatic systems. $k_H/k_D = 6.2–7.4$ was found for the desilylation in $CF_3CO_2L–L_2O$,[19] and a value of $k_H/k_D = 3.7$ has been taken as a proof of the A-SE2 mechanism for the deboronation reaction in sulfuric acid.[20]

For the *tert*-butyl derivatives **1** and **2**, surprisingly high inverse solvent isotope effects were obtained. In the case of O-protonated substrates, for the acid-catalyzed reactions where proton transfer to the substrate may be regarded as complete before attainment of the transition state, solvent isotope effects were found to be in the range of $k_H/k_D = 0.3–0.5$.[21] There are, however, no data available for the similar effects on the preequilibrium protonation at an aromatic carbon. Also, since the acidity function of $DClO_4$ in D_2O is not known, identical composition of $HClO_4/H_2O$ and $DClO_4/D_2O$ solutions does not correspond necessarily to the same acidity for these two systems. The inverse solvent isotope effect shows unambiguously that the protode-tert-butylation reaction does not proceed according to the A-SE2 mechanism,[22] but most likely according to an A-1 reaction path; this is precisely the same conclusion that has been reached from the transition-state activity coefficient behavior. It is interesting to note, that the solvent isotope effect for *o-tert*-butylphenol (**2**) decreases with an increase in acidity, which might indicate that the second step of the reaction is only partially rate determining. The behavior of the transition-state activity coefficient of this compound is also intermediate in character (Figure 1) suggesting the borderline mechanism between "pure" A-1 and A-SE2 reactions.

For reactions proceeding in strongly acidic media, mechanistic conclusions are frequently drawn from an examination of the rate–acidity dependence. Such plots of log k_ψ vs. acidity function for the protodeboronation,[20] protodedeuteration,[18] and protode-tert-butylation are presented in Figure 2.

The slopes of all plots are remarkably similar, and the rate profiles give no indication about the possible mechanism change within this series of electrophilic substitutions. On the other hand, examination of the transition-state activity coefficient behavior provides clear evidence for the A-1 mechanistic pattern in case of the protode-tert-butylation reaction. In conclusion, we believe that we have demonstrated that the transition-state activity coefficient approach can be successfully used as a mechanistic criterion for acid-catalyzed reactions in aromatic systems.

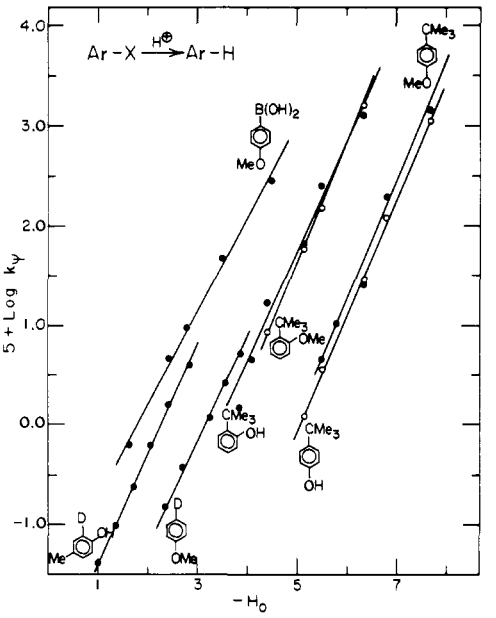


Figure 2. Rate–acidity profiles for protodeboronation, protodedeuteration, and protode-tert-butylation reactions.

Experimental Section

Analyses were performed by A. G. Gygli, Toronto 180, Ontario.

Reagents. Aqueous solutions of $HClO_4$ were prepared by diluting the concentrated acid of AnalaR Grade with distilled water. Concentrations of these solutions were determined from their densities measured with a DMA 02C digital precision density meter at 25.0 °C. Solutions of $DClO_4$ in D_2O were prepared by diluting the concentrated perchloric acid-*d* (68% in D_2O, 99+ atom % D, Diaprep, Aldrich Chem. Co.) with deuterium oxide (min 99.75 atom % D, J. T. Baker Chem. Co.), and their concentrations were determined by standard titration against potassium hydroxide. Cyclohexane, chloroform, and methanol were of ACS Spectranalyzed grade. *p-tert*-Butylphenol (**1**) (Aldrich) and *p*-tritylphenol (**5**) (Aldrich) were recrystallized from water and acetic acid, respectively. *o-tert*-Butylphenol (**2**) (Aldrich) was distilled immediately before use, bp 63 °C (1 mm). *p-tert*-Butylanisole (**3**) was prepared by the standard methylation of *p-tert*-butylphenol with dimethyl sulfate; bp 62–63 °C (0.9 mm). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 81.15; H, 9.61. Ir and NMR spectra showed no trace of unreacted substrate.

o-tert-Butylanisole (**4**) was prepared by methylation of *o-tert*-butylphenol with the excess of dimethyl sulfate. Ir and TLC showed that the reaction product always contained significant amounts of unreacted phenol, which could not be removed by fractional distillation. The crude reaction product was separated on the chromatographic column (Florisil, 60–100 mesh, hexane/methylene chloride, 5:1) the product **4** collected as a first fraction and distilled, bp 57–58 °C (1 mm). Anal. Found: C, 80.95; H, 9.68. Ir and NMR spectra showed no trace of unreacted phenol.

Product Determination. For compounds **1–4** the uv spectra of the solution of the substrate in aqueous perchloric acid were recorded at 230–300 nm. The spectra changed with time, and after the reaction was complete the absorption curves were exactly superimposable with those of the corresponding reaction products (phenol or anisole) of the same concentration.

For compound **5** the absorption spectrum of the reaction product at 250–500 nm in perchloric acid–trifluoroacetic acid mixture was,

after suitable time, identical with the spectrum of the trityl ion obtained from triphenylcarbinol in the same medium.

Kinetic Methods. For compounds **1–4** ca. 10 μl of the stock solution of the substrate in methanol (0.05–0.10 M) was introduced to 3.0 ml of aqueous acid in 1 cm uv cell thermostated at 25 ± 0.1 °C in a Cary 16 Model spectrophotometer with an external recorder. The decrease in ultraviolet absorption was measured at 276–280 nm; good linear plots of log A vs. time were obtained in all cases ($r > 0.99$). For compound **5** ca. 5 μl of the stock solution in methanol (ca. 10^{-3} M) was introduced in the same way to the mixture of aqueous perchloric acid and trifluoroacetic acid, and the increase in the absorption at 403 nm was measured. Excellent linear plots of log A vs. time were obtained ($r > 0.999$).

Activity Coefficient Measurements. For compounds **1**, **2**, **3**, and **5**, the distribution method was applied. For the *tert*-butyl derivatives **1–3**, 1 ml of ca. 0.2 M solutions of substrates in cyclohexane was shaken mechanically with 5 ml of water or aqueous acid for 2 min at 25 ± 0.1 °C. The absorbance of substrates in aqueous and organic layers was measured at 276–280 nm, using a Cary 14 recording spectrophotometer. At higher acidities (above 8 M) various shaking periods from 1–3 min were applied, and the observed absorbances were extrapolated to zero shaking time. For compound **5**, 1 ml of 1.6×10^{-2} M solution in chloroform was shaken with 12 ml of water or aqueous acid for 2 min, and the absorbance of substrate in aqueous layer was measured at 270 nm using 10-cm uv cells. The values of the activity coefficients were calculated from the ratio of distribution coefficients in pure water to that in a given acid solution. For compound **5**, the concentration in the chloroform layer was taken as constant (distribution coefficient $< 10^{-3}$). Because of the very low solubility of compound **4** in water, activity coefficient values were obtained by solubility method. **4** (0.1 ml) was shaken with 5 ml of water or aqueous acid at 25 ± 0.1 °C for 1 h. Separate experiments showed this time to be sufficient to obtain equilibration. The concentration of the substrate in aqueous phase was then determined from the absorbance at 270 nm. At acidities above 5 M various shaking periods (1–3 h) were applied, and the observed absorbances were extrapolated to zero shaking time; extrapolation never exceeded 10% of the measured absorption values.

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Contact vs. Pseudocontact Contributions to Lanthanide-Induced Shifts in the Nuclear Magnetic Resonance Spectra of Isoquinoline and of *endo*-Norbornenol

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Abstract: The differences between calculated and observed behavior of lanthanide shift reagents vs. isoquinoline and *endo*-norbornenol have been recorded. These differences are interpreted as contact shifts. The magnitudes of the shifts are compared with several independent theoretical and experimental determinations of contact/pseudocontact ratios. Contact shifts are evident in the ^{13}C magnetic resonances of the hard base isoquinoline and the softer base norbornenol. Of the eight lanthanides studied $Yb(dpm)_3$ was found to be the most effective for determining pseudocontact indexes.

Introduction

Effects of paramagnetic ions on magnetic resonance spectra have been of research interest for more than 2 decades. The literature contains numerous articles which deal with the theoretical bases for and the experimental applications of paramagnetic ion effects to chemical problems.[2] A renewed interest in paramagnetic ion effects has been generated by reports of easily understood dispersions of the nuclear magnetic resonance signals of many organic molecules by paramagnetic lanthanide shift reagents (LSR's).[3] In this paper we will examine the source of these lanthanide-induced chemical shifts.

The total isotropic shift induced by a paramagnetic species in the NMR resonance of a molecule can be discussed in terms of two distinct effects, a through-bond effect (Fermi contact shift)[4] and a through-space effect (dipolar or pseudocontact