involving ammine complexes of metals other than cobalt appear to be available with which eq 7 could be further tested at the present time.

As will be discussed in detail elsewhere,[25] the relative success of the Marcus correlation (a) (and therefore also eq 7) found for some systems here and in ref 1 and 2 may be misleading inasmuch as a quite different result would probably be obtained if a comparison could be made between rate constants that were corrected for the free energy of the approach of the reactants and products. Thus the measured entropies of activation for the homogeneous reactions listed in Table I are uniformly large and negative[12–20] which probably arises chiefly from solvent ordering attending the approach of the multicharged cationic reactants, whereas the corresponding entropic term for the electrode reactions is probably small.[25,26] Consequently, comparison between the (few available) enthalpies of activation for the corresponding electrochemical and homogeneous self-exchange systems indicates that the former values are substantially greater than half of the latter values, in contradiction to the reasoning behind correlation (a) above.[1] Therefore it is likely that the relative success of correlation (a)[1,2] and eq 7 is due to the unfavorable activation entropy for the chemical systems effectively compensating for the additional activation enthalpy in the electrochemical systems which may arise because the reactant is unable to penetrate the solvent layer adjacent to the electrode surface.[1] The relative importance of these effects may well vary with the size and structure of the reactants, as well as the charge carried by the reactants.

The discrepancies notwithstanding, there do appear to be similar trends exhibited by $(k^{\mathrm{chem}}{}_{\mathrm{AB}})_{\mathrm{calcd}}$ and $(k^{\mathrm{chem}}{}_{\mathrm{AB}})_{\mathrm{obsd}}$ for a series of related heteronuclear reactions. This correlation may therefore be utilized with some confidence to estimate approximate outer-sphere rates for either electrochemical or chemical reactions given rate data for either of these reaction types that is known to refer to an outer-sphere pathway. For example, the electroreduction of $Cr(OH_2)_5F^{2+}$ (in addition to $Cr(OH_2)_5SO_4^+$ and $Cr(OH_2)_6^{3+}$) proceeds by an outer-sphere mechanism at a mercury electrode,[27,28] and the electrochemical rate data[9,27,28] can be inserted into eq 7 to yield a calculated rate constant for the outer-sphere homogeneous reaction between $Cr(OH_2)_5F^{2+}$ and Cr^{2+} of 10^{-9} M^{-1} s^{-1}, markedly slower than the inner-sphere rate constant observed to be 2.6×10^{-3} M^{-1} s^{-1} for this reaction involving bridging by F^-.[29] This example illustrates one exploitable aspect of eq 7 in using electrochemical rate data to estimate outer-sphere rates for homogeneous reactions in that rate measurements of reactions with very small second-order rate constants ($<10^{-4}$ M^{-1} s^{-1}) are difficult and often impossible to obtain due to chemical instability of the reactants, competing reactions such as acid-dependent pathways, etc. However, the rate measurements for the corresponding heterogeneous electrochemical reactions are easily performed with measurement times in the subsecond region (thus minimizing any influence of following chemical reactions) and acid-dependent pathways are usually unimportant,[30] probably due to the ineffectiveness of hydroxyl as a bridging group at electrode surfaces.

It is also anticipated that eq 7 will prove to be useful in extending the Marcus correlation between electrochemical and chemical reactivities to a greater variety of redox processes than have hitherto been considered, e.g., to metal ion–nonmetal and bioinorganic reactions. A number of such applications await the further acquisition of good-quality electrochemical rate data.

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Oxygen- and Nitrogen-Bonded Borane Cations of Betaines and Amino Acid Esters

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In the few years since the initial elucidation[1] of the first borane cation $H_2B(NH_3)_2^+$ in the "diammoniate of diborane" many structural classes of cations have been discovered,[2] but few of these have functional substitution. It is of interest then to report a newly defined class of cations derived from betaines $(CH_3)_3NBH_2O_2C(CH_2)_nN(CH_3)_3^+$ and to extend the known amino acid ester derived cations[3] to the series $(CH_3)_3NBH_2N(CH_3)_2(CH_2)_nCO_2C_2H_5^+$. Comparison of the physical and chemical properties of the series provides insight into potential chemical transformations of the ester function.

The first member of ω-dimethylamino acid ester derived cations, namely, $(CH_3)_3NBH_2N(CH_3)_2CH_2CO_2C_2H_5^+$, was characterized as a water-stable species[3d] that hydrolyzes in dilute base to form a novel five-membered heterocycle $H_2\overline{BN(CH_3)_2CH_2CO_2}$.[3b] Extension of the series to $n = 2$–4 is now reported (Table I). Of these cations, only one, where $n = 2$, forms a crystalline hexafluorophosphate salt; the others remain as viscous oils (and, in our experience, are essentially

Table I

	Yield, %	Mp, °C	% calcd C	% calcd H	% calcd N	% found C	% found H	% found N
		Amino Ester Cations						
$C_2H_5O_2C(CH_2)_2N(CH_3)_2BH_2N(CH_3)_3{}^+PF_6{}^-$	47[c]		33.2	7.2	7.7	33.2	7.1	7.7
$C_2H_5O_2C(CH_2)_3N(CH_3)_2BH_2N(CH_3)_3{}^+PF_6{}^-$		Viscous oil	35.1	7.5	7.4	33.3	7.5	7.2
$C_2H_5O_2C(CH_2)_4N(CH_3)_2BH_2N(CH_3)_3{}^+PF_6{}^-$	68[c]	Viscous oil	36.9	7.7	7.2	35.6	7.5	6.9
		Betaine Cations						
$(CH_3)_3NCH_2CO_2BH_2N(CH_3)_3{}^+PF_6{}^-$	98[a]	152–153 dec	28.8	6.6	8.4	28.8	6.6	8.4
$(CH_3)_3N(CH_2)_2CO_2BH_2N(CH_3)_3{}^+PF_6{}^-$	78[a]	159–172 dec[b]	31.1	7.0	8.0	31.2	7.1	7.9
$(CH_3)_3N(CH_2)_3CO_2BH_2N(CH_3)_3{}^+PF_6{}^-$	>30[c]	149–151 dec	33.2	7.2	7.7	33.0	7.4	7.3
$(CH_3)_3N(CH_2)_4CO_2BH_2N(CH_3)_3{}^+PF_6{}^-$	34[c]	127–132 dec	35.1	7.5	7.4	33.4	7.1	6.6

[a] Based on original iodide salt isolated. [b] Melting point is a function of time of heating. [c] Based on $PF_6{}^-$ salt.

Table II. Hydrolysis[a] of $(CH_3)_3NBH_2N(CH_3)_2(CH_2)_2CO_2C_2H_5{}^+PF_6{}^-$ (29.8 °C; $I = 0.90$)

(OH^-), M	10^3k_1,[b] s^{-1}	10^2k_2,[c] $M^{-1}\ s^{-1}$	% H_2 measd
0.20	4.3	2.2	50
0.40	6.9	1.7	40

[a] Apparatus and procedure reported previously.[3b] [b] Pseudo-first-order constant; linear to only 1–2 half-lives. [c] $k_1/(OH^-)$.

the only cations that have resisted crystallization as hexafluorophosphate salts). They were prepared by iodide displacement from $(CH_3)_3NBH_2I$ followed by metathesis in aqueous solution.

Kinetics for aqueous hydrolysis (Table II) of $(CH_3)_3NBH_2N(CH_3)_2CH_2CH_2CO_2C_2H_5{}^+PF_6{}^-$ reveals a markedly different behavior than that of its glycine analogue ($n = 1$). Hydrolysis is rapid (surprisingly with k_2 similar to that for $\overline{H_2BN(CH_3)_2CH_2CO_2}$, but only half the expected hydrogen is collected; there is no evidence for a six-membered heterocyclic intermediate,[4] $\overline{H_2BN(CH_3)_2CH_2CH_2CO_2}$; and there is little noticeable trimethylamine liberated. Taken together, the observations suggest an intact hydrolyzed species with BH, amino acid, and trimethylamine moieties, but no characterizable species of that type could be isolated from the hydrolysates.

Because of the good aqueous stability of cyclic amino acid boranes,[3a] $(CH_3)_2\overline{N(CH_2)_nCO_2BH_2}$, it seemed likely that betaines, $(CH_3)_3N^+(CH_2)_nCO_2{}^-$, could also function as bases in borane cations and lead to isolable species. Indeed, this was realized and the cations $(CH_3)_3NBH_2O_2C(CH_2)_nN(CH_3)_3{}^+$, where n = 1–4, were characterized as relatively water-stable species forming crystalline, white hexafluorophosphate salts (Table I). Synthesis proceeded smoothly by iodide displacement from $(CH_3)_3BH_2I$ in chloroform even though the betaines have little or no solubility in the solvent. Formally this series differs from that of the amino acid ester cations by interchange of the $(CH_3)_3NBH_2$– and *N*-alkyl moieties. Crystallinity of the hexafluorophosphates of the higher betaine cations, as contrasted to the oily nature of the ester analogues, must reflect better, probably more compact packing arrangements of cations with positive "tails" than cations with lipophilic "tails". Qualitative order of stabilities toward aqueous base of the betaine cations ($n = 1, 2 > n = 3, 4$) is inverted from that of ester-derived cations ($n = 2, 3, 4 > n = 1$). However, until more detailed kinetic data are available, not much ought to be interpreted—especially in view of the spread of hydrolysis mechanisms already established.

Proton NMR and infrared spectra support the assigned structures (Tables III, IV).

Experimental Details

The ethyl ω-dimethylamino-substituted esters of acetic, propionic, butyric, and valeric acids were prepared from 2 molar amounts of dimethylamine and the corresponding ethyl ω-halo-substituted acids (Table V). The bromo-substituted acids (n = 1, 2) reacted in ether (500 ml for 0.3-mol run) at room temperature, but the chloro-substituted acids had to be heated with dimethylamine to 60 °C (n = 4) or converted to the iodo derivative (n = 3; with sodium iodide in acetone) which reacts with dimethylamine in ether at room temperature. Workup was analogous to that reported for ethyl dimethylaminoisobutyrate.[3b]

Table III. ^1H NMR Resonances[a]

Compd, solvent	Chem shift,[b] ppm, and assignment	Obsd rel intens
$(CH_3)_3NBH_2N(CH_3)_2(CH_2)_3$-$CO_2C_2H_5{}^+PF_6{}^-$, CH_2Cl_2	1.23, triplet (1:2:1), CH_3 of C_2H_5; $J_{HCCH} = 7$ Hz	2.7
	1.83–2.50, many, unresolved, $(CH_2)_3$	1.5
	2.82–2.85, unsym doublet $N(CH_3)_2$ $N(CH_3)_3$	15.0
	2.92–3.20, small multiplet $(CH_2)_3$	4.5
	2.48, quartet (1:3:3:1), CH_2 of C_2H_5; $J_{HCCH} = 7$ Hz	2.1
$(CH_3)_3NBH_2O_2CCH_2$-$N(CH_3)_3{}^+PF_6{}^-$, CD_3CN	2.58, B–$N(CH_3)_3$	9
	3.25, C–$N(CH_3)_3$	9
	4.05, CH_2	2.0
$(CH_3)_3NBH_2O_2C(CH_2)_2$-$N(CH_3)_3{}^+PF_6{}^-$, CD_3CN	2.57, B–$N(CH_3)_3$	9
	2.57–3.0, unresolved small multiplet, $(CH_2)_2$	1.8
	3.07, C–$N(CH_3)_3$	9
	3.47–3.72, three small, broad peaks, $(CH_2)_3$	1.9
$(CH_3)_3NBH_2O_2C(CH_2)_3$-$N(CH_3)_3{}^+PF_6{}^-$, CD_3CN	2.17, 2.28, 2.37, small, broad, $(CH_2)_3$	2.7
	2.57, B–$N(CH_3)_3$	9
	3.08, C–$N(CH_3)_3$	9
	3.17–3.50, unresolved multiplet, $(CH_2)_3$	3.4

[a] Obtained with a Varian A-60A spectrometer. [b] Downfield from internal tetramethylsilane.

Betaines were prepared by quaternization of the ω-dimethylamino acid esters with methyl iodide in ether to form $(CH_3)_3N(CH_2)_nCO_2C_2H_5{}^+I^-$, followed by passage through strong-base anion-exchange resin [Rexyn 201 (OH), 16–50 mesh]. The exchange effluent $[(CH_3)_3N^+(CH_2)_nCO_2{}^-]$ was concentrated under vacuum, finally heating to 80 °C under high vacuum (less than 10^{-5} mm) for several hours. Yields for the exchange step were 82–88% (n = 1, 3, 4) and 33% (n = 2).

Cations were synthesized by addition of molar amounts of soluble amino acid ester or insoluble betaine to a chloroform or methylene chloride solution of $(CH_3)_3NBH_2I$ (prepared from iodine and trimethylamine–borane). Details for synthesis of a cation of each type are given.

Table IV. Infrared Absorptions,[a] cm^{-1}

	BH	CO	Fingerprint (1300-900)
$(CH_3)_3NBH_2N(CH_3)_2(CH_2)_2CO_2C_2H_5{}^+PF_6{}^-$	2460 m, 2424 vw, 2380 vw, 2340 w	1720 s	1320 s, 1240 m, 1210 s, 1170 s multiplet, 1105 w, 1050 w, 1020 m, 1005 m, 970 m, 940-950 w doublet
$(CH_3)_3NBH_2N(CH_3)_2(CH_2)_3CO_2C_2H_5{}^+PF_6{}^-$	2460 m, 2380 vw, 2340 w	1720 s	1370 m, 1240 s, 1190 s, 1105 vw, 1070 vw, 1030 w, 1000 m, 980 m
$(CH_3)_3NBH_2O_2CCH_2N(CH_3)_3{}^+PF_6{}^-$	2410 m, 2300 vw	1690 s	1300 m, 1240 w, 1230 w, 1190 vw, 1170 s, 1125 w, 1110 vw, 1020 w, 985 m, 930 m
$(CH_3)_3NBH_2O_2C(CH_2)_2N(CH_3)_3{}^+PF_6{}^-$	2440 m, 2380 vw, 2310 vw	1675 s	1290 vw, 1265 w, 1255 m, 1195 s, 1175 m, 1125 vw, 1110 w, 995 m, 980 w, 950 vw, 930 m
$(CH_3)_3NBH_2O_2C(CH_2)_3N(CH_3)_3{}^+PF_6{}^-$	2380 m, 2290 w	1680 s	1320 s, 1250 m, 1225 w, 1190 m, 1160 s, 1140 w, 1120 vw, 1010 vw, 1020 vw doublet, 1005 w, 980 w, 965 w
$(CH_3)_3NBH_2O_2C(CH_2)_4N(CH_3)_3{}^+PF_6{}^-$	2410 m, 2300 w	1675 s	1285 w, 1240 w, 1195 w, 1160 s, 1120 vw, 1105 vw, 990 w, 970 w

[a] Run on a Perkin-Elmer 237B spectrophotometer neat or in mineral oil mulls. Abbreviations: s, strong; m, medium; w weak; vw, very weak.

Table V

ω-Dimethylamino acid ester	Starting material[a]	Bp, °C (pressure, mm)	Yield, %
$(CH_3)_2NCH_2CH_2CO_2C_2H_5$	$BrCH_2CH_2CO_2C_2H_5$	71 (21); lit.[5] 56-57 (12)	76
$(CH_3)_2N(CH_2)_3CO_2C_2H_5$	$Cl(CH_2)_3CO_2C_2H_5$	77-79 (14); lit.[6] 78-79 (18)	33
$(CH_3)_2N(CH_2)_4CO_2C_2H_5$	$Cl(CH_2)_4CO_2C_2H_5$	76-77 (6)	43

[a] Commercial material: Aldrich Chemical Co.

Betaine-Derived Cation, $(CH_3)_3NBH_2O_2C(CH_2)_2N(CH_3)_3{}^+PF_6{}^-$. A mixture of 327 mg (2.50 mmol) of betaine, $(CH_3)_3N(CH_2)_2CO_2$, and 20 ml of a chloroform solution of 2.59 mmol of $(CH_3)_3NBH_2I$ (from 3.31 mg of iodine added as a solid slowly to 188 mg of trimethylamine–borane in 20 ml of chloroform) was stirred 2 days. The insoluble iodide salt product (643 mg) was collected by filtration, dissolved in water, and metathesized to the title hexafluorophosphate salt with addition of excess solid ammonium hexafluorophosphate. The hexafluorophosphate salt was recrystallized from hot water before analysis. No more product was found in the chloroform reaction solution.

Other borane cations derived from betaines were soluble in chloroform as iodide salts. Workup involved solvent evaporation followed by dissolution in water and metathesis.

Amino Acid Ester Derived Cation, $(CH_3)_3NBH_2N(CH_3)_2(CH_2)_2CO_2C_2H_5{}^+PF_6{}^-$. A solution of 3.66 g (18.4 mmol) of $(CH_3)_3NBH_2I$ in 7 ml of methylene chloride was treated with 3.5 ml of ethyl ω-dimethylaminopropionate and allowed to stand overnight. Volatiles were removed under vacuum, and the resulting syrup was nearly crystalline on standing 1 day; it was dissolved in acidified water and metathesized to the title salt with ammonium hexafluorophosphate, giving a precipitate which slowly crystallized. The yield was 3.13 g (47%). A 1.0-g sample recrystallized from 100 ml of water (acidified with 4 drops of 6 M HCl) at 80 °C yielded 0.318 g of purified product. Salts of the higher acid esters did not crystallize from water, ethanol, methylene chloride, or acetonitrile and were purified by water washing and prolonged (8 h) drying under high vacuum.

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Registry No. $C_2H_5O_2C(CH_2)_2N(CH_3)_2BH_2N(CH_3)_3{}^+PF_6{}^-$, 58815-52-4; $C_2H_5O_2C(CH_2)_3N(CH_3)_2BH_2N(CH_3)_3{}^+PF_6{}^-$, 58815-54-6; $C_2H_5O_2C(CH_2)_4N(CH_3)_2BH_2N(CH_3)_3{}^+PF_6{}^-$, 58815-56-8; $(CH_3)_3NCH_2CO_2BH_2N(CH_3)_3{}^+PF_6{}^-$, 58815-59-1; $(CH_3)_3N(CH_2)_2CO_2BH_2N(CH_3)_3{}^+PF_6{}^-$, 58815-62-6; $(CH_3)_3N(CH_2)_3CO_2BH_2N(CH_3)_3{}^+PF_6{}^-$, 58815-65-9; $(CH_3)_3N(CH_2)_4CO_2BH_2N(CH_3)_3{}^+PF_6{}^-$, 58815-68-2; $(CH_3)_2NCH_2CH_2CO_2C_2H_5$, 20120-21-2; $(CH_3)_2N(CH_2)_3CO_2C_2H_5$, 22041-23-2; $(CH_3)_2N(CH_2)_4CO_2C_2H_5$, 58735-52-7; betaine, 6458-06-6; $(CH_3)_3NBH_2I$, 25741-81-5.

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Spectroscopic and Magnetic Studies of a Mixed-Valence Iron Fluoride, $Fe_2F_5 \cdot 7H_2O$[1a]

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In 1958 Brauer and Eichner[2] reported that the reaction of metallic iron with hot, concentrated hydrofluoric acid produced a yellow mixed-valence iron fluoride, $Fe_2F_5 \cdot 7H_2O$, and that this material could be dehydrated to a red trihydrate and a blue-gray anhydrous complex. Since the color changes observed upon dehydration suggest variation in the extent of iron–iron interactions, these systems may prove to be valuable probes for studying interactions in mixed-valence complexes. Although the dehydration of this material has been shown to be much more complex than originally proposed,[1,3,4] the existence of the heptahydrate has been repeatedly confirmed. In this note we report a variety of physical evidence bearing on the structure of the heptahydrate.

Experimental Section

The complex was prepared as described by Brauer and Eichner[2] and crystallized from solutions of iron in concentrated HF upon standing at room temperature. Anal. Calcd for $Fe_2F_5(H_2O)_7$: Fe, 33.56; F, 28.59; H_2O, 37.88. Found: Fe, 33.56; F, 28.54; H_2O, 37.89.

Magnetic susceptibilities were measured by the Faraday method. The balance was calibrated using $HgCo(NCS)_4$.[5] Mössbauer spectra