against flocculation. The results described here give some possible explanations for the roles of the reductant and the stabilizer and greatly expand the subfamily of MnO_4^-–reductant oscillating chemical reactions.

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"Gas-Phase-like" Behavior in Solution Chemistry[†]

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Abstract: Using data from this work and from the literature, the standard free-energy changes for reactions i and ii, $\Delta G_{H^+}(g)$ and $\Delta G^\circ_{I_2}(\text{soln})$, are compared: $B(g) + H^+(g) \rightleftarrows BH^+(g)$ (i); $B(\text{soln}) + I_2(\text{soln}) \rightleftarrows B\cdots I_2(\text{soln})$ (ii). B's are $S(sp^3)$ and $N(sp^2$ and $sp^3)$ n-donor bases (all compounds for which data sets are extensive and reliable), spanning a range of $\Delta G_{H^+}(g)$ of ca. 65 kcal·mol^{-1}. Within families, $\Delta G_{H^+}(g)$ and $\Delta G^\circ_{I_2}(\text{soln})$ are linearly related. Thus, a pattern of reactivity similar to that prevailing in the gas phase can be found in acid–base reactions in solution, provided charge dispersal through hydrogen bonding to the solvent is minimized.

I. Introduction

The development of experimental techniques for the study of proton-transfer reactions in the gas phase[1] has allowed the determination of gas-phase basicities (GB) and proton affinities (PA) for a substantial number of compounds. For a given base B, these magnitudes are defined as $GB(B) = \Delta G_{H^+}(g)$ and $PA(B) = -\Delta H_{H^+}(g)$, $\Delta G_{H^+}(g)$ and $\Delta H_{H^+}(g)$ being the standard free-energy and enthalpy changes for the reactions

$$B(g) + H^+(g) \rightarrow BH^+(g) \quad \Delta G_{H^+}(g),\ \Delta H_{H^+}(g) \qquad (1)$$

The pattern of structural effects on the aqueous basicities of organic compounds is dominated by the solvation of the onium ions, largely by charge dispersal through hydrogen bonding to water.[2] When solvation is not sterically hindered and the basic center as well as the number of acidic hydrogens are kept constant, as it is the case for pyridinium ions,[3] gas-phase and aqueous basicities are linearly related, provided allowance is made for an almost complete loss of polarizability[3] stabilization in aqueous solution. It is also known that extensive charge delocalization within the protonated base provides an efficient "internal solvation" leading to a very precise matching of structural effects on gas-phase and aqueous solution basicities.[4]

It is then fair to ask whether a *general* "gas-phase pattern of reactivity" can be observed in solution. From the above *it is clear that if a general "gas-phase ranking" of basicities is ever to be found in solution chemistry, charge dispersal through hydrogen bonding to the solvent has to be avoided.* This is a very difficult requirement for protonation reactions to fulfill,[5] but charge-transfer (CT)[7] association between neutral bases B and molecular iodine in solution (reaction 2) is a Lewis acid–base reaction that seems promising for this purpose.

$$B + I_2 \underset{\text{soln}}{\overset{K_c}{\rightleftarrows}} B\cdots I_2 \qquad \Delta G^\circ_{I_2}(\text{soln}) \qquad (2)$$

This work is thus aimed at comparing gas-phase proton basicity and solution molecular iodine basicity [defined as $IB = \Delta G^\circ_{I_2}(\text{soln})$] as determined in "inert" media (saturated hydrocarbons or dichloromethane).

Because data on $N(sp^2)$, $N(sp^3)$, and $S(sp^3)$ n-donor bases are more numerous and span a range of GBs of some 65 kcal·mol^{-1}, we have chosen to carry out a thorough study of these compounds.

II. Experimental Results and Discussion

For the purpose of extending the range of structural variations, a number of new IB values were determined in this study. They are presented in Table I together with data from other workers.

Most GB values given in Table I are taken with respect to the

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Table I. Thermodynamic Data for Reactions 1 and 2

	$\Delta G^\circ_{I_2}$(soln),[a,b] kcal·mol^{-1}							$\Delta G^\circ_{I_2}$(soln),[a,b] kcal·mol^{-1}					
B S(sp^3) bases	CCl_4, 298 K	ref	CH_2Cl_2, 298 K	ref	−δPA,[a] kcal·mol^{-1}	ref	B S(sp^3) bases	CCl_4, 298 K	ref	CH_2Cl_2, 298 K	ref	−δPA,[a] kcal·mol^{-1}	ref
H_2S			−0.16	13	32.9	8	Et_2S	−3.04	14	−3.55	14	−0.4	8
EtSH	−1.00	14	−1.51	14	14.2	8	*n*-Pr_2S	−3.04	15	−3.71	14	−2.3	8
Me_2S	−2.53	15	(−3.09)	16	4.9	8	$(CH_2)_3S$	−2.65	17	(−3.22)	16	4.6	8
McSEt	−2.91	15	(−3.49)	16	1.7	8	$(CH_2)_4S$	−3.11	14	−3.77	14	0.7	8
MeSi-Pr	−2.88	15	(−3.57)	16	−0.7	8	$(CH_2)_5S$	−2.91	20	(−3.49)	16	−0.5	8

	$\Delta G^\circ_{I_2}$(soln),[a,b] kcal·mol^{-1}					$\Delta G^\circ_{I_2}$(soln),[a,b] kcal·mol^{-1}					$\Delta G^\circ_{I_2}$(soln),[a,b] kcal·mol^{-1}			
N(sp^3) bases	*n*-C_7H_{16}, 293 K	ref	−δPA,[a] kcal·mol^{-1}	ref	N(sp^3) bases	*n*-C_7H_{16}, 293 K	ref	−δPA,[a] kcal·mol^{-1}	ref	N(sp^3) bases	*n*-C_7H_{16}, 293 K	ref	−δPA,[a] kcal·mol^{-1}	ref
NH_3	−2.45	22	0	8	Me_2NH	−5.14	22	−16.7	8	Quinuclidine	−7.20	23	−29.0	8
$MeNH_2$	−3.65	22	−9.6	8	Me_3N	−5.39	22	−21.2	8	DABCO[c]	−6.07	24	−23.6	25

	$\Delta G^\circ_{I_2}$(soln),[a,b] kcal·mol^{-1}									
N(sp^2) bases X-pyridines, X =	CH_2Cl_2, 303 K	ref	$CHCl_3$, 299 K	ref	CCl_4, 298 K	ref	*n*-C_7H_{16}, 298 K	ref	−δPA,[a] kcal·mol^{-1}	ref
H	−2.80	26	−2.43	31	−2.78	27	−3.03	32	−16.8	8
4-Me	−3.32	26	−2.85	31	−3.18	30	−3.49	32	−20.3	8
4-Et			−2.90	31	3.29	33	−3.55	34	−21.0	3a
4-*i*-Pr			−3.03	31	−3.43	14	(−3.69)	35	−21.9	3a
4-*t*-Bu			−3.04	31	−3.37	30	(−3.66)	36	−22.5	3a
4-CH:CH_2	−3.24	26					(−3.41)	16	−19.2	3a
3-Me	−3.21	26	−2.77	31	−3.15	30	−3.37	32	−19.7	3a
3-Et					−3.25	30	(−3.48)	16	−19.9	3a
4-NH_2	−4.53	26	−3.72	31			(−4.45)	37	−28.2	3a
4-MeO	−3.41	26					(−3.55)	16	−23.9	3a
4-Cl	−1.97	26					(−2.36)	16	−13.4	3a
4-CN							−1.29	38	−5.7	3a
4-NO_2	−0.55	26					(−1.18)	16	−4.2	3a
3-Cl	−1.44	26			−1.66	30	−1.85	32	−10.6	3a
3-CN	−0.62	26					−1.35	38	−4.8	3a
3-NO_2	−0.39	26					(−1.04)	16	−3.3	3a
4-NMe_2							−5.14	38	−33.2	8

	$\Delta G^\circ_{I_2}$(soln),[a,b] kcal·mol^{-1}							$\Delta G^\circ_{I_2}$(soln),[a,b] kcal·mol^{-1}					
1-X-imidazoles X =	$CHCl_3$, 299 K	ref	*n*-C_7H_{16}, 298 K	ref	−δPA,[a] kcal·mol^{-1}	ref	1-X-imidazoles X =	$CHCl_3$, 299 K	ref	*n*-C_7H_{16}, 298 K	ref	−δPA,[a] kcal·mol^{-1}	ref
H	−3.06	39	(−3.71)	16	−19.6	40	*t*-Bu			−4.19	14	−26.2	41
Me			−3.89	14	−23.0	41	1-adamantyl			−4.64	14	−31.4	41

	ΔG_{I_2}(soln),[a,b] kcal·mol^{-1}							ΔG_{I_2}(soln),[a,b] kcal·mol^{-1}					
diazines	CH_2Cl_2, 303 K	ref	*n*-C_7H_{16}, 298 K	ref	−δPA,[a] kcal·mol^{-1}	ref		CH_2Cl_2, 303 K	ref	*n*-C_7H_{16}, 298 K	ref	−δPA,[a] kcal·mol^{-1}	ref
1,2-pyridazine	−1.40	42	(−1.86)	16	−11.5	8	pyrazole			−2.58	14	−9.1	8
1,3-pyrimidine	−0.89	42	−1.38	43	−6.8	8	isoquinoline			−3.35	32	−22.5	8b
1,4-pyrazine	−0.54	42	−1.22	45	−4.5	8							

	$\Delta G^\circ_{I_2}$(soln),[a,b] kcal·mol^{-1}					
	CCl_4, 298 K	ref	*n*-C_7H_{16}, 298 K	ref	−δPA,[a] kcal·mol^{-1}	ref
thiazole	−1.65	46	(−1.85)	16	−9.5	8

[a] Corrected for symmetry changes as indicated in the text. [b] Uncertainties estimated at 0.15–0.20 kcal·mol^{-1} at the most.[12] [c] 1,4-Diazabicyclo[2.2.2]octane.

same "basicity ladder".[8] Uncertainties in GBs are estimated at 0.1–0.2 kcal·mol^{-1}.

Equilibrium constants K_c for reaction 2 were determined using standard UV–visible techniques previously described.[9] We recall that IB = $\Delta G^\circ_{I_2}$(soln) = $-RT \ln K_c$.

There are several difficulties inherent to the determination of solution K_c values. In principle, very "inert" solvents such as alkanes and cycloalkanes are highly desirable. In practice, this reduces the solubility of strongly dipolar solutes (including both the bases B and the complexes $B \cdots I_2$), it is then necessary to use solvents such as di-, tri-, and tetrachloromethane. In these cases, the danger of a complete ionization of the complex is often present,[10] a fact reducing the applicability of this method. In short, this frequently implies difficulties at determining all K_c values in the same solvent, for families of compounds spanning a wide range of reactivities.

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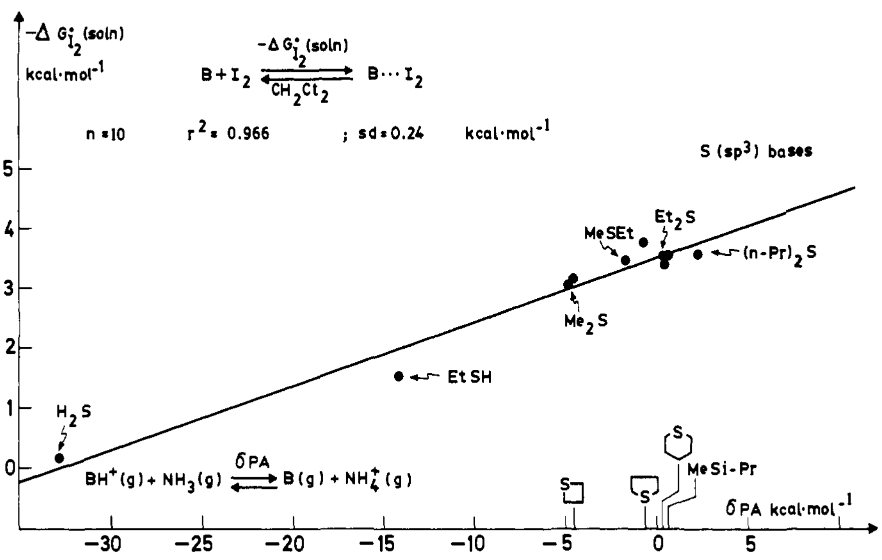

Figure 1. Standard free-energy changes (corrected for changes in symmetry numbers) for iodine complexation of S(sp^3) bases in CH_2Cl_2 solution at 298 K versus differential gas-phase proton affinities for the same compounds.

It is fortunate, however, that for families of structurally related compounds, $\Delta G^\circ_{I_2}$(soln) values determined in two different solvents are related to a high degree of precision.[11] In Table I we present the experimental $\Delta G^\circ_{I_2}$(soln)s together with the values (in parentheses) obtained through these correlations. Specifically, (i) data for S(sp^3) bases were obtained in CCl_4 and CH_2Cl_2. Because the crucial datum for H_2S was determined in the latter at 298 K, all values (in kcal·mol^{-1}) were referred to this solvent and temperature through the equation:

$$\Delta G^\circ_{I_2}(CH_2Cl_2) = (-0.46 \pm 0.14) + (1.04 \pm 0.05)\Delta G^\circ_{I_2}(CCl_4) \qquad (3)$$
$$n = 4,\ r^2 = 0.995,\ \text{std} = 0.095$$

(ii) Values for N(sp^2) bases were originally determined in n-C_7H_{16}, CH_2Cl_2, $CHCl_3$, and CCl_4. These data were referred to n-C_7H_{16} solution at 298 K using the equations (values in kcal·mol^{-1}):

$$\Delta G^\circ_{I_2}(n\text{-}C_7H_{16}) = (-0.72 \pm 0.04) + (0.83 \pm 0.05)\Delta G^\circ_{I_2}(CH_2Cl_2,\ 303\ K) \qquad (4)$$
$$n = 9,\ r^2 = 0.997,\ \text{std} = 0.07$$

$$\Delta G^\circ_{I_2}(n\text{-}C_7H_{16}) = (-0.37 \pm 0.02) + (1.09 \pm 0.03)\Delta G^\circ_{I_2}(CHCl_3,\ 299\ K) \qquad (5)$$
$$n = 4,\ r^2 = 0.995,\ \text{std} = 0.03$$

$$\Delta G^\circ_{I_2}(n\text{-}C_7H_{16}) = (-0.10 \pm 0.06) + (1.05 \pm 0.02)\Delta G^\circ_{I_2}(CCl_4,\ 298\ K) \qquad (6)$$
$$n = 6,\ r^2 = 0.995,\ \text{std} = 0.03$$

All values are given at 298 K. When necessary, the appropriate corrections were applied to the original data, using the association enthalpies for the same or closely related compounds. The squares of the correlation coefficients for eqs 3–6 are always higher than 0.99. The data used to obtain these equations and not included in Table I are as follows: 3,4-dimethylpyridine–I_2 in CH_2Cl_2 at 303 K, $\Delta G^\circ_{I_2}$(soln) = −3.75 kcal·mol^{-1},[26] in CCl_4 at 298 K, $\Delta G^\circ_{I_2}$(soln) = −3.58 kcal·mol^{-1},[30] and in n-C_7H_{16} at 298 K,

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[36] Average value obtained from $\Delta G^\circ_{I_2}$ = −3.64 kcal·mol^{-1} calculated from the CCl_4 datum using eq 6 and $\Delta G^\circ_{I_2}$ = −3.68 kcal·mol^{-1} calculated from the $CHCl_3$ datum using eq 5.

[37] Average value obtained from $\Delta G^\circ_{I_2}$ = −4.42 kcal·mol^{-1} calculated from the $CHCl_3$ datum using eq 5 and $\Delta G^\circ_{I_2}$ = −4.48 kcal·mol^{-1} calcualted from the CH_2Cl_2 datum using eq 4.

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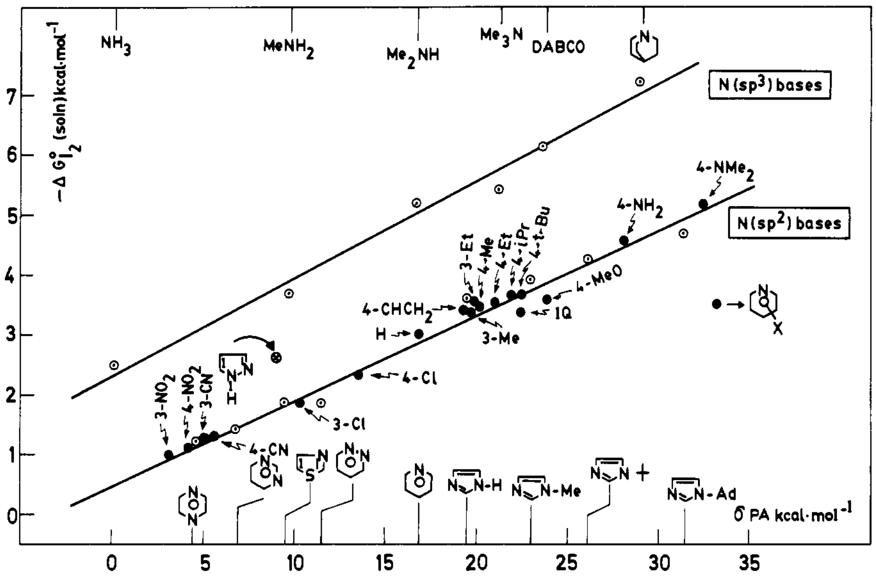

Figure 2. Standard free-energy changes (corrected for changes in symmetry numbers) for iodine complexation of N(sp^2) and N(sp^3) bases in n-C_7H_{16} solution at 298 K versus differential gas-phase proton affinities for the same compounds. IQ is isoquinoline.

$\Delta G^\circ_{I_2}$(soln) = −3.88 kcal·mol^{-1} (from K_c = 697 ± 81 L·mol^{-1});[14] 3,5-dichloropyridine–I_2 in CH_2Cl_2 at 303 K, $\Delta G^\circ_{I_2}$(soln) = −0.50 kcal·mol^{-1}[26] and in n-C_7H_{16}, $\Delta G^\circ_{I_2}$(soln) = −1.11 kcal·mol^{-1} (from K_c = 6.5 ± 0.5 L·mol^{-1}).[14]

Symmetry numbers σ are often different for neutral and protonated (iodinated) bases. Thus, the values of ΔG_{H^+}(g) and $\Delta G^\circ_{I_2}$(soln) given in Table I were corrected for changes in σ. In the case of gas-phase proton-transfer, this amounts to using PAs instead of GBs.[8b] In what follows, differential proton affinities, δPA, relative to ammonia are used. For any base B, δPA = PA(B) − PA(NH_3).

Figures 1 and 2 are plots of $\Delta G^\circ_{I_2}$(soln) versus δPA for the three families of bases studied herein. They define three good linear relationships (in kcal·mol^{-1}), embodied in eqs 7–9. For S(sp^3) bases:

$$\Delta G^\circ_{I_2}(\text{soln}) = (-3.67 \pm 0.09) - (0.113 \pm 0.007)\delta\text{PA} \qquad (7)$$
$$r^2 = 0.960,\ n = 10,\ \text{std} = 0.24\ \text{kcal·mol}^{-1}$$

For N(sp^3) bases:

$$\Delta G^\circ_{I_2}(\text{soln}) = (-2.29 \pm 0.20) - (0.162 \pm 0.011)\delta\text{PA} \qquad (8)$$
$$r^2 = 0.976,\ n = 6,\ \text{std} = 0.25\ \text{kcal·mol}^{-1}$$

For N(sp^2) bases:

$$\Delta G^\circ_{I_2}(\text{soln}) = (-0.58 \pm 0.08) - (0.138 \pm 0.004)\delta\text{PA} \qquad (9)$$
$$r^2 = 0.980,\ n = 26,\ \text{std} = 0.18\ \text{kcal·mol}^{-1}$$

Oxygen bases were not included in this study for the following reasons: (i) Iodine complexation of both O(sp^2)[47] and O(sp^3)[48] bases is known to be extremely sensitive to steric effects [Inspection of Figure 1 strongly suggests that some steric effects are still present in the association of S(sp^3) bases with I_2]. (ii) This makes it important to determine the association constants for small molecules such as H_2O, MeOH, and H_2CO. These constants are expected to be very small. Now, K_c values for MeOH are uncertain because of self-association of the alcohol,[49] and useful concentrations of monomeric water in "inert" solvents seem unattainable. Polymerization problems precluded the study of H_2CO. This notwithstanding, the trend of decreasing (i.e., becoming more negative) $\Delta G^\circ_{I_2}$(soln) with increasing PA is also observed in the case of oxygen bases.

Relevant conclusions derived from eqs 7, 8, and 9 are as follows.

1. Within families of bases, the gas-phase basicity ranking is well reproduced in solution, even when substantial structural differences exist between their members.

2. This fact strongly supports the concept that gas-phase-like behavior can indeed be observed in solution chemistry provided charge dispersal through hydrogen bonding to the solvent is excluded. On this basis, we have just shown the existence of excellent "generalized Brønsted" correlations between gas-phase PAs and the standard free energies of activation for the quaternization of N(sp^2) and N(sp^3) bases with MeI in MeCN.[50]

3. Gas-phase lithium cation basicities for O(sp^2) bases with important dipole moments such as DMF[51] are much higher than those for nitrogen (sp^2 or sp^3) and sulfur (sp^3) bases of comparable GBs.[52] The opposite holds for IBs. Recently, gas-phase iodine cation (I^+) basicities have become available.[53a] For a given GB, the ranking of basicities toward I^+(g) is O(sp^2) < N(sp^2) < N(sp^3) < S(sp^3). These facts and the present findings seem to indicate that the ratio of covalent/electrostatic interactions[53b] increases along the series Li^+(g) < I_2(soln) < I^+(g).

4. The slope in eq 7 is appreciably smaller than those in eqs 8 and 9, seeming to indicate that a smaller amount of charge is being transferred in the complexes involving S(sp^3) bases, even though CH_2Cl_2 is a solvent more favorable to charge separation than n-C_7H_{16}. This notwithstanding, the covalent character of the S–I_2 bond may still be significant because the strong (pπ–dπ and dπ–dπ) back-donation from I_2 to S[54] *reduces* the *net* amount of charge transfer and strengthens the bond.

5. It has recently been reported[52,55] that in the gas phase, 1,2-diazines form bidentate, highly electrostatic, adducts with Li^+. It can be seen in Figure 2 that the IBs of the three diazines (1,2-,

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1,3-, and 1,4-) fall on the line defined by eq 9. This supports the concept that the N–I_2 bonds are directional and largely covalent and that no di-coordination of I_2 is involved.

6. Lone-pair/lone-pair repulsion in pyridazine (1,2-diazine) is lost or reduced in reactions 1 and 2. This is an important contributor to its enhanced (relative to the other diazines) GB[56] and IB. At variance with this, protonation of pyrazole is followed by the formation of two adjacent, mutually repelling N–H^+ bonds.[56] The energy of this repulsion is estimated at 6.5 kcal·mol^{-1}. Figure 2 reveals that the only significantly deviant datum from eq 9 is in pyrazole which has an IB that seems "too large". In fact, it has the value that would correspond to pyrazole were its PA some 6.0 kcal·mol^{-1} higher. It is clear that although some charge is drained from the lone pair of the nitrogen, the repulsion between the N–H and N–I_2 bonds is proportionally much smaller than that between the two N–H^+ bonds. Also, as suggested by one of the referees, a hydrogen-bonding effect is possible; it would correspond to the (resonance structure extreme) $N\cdots I^+—I^-\cdots HN$. This would occur only here, of all the bases used, owing to the proximity of the basic site with an adjacent hydrogen bond donor site.

III. Conclusion

1. "Gas-phase-like" structural effects can be observed in solution chemistry.

2. The comparison of gas-phase and solution basicities under conditions of small charge dispersal leads to valuable insights in the field of structure–reactivity relationships.

IV. Experimental Section

1-*tert*-Butylimidazole[57] and 1-adamantylimidazole[58] have been synthesized by methods previously described. The remaining bases were commercial products of the highest purity available. All these compounds have been carefully purified by standard methods. In all cases, the structures were confirmed by spectroscopic techniques (MS, IR, NMR).

Solvents of spectrograde quality were refluxed over and distilled from sodium (n-C_7H_{16}) or P_4O_{10} (CCl_4, CH_2Cl_2).

Equilibrium constants K_c for reaction 2 are the average of at least six different measurements.

The absence of I_3^- was carefully checked. Experiments were performed at 25.0 and 30.0 °C on a Cary 219 spectrophotometer using matched 1-cm silica window cells. Temperature was kept constant within 0.1 °C by a Lauda S-15 thermostat.

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Electrode Potentials and the Thermodynamics of Isodesmic Reactions

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Abstract: The free energies of isodesmic reactions can be calculated from appropriate electrode potential differences without the necessity of evaluating reference electrode potentials or the free energies of any chemical or physical processes. Class I reactions involve different oxidation states of the same species while reactions involving different species at the same oxidation state level are grouped in Class II. The free energy change of $H^\bullet$ exchange (i) above the double line is equal to that for electron transfer (ii) below the double line. The first aryl group appearing on both sides of the equations is designated with an asterisk

$$\begin{array}{lll} \mathrm{Ar^*CH_3^{\bullet+} + ArCH_2^\bullet = Ar^*CH_2^+ + ArCH_3} & \Delta G^\circ = \Delta \mathrm{BDE} & \text{(i)} \\ \hline\hline \mathrm{Ar^*CH_3^{\bullet+} + ArCH_2^\bullet = Ar^*CH_3 + ArCH_2^+} & \Delta G^\circ = -F\Delta E^\circ & \text{(ii)} \end{array}$$

for clarity, i.e. the compositions of Ar* and Ar are identical. Similar equations relate differences in acid dissociation constants to an appropriate electrode potential difference. For class II reactions, an electrode potential difference can be related to the sum of the free energies of two isodesmic reactions involving the transfer of atoms, ions, or groups. The Cr–H bond dissociation energies of chromium hydride complexes which have recently been evaluated experimentally were selected as standard processes for the evaluation of other BDE. The reversible oxidation of the 2,6-di-*tert*-butyl-4-nitrophenoxide ion was used to relate thermochemical quantities determined in acetonitrile to those in dimethyl sulfoxide.

Introduction

Thermochemical cycles incorporating electrode potentials often provide a means of obtaining reliable estimates of thermodynamic quantities that are either difficult or sometimes impossible to obtain directly. There has been a recent surge of activity in this area to obtain equilibrium and bond energy information in a variety of different systems. A seminal effort in this area by Breslow established the use of thermochemical cycles to estimate pK_a values of weak carbon acids in aprotic solvents as well as equilibrium constants for the dissociation of alcohols to carbenium ions.[2] Arnold devised three different thermochemical cycles to estimate

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