The relatively low barrier for interconversion of **1** to **2** is also consistent with experimental[11] and theoretical[12] studies on the importance of carbon–metal σ–π conjugation in the stabilization of mercurinium ions.[13] The extent of perturbation of the double bond by $HgCH_3^+$ may be estimated by a comparison of the Mulliken overlap population for ethylene, $\rho_\pi = 0.503$, with that of the π system of the mercurinium ions **1–3**. The Mulliken overlap population for the C_1–C_2 π bond in **1** has been reduced to 0.368. In the unsymmetrical ion **2** this value is slightly increased to 0.381. The overlap population between the carbon 2p π orbital on C_1 and electron density on mercury is only 0.110 in **2**. Thus, 78% of the stabilization of the positive charge on C_1 in **2** is due to delocalization of the polarizable carbon–mercury σ bond and only 22% to neighboring group participation by mercury. With the classical ion **3** ρ_π is 0.346 and the overlap population between the neighboring group $HgCH_3$ and the π orbital on carbon, ρ_{C_1-Hg}, is reduced to 0.052. Thus, in **3** both σ–π conjugative stabilization and neighboring group participation are reduced. The increase in energy of **3** is also reflected in an increase in positive charge on C_1 which is 0.114, 0.123, and 0.177 for ions **1**, **2**, and **3**, respectively.

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Activity Coefficient Effects in Spectral and Solubility Studies of Molecular Complex Equilibria

Sir:

Information about molecular complexes of iodine has played a key role in the development of theories of electron donor–acceptor interaction.[1] Yet, in spite of

(1) For general references, see (a) R. S. Mulliken and W. B. Person, "Molecular Complexes. A Lecture and Reprint Volume," Wiley-Interscience, New York, N. Y., 1969; (b) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, London and New York, 1969; (c) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

the importance of these adducts, there remains considerable disagreement regarding the magnitudes of spectral and thermodynamic constants of iodine complexes in nonpolar media.[1-6] When different physical methods are employed to study the same series of complexes, discrepancies are particularly large. For example, formation constant (K_c) values determined by the solubility method are as much as twice as great as those inferred from spectral techniques.[4,5]

It has been stated that the solubility method and similar thermodynamic techniques yield K_c values which account for the total effect of donor–acceptor interactions (specific plus nonspecific),[5b] whereas K_c values determined spectrally reflect only the effects of donor–acceptor contacts occurring in excess of random collisions.[7] This communication treats explicitly the effect of variation in activity coefficients on values of thermodynamic constants inferred from the solubility method and compares the corrected solubility results with constants determined spectrally.

Consider the reaction $D + I_2 \rightleftharpoons DI_2$ which occurs between dissolved donor (D) and iodine in dilute solution in a solvent (e.g., heptane). The thermodynamic equilibrium constant for the reaction (in reciprocal molarity units) is

$$K_c = a_{DI_2}/(a_D a_{I_2}) = (c_{DI_2}/c_D c_{I_2})(\gamma_{DI_2}/\gamma_D \gamma_{I_2})$$

where a_i, c_i, and γ_i represent the activity, molar concentration, and activity coefficient of a solute species i (DI_2, D, or I_2). The activity coefficients are based on ideal dilute solution (unit molarity) standard states; the γ_i values individually approach unity as the total solute concentration approaches zero. In conventional spectral studies it is common to assume that $\gamma_{DI_2} \simeq \gamma_D \gamma_{I_2}$, even in treating data for quite concentrated solutions. This assumption has been criticized and defended by various workers.[8-10] At first glance, it would appear that constants derived from solubility results should be less influenced by activity coefficient effects, since meaningful measurements of solubility increases can be made in the very dilute solution range.[5] However, the total concentration of dissolved iodine, at constant activity in the presence of an added donor, can be expressed as

$$[I_2] = c_{I_2} + c_{DI_2} = (a_{I_2}/\gamma_{I_2}) + c_{DI_2} \qquad (1)$$

where a_{I_2} is fixed and known.[11] As more donor is

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(11) In the polyiodide solubility method, mixtures of tetramethylammonium polyiodides are utilized to maintain a constant activity of iodine in a solution phase or gaseous phase containing added donor.[5,12] Studies of aromatic donor–iodine complexes in heptane are conveniently performed by using tetramethylammonium triiodide and pentaiodide solid mixtures, which in contact with liquid heptane at 25° give an equilibrium concentration of molecular iodine equal to 1.97 × 10⁻⁴ M. In these experiments, $c_D \gg c_{I_2}$ or c_{DI_2}, which implies that activity coefficient effects in the solution phase are determined by the relative concentrations of heptane and donor.

added, c_{DI_2} will increase, but owing to nonspecific effects, γ_{I_2} may vary also. It can be shown that in very dilute solutions both c_{DI_2} and γ_{I_2} (or its reciprocal) vary linearly with donor concentration;[13,14] therefore, the total solubility increase reflects both specific and nonspecific effects. It should be obvious from eq 1 that knowledge of γ_{I_2} would permit the unambiguous determination of c_{I_2} and, by difference, c_{DI_2}; knowledge of c_{DI_2} permits determination of the concentration of uncomplexed donor (c_D). Therefore, if γ_{I_2} were known as a function of c_D, it would be possible to obtain values of $c_{DI_2}/(c_D c_{I_2})$ in the very dilute concentration region and to extrapolate these values to infinite dilution to obtain the thermodynamic equilibrium constant K_c.

The equations of solubility parameter theory (for a mixed solvent)[15] may be used to estimate γ_{I_2} as a function of c_D for several aromatic donor–iodine systems for which K_c has been determined by both the polyiodide solubility method and the Benesi–Hildebrand (BH) spectral technique.[16] Table I shows values of K_c

Table I. Equilibrium Constants for Several Donor–Iodine Complexes in Heptane at 25°[a]

Donor	$K_c^{(s)}$,[b] 1. mol^{-1}	$K_c^{(corr)}$,[c] 1. mol^{-1}	$K_c^{(BH)}$,[d] 1. mol^{-1}
Benzene	0.37	0.15	0.20
Toluene	0.50	0.28	0.32
o-Xylene	0.64	0.37	0.42
p-Xylene	0.64	0.40	0.41
m-Xylene	0.70	0.46	0.54
Mesitylene	0.98	0.71	0.74

[a] From ref 5b. [b] $K_c^{(s)}$ values are obtained directly from the polyiodide solubility results, assuming $\gamma_{I_2} = 1$. [c] $K_c^{(corr)}$ values have been corrected for γ_{I_2}, estimated from solubility parameter theory. [d] $K_c^{(BH)}$ values have been inferred using the Benesi–Hildebrand analysis, assuming $\gamma_{DA} = \gamma_D \gamma_A$.

obtained directly from the uncorrected solubility method, values corrected for changes in γ_{I_2}, and values obtained using the BH analysis of spectral data for more concentrated solutions. The agreement between the corrected solubility results and the BH results is remarkably good, indicating that $\gamma_{DI_2} \simeq \gamma_D \gamma_{I_2}$ in these systems. This is not to suggest that activity coefficient effects will in general cancel so neatly, but, at least in the case of the important aromatic hydrocarbon complexes, the spectral and solubility results can be brought into near agreement by estimating γ_{I_2} from simple nonelectrolyte solution theory.

Finally, it should be noted that properties of the electronic spectral bands of donor–iodine complexes inferred from the uncorrected solubility results (ignoring activity coefficient effects) are in better agreement with trends predicted from the Mulliken theory[1,17] than are results inferred from the BH or corrected solubility

methods.[5,18] In the case of relatively weak complexes it may be argued that the total effect of donor–iodine interactions (random plus specific) should be considered in relating spectral intensities and frequency shifts to donor strength. Since the uncorrected solubility results comprise both types of effects, they should therefore be simpler to interpret theoretically. This point of view is not very different from that expressed by Orgel and Mulliken,[2] who introduced the concept of "contact charge transfer" to explain the anomalous variation of spectral band intensities with donor strength for weak complexes which had been investigated with the BH technique.

(18) A puzzling result of the BH spectral studies is that in a series o, weak complexes such as those between the aromatic donors and iodinef the molar absorptivities of the charge-transfer band do not increase uniformly as the donor strength increases;[1,2] in fact, there is an abrupt drop in absorptivity in the series benzene·I₂–toluene·I₂–xylene·I₂, and the absorptivity rises again as more highly alkylated donors are employed. The polyiodide solubility results yield absorptivity values which are all in the range 6900 ± 1200 1. mol^{-1} cm^{-1} for the complexes listed in Table I.[5b] Moreover, the uncorrected solubility results lead to simple correlations between complex stability and the intensities and frequency shifts of the blue-shifted iodine bands of the aromatic donor complexes.[5b]

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Substituent Effects in Gas-Phase Ionic Nitration and Acetylation of Aromatics

Sir:

We report the observation using ion cyclotron resonance (icr) spectroscopy of marked substituent effects on the gas-phase reaction rates of $(NO_2)^+$ and $(CH_3CO)^+$ transfer to a variety of substituted benzenes and heteroaromatic compounds. Although substituent effects in gas-phase ionic reactions have never been examined under conditions comparable to those employed in this work a number of studies have dealt with ion–molecule reactions involving aromatic compounds.[1–10] Of particular interest are the results of Cacace,[4,5] *et al.*, on tritiation by strong Brønsted acids, in which a substantial positional selectivity is observed, but little rate selectivity.

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