ized light does not necessarily represent the circular dichroism of the chromophore in isotropic solution. Discrepancies between the two may occur if the electric dipole transition moments in the absorption band and in the emission band are not parallel or perpendicular to each other. Whether or not such complications occur in a system under investigation may be checked by measurement of the linear polarization of the fluorescence. It may be noted that CD is often used in biochemistry as a diagnostic tool for conformation without an attempt at a physical interpretation of the data, as such discrepancies between CD and fluorescence-detected CD may be of no consequence. In spectroscopic studies of chiral molecules, however, such discrepancies should not be ignored. It is of interest to note that the study of CD by fluorescence in frozen systems has the elements of measuring CD of a nonisotropically distributed molecular assembly; discrepancies between such data and CD obtained conventionally may therefore in principle yield molecular parameters not obtainable from CD alone.[10]

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$$\frac{\Delta I}{I} = 4\,\frac{7P_1{}^{ab}\tilde{M}_1{}^{ab} + 7P_2{}^{ab}\tilde{M}_2{}^{ab} + 6P_3{}^{ab}\tilde{M}_3{}^{ab}}{7(P_1{}^{ab})^2 + 7(P_2{}^{ab})^2 + 6(P_3{}^{ab})^2}$$

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The Relative Stability of Alkyl-Substituted Benzene Anions in the Gas Phase

Sir:

The negative ions of benzene and the alkylbenzenes may be formed in the gas phase by capture of an impacting electron into the low-lying π^* orbitals. The ions, however, are short-lived and decay by ejecting the electron back into the continuum in times of typically 10^{-14} s. Despite the transient character of these ions, their formation is easily observed as a sharp variation, or "resonance", in the cross section for electron scattering from the neutral molecule. The impact energy at which the resonant structure is observed yields the magnitude of the gas phase electron affinity; the sign of the electron affinity is taken by convention to be negative for an unstable anion. In this communication, we have determined the electron affinities of a series of alkyl-substituted benzenes using high resolution electron transmission spectroscopy.[1-3] For a detailed discussion of this method as applied to certain hydrocarbons, we refer the reader to a recent paper by Nenner and Schulz.[2]

The motivation for this study is provided by recent work[4,5] demonstrating that the relative stability of certain anions such as alkoxides may display opposite ordering in the gas phase and in solution. It is of interest to determine whether solvation energies oppose the intrinsic gas phase orderings for other classes of anions. An investigation of the relative stabilities of the benzene anion and its alkyl derivatives is particularly timely since the ordering of these anions in solution has recently been established. Lawler and Tabit[6] have determined the relative electron affinities from equilibrium studies:

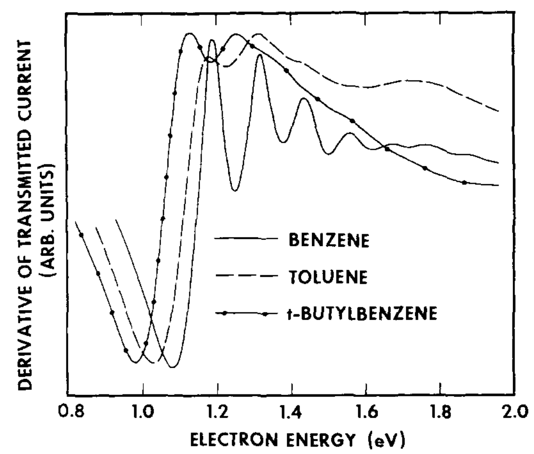

Figure 1. The derivative with respect to energy of the electron current transmitted through the gas cell is plotted as a function of electron energy. The results for benzene and two substituted benzenes, toluene and *tert*-butylbenzene, are shown. These results demonstrate that the anions of the substituted compounds are formed at lower electron energy than that of benzene.

$$C_6H_6 + R_1R_2C_6H_4\cdot^- \rightleftarrows C_6H_6\cdot^- + R_1R_2C_6H_4$$

Solutions with known concentrations of benzene and alkylbenzenes were reduced by sodium-potassium alloy in tetrahydrofuran-dimethoxymethane and the ESR spectra taken to determine the equilibrium constants. The measured free energy changes $\Delta G°$ indicate[7] that the introduction of alkyl groups onto the ring makes one-electron reduction more difficult or, equivalently, destabilizes the negative ion in solution. We note that this result is frequently rationalized by "the electron release by the alkyl groups to the ring".

In Figure 1 we present the electron transmission spectra of benzene, toluene, and *tert*-butylbenzene. These spectra are acquired by sending a high resolution electron beam into a cell containing gas at sufficient density to scatter approximately 60% of the electron beam. The *unscattered* or transmitted portion of the beam, which is collected, is related exponentially to the total scattering cross section. To enhance the visibility of the sharp variations in the cross section, the derivative with respect to energy of the transmitted current is plotted in Figure 1 as a function of electron impact energy. The means by which the derivative data are taken is fully described elsewhere.[1]

Our benzene spectrum is in good agreement with those published by Schulz et al.[1,2] The structure corresponds to the capture of an incident electron into the doubly degenerate e_{2u} π^* orbital, yielding the ground electronic state of the benzene anion. The lifetime of the anion is sufficiently long that a progression of vibrational levels of the ν_2 symmetric breathing mode is observed. The spectra of the alkyl-substituted benzenes, two of which are shown in Figure 1, differ from that of benzene in two respects. For the purpose of this communication, the more significant feature is that the anions are formed at *lower* electron impact energies, that is, the alkylbenzene anions are energetically *more* stable than $C_6H_6^-$ in the gas phase. This is opposite to the behavior in solution observed by Lawler and Tabit.[6] A summary of the gas and liquid phase results is presented in Table I.

The visibility of the vibrational structure in the substitut-

Table I. Stability of Anions of Alkyl-Substituted Benzenes Relative to $C_6H_6^-$ in Gas Phase and Solution[a]

Compound	ΔEA (Solution)[b]	ΔEA (Gas phase)[c]
Toluene	−0.022	0.04 ± 0.02
p-Xylene	−0.033	0.08 ± 0.02
m-Xylene	−0.059	0.09 ± 0.02
o-Xylene	−0.100	0.03 ± 0.03
tert-Butylbenzene	−0.070	0.09 ± 0.02
Isopropylbenzene	−0.055	0.07 ± 0.02
1,2,4-Trimethylbenzene		0.08 ± 0.03
1,3,5-Trimethylbenzene		0.12 ± 0.02

[a] All energies in eV. ΔEA = E.A. (substituted benzene) − E.A. (benzene), thus a negative ΔEA implies a negative ion less stable than $C_6H_6^-$. [b] Reference 6. [c] These shifts are determined with respect to an electron affinity of −1.15 eV for benzene. We estimate the absolute error in this reference value to be ±0.030. Our electron affinity is in excellent agreement with previous measurements of ref 1 and 2.

ed anions is considerably weaker than that of benzene. Space does not permit a detailed discussion of this aspect; however, it is consistent with a decrease in anion lifetime. Similar effects were observed by us in other molecules such as ethylene, butadiene, and formaldehyde under methyl substitution.[8] The interpretation is more complicated in the substituted benzenes because of the small splitting associated with the lifting of the degeneracy of the $^2E_{2u}$ electronic state. A calculation by Alper and Silbey[9] of the pseudo-Jahn-Teller effect in the toluene anion yielded a vibronic splitting of 0.033 eV. From our instrumental energy resolution, approximately 0.040 eV, and the characteristics of the transmission spectrum in benzene, we infer that the finite lifetime of the benzene anion corresponds to a spread in energy in excess of 0.040 eV. For the toluene anion, the energy spread is likely to be even greater. It is worth noting here that the effect of the finite lifetime has not been previously taken into account in the theoretical calculations.

With regard to the ordering of the two states, it has been suggested, from nodal arguments, that the antisymmetric (A) π^* orbital[10] is unperturbed through first order by the substituents in the monoalkyl- and *p*-dialkylbenzenes.[11] ESR studies[12] locate the symmetric (S) state above the A state in solution and indicate a small splitting ($\lesssim 0.1$ eV) between them. It is not certain that this ordering is also correct in the gas phase. The most elaborate calculations have been parametrized with ESR data and hence incorporate solvation effects. For example, Purins and Karplus[11] in their "pure hyperconjugation model" found the S state of the anion to lie below the A state for usual values of the parameters, but since this result disagreed with the ESR results, they concluded that it was also necessary to include induction. The possibility that the S state is more stable for the gas phase substituted anions should be reconsidered as suggested by the original Purins and Karplus[11] calculation.

The shifts in electron affinity due to alkyl substitution are quite small, and it is not clear that there is a simple physical model capable of predicting the relative values. For this series of compounds, the observed shifts are likely due to the subtle contribution of several factors, including electron correlation.

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Metal Clusters in Catalysis. IV.[1] Catalytic Hydrogen Reduction of Carbon Monoxide to Alkanes

Sir:

We have advanced[1] a detailed thesis that the class of discrete metal cluster complexes are, to a first approximation, reasonable models for metal surfaces in such processes as chemisorption and heterogeneous catalysis. This thesis has been preliminarily documented in our studies of the catalytic properties of a nickel cluster,[2] $Ni_4[CNC(CH_3)_3]_7$, and of the cluster prototypes $(\eta^3\text{-}C_3H_5Fe(CO)_2L)_2$,[3] in the Roundhill et al.[4] demonstration of activity of $Rh_6(CO)_{16}$ in catalytic oxidations, and in the extremely intriguing $Os_3(CO)_{12}$ chemistry[5] with alkenes which relates[1] importantly to chemisorption phenomena. We[1] have also noted two distinctive catalytic capabilities of surfaces vis-a-vis mononuclear coordination catalysts which are catalytic reactions of aliphatic hydrocarbons[6] and the hydrogen reduction of carbon monoxide.[7] Herein we describe the catalytic hydrogen reduction of carbon monoxide to alkanes by discrete metal clusters. Observed rates were very low but the imposed reaction conditions were mild and the systems were unambiguously homogeneous.

Reduction of carbon monoxide by hydrogen to alcohols or alkanes is a highly favorable thermodynamic process, yet practical operation of this reaction with heterogeneous catalysts as in methanol production or the Fischer–Tropsch process requires rather extreme operating conditions[7] (200–400° and 10–200 atm of pressure). If such conditions are truly required, many of the traditional homogeneous coordination or organometallic catalysts would be excluded on stability grounds. There is, however, a mechanistic constraint that may severely limit a mononuclear complex as a catalyst in the $CO\text{-}H_2$ reaction. Well established mechanistic features of the hydroformylation reaction[8] suggest that a mononuclear catalyst might take CO and H_2 to CH_2O[9] although there is no evidence for direct formation of formylmetal complexes.[10] No precedent[11] exists in homogeneous catalysis for a reaction mode that would convert a formylmetal species to CH_3OH, and furthermore, formation of CH_4 would seem to require a second metal center for scission of the carbon-oxygen bond. In metal clusters (and metal surfaces), there is the possibility of a $\mu_2(\eta^2)$-CO bonding mode wherein conversion, through hydrogen atom transfer, to CH_3OH or CH_4, could be readily achieved. We have demonstrated a $\mu_2(\eta^2)$-bonding mode for isocyanides[2]