droxyhomotropylium cations are quite different. Such differences in behavior can most reasonably be attributed to the effect the hydroxy group has on the "degree of openness" of the internal "cyclopropane" bond of these systems.[16]

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Experimental Study of the Negative Ion States of Styrene. A Test of the Pairing Theorem

Sir:

Low energy electron scattering methods provide a means to determine the energies of the temporary negative ion states associated with the low-lying, normally unfilled π^* orbitals of unsaturated hydrocarbons. In this communication we report values for the four lowest electron affinities (EA's) of styrene as determined by electron transmission spectroscopy (ETS) in the format devised by Sanche and Schulz.[1] This technique has been employed in recent measurements of the EA's of benzene[2,3] and its azine analogues,[3] substituted benzenes,[4] ethylene,[5] butadiene,[5] formaldehyde,[6] and selected cyclic dienes.[7]

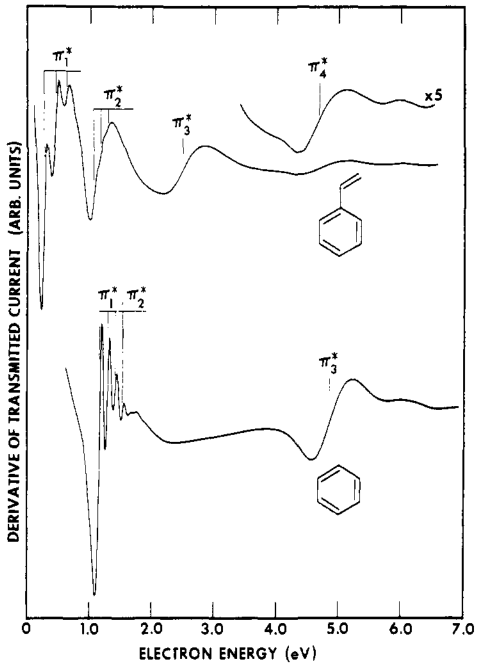

Figure 1. The derivative with respect to energy of the electron current transmitted through styrene (upper curve) and benzene (lower curve) as a function of electron impact energy.

In applying this technique to more complicated molecules, styrene is of interest since it may be viewed as two interacting functional groups, namely, the ethylenic and phenyl moieties. Each of the "constituent" molecules, ethylene and benzene, has already been well characterized in the gas phase by ETS. Furthermore, because styrene is an alternant hydrocarbon, its π and π^* orbitals, as described by PPP theory, obey the pairing theorem.[8] Our determination of the anion energies, together with the known ionization potentials (IP's), allows a direct experimental test of this relationship.

In Figure 1, we present the electron transmission spectra of styrene and, for comparison, benzene. The ethylene spectrum has been published elsewhere.[5] The temporary occupation of one of the unfilled π^* orbitals in these molecules is manifested by a rapid, "resonant", variation in the total scattering cross section. The visibility of such variations is enhanced by measuring the derivative with respect to energy of the electron current transmitted through a cell containing the appropriate gas.[1]

The structure near 1 eV in the benzene spectrum corresponds to the capture of an incident electron into the doubly

Table I. Vertical Electron Affinities and Ionization Potentials of Ethylene, Benzene and Styrene

Compound	Electron affinity (eV) Exptl	Electron affinity (eV) Theory[a]	Ionization potential (eV) Exptl[b]	Ionization potential (eV) Theory[a]	EA + IP Exptl	EA + IP Theory[a]
Ethylene	−1.78 ± 0.1[c]	−1.60	10.52	9.73	8.74	8.13
Benzene	−1.15 ± 0.05	−1.07	9.24	9.19	8.09	8.12
	−4.85 ± 0.1	−3.97	12.20	12.15	7.35	8.18
Styrene	−0.25 ± 0.05	−0.39	8.43	8.49	8.18	8.10
	−1.05 ± 0.1	−1.09	9.18	9.20	8.13	8.11
	−2.48 ± 0.1	−2.27	10.45	10.41	7.97	8.14
	−4.67 ± 0.1	−4.21	12.30[d]	12.39	7.63	8.18

[a] The theoretical values were obtained from the semiempirical method of Younkin, Smith, and Compton (ref 14). We have readjusted the empirical relationship between the energies of the occupied orbitals and the IP's to obtain somewhat better agreement with experiment. [b] Ethylene (ref 11), benzene (ref 12), styrene (ref 13). [c] Reference 5. [d] It has not been unambiguously demonstrated that the 12.30 eV IP corresponds to ejection of a π electron.

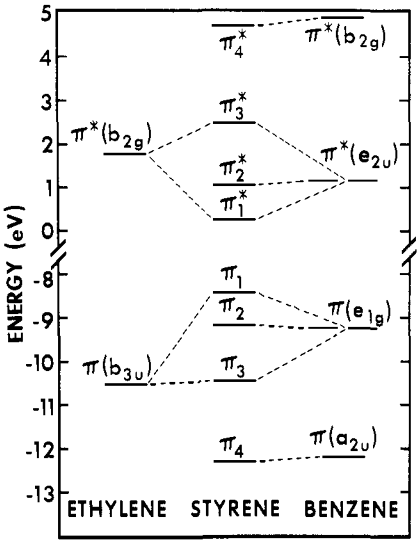

Figure 2. Correlation diagram showing experimental values for the anion and cation energies in ethylene, styrene, and benzene.

degenerate $e_{2u}(\pi^*)$ orbital, yielding the X^2E_{2u} ground state of the benzene anion. The lifetime of the anion is sufficiently long that a progression of vibrational levels of the symmetric breathing mode is observed. The feature near 4.85 eV is associated with the capture of an electron into the $b_{2g}(\pi^*)$ orbital.[9]

In styrene we expect four low-lying negative ion states. The bonding combination of the ethylene π^* orbital and the b_1 member[10] of the $e_{2u}(\pi^*)$ benzene orbital should lead to a negative ion ground state which is stabilized with respect to that of benzene. Similarly, the antibonding combination yields a state less stable than the X^2B_{2g} ethylene anion. We expect that the a_2 component[10] of the benzene $e_{2u}(\pi^*)$ orbital will be essentially unperturbed since, from symmetry considerations, it cannot mix directly with the ethylenic π^* orbital. Finally, the high-lying b_{2g} benzene orbital should be relatively unperturbed.

The four negative ion states of styrene are clearly distinguished in Figure 1 and are labeled as π_1^*–π_4^*. The lifetimes of the two lower states are sufficiently long to yield evidence of vibrational motion of the anion. The correlation diagram given in Figure 2 shows the experimentally determined anion and cation energies of styrene, benzene, and ethylene, and is in excellent agreement with the interaction picture described above. The EA's and IP's[11-13] for these three molecules are summarized in Table I.

In the right-hand column of the table, we list the values of (IP + EA) associated with each π, π^* pair. According to PPP theory, this quantity should be a constant for alternant hydrocarbons.[8] For comparison with the experimental data, the EA's and IP's generated by the semiempirical method of Younkin et al.[14] are also included. Although these calculations are based on the PPP method, certain modifications were introduced which cause the values of (IP + EA) to vary slightly. The spread is small, however, amounting to only 0.08 eV for the three molecules discussed here.

For styrene, the first three values of (IP + EA) determined from the experimental data are indeed consistent with a constant, 8.08 eV, to within ±0.11 eV, a spread which is commensurate with the experimental errors. Pairing of the lower-lying π and π^* levels in other alternant hydrocarbons we have studied also holds to good approximation and should allow the energies of stable anions to be predicted from those of the temporary anions. A detailed discussion of the negative ion states in the gas phase of several alternant hydrocarbons is in preparation.

The fourth anion state of styrene, as well as the third anion of benzene, lies considerably higher than the theoretical prediction. This displacement may result from the inadequacy of the theory in taking account of the increased diffuseness of the wave functions belonging to the high-lying states. Alternatively, the shift may be due to mixing with nearby doubly excited anion states.

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Concerning the Formation of Compounds Containing Metal-to-Metal Multiple Bonds. A Stereospecific Alkyl-for-Chlorine Exchange Reaction Involving Compounds with Tungsten-to-Tungsten Triple Bonds

Sir:

The ability of metals to form multiple bonds with themselves and each other is now well documented.[1] However, the mechanisms leading to compounds with M–M multiple bonds are generally not known and have received little attention.[2] For example, the first compounds which were shown to contain M–M triple bonds unsupported by bridging ligands, $M_2(CH_2SiMe_3)_6$, where M = Mo and W, were unexpected products obtained from metathetic reactions involving $MoCl_5$ and WCl_6, respectively.[3] Recently the compounds $M_2(NR_2)_6$, where M = Mo[4] and W[5] and NR_2 = NMe_2, NMeEt, and NEt_2, have been isolated from similar reactions (MCl_n + nLiNR$_2$; M = Mo, n = 5; W, n = 6 and 4). The reaction pathway leading to the dinuclear compounds M_2L_6 (L = CH_2SiMe_3 and NR_2) is clearly of interest. We now report that the reaction between *anti*-$W_2Cl_2(NEt_2)_4$ and $LiCH_2SiMe_3$ (2 equiv) proceeds to give *anti*-$W_2(CH_2SiMe_3)_2(NEt_2)_4$, which under thermodynamic control isomerizes according to eq 1. This observation is significant in both its synthetic and mechanistic implications.

$$\underset{\text{a-I}}{anti\text{-}W_2(CH_2SiMe_3)_2(NEt_2)_4} \rightleftarrows \underset{\text{g-I}}{gauche\text{-}W_2(CH_2SiMe_3)_2(NEt_2)_4} \quad (1)$$

$$K \cong 4 \text{ at } 25\ ^\circ\text{C}$$