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THEORETICAL STUDIES OF $(CuC_2H_4)^+$ AND $(CuC_2H_4)^0$: APPLICATION OF CuCl ON POLYSTYRENE *

J.A. KELBER, L.A. HARRAH and D.R. JENNISON
*Sandia Laboratories **, Albuquerque, NM 87185 (U.S.A.)*

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Summary

Ab initio restricted Hartree-Fock self-consistent field molecular orbital calculations have been carried out on $(Cu_2H_4)^+$ and $(CuC_2H_4)^0$. $(CuC_2H_4)^+$ has a calculated binding energy of 1.31 eV, versus 0.05 eV for $(CuC_2H_4)^0$. The primary bonding interaction is σ-bonding (ligand to metal charge donation); π-backbonding is negligible. Ultraviolet absorption and emission studies carried out on solutions of CuCl and polystyrene in tetrahydrofuran indicate the existence of a Cu^+-polystyrene charge transfer complex for which $(CuC_2H_4)^+$ is a good theoretical first approximation.

Introduction

In the study of the bonding of transition metals and metallic ions, the relative importance of σ-bonding [1] (ligand to metal charge donation) and π-backbonding [1] (metal to ligand charge donation) is of interest to workers in such fields as catalysis and adhesion. The bonding in $(CuC_2H_4)^+$ is a topic of some controversy and practical importance. Bigorgne [2] has recently concluded, on the basis of infrared measurements, that Cu^+ is a stronger π-donor than σ-acceptor in $CuCl(C_2H_4)$. In contrast, molecular orbital calculations by Basch [3] on $(AgC_2H_4)^+$ indicate σ-bonding to be more important than π-backbonding. The interaction of Cu and Cu^+ with aromatic side chain polymers such as polystyrene is of considerable industrial interest, and recent work [4,5] suggests that the oxidation state of the copper greatly affects the ability of the metal to bind to the polymer. Results of studies on $(CuC_2H_4)^+$ should be applicable to such aromatic polymer systems. This is because molecular orbital symmetry

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considerations [6] dictate that in aromatic charge transfer complexes charge acceptors such as Ag^+ and Cu^+ (with empty *S*-like acceptor orbitals) should occupy a position of local C_{2v} symmetry, midway between and above two carbon atoms on the edge of the benzene ring. This has been experimentally confirmed for $C_6H_6 \cdot AgClO_4$ [7] and $C_6H_6 \cdot CuAlCl_4$ [8]. Considering only nearest neighbor interactions, the metal ion is in an ethylene-like environment and $(CuC_2H_4)^+$ is a good first approximation to a Cu^+-polystyrene charge-transfer complex.

In order to determine the relative importance of σ- vs. π-backbonding, we have carried out ab initio restricted Hartree-Fock self-consistent field molecular orbital calculations on $(CuC_2H_4)^+$ and, for comparison, $(CuC_2H_4)^0$. The results are presented in the section on molecular orbital calculations. We have investigated the possible existence of a Cu^+-polystyrene charge transfer complex by examining the ultraviolet absorption and emission from solutions of CuCl and polystyrene in tetrahydrofuran. These results are presented in the section on ultra violet spectra and discussed in light of the theoretical calculations.

Molecular orbital calculations

A. Method, basis set, and geometry

Ab initio molecular orbital calculations were carried out on $(CuC_2H_4)^+$ and $(CuC_2H_4)^0$ within the restricted Hartree-Fock self-consistent field formalism. A restricted calculation should give a reasonable value for the dissociation energy of $(CuC_2H_4)^+$ since the complex and both dissociation fragments (Cu^+ and C_2H_4) are closed shell entities. The binding energy calculated for $(CuC_2H_4)^0$ will be less accurate, but can be compared with the configuration interaction calculations reported by Basch et al. [9] and Upton and Goddard [10] on $(NiC_2H_4)^0$, in which the metal atom also has a $4s^1$ configuration. All calculations were carried out on a CDC-7600 computer using a locally modified version of HONDO [11].

The atomic orbital basis set used for carbon in these calculations was the Gaussian Type Function (9*s*, 5*p*) basis set of Huzinaga contracted to (3*s*, 2*p*) by Dunning [12]. For Cu, the Gaussian type function (12*s*, 6*p*) basis set of Roos, et al. [13] contracted to (5*s*, 2*p*) was used, together with the augmented (5*d*) basis set of Hay [14] contracted to (3*d*). This was done to allow a more diffuse set of 3*d* orbitals than is obtained with exponents optimized for atomic calculations [13,14]. For the same reason [13], the atomic basis functions heavily used in the 4*s* wave function were replaced by two 1*s* functions of exponents 0.32 and 0.08 as suggested by Roos, et al. [13]. Two 4*p* wave functions, also with exponents 0.32 and 0.08 were added to allow for Cu 4*s*—4*p* hybridization.

For Cu^+ (^1S), a total energy of —1636.1323 a.u. was obtained using the basis set described above. For Cu^0, a total energy of —1636.2934 a.u. was obtained. This latter figure should be compared to the value of —1635.3810 a.u. obtained [13] by Roos et al. for neutral Cu using their (12*s*, 6*p*, 4*d*) basis set contracted to (5*s*, 2*p*, 2*d*), the difference resulting principally from the 5*d* vs. 4*d* basis.

All geometric configurations examined were of C_{2v} symmetry with the Cu ion or atom situated above and midway between the two carbon atoms. For

$(CuC_2H_4)^+$, three geometric configurations of the C_2H_4 unit were examined. The first was the standard planar ethylene geometry [12]. The second configuration had the hydrogens bent back out of the plane by 5°, and the third had the hydrogens bent by 20°. For $(CuC_2H_4)^0$, only the planar C_2H_4 configuration was examined. The Cartesian coordinates of the atoms in the various configurations are listed in Table 1. The total energy of each configuration was calculated as a function of R, the distance from Cu to the midpoint of the C—C bond, with R varied from 2.00 Å to 3.20 Å. The binding energies were calculated relative to planar C_2H_4 and Cu^+ (or Cu^0) at infinite separation.

B. Results

The binding energy curves calculated for $(CuC_2H_4)^+$ and $(CuC_2H_4)^0$ are shown in Figure 1. The lowest energy configuration for $(CuC_2H_4)^+$ has R = 2.32 Å and C_2H_4 in the planar configuration. The calculated binding energy is 1.31 eV. The R value of 2.32 Å is about 10 percent higher than that observed [8] for $C_6H_6 \cdot CuAlCl_4$. The binding energy is close to that calculated for $(AgC_2H_4)^+$ [3]. The eigenvalues, symmetries, and composition of the molecular orbitals of $(CuC_2H_4)^+$, together with corresponding eigenvalues for free Cu^+ and C_2H_4 are listed in Table 2.

As Figure 1 shows, the binding energy curve for $(CuC_2H_4)^0$ is extremely shallow, with a minimum near 3.00 Å and a binding energy of only 0.05 eV. Inaccuracies are involved in applying the restricted Hartree-Fock self-consistent field formalism to an open shall configuration, but the results obtained here are in general accord with experiment since no room temperature stable Cu^0-olefin complexes are known, although such complexes have been formed at low temperatures in matrix isolation [15]. The theoretical results obtained for

TABLE 1

CARTESIAN COORDINATES (IN a.u.) FOR $(CuC_2H_4)^+$ AND CuC_2H_4

Atom	x	y	z
Planar configuration			
Cu or Cu^+	0.0	R	1.27551
C(1)	0	0	0
C(2)	0	0	2.55102
H(1)	1.72540	0	−1.05733
H(2)	−1.72540	0	−1.05733
H(3)	−1.72540	0	3.60835
H(4)	1.72540	0	3.60835
Bent ~5°			
H(1)	1.65150	−0.17510	−1.15610
H(2)	−1.65150	−0.17510	3.70710
H(3)	1.65150	−0.17510	3.70710
H(4)	1.65150	−0.17510	3.70710
Bent ~20°			
H(1)	1.64680	−0.69211	−0.95070
H(2)	−1.64680	−0.69211	3.50180
H(4)	1.64680	−0.69211	3.50180

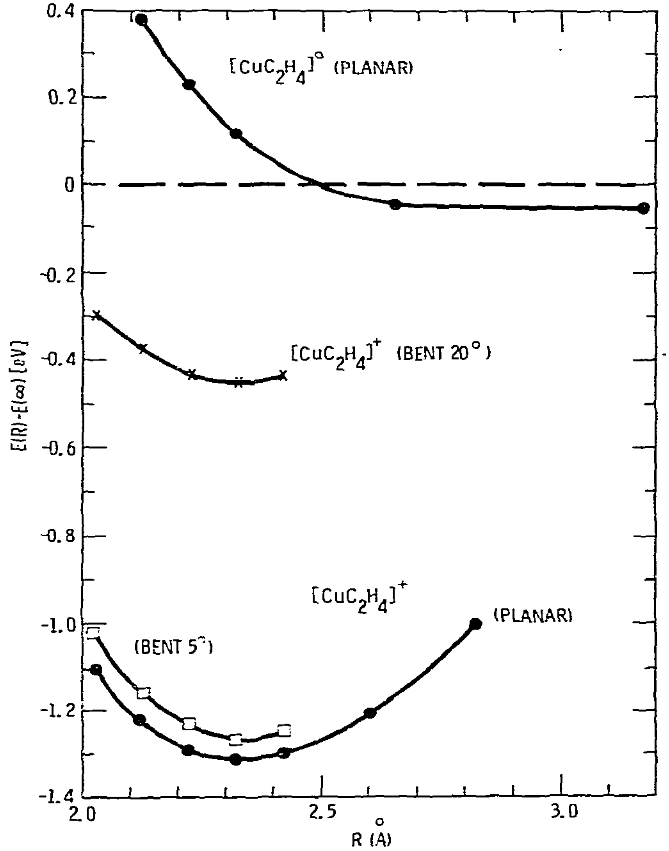

Fig. 1. Binding energy curves for $(CuC_2H_4)^+$ and $(CuC_2H_4)^0$; solid lines are guides to the eye.

$(CuC_2H_4)^0$ are similar to those obtained [9] for $(NiC_2H_4)^0$ using both Hartree-Fock and configuration interaction methods. The self-consistent field calculations showed the complex (with planar ethylene) to be unbound [9]. The configuration interaction calculation yielded a binding energy [9] of ~0.23 eV. This result is different from the ~0.6 eV binding energy obtained using the Generalized Valence Bond method with configuration interaction [10], but the reasons for the disagreement are difficult to evaluate due to lack of detail in reference 10.

C. σ- vs π-back bonding

The nature of the bonding mechanism in $(CuC_2H_4)^+$ and $(CuC_2H_4)^0$ is revealed by an examination of the results of the molecular orbital calculation for $(CuC_2H_4)^+$. As Table 2 shows, the only substantial mixing of Cu and ethylene basis orbitals occurs in the highest occupied molecular orbital, which is mainly π(ethylene)-like but has some 4*s* (Cu) character mixed in. (The mixing in molecular orbitals number 18 and number 15 is between two fully occupied basis orbitals of a_1 character and involves no transfer of charge.) A comparison of eigenvalues of the Cu basis orbitals in the free ion relative to the complex

TABLE 2

ORBITAL ENERGIES, SYMMETRIES, AND COMPOSITION FOR $(CuC_2H_4)^+$

No.	Energy (eV)	Symmetry	Composition	Cu^+	C_2H_4
22	−16.46	A_1	π, Cu4s	−6.14	−10.24
21	−19.46	A_2	C—H		−13.95
20	−20.91	B_1	Cu3d_{yz}		
19	−20.94	B_2	Cu3d_{xy}		
18	−20.99	A_1	σ_{C-C}, Cu3$d_{y^2-z^2}$	(3d) − 22.44	
17	−21.04	A_1	Cud_{x^2}		
16	−21.06	A_2	Cu3d_{xz}		
15	−21.84	A_1	σ_{C-C}, Cu3$d_{y^2-z^2}$		−16.06
14	−23.47	B_2	H—C—C—H		−17.70
13	−27.44	B_1	C—H		−21.77
12	−34.31	A_1	C—C, C—H		−28.24
11	−97.87	B_2	Cu3p_x		
10	−97.88	B_1	Cu3p_z	(3p) − 99.29	
9	−97.89	A_1	Cu3p_y		
8	−140.71	A_1	Cu3s	(3s) − 142.05	
7	−311.91	B_1	σ^*_{C-C}, 2s, 1s		−306.16
6	−311.95	A_1	σ_{C-C}, 2s, 1s		−306.21
5	−974.44	A_1	Cu2p_y		
4	−974.48	B_2	Cu2p_x	(2p) − 975.65	
3	−974.48	B_1	Cu2p_z		
2	−1098.06	A_1	Cu2s	(2s) − 1099.17	
1	−8942.27	B_1	Cu1s	(1s) − 8943.34	

(Table 2) shows the orbital energies of the complex to be higher (less negative) by 1 eV. The orbital energies of the C_2H_4 basis orbitals are generally lower in the complex by 5 to 6 eV relative to free C_2H_4, mostly due to electrostatics. In the Hartree-Fock self-consistent field approximation for closed shell configurations, the orbital energy is equal to the appropriate core electron binding energy if the instantaneous rearrangement of the remaining electrons is neglected [16]. The core electron binding energy generally increases with positive atomic charge [17,18]. Therefore, the results listed in Table 2 suggest that in $(CuC_2H_4)^+$ the Cu^+ unit may be more negative than the free ion and the C_2H_4 unit more positive than free ethylene. This is what one would predict for a complex in which the σ-bonding mechanism [$\pi(C_2H_4) \rightarrow 4s(Cu^+)$ charge transfer] is stronger than π-back bonding [$3d(Cu^+) \rightarrow \pi(C_2H_4)$].

Further evidence concerning the bonding in $(CuC_2H_4)^+$ can be obtained from a Mulliken orbital population analysis [19]. In Table 3 are listed the orbital overlap populations between various molecular orbitals of $(CuC_2H_4)^+$ compared to those in free C_2H_4. At the bottom are listed the gross atomic charges. The relative changes in charges and overlap populations clearly indicate that, in the complex, the C_2H_4 unit is being polarized, with the electronic charge being drawn towards the Cu^+ ion. Electronic charge is being promoted out of both major C—C bonding orbitals (the σ and π bonds in free C_2H_4) in order to form a σ-bond with Cu^+. Since this σ-bond overlap contributes only about 0.17 electrons to the additional (relative to the free ion) Cu^+ atomic charge of 0.32 electrons, the amount of charge back donation from the $3d(Cu^+)$ must be negligible. The repulsion from the single 4s electron in $(CuC_2H_4)^0$ and $(NiC_2H_4)^0$

TABLE 3

ORBITAL OVERLAP POPULATIONS FOR $Cu^+C_2H_4$(A) COMPARED TO C_2H_4(B)

Orbital no.	Cu^+—C [a]	C=C(A)	C=C(B)	C—H(A)	C—H(B)
22	0.3024	0.3619	0.5286	0.0046	0.0000
21	−0.0016	−0.2253	−0.1520	0.2374	0.2267
15	0.0298	0.2745	0.3598	0.0964	0.0960
14	0.0328	0.1796	0.1676	0.1526	0.1644
13	0.0240	−0.1826	−0.1502	0.1989	0.2097
12	0.0014	0.6460	0.6129	0.0217	0.0305
Totals from all M.O.'s	0.3384	1.1314	1.3658	0.7277	0.7271
	Cu^+	C(A)	C(B)	H(A)	H(B)
Atomic charges	28.3215	6.3283	6.3589	0.7555	0.8206

[a] Includes overlap with both carbons.

accounts for the weak binding energies of these complexes. More quantitative evidence concerning the amount of charge donation from the $3d(Cu^+)$ orbital is presented in Table 4, which lists the gross atomic populations from d-like basis functions in molecular orbitals with substantial $3d(Cu^+)$ character. (In computing these figures, the s-like charge originating from the $x^2 + y^2 + z^2$ combination of d-like Gaussians was subtracted from the total [3].) The only substantial $3d$-(Cu^+) interaction with $2p$(C) orbitals (Table 4) occurs for a d orbital of totally symmetric character (the y axis being the molecular two-fold rotation axis) and therefore does not involve any charge transfer to the $\pi^*(C_2H_4)$ orbital.

Our results are in disagreement with those of Ziegler and Rauk [20], who performed a Hartree-Fock-Slater transition state calculation on $(CuC_2H_4)^+$ and found significant π-back bonding to occur. The most likely reason for this disagreement is a difference in basis sets. The Hartree-Fock-Slater results [20] place the Cu $3d$ orbitals approximately 6.5 eV above the π in energy. We have achieved similar results (an energy separation of 5.2 eV) using a minimal Gaussion type basis set with fully contracted $3d$-like basis functions and no $4s$ or $4p$-like functions. The use of a larger basis set, including the augmented ($5d$) basis set of Hay [14] (see section A above), in our calculations stabilizes the $3d$ (Cu^+) orbital energies so that these orbitals lie over 4 eV below the π (Table 1). Thus any possibility of π-back bonding is removed. As discussed in reference 14 and section A above, this stabilization is due to the fact that use of the augmented basis set allows for a more diffuse set of $3d$ molecular orbitals. The

TABLE 4

GROSS ATOMIC D-LIKE CHARGE ON COPPER IN MOLECULAR ORBITALS WITH SUBSTANTIAL $3d$ CHARACTER

Orbital type	$\sigma_{C—C}$, $3d_{y^2-z^2}$	$3d_{xz}$	$3d_{x^2}$	$\sigma_{C—C}$, $3d_{y^2-z^2}$	$3d_{xy}$	$3d_{yz}$
Energy (eV)	−21.84	−21.06	−21.05	−20.99	−20.94	−20.91
Gross atomic 3D-like charge (electrons)	0.196	1.974	1.956	1.789	1.964	1.989

qualitative agreement of the Hartree-Fock-Slater calculation [20] with Basch's Hartree-Fock calculation on $(AgC_2H_4)^+$ may be due to the fact that with the more diffuse 4*d* wavefunctions the choice of basis set is not so critical.

The bond overlap figures listed in Table 3 may be compared with infrared measurements [2] of $(C_2H_4)CuCl$. The observed [2] decrease in $\nu(C{=}C)$ (relative to free C_2H_4) of 345 cm^{-1} is consistent with a weakening of both the σ and π bonds of the C—C double bond. A small observed decrease (50 cm^{-1}) in the C—H symmetric stretching frequency was attributed [2] to π back donation from Cu^+. The results listed in Table 3 would suggest that this decrease may also be due to other factors (e.g., weakening the C—C bond or a change in geometry or atomic charge). A photoelectron spectrum of $(C_2H_4)CuCl$ would be most useful.

Ultraviolet spectra

A. Experimental

Ultraviolet absorption and emission spectra were taken of solutions of CuCl and polystyrene in tetrahydrofuran. Polystyrene beads (Polysciences, Inc.) were used. The tetrahydrofuran (Matheson, Coleman, and Bell) was distilled under nitrogen and stored under He until used. CuCl (Merk, reagent grade) was recrystallized from hot HCl and stored in a desiccator until needed. All solutions were prepared under He atmosphere. Ultraviolet emission spectra were recorded on a Carey 17 double beam spectrophotometer. Samples were contained in fused quartz cells (1 cm path length) with Teflon caps to prevent exposure to air and water vapor. Emission spectra were recorded using an apparatus previously described [21].

B. Ultraviolet absorption

Samples and reference solutions were made up by adding 6.25 g polystyrene to 250 ml tetrahydrofuran. To 100 ml of this solution was added 2.5×10^{-4} g

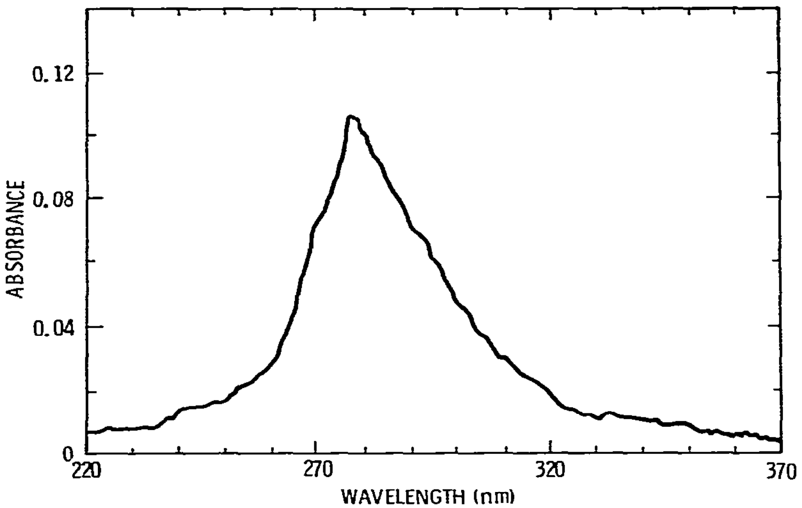

Fig. 2. UV absorption: sample = (PS + CuCl) in THF; reference = PS in THF.

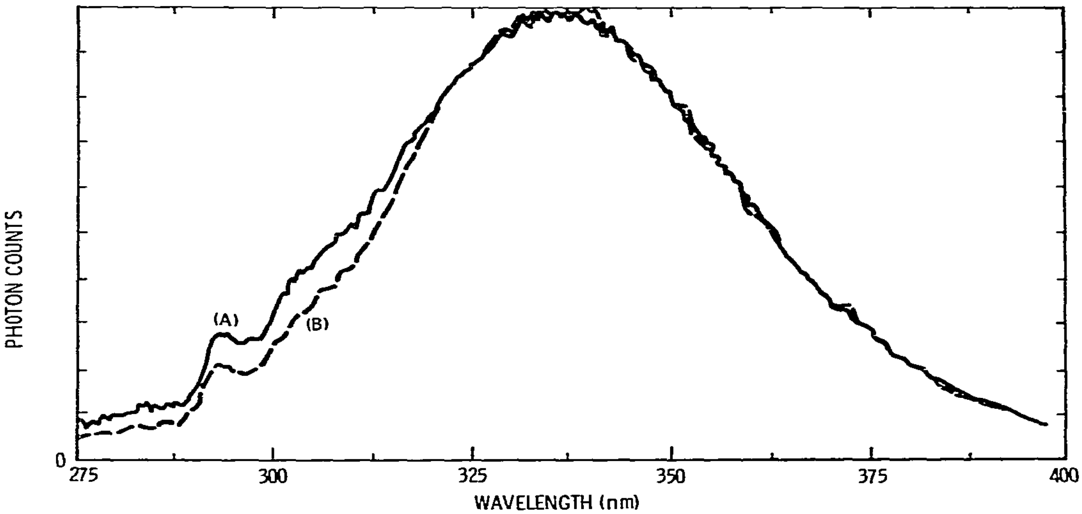

Fig. 3. UV emission (excitation at 2650 Å); A = (PS + CuCl) in THF, B = PS in THF. Individual spectra are normalized to a maximum relative intensity of 1.0.

CuCl. Most of the CuCl remained undissolved, so that the actual concentration of CuCl in solution was unknown. Spectra were recorded between 400 nm and 210 nm with the (polystyrene + CuCl) solution as sample and the parent polystyrene solution as reference. No change in the spectra was observed after leaving the cells in air (with Teflon plugs in place) for 7 hours. Solutions exposed to air or water vapor turned a yellow-green within a matter of minutes, indicating oxidation to Cu^{2+}.

The absorption spectrum is shown in Figure 2. The absorption maximum occurs at 277 nm with an absorbance of 0.105. No such band was observed for the yellow-green solutions.

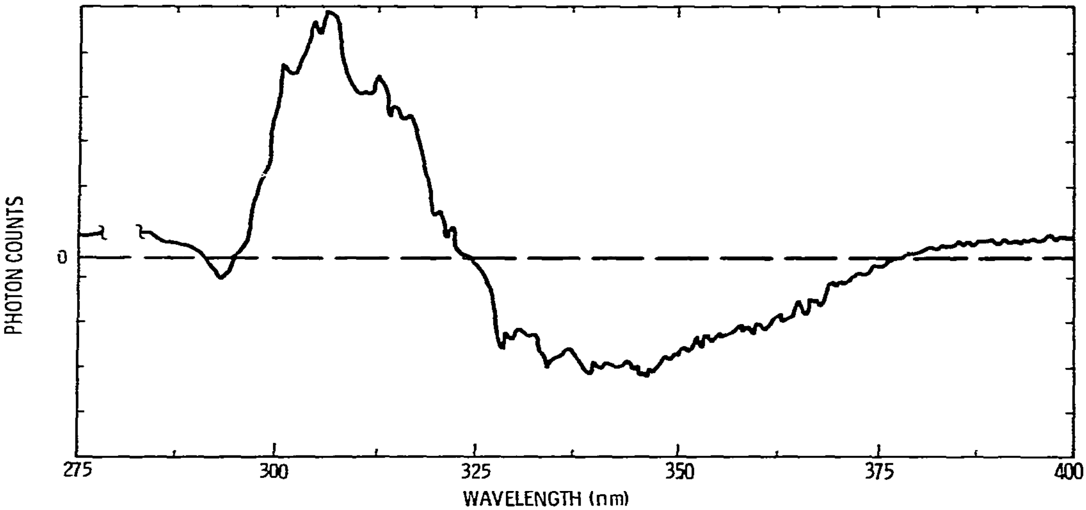

Fig. 4. Difference of normalized emission spectra (A — B, Fig. 3). Break at left is due to Hg emission line.

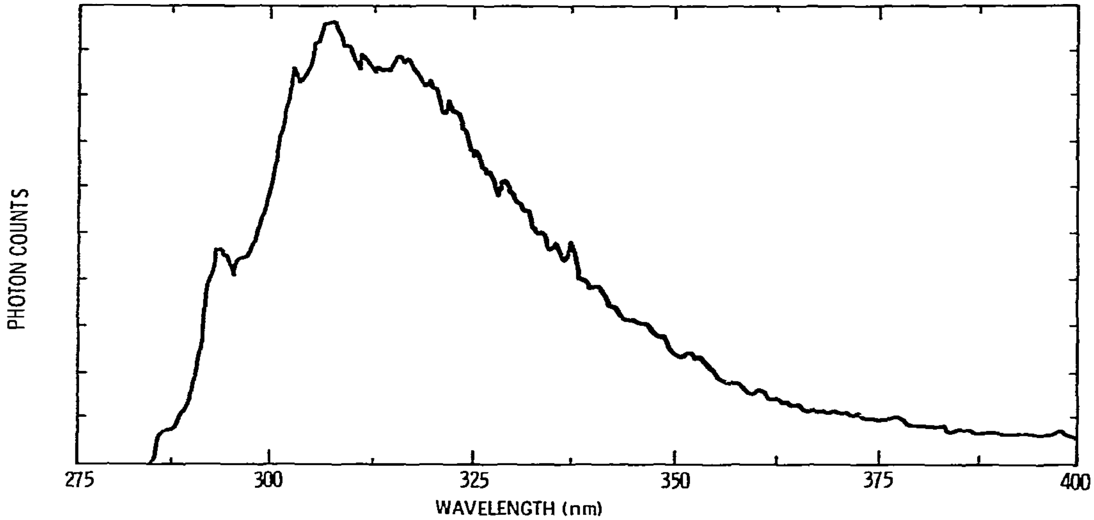

Fig. 5. Emission spectrum of (PS + CuCl) in THF (excitation at 2800 Å, cf., Fig. 2). Region to left of 297 nm is set to zero due to presence of Hg emission line.

C. Ultraviolet emission

Solutions for the emission experiments were made up as described above. Emission spectra of both the polystyrene + CuCl solution and the polystyrene solution were taken between 2750 Å and 4000 Å at 5 Å intervals with an excitation radiation of 2650 Å (the $\pi \rightarrow \pi^*$ transition for benzene [22]). The polystyrene + CuCl solution displayed an emission maximum near 3300 Å, while the maximum for the polystyrene solution occurred near 3350 Å. The maximum of each solution was scaled to a relative intensity of 1.0. The normalized spectra are displayed in Figure 3. The difference between these normalized spectra [(polystyrene + CuCl) — (polystyrene)] is plotted in Figure 4. It is evident from Figure 4 that an extra emission band with a peak near 3060 Å is present in the polystyrene + CuCl solution and that longer wavelength emission (due to excimer formation [22]) is partially quenched.

To determine if the emission peak in Figure 4 was due to a charge transfer transition, the polystyrene + CuCl solution was excited at 2800 Å (near the peak of the charge transfer absorption band, Fig. 3) and the emission spectrum measured between 2750 Å and 4000 Å at 5 Å intervals. (The absorption of pure polystyrene in tetrahydrofuran is negligible at 2800 Å). The result is shown in Fig. 5. A rather broad band is again observed, with a maximum near 3060 Å.

Discussion

The peak observed in the absorption spectra at 277 nm (Fig. 2) is not observed in a solution containing only polystyrene or only CuCl and, therefore, indicates a charge transfer interaction between the copper and the polystyrene. Moreover, if the observed band were due to impurities in the polymer, exciting the two different solutions at 280 nm would yield identical spectra.

That the charge transfer is due to the presence of Cu^+, and not some other oxidation state of Cu, cannot be completely ruled out since the limited solubility of CuCl in the solutions prevented monitoring absorption or emission intensities as a function of CuCl concentration. That the absorption was due to Cu^{2+} can be ruled out, however, since no such absorption was observed for the oxidized yellow-green solutions. That the absorption was due to the presence of Cu^0 is unlikely, since Cu^0 olefin complexes are unstable at room temperature [15]. Moreover, the position of the absorption maximum, when compared to that of CuCl and nornobornadiene [23] and Cu^+ and ethylene [24], reveals the red shift of the charge-transfer transition expected for increasing conjugation of the olefin [25]. The evidence strongly indicates that the charge transfer transition is due to Cu^+ and polystyrene.

The ultraviolet absorption and emission spectra, together with the molecular orbital calculations on $(CuC_2H_4)^+$, show that the observed charge transfer excitation is of a ligand-to-metal rather than metal-to-ligand ($3d(Cu^+) \rightarrow \pi^*$) nature. The benzene $\pi \rightarrow \pi^*$ excitation (2650 Å) occurs at higher energy than the charge transfer excitation (2800 Å). The same relationship holds for the emission [20] spectra (2750 Å, $\pi \rightarrow \pi^*$, 3060 Å, charge transfer). The molecular orbital calculations (Table 1) place the $3d$ (Cu^+) orbitals over 4 eV below the π. A metal-to-ligand charge transfer would thus occur at a higher energy than the $\pi \rightarrow \pi^*$ excitation, opposite to what is in fact observed. A ligand-to-metal charge transfer assignment is consistent with the observed quenching of excimer emissions (Fig. 4). Radiationless transfer from the π^* to the $4s$ (Cu^+) followed by radiative decay to the ground state would give just the observed spectrum.

As a check on the accuracy of the calculated binding energy, the observed charge transfer excitation energy (E_{CT}) can be estimated from the following steps:

$$(CuC_2H_4)^+ \rightarrow Cu^+ + C_2H_4;\ E_1 \tag{1}$$

$$C_2H_4 \rightarrow C_2H_4^+ + e^-;\ E_2 \tag{2}$$

$$Cu^+ + e^- \rightarrow Cu;\ E_3 \tag{3}$$

$$Cu \div C_2H_4^+ \rightarrow C_2H_4^+ \ldots Cu:\ E_4 \tag{4}$$

E_1 is obviously the calculated binding energy for $(CuC_2H_4)^+$, 1.31 eV. E_2 and E_3 are the ionization potentials for ethylene [26] (10.51 eV) and neutral copper [27] (7.72 eV). E_4 is difficult to estimate, but our results and those [9] for Ni suggest it should not be very large relative to E_1, and we neglect it. We then have $E_{CT} = E_1 + E_2 - E_3 = 4.10$ eV or 3050 Å; neglecting solvation effects. (The observed value [24] for $(CuC_2H_4)^+$ is 2280 Å in aqueous solution.)

Conclusions

Ab initio Hartree-Fock self-consistent field calculations carried out on $(CuC_2H_4)^+$ and (CuC_2H_4) show that the charged complex is bound by 1.31 eV and the neutral complex is bound by only 0.05 eV. The amount of π-backbonding in $(CuC_2H_4)^+$ is negligible. Ultraviolet absorption and emission spectra indicate that CuCl forms a charge transfer complex with the phenyl group in polystyrene, with a ligand-to-metal charge transfer excitation at 2800 Å, consistent with the calculated 1.31 eV binding energy for Cu^+ interacting with a C—C double bond.

These results suggest that a possible reason for improved adhesion of Cu to oxygen-plasma pretreated polystyrene is oxidation of the interfacial copper to Cu^+, followed by formation of a charge transfer complex with the phenyl groups. Determination of the charge on the copper in the Cu—O—C complex would be of great interest.

References

1 J. Chatt and L.A. Duncanson, J. Chem. Soc., (1953) 2939.
2 M. Bigorgne, J. Organometal. Chem., 160 (1978) 345.
3 H. Basch, J. Chem. Phys., 56 (1972) 441.
4 J.M. Burkstrand, J. Vac. Sci. and Tech., 15 (1978) 223.
5 J.M. Burkstrand, Appl. Phys. Lett., 33 (1978) 387.
6 R.S. Mulliken, J. Amer. Chem. Soc., 74 (1952) 811.
7 H.G. Smith and R.E. Rundle, J. Amer. Chem. Soc., 80 (1958) 5075.
8 R.W. Turner and E.L. Amma, J. Amer. Chem. Soc., 88 (1966) 1877.
9 H. Basch, M.D. Newton and J.W. Moskowitz, J. Chem. Phys., 69 (1978) 584.
10 T.A. Upton and W.A. Goddard III, J. Amer. Chem. Soc., 100 (1978) 321.
11 M. Dupuis, J. Rys and H. King, QCPE, 10 (1977) 336.
12 S. Huzinaga, J. Chem. Phys., 42 (1965) 1293 and T.H. Dunning, Jr., J. Chem. Phys., 53 (1970) 2834.
13 B. Roos, A-Veillard and G. Vinot, Theoret. Chim. Acta., 20 (1971) 1.
14 P.J. Hay, J. Chem. Phys., 66 (1977) 4377.
15 G.A. Ozin, H. Huber, D. McIntosh, Inorg. Chem., 16 (1977) 3070.
16 E. Clementi, J. Chem. Phys., 47 (1967) 4485.
17 K. Siegbahn. C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.E. Karlsson, I. Lindgren and B. Lindberg, Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy, Almquist and Wiksells, Upsalla, 1967.
18 H. Basch, Chem. Phys. Lett., 5 (1970) 337.
19 R.S. Mulliken, J. Chem. Phys., 23 (1955) 1833.
20 T. Ziegler and A. Rauk, Inorg. Chem., 18 (1979) 1559.
21 C.W. Frank and L.A. Harrah, J. Chem. Phys., 61 (1974) 1526.
22 I.A. Berlman, Handbook of Flourescence Spectra of Aromatic Molecules (Second ed.), Academic Press, New York, 1971, p. 69.
23 D.P. Schwendiman and C. Kutal, J. Amer. Chem. Soc., 99 (1977) 5677.
24 G.V. Buxton, J.C. Green and R.M. Sellers, J. Chem. Soc. Dalton Trans., (1976) 2160.
25 J.K. Hurstand and R.H. Lane, J. Amer. Chem. Soc., 95 (1973) 1703.
26 J.W. Robinson, Handbook of Spectroscopy, Vol. 1 CRC Press, Cleveland OH. (1974).
27 C.E. Moore, NBS Circular 467, Vol. 2 (1952) 111.