

**1183.** *Electronic Spectra of Silver-Hydrocarbon Complexes.*

By J. N. MURRELL and S. CARTER.

The spectra of the  $\text{Ag}^+$  complexes with benzene and styrene are reported. On complexing, the benzene 2550-Å band doubles in intensity but is unchanged in energy. Also, a new band appears at 2330 Å ( $\epsilon = 1500$ ) which we attribute to a charge-transfer transition. The predominant effect of  $\text{Ag}^+$  on the styrene spectrum is to decrease the intensity of the 2450-Å band by  $\epsilon = 4000$  and shift it to lower energies by 200 Å. Calculations are in good agreement with experiment if it is assumed that the silver ion lies directly over one C-C bond in the benzene complex and over the exocyclic C-C bond in the styrene complex.

We present and analyse the spectra of the silver-benzene and silver-styrene complexes. Although the stability of these complexes has been attributed to a charge-transfer inter-

action,<sup>1</sup> no charge-transfer band has previously been reported for them. Hosoya and Nagakura<sup>2</sup> have published a spectrum of the Ag<sup>+</sup>-cyclohexene complex in which they assign an absorption shoulder at 2250 Å to a charge-transfer transition; Torre-Mori, Janjic, and Susz<sup>3</sup> have also attributed a band at 2740 Å to a charge-transfer transition of the benzene-silver perchlorate complex, but we believe that this is due to a transition localised on the hydrocarbon.

It is to be expected that complex formation will alter the absorption spectrum of the components of the complex but this effect has not been much investigated. Useful information can be obtained about the structure of the silver-hydrocarbon complexes from the changes in the hydrocarbon spectra.

Spectra of the Ag<sup>+</sup>-hydrocarbon complexes are difficult to study because they are completely overlain by the spectra of the uncomplexed components always present in solution. We used silver perchlorate as this is the most transparent silver salt below 2300 Å, but even so we required cells of path length 0.10–0.01 cm. to keep down the absorption due to silver ion.

### EXPERIMENTAL

Aqueous solutions were made up from dry silver perchlorate and their ionic strengths adjusted to unity with sodium perchlorate. About 2 ml. of the hydrocarbon was added to 100 ml. portions of each solution and the aqueous layer saturated with the hydrocarbon by mechanical agitation of the mixtures for 4–5 hr. at room temperature. The spectrum of the aqueous layer was run against a reference which was another portion of the same solution after the hydrocarbon had been extracted with cyclohexane. This was found to be the most accurate method of subtracting the absorption due to the AgClO<sub>4</sub>. The optical path length was chosen such that at 2300 Å the AgClO<sub>4</sub> was absorbing not more than 60% of the light. The amount of hydrocarbon in each aqueous layer was determined by a method of Andrews and Keefer.<sup>4</sup> 5-ml. Samples of the aqueous layer were extracted with 20-ml. samples of spectroscopic cyclohexane (a single extraction removed all the hydrocarbon) and the concentration of hydrocarbon in the cyclohexane was determined spectroscopically using the following data: benzene  $\lambda = 2550$  Å,  $\log_{10} \epsilon = 2.3$ ; styrene  $\lambda = 2910$  Å,  $\log_{10} \epsilon = 2.7$ .

The spectra and concentrations of the two hydrocarbons in aqueous sodium perchlorate solutions were also recorded. The spectra were recorded on a Perkin-Elmer model 137 instrument.

The spectrum as measured of the hydrocarbon in AgClO<sub>4</sub> solutions consists of the spectrum due to the complex and that of the free hydrocarbon. (We have assumed that the relatively small percentage of the Ag<sup>+</sup> which is complexed has the same spectrum as that which is uncomplexed.) Following Andrews and Keefer, we assumed that the concentration of uncomplexed hydrocarbon was constant in the experiments, equal to that in pure NaClO<sub>4</sub> solutions. This assumption is supported by the fact that the amount of hydrocarbon that goes into the aqueous layer is almost linear in the silver concentration (there is a slight curvature which Andrews and Keefer attributed to a complex with two silver ions per hydrocarbon). The absorption spectra of the complexes were then readily obtained from the average of all the experiments, and they are shown in Figs. 1 and 2. The equilibrium constants of the 1:1 complexes which we calculate from our data are for benzene  $K_1 = 2.25$  and for styrene  $K_1 = 22.7$  l. mole<sup>-1</sup> [Andrews and Keefer found, using AgNO<sub>3</sub>-NaNO<sub>3</sub> solutions,  $K_1$  (benzene) = 2.41 and  $K_1$  (styrene) = 18.2 l. mole<sup>-1</sup>].

### RESULTS AND DISCUSSION

*Spectrum of the Benzene Complex.*—There are two important features. On complex formation the benzene 2550-Å band is increased in intensity by about a factor of two, but is unchanged in frequency. Also, a new band with no vibrational fine structure is observed with a maximum at 2330 Å. This second band is still rather weak compared with the 2000-Å or 1850-Å bands of benzene and is certainly far removed from them. Since the 2550-Å band

<sup>1</sup> R. S. Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811.

<sup>2</sup> H. Hosoya and S. Nagakura, *Bull. Chem. Soc. Japan*, 1964, **37**, 249.

<sup>3</sup> B. G. Torre-Mori, D. Janjic, and B. P. Susz, *Helv. Chim. Acta*, 1964, **47**, 1172.

<sup>4</sup> L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, 1950, **72**, 5034.

is not shifted by complexing, it is unlikely that the 2330-Å band is to be associated with one of the benzene absorption bands and we therefore assign it to a charge-transfer band of the complex. Below 2300-Å the  $\text{AgClO}_4$  is absorbing a large fraction of the light and the spectrum becomes increasingly less accurate. We feel confident, however, in the position of the absorption maximum of this proposed charge-transfer band.

The band at 2330 Å is slightly lower in energy than that which has been postulated as a charge-transfer band for the  $\text{Ag}^+$ -cyclohexene complex (2250 Å). Such bands of benzene and cyclohexene with the same acceptor usually occur at about the same wavelength, as can be

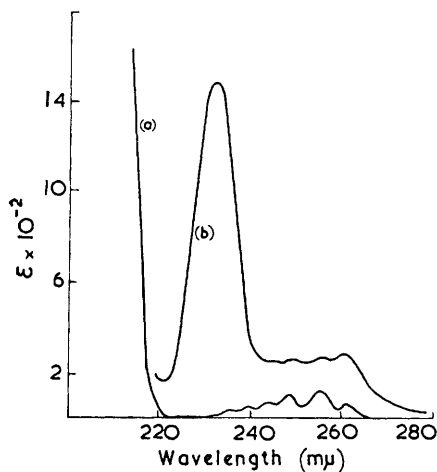


FIG. 1. Ultraviolet absorption spectra of (a) uncomplexed benzene (b) the  $\text{Ag}^+$ -benzene complex.

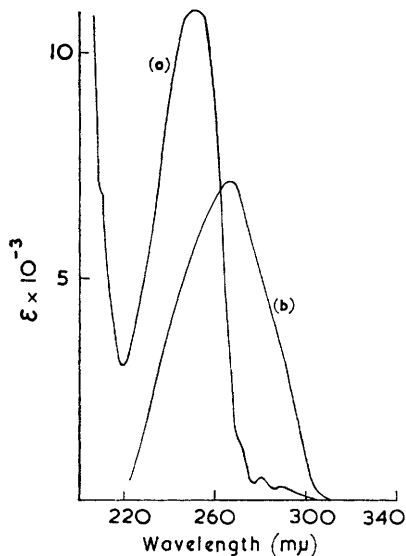


FIG. 2. Ultraviolet absorption spectra of (a) uncomplexed styrene (b) the  $\text{Ag}^+$ -styrene complex.

seen from the Table. Although the ionisation potential of cyclohexene is about 0.3 eV lower than that of benzene, the charge-transfer bands are not always at lower energies for cyclohexene than for benzene. It appears that  $\text{Ag}^+$  provides a further example where the charge-transfer frequency does not follow the difference in ionisation potentials.

Hosoya and Nagakura have attempted to calculate the position of the charge-transfer band of  $\text{Ag}^+$ -cyclohexene taking the acceptor orbital to be the 5s of the  $\text{Ag}^+$ . They find it necessary to assume that about 4.5 eV of solvation energy of  $\text{Ag}^+$  is lost on going from the ground state to the charge-transfer state. A similar calculation will therefore give as good an

Charge-transfer band energies for benzene and cyclohexene complexes (ev).

Acceptor	Benzene $I_D = 9.2$ ev	Cyclohexene $I_D = 8.9$ ev	Solvent	Ref.
$I_2$	4.30	4.33	n-Heptane	5
$SO_2$	4.50	4.56	n-Heptane	6
Trinitrobenzene	4.30	4.0	$CCl_4$	7
Tetracyanoethylene	3.23	2.94	$CH_2Cl_2$	8
$Ag^+$	5.32	5.51	Water	This work

energy for the  $Ag^+$ -benzene band. There is just one complicating feature which is that the highest occupied orbitals of benzene are degenerate, having wave-functions (in real form) as follows:



If  $Ag^+$  is taken to lie over the centre of the 2-3 bond (see later) then the transition  $\psi_1' \rightarrow 5s$  is symmetry-forbidden. We therefore assume that the charge-transfer band, which has an observed intensity of about 1500, arises from the allowed transition  $\psi_1 \rightarrow 5s$ .

The intensity of the benzene 2550-Å band is weak because it arises from a symmetry-forbidden transition ( ${}^1A_{1g} \rightarrow {}^1B_{2u}$ ). If the silver complex has a lower symmetry than benzene, then it is to be expected that this band will increase in intensity. It is seen from Fig. 1 that the vibrational structure of the band is not as marked as in benzene, which is to be expected if the band is no longer symmetry-forbidden. X-Ray analysis<sup>9</sup> of the  $Ag^+$ -benzene crystal shows that the  $Ag^+$  is almost directly above the centre of one C-C bond, the distance from the plane of the benzene ring being *ca.* 2.48-Å. We have calculated what increase would be expected in the intensity of the  ${}^1A_{1g} \rightarrow {}^1B_{2u}$  transition due to an  $Ag^+$  at that position.

The  ${}^1A_{1g} \rightarrow {}^1B_{2u}$  transition will gain intensity mainly through the mixing of the  ${}^1B_{2u}$  and  ${}^1E_{1u}$  (1850 Å) states.<sup>10,11</sup> The energy of the  ${}^1B_{2u} \rightarrow {}^1E_{1u}$  transition density in the potential field of the  $Ag^+$  was calculated by assuming the  $Ag^+$  was a point positive charge, and taking Slater wave-functions for the carbon  $2p\pi$  atomic orbitals. Except for the two carbon atoms nearest to the  $Ag^+$  the  $(2p\pi)^2$  charge densities can be represented by point charges at the carbon nuclei. The integrals were evaluated using Roothaan's formulae.<sup>12</sup>

This perturbation transferred approximately 1.3% of the intensity of the 1850-Å band to the 2550-Å band. If the extinction coefficient of the 1850-Å band is 50,000 this would give  $\epsilon \sim 650$  for the 2550-Å band of the complex. Experimentally the increase in extinction coefficient of the benzene band on complexing is about 150, so that our calculation overestimates this increase. If the distance of the silver ion from the benzene ring is increased to 3 Å then there is agreement between the calculation and experiment. Also, if the silver is moved closer to the six-fold axis of the benzene ring the transferred intensity will be smaller. However, the type of calculation we have carried out is only expected to give a rough measure of the transfer of intensity to the 2550-Å band. Therefore, although the calculation gives some indication that the most probable configuration of the silver-benzene complex in solution has the silver ion slightly displaced from its position in the solid, we do not state this with confidence.

<sup>5</sup> J. Ham, *J. Amer. Chem. Soc.*, 1954, **76**, 3875.

<sup>6</sup> D. Booth, F. S. Dainton, and K. J. Ivin, *Trans. Faraday Soc.*, 1959, **55**, 1293.

<sup>7</sup> G. Briegleb and J. Czekalla, *Z. Electrochem.*, 1959, **63**, 6.

<sup>8</sup> R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, 1958, **80**, 2778.

<sup>9</sup> H. G. Smith and R. E. Rundle, *J. Amer. Chem. Soc.*, 1950, **72**, 5337; 1958, **80**, 5075.

<sup>10</sup> A. L. Sklar, *J. Chem. Phys.*, 1942, **10**, 135.

<sup>11</sup> T. Förster, *Z. Naturforsch.*, 1942, **2a**, 149.

<sup>12</sup> C. C. J. Roothaan, *J. Chem. Phys.*, 1951, **19**, 1445.

The transfer of 0.32% of the intensity of the 1850-Å band to the 2550-Å band will be accompanied by a red shift of only about 25 cm.<sup>-1</sup> in the latter. This could not be determined in a solution spectrum.

We have also investigated the interaction between the charge-transfer state and the locally excited states of benzene: this will arise through the overlap of the benzene and the silver orbitals. The interaction matrix element was calculated using the method given earlier.<sup>13</sup> With the geometry of the complex so far assumed, the charge-transfer state can only interact with the <sup>1</sup>B<sub>2u</sub> and one component of the <sup>1</sup>E<sub>1u</sub> states. For example, the perturbed <sup>1</sup>B<sub>2u</sub> state will have the form

$$\Psi'_{(^1B_{2u})} = \Psi_{(^1B_{2u})} + \lambda \Psi_{(C-T)} \quad (1)$$

where  $\lambda$  is given by

$$\langle \Psi_{(C-T)} | V' | \Psi_{(^1B_{2u})} \rangle - \langle \Psi_{(C-T)} | \Psi_{(^1B_{2u})} \rangle \langle \Psi_{(^1B_{2u})} | V' \{ \Psi_{(^1B_{2u})} \} \rangle / \Delta E \quad (2)$$

The subscript C-T stands for charge-transfer;  $\Delta E$  is the difference in energy between these zero-order states and  $V'$  is the potential field of the Ag<sup>+</sup>. These matrix elements were evaluated using the usual Goppert-Mayer-Sklar wave-function for  $\Psi_{(^1B_{2u})}$  and a wave-function for  $\Psi_{(C-T)}$  appropriate to the transfer of the electron from  $\psi_1$  to 5s as deduced earlier. Reducing the many electron integrals in the usual way and neglecting all terms which depend on both an overlap density and a transition density we have

$$\lambda = -\sqrt{\frac{1}{2}} \left\{ \int \psi_{-1} \cdot \psi_{5s} V' d\tau - \int \psi_{-1} \cdot \psi_{5s} d\tau \int \psi_1^2 V' d\tau \right\} / \Delta E \quad (3)$$

where  $\psi_{-1}'$  is the paired antibonding orbital to  $\psi_1$ , in the alternant hydrocarbon scheme. These integrals were evaluated by use of the same potential as described earlier, and a 5s orbital chosen by the Slater recipe

$$\psi_{5s} = 0.079 r^3 \exp(-0.925r) \quad (4)$$

The overlap and resonance integrals were then calculated using formulae given in refs. 12 and 14.

The calculation gives  $\lambda = 0.033$ , which would lead to negligible exchange of intensity between the charge-transfer and <sup>1</sup>B<sub>2u</sub> bands. Also the corresponding depression of the <sup>1</sup>B<sub>2u</sub> band would be given by  $\lambda^2 \Delta E = 4$  cm.<sup>-1</sup>, which is again undetectable.

A similar calculation was made on the interaction between the charge-transfer state and the component of the <sup>1</sup>E<sub>1u</sub> state of the same symmetry. The perturbed <sup>1</sup>E<sub>1u</sub> state is given by the formula

$$\Psi'_{(^1E_{1u})} = \Psi_{(^1E_{1u})} + \lambda \Psi_{(C-T)} \quad (5)$$

where  $\lambda$  has the same form as (3). The perturbed charge-transfer state must be orthogonal to (5), hence

$$\Psi'_{(C-T)} = \Psi_{(C-T)} + \mu \Psi_{(^1E_{1u})} \quad (6)$$

where, to first order

$$\mu = -\lambda - \langle \Psi_{(C-T)} | \Psi_{(^1E_{1u})} \rangle$$

The calculation gives  $\mu = 0.11$  which would lead to a negligible shift in the energy of the charge-transfer band but a transfer of intensity of about  $\epsilon = 254$ , which accounts for about one-sixth of the intensity of the charge-transfer band.

To summarise: the calculations show that if the complex in solution has roughly the same structure as in the solid state then calculation gives about the right increase in intensity of the 2550-Å band and predicts no change in frequency of this band on complexing, in agreement with experiment. Further calculations suggest that about one-sixth of the intensity of the charge-transfer band is derived from the <sup>1</sup>E<sub>1u</sub> band, but that the interaction between the

<sup>13</sup> J. N. Murrell, *J. Amer. Chem. Soc.*, 1959, **81**, 5037.

<sup>14</sup> R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.

charge-transfer state and the locally excited states of benzene have no effect on the energy of the charge-transfer band.

*Spectrum of the Styrene Complex.*—The predominant feature is a shift to lower energies and a reduction in the extinction coefficient of the band near 2500 Å, compared with the uncomplexed styrene spectrum. The weak  ${}^1L_b$  band of styrene (2780 Å) is largely overlain by the more intense 2500-Å band ( ${}^1L_a$ ) in the complex. Although there is some indication that the intensity of this band is increased, we can make no accurate estimate of this as was possible for the benzene complex.

There is no obvious band in the spectrum that we can attribute to charge-transfer, so that this is either below 2200 Å or it underlies the intense 2500-Å band. We shall show by calculation that the former supposition is probably correct.

There is no X-ray evidence for the structure of the  $\text{Ag}^+$ -styrene complex. If charge-transfer interaction is mainly responsible for the stability of the complex then it is to be expected that the  $\text{Ag}^+$  will sit at such a position that the overlap between the 5s orbital and the highest occupied orbital of the styrene is a maximum. If we further assume that the  $\text{Ag}^+$  will lie over the centre of a C-C bond as it does in benzene then this bond is expected to be the exocyclic double bond. We will base our calculations on this structure, taking the distance of the  $\text{Ag}^+$  from the C=C bond to be the same as for benzene.

If the charge-transfer energy of the styrene differs from that of benzene only through a difference in ionisation potential of the donor, then we would predict a charge-transfer band for styrene in the region of 2800 Å. This ignores, however, the interaction between the charge-transfer state and the 2450-Å  ${}^1L_a$  state which would lower the energy of the charge-transfer band still further, and raise the energy of the  ${}^1L_a$  band. Similar calculations to those carried out for benzene then predict a charge-transfer band at 3170 Å with an intensity  $\epsilon \sim 2500$ , and a  ${}^1L_a$  band at 2150 Å with an intensity of  $\epsilon \sim 11,000$ . This clearly has no similarity to the observed spectrum.

We have seen, however, that the energies of the charge-transfer bands of the benzene and cyclohexene complexes do not follow the difference in the ionisation potentials of the hydrocarbon so our initial estimate of 2800 Å for the position of the band may be wrong. We have therefore examined a further possibility, that the zeroth-order charge-transfer energy of the styrene complex is the same as that of the benzene complex. The interaction between the  ${}^1L_a$  state and the charge-transfer state then gives rise to a state given by

$$\Psi'_{({}^1L_a)} = \Psi_{({}^1L_a)} + 0.86 \Psi_{(\text{C-T})}$$

which would give a band at 2800 Å with an intensity less by  $\epsilon = 5000$  than the styrene  ${}^1L_a$  band. This is in very good agreement with experiment. (Although one would not assign this band to a charge-transfer transition one can see from the wave-function that it has a large amount of C-T character.) The higher-energy component of the  ${}^1L_a$ -C-T interaction is predicted to be at 2050 Å, so would not be observed.

*Conclusions.*—The observed spectra of the  $\text{Ag}^+$ -benzene and  $\text{Ag}^+$ -styrene complexes are in good agreement with the calculated spectra which are based on the assumption that the zeroth-order charge-transfer states for both systems (and also for the cyclohexene complex) occur at about 2330 Å. The most likely reason for the failure of this band to show the expected linear variation with the ionisation potential of the hydrocarbon is that the solvation energy of the ground state relative to the charge-transfer state, which in the case of benzene and cyclohexene must be about 4.5 eV, varies in such a way as to cancel out the variation in the ionisation potential.

S. Carter thanks the D.S.I.R. for a maintenance grant. J. N. Murrell thanks the Royal Society for a Mr. and Mrs. John Jaffé Research Fellowship.