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Some Aspects of Gaseous TCNE Complexes Including the Butene-TCNE

Jun-ichi AIHARA,*1 Motoyuki TSUDA*1 and Hiroo INOKUCHI

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Tokyo

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The absorption spectra of the gaseous olefin-TCNE complexes were successfully observed for the first time: the absorption maximum of the butene-TCNE complex was found at 28700 cm^{-1}. The CT band of the methyl derivatives was shifted to a higher-energy region because of their steric effect. The systematic collection of the gaseous data made it possible to estimate the magnitude of the steric effect.

1. The Absorption Spectra of the Gaseous Butene-TCNE Complex. Since Lang and Strong first measured the electronic absorption spectra of gaseous diethyl ether-iodine and also gaseous benzene-iodine complexes, various charge-transfer complexes have been investigated in the gas phase.[1-3] We have also measured the spectra of a series of gaseous aromatics-TCNE(tetracyanoethylene) and anthracene-chloranil complexes. These results have been reported in previous papers.[4-6]

Recently, Kroll studied the gaseous charge-transfer complexes, using TCNE as an electron acceptor.[7] However, according to his article, he failed to find the charge-transfer spectra for a gas-phase mixture of ethylene and TCNE, nor did he find the characteristic spectra for a gaseous mixture of butadiene and TCNE. Of course, it is widely known that ethylenic hydrocarbons form charge-transfer complexes with various acceptors in solution.[8,9]

We attempted to detect the charge-transfer band of the gaseous TCNE complex with one of the ethylenic hydrocarbons, *cis*-2-butene, and succeeded in the measurement of its spectrum. The experimental apparatus and procedures were the same as those employed in the previous experiments.[4] The *cis*-2-butene used was a commercial material, while the TCNE was purified by sublimation *in vacuo*. The spectroscopic measurements were made as rapidly as possible in order to observe the clean species. The electric furnace containing the optical cell was maintained at 200°C.

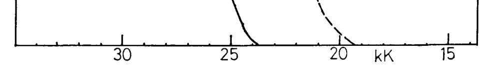

Fig. 1. The CT band of the butene-TCNE complex.

Figure 1 shows the gaseous spectrum of the butene-TCNE complex. The solution spectrum in carbon tetrachloride is added for the sake of comparison. To obtain the solution data, a sufficient amount of gaseous butene was introduced into a solution saturated with TCNE. In the gaseous phase, the characteristic charge-transfer band was observed in the near-ultraviolet region, where neither the vapour of butene nor that of TCNE absorbs. A peak is found at 28700 cm^{-1}; it corresponds to a blue shift of 4300 cm^{-1} from that found when both components are dissolved in carbon tetrachloride. The half-width determined from the long-wavelength part of the band is approximately 2200 cm^{-1}. It can be seen in Fig. 1 that gas and solution bands would coincide almost exactly if

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[*1] Present address: Hokkaido University, Department of Chemistry, Faculty of Science, Sapporo, Japan.

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TABLE 1. ADDENDUM TO THE LIST OF THE GASEOUS TCNE COMPLEXES

Donor	CT band (cm^{-1})		Gas-to-solution shift (cm^{-1})
	in gas phase	in CCl_4 solution	
cis-2-Butene	28700	24400	−4300
Acenaphthene	18100	15300	−2800

superimposed. In all respects, the nature of the butene-TCNE complex seems like that of usual TCNE complexes.

We also observed the spectra of another TCNE complex, that with acenaphthene at 200°C. These results are summarised in Table 1.

2. Steric Effects of Charge-transfer Complexes in the Gas Phase. Now, a fair amount of data on the gaseous TCNE complexes are available. Therefore, we can survey them from a different point of view. The observed band maxima($h\nu$) of the charge-transfer transition are plotted against the ionization potentials (Ip) of the donor molecules in Fig. 2. As usual, a linear relation between them can be derived:[10]

$$h\nu = aI_p - b \tag{1}$$

Here, a and b are assumed to be characteristic constants for the complexes of any one acceptor.

The ionization potentials of the donors used were determined by Watanabe, Terenin and Vilessov, and Briegleb.[11–13] We newly determined those of pyrene (7.53±0.03 eV) and acenaphthene (7.66±0.03 eV) by the photoionization method. This simplified equation, which can often be a sufficient approximation, has been used to determine the unknown ionization potential of any donor. In the case of typical polycyclic aromatic hydrocarbons especially, the ionization potentials derived from Eq. (1) coincide well with those obtained from the polarographic oxidation potentials.[14] On the other hand, it is generally admitted that polymethyl-benzenes obey a slightly different equation; that is, they give higher transition energies than the values to be expected from the equation based on typical hydrocarbons.[15,16]

As is illustrated in Fig. 2, we can also broadly classify the gaseous data into two groups; one is the group to which typical aromatic hydrocarbons belong, and the other is that to which their derivatives belong. Benzene, naphthalene, and pyrene can be ascribed to the former, while the other compounds belong mainly to the latter, though there are some exceptions.

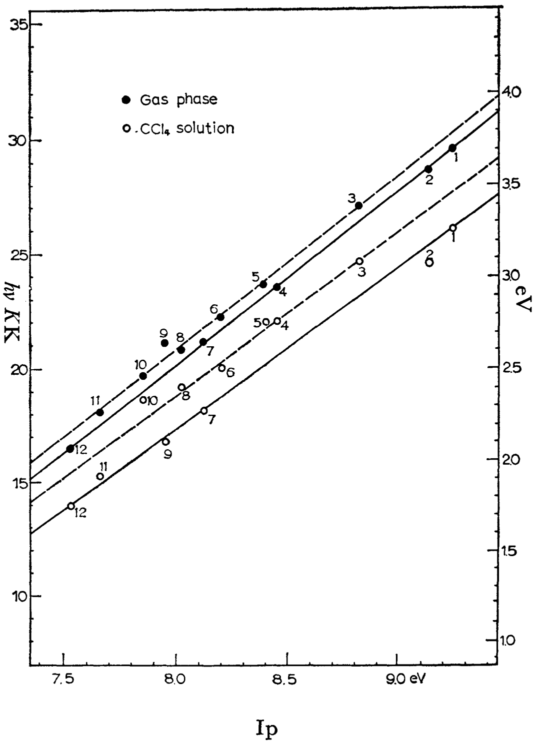

Fig. 2. Plots of CT absorption maxima *versus* ionization potentials of donors.

1. benzene, 2. *cis*-2-butene, 3. toluene, 4. *p*-xylene, 5. mesitylene, 6. diphenyl, 7. naphthalene, 8. durene, 9. stilbene, 10. hexamethylbenzene, 11. acenaphthene, 12. pyrene.

● Gas phase

○ CCl_4 solution

For the typical hydrocarbons, we obtained the following relations:

$$h\nu = 0.948I_p - 5.07 \text{ (eV)} \tag{2}$$

for the TCNE complexes in the gas phase, and

$$h\nu = 0.877I_p - 4.87 \text{ (eV)} \tag{3}$$

for those in the carbon tetrachloride solution. The complexes with these compounds rigorously maintain a linear relation both in gas and in solution. The coefficient, "a", in the gas phase is almost equal to unity. This means that the charge-transfer transition of the TCNE complexes can be interpreted primarily in terms of a simple electron donation from the donor to the acceptor molecule. In other words, it can be expressed by the ionization potential of the donor minus the electron affinity of the acceptor and minus the Coulomb energy.

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In the case of complexes with substituted derivatives, the gradients of Eqs. (2) and (3) are not changed. However, the constant terms in them increase by approximately the amounts of 0.075 and 0.19 eV respectively. These situations are shown by the dotted lines in Fig. 2. The data for benzene, *p*-xylene, mesitylene, and hexamethylbenzene are cited from Ref. (7).

In order to explain the above tendencies, it is instructive to consider the steric effect of the substitutents of the donor molecules. Though our information on the stereochemistry of the gaseous complexes is quite deficient, the substitutents should often change the distance between the molecular planes in the complex to some extent.

According to Pauling's idea, the half-thickness of the aromatic ring is 1.85 Å, while the van der Waals radius of the methyl group is about 2.0 Å.[17] Briegleb has suggested that, if the intermolecular distance, R, between the donor and the acceptor increases by 0.01 Å near R=3.2 Å, the Coulombic attraction term contributing to the charge-transfer transition will decrease by 100 cm^{-1}.[15] On the basis of this statement, it may be concluded that the R of the methyl derivatives increases by 0.06 Å on the average. Though R must be interpreted as the distance between the centres of the donor and of the acceptor molecules, the interplanar distance of the complex might be roughly regarded as the same. Exceptionally, *p*-xylene and butene behave as if they are not affected by the steric effect. On the other hand, diphenyl and acenaphthene are apparently affected under these circumstances. This behaviour is reflected in the subsequent polarization energy, P, in the carbon tetrachloride solution. As the dipole moments of the complex are dependent on the ionization potential of the donor, the polarization energy will necessarily depend on it. In fact, the dipole moments in the ground state are 1.28D for the naphthalene-TCNE, 1.35D for the hexamethylbenzene-TCNE, and 2.0D for the pyrene-TCNE complex.[18,19] Theoretical studies have suggested that the dipole moments in the excited state also vary systematically.[15] The actual *Ip* dependence of the polarization energy was derived by Eqs. (2) and (3) for typical complexes:

$$\mathrm{P} = 0.071 I_p - 0.20 \ (\mathrm{eV}) \qquad (4)$$

The polarization energy of the complex with the substituted compound is somewhat smaller than that of the typical complex. Supposing that Onsager's approximation is applicable to the dielectric media containing the charge-transfer complex, the solvent shift is inversely proportional to the cube of the cavity radius.[20,21] This assumption has been confirmed by an analysis of the TCNE complex in the solvent, a discussion presented in a previous paper.[5] Therefore, the change in the polarization energy can be shown by the augmentation of the molecular dimensions. The decrease of 30 percent in the polarization energy is equivalent to the increase of 13 percent in the cavity radius. This behaviour is also ascribable to the steric effect of the substitutents.

In the above discussion, we neglected various factors affecting the charge-transfer complex. Accordingly, we must admit that the criterion for the judgement of the steric effects seems somewhat obscure, as the several exceptions show. Such an amount of spectral change may occur by means of the geometrical variation of the complex.[22]

In the case of the stilbene-TCNE, the temperature dependence of the intensity ratio of the first and the second CT bands has been found in a methylene chloride solution.[23] This phenomenon has been explained in terms of geometrical isomerism. This isomerism may cause the location for it to deviate from the linearities. Strictly speaking, we need to examine the individuality of each complex in detail. Therefore, it seems very natural that the gaseous species behave well with fewer exceptions, since they are not influenced by a variety of ways of solvation and so on.

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