Gas-Phase Charge-Transfer Complexation of Carbonyl Cyanide as Acceptor

Takayuki Fueno and Yoshiro Yonezawa

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka

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Charge-transfer complexations of carbonyl cyanide with furan, tetrahydrofuran, diethyl ether, and their sulfur homologs have been investigated in gaseous phase at temperatures 22—82°C. Thermodynamic data showed that the complexations are enthalpy-controlled in the temperature range studied and that the complexes formed from *n*-donors are fairly strongly bound. Both the transition and bonding energies could be interpreted in terms of the usual two-state resonance model. It has been deduced that the spatial arrangements of the components do not greatly differ for the various donors studied, despite the difference in precise nature of the bondings involved.

Intermolecular interactions leading to the formation of "charge-transfer (CT)" complexes have been attracting increasing interests of both physical and organic chemists.[1] Studies have recently been conducted in gaseous phase, which have served to disclose the role of solvents in the CT complexations formerly observed in condensed phases. The gas-phase CT complexations studied so far include those with iodine,[2–8] sulfur dioxide,[9] tetracyanoethylene,[6,10,11] and carbonyl cyanide[12,13] as electron acceptor.

From a particular interest in the role of molecular complexation in the kinetics of some gas-phase reactions,[14,15] we investigated the bonding character of the gas-phase CT complexes of carbonyl cyanide, $(CN)_2CO$. This compound was chosen as acceptor because of relative unfamiliarity with respect to its structure and reactivity. The donor compounds here investigated are furan, tetrahydrofuran, diethyl ether and their sulfur homologs, *i.e.*, a series of C_2XC_2-type compounds with $X=O$ or S. Carbonyl cyanide, being highly electron-deficient at its carbonyl carbon atom, gives fairly strong complexes with some of the donor molecules studied. Nonetheless, it has been found that the usual assumption of weak complexation is still valid for characterizing the present CT interaction systems.

Experimental

Materials. Carbonyl cyanide was synthesized from tetracyanoethylene according to the method of Linn, Webster, and Benson.[16] It was distilled under reduced pressure in an all-glass apparatus and stored in a reservoir which was screened from sunlight and cooled with Dry Ice-methanol.

Furan, thiophene, tetrahydrofuran, tetrahydrothiophene, diethyl ether, and diethyl sulfide were all purchased and purified by drying and distillation.

Apparatus and Procedure. The apparatus used is diagrammatically shown in Fig. 1. The absorption cell made of cylindrical quartz is 2 cm in diameter and 10 cm in light-path length. The side arm of the absorption cell has a sampling part for donors and two capillary parts, S_1 and S_2, for sealing off. The volumes of the absorption cell and of the glass tube between sealing-off points were measured before the absorption cell was connected with the vacuum line. The sampling part for donors consists of a glass tube stoppered with silicone gum and tightened with stainless steel fittings having a hole for a microinjector. The whole apparatus maintained vacuum under 10^{-3} mmHg.

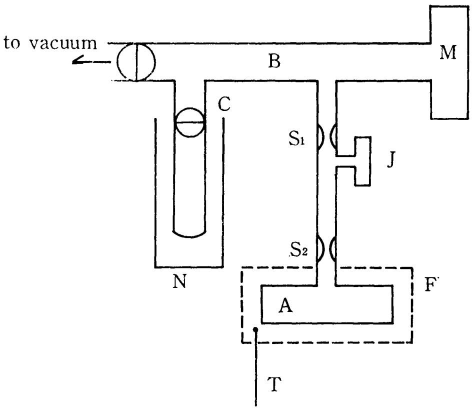

Fig. 1. Apparatus used for the gas-phase complexation measurements.
A, absorption cell; B, auxiliary tube; C, reservoir; M, oil manometer; F, electric heater; J, sampling part; T, thermocouple; N, liquid N_2 vessel; and S_1, S_2, seal-off parts

Gaseous mixtures of carbonyl cyanide and donor were prepared by the following method. The carbonyl cyanide vapor was metered into the evacuated absorption cell, using an oil manometer. The absorption cell was sealed off at capillary point S_1 from the vacuum line. While carbonyl cyanide in the absorption cell was condensed in the cell cooled with Dry Ice-methanol, liquid donor was introduced into the sampling part by use of a 25-μl microinjector. The cell was then sealed off at capillary point S_2. The concentration of carbonyl cyanide was calculated from its vapor

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pressure and the predetermined cell volume, assuming that the vapor is an ideal gas. Concentrations of donor vapors were also calculated from the weight of the liquid samples and cell volume. The absorption cell was covered with a heat jacket whose temperature was read with a thermocouple. Spectral measurements were carried out at varying temperatures between 22 and 82°C.

Absorption spectra of gaseous mixtures were recorded on a Shimadzu-MPS-50L spectrophotometer. The spectrophotometric equation which can be applied to this study is[17)]

$$\frac{c_a c_b}{d-d_0} = \left(c_a + c_b - \frac{d-d_0}{\varepsilon-\varepsilon_0}\right)\frac{1}{\varepsilon-\varepsilon_0} + \frac{1}{K_c(\varepsilon-\varepsilon_0)} \qquad (1)$$

where c_a and c_b are the initial concentrations of carbonyl cyanide and donor, respectively; ε and d_0 are the extinction coefficients of the complex and free carbonyl cyanide, respectively; d is the absorbance per unit length; d_0 is $\varepsilon_0 c_a$; and K_c is the equilibrium constant of complex formation. c_a was varied from 1.1 to 2.3 mM, and c_a from 1.4 to 9.3 mM.

In evaluating ε and K_c from Eq. (1), we adopted the method of Lang.[18)] An approximate value of ε was obtained by solving an appropriate pair of simultaneous equations based on Eq. (1). The values of $c_a c_b/(d-d_0)$ obtained from measurements at various c_a and c_b were then plotted against the values of $c_a+c_b-(d-d_0)/(\varepsilon-\varepsilon_0)$. From the slope calculated by the least squares method, a better value of ε was obtained. The procedure was repeated until the resulting value of ε coincided with the assumed. Usually, two iterations sufficed for the present purpose. The values of K_c at various temperatures were calculated from Eq. (1) by use of the ε value finally obtained. In the temperature range studied, ε of each complex did not vary appreciably with temperature.

Results

Figure 2 shows the absorption spectra of gaseous CT complexes of carbonyl cyanide with a series of donors at 62°C. The intensities of absorption increased (decreased) with the lowering (rising) in temperature and were essentially reproducible at temperatures between 22 and 82°C. This indicates that the complexes can exist in equilibrium with the free donor (D) and acceptor (A) species. Above 90°C, however, the absorbance in the shorter-wavelength region tended to show a gradual decrease with the elapsing time, indicating the occurrence of an irreversible reaction.

Prochorow *et al.*[19)] investigated the absorption spectrum of carbonyl cyanide in both gaseous phase and

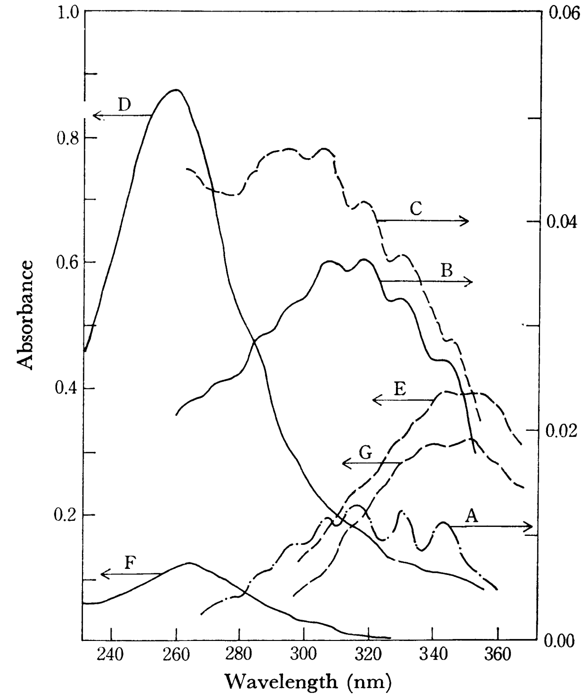

Fig. 2. Absorption spectra of the gas-phase CT complexes of $(CN)_2CO$ at 62°C.
A, $(CN)_2CO$ (1.50 mM) alone
B, $(CN)_2CO$ (1.80 mM) +furan (6.88 mM)
C, $(CN)_2CO$ (2.00 mM) +thiophene (6.30 mM)
D, $(CN)_2CO$ (1.64 mM) +tetrahydrofuran (4.17 mM)
E*, $(CN)_2CO$ (1.58 mM) +tetrahydrothiophene (2.11 mM)
F, $(CN)_2CO$ (1.39 mM) +diethyl ether (8.02 mM)
G, $(CN)_2CO$ (2.24 mM) +diethyl sulfide (4.02 mM)
* Measured at 72°C

TABLE 1. SPECTRAL AND THERMODYNAMIC DATA OF THE GAS-PHASE CT COMPLEXES OF $(CN)_2CO$

Donor	λ_{max} nm	ε $M^{-1}cm^{-1}$	K_c[a)] M^{-1}	$-\Delta H°$[a)] kcal mol^{-1}	$-\Delta S°$[a)] e.u.	I_D eV
Furan	315	20	16.1±2.5	2.6±1.0	2.5±1.5	9.0[b)]
Thiophene	295	20	30.6±3.5	6.0±2.2	11.8±2.1	9.0[b)]
Tetrahydrofuran	260	100	322±100	8.2±1.3	13.8±6.1	10.1[c)]
Tetrahydrothiophene	345	40	8020±500	14.3±4.4	26.2±6.2	8.6[d)]
Diethyl ether	262	30	39.3±1.0	4.4±0.5	6.1±2.7	9.7[e)]
Diethyl sulfide	350	50	740±250	16.8±2.8	38.4±4.5	8.3[f)]

a) At 52°C. The uncertainties indicate the probable errors.
b) W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (London), **A179**, 201 (1941).
c) J. Hissel, *Bull. Soc. Roy. Sci. Liège*, **21**, 457 (1952) [F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y. (1957), p. 283].
d) E. J. Gallegos and R. W. Kiser, *J. Phys. Chem.*, **66**, 136 (1962).
e) J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).
f) Calculated from $I_D = AP - D_{C-S}$, where AP (11.15 eV) is the appearance potential of $C_2H_5S^+$ from $(C_2H_5)_2S$ [J. L. Franklin and H. E. Lumpkin, *J. Amer. Chem. Soc.*, **74**, 1023 (1952)] and where D_{C-S} (2.83 eV) is the C-S bond energy [J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y. (1965), p. 77].

[17)] N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.*, **81**, 6138 (1959).
[18)] R. P. Lang, *ibid.*, **84**, 1185 (1962).
[19)] J. Prochorow, A. Tramer, and K. L. Wierzchowski, *J. Mol. Spectrosc.*, **19**, 45 (1966).

n-hexane solution and attributed the weak absorption with vibrational structure appearing in the 260—400 nm region to the symmetry forbidden n-π^* transition of the carbonyl group. The extinction coefficient at the absorption maximum $\lambda_{max}=330$ nm was reported to be $3.0\ \text{M}^{-1}\text{cm}^{-1}$. The vibrational structure of carbonyl cyanide remains clearly in the CT complexes with furan (Fu) and thiophene (Th). It is also discernible in the complexes with tetrahydrothiophene (THT) and diethyl sulfide (DES), but absent in the tetrahydrofuran (THF) and diethyl ether (DEE) complexes.

Table 1 summarizes the spectral and thermodynamic data of the CT complexes observed. Prochorow and Tramer[13] have already reported that the gaseous CT complex of carbonyl cyanide with DEE has $\lambda_{max}=262$ nm, $\varepsilon \simeq 65\ \text{M}^{-1}\text{cm}^{-1}$ and $K_c \simeq 45\ \text{M}^{-1}$ at an unspecified temperature. The ε value we obtained is about half as great as theirs, but the K_c values observed in both studies are in rough accord with each other.

Figure 3 gives a plot of the wavenumbers of the CT band maxima, $\tilde{\nu}_{max}$, against the ionization potentials I_D of donor compounds. For the sake of reference, the points for benzene, toluene, and *p*-xylene[13] have been included. The points including those of the benzene derivatives fit approximately the simple theoretical formula[20,21]

$$hc\tilde{\nu}_{max} = I_D - C_1 + \frac{C_2}{I_D - C_1} \qquad (2)$$

with $C_1=5.7$ eV and $C_2=2.5$ (eV)^2.

Inspection of the equilibrium data given in Table 1 indicates that the K_c values of saturated donors are appreciably greater than those of unsaturated donors. The K_c values of the sulfur compounds are uniformly greater than those of the corresponding oxygen homologs. The results are in agreement with those found for the gas-phase CT complexes of iodine as acceptor.[2,4,6] The CT complexations here observed may be characterized by the relatively large equilibrium constants K_c for some donors and the correspondingly large enthalpy change of complexation, $-\Delta H°$.

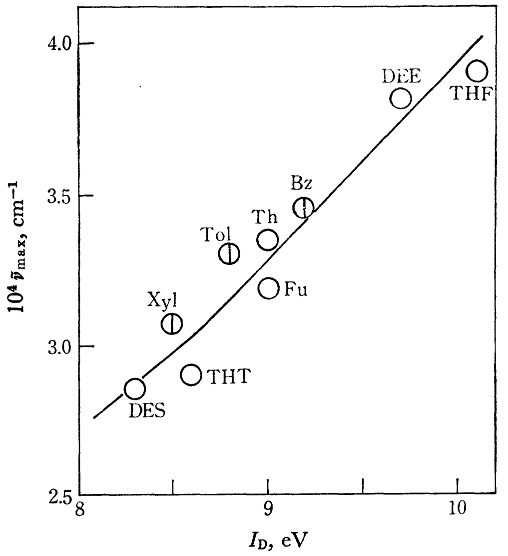

Fig. 3. Plots of the wavenumber of the CT band maxima *vs.* the ionization potential of donors.
Fu, furan; Th, thiophene; THF, tetrahydrofuran; THT, tetrahydrothiophene; DEE, diethyl ether; DES, diethyl sulfide; Bz, benzene[13]; Tol, toluene[13]; Xyl, *p*-xylene[13]

In Fig. 4, the observed values of $\Delta H°$ are plotted against the values of $\Delta S°$. Although errors inherent to these thermodynamic quantities are too large to permit any quantitative considerations, it does appear that an extrathermodynamic relationship[22] holds between the $\Delta H°$ and $\Delta S°$ values observed. The "isokinetic" temperature as determined from the slope is *ca.* 435°K. The results indicate that the relative complexation abilities of the series of donor compounds here investigated are enthalpy-controlled in the temperature range studied.

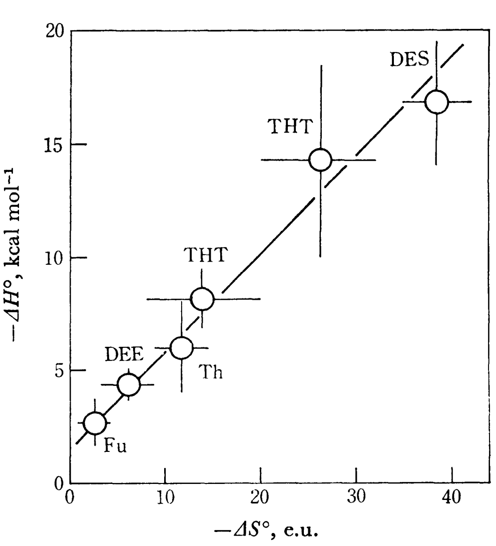

Fig. 4. Plots of $\Delta H°$ *vs.* $\Delta S°$.
The vertical and horizontal lines drawn on the circles indicate the ranges of the probable errors. For the symbols appended, see Fig. 3.

Discussion

The observed dependence of $\tilde{\nu}_{max}$ on I_D (Fig. 3) confirms that the absorption bands in question are essentially due to the intermolecular charge transfer transitions. The constants C_1 and C_2 appearing in Eq. (2) are given by[20,21]

$$C_1 = E_A - E_C + W_0 \qquad (3)$$

and

$$C_2 = 2\beta^2 \qquad (4)$$

where E_A is the electron affinity of the acceptor; E_c is the Coulombic energy involved in the ionic state, D^+A^-; W_0 is the van der Waals interaction energy of the no-bond state, DA; and β is the exchange interaction between the two extreme states.

If the simple two-state resonance model, on which

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[22] J. E. Leffler and E. Grundwald, "Rates and Equilibria of Organic Reactions," John Wiley, New York, N .Y. (1963), Chapter 9.

Eq. (2) is based, is also an adequate description of the bondings in the present complexations, then the binding energy should be given approximately by just a half the second term of Eq. (2)[23]:

$$\Delta E_R = C_2/2(I_D - C_1) \qquad (5)$$

Substitution of the spectroscopically determined values of $C_1=5.7$ eV and $C_2=2.5(\text{eV})^2$ into Eq. (5) gives $\Delta E_R=8.7$(Fu), 8.7(Th), 6.6(THF), 9.9(THT), 7.2 (DEE), and 11.1(DES) kcal mol^{-1}. Although the values of ΔE_R thus calculated are all in order-of-magnitude agreement with the observed heats of complexation (Table 1), one can hardly see any quantitative correlation between these two sets of data.

One possible reason for the absence of correlation between ΔE_R and ΔH° might be sought in the premise that the C_1 and C_2 values can be assumed to be constant for the different types of donor compounds. Some of the donors studied in this work are unsaturated compounds which should fall in the category of the so-called π-donors (Fu and Th), while others are saturated n-donors (THF, THT, DEE, and DES). There is no justification for expecting the bonding characters of these two types of donors in complexes to be nearly the same.

In order to find logical consistency, we have solved Eqs. (2) and (5) simultaneously with respect to C_1 and C_2. The results are listed in Table 2.

TABLE 2. VALUES OF C_1 AND C_2[a)]

Donor	C_1, eV	C_2, (eV)^2
Furan	5.3	1.0
Thiophene	5.3	1.9
Tetrahydrofuran	6.0	2.9
Tetrahydrothiophene	6.2	2.9
Diethyl ether	5.3	1.7
Diethyl sulfide	6.2	3.0

a) Calculated from the experimental vaules of ν_{max} and ΔH° through Eqs. (2) and (5).

Although no quantitative significance should be attached to the C_1 and C_2 values thus derived, it is worth noting that the π-donors take $C_1=5.3$ eV and $C_2=1.4$ (eV)^2 on the average, while three n-donors (THF, THT, and DES) possess values centered on $C_1=6.1$ eV and $C_2=2.9$ (eV)^2. The case of DEE is apparently closer to the π-donor case, which might be accidental. The values $C_1=5.7$ eV and $C_2=2.5$ (eV)^2 obtained from Fig. 3 should be taken merely as the averages of these individual values.

That the n-donors have greater values of C_1 and C_2 than the π-donors can best be reconciled by assuming that the former are complexed with $(CN)_2CO$ at an intermolecular distance somewhat shorter than in the case of the latter. In the present π-donor complexes it is likely that the component molecules are located on two parallel planes as in most π-donor-π-acceptor complexes. Taking the interplanar distance in our π-donor complexes to be the same (3.50 Å) as in crystalline naphthalene-TCNE[24] and assuming the W_0 to be negligibly small, we obtain $E_A=1.2$ eV for $(CN)_2CO$. This value of E_A in turn gives the intermolecular distance of *ca.* 3.0 Å for the n-donor-$(CN)_2$-CO complexes, a not unreasonable distance.

The constant $C_2=2.9$ (eV)^2 reduced for the present n-donor-$(CN)_2CO$ interactions is perhaps the greatest of the values hithero recorded.[1] For such a large C_2 value, the usual assumption of weak complexes would no longer be reliable, and thus both Eqs. (2) and (5) would need to be modified accordingly. Nevertheless, in view of the approximate nature of the present treatment, we may be satisfied for the present with such semiquantitative arguments as presented above on the basis of the assumption of weak complexation.

Discussion so far has been based on the assumption that charge transfer is the only cause of intermolecular bonding energies. However, Dewar and Thompson[25] argued that charge transfer is not generally the main factor responsible for the intermolecular bondings in donor-acceptor complexes. Lippert, Hanna, and Trotter[26] theoretically demonstrated that the Coulombic, induction, dispersion, charge-transfer, and exchange-repulsion energies all contribute to the total binding energies of the aromatic-TCNE as well as aromatic-halogen complexes.

Charge transfer spectra certainly provide no direct evidence for dominancy of the role of charge transfer in intermolecular bondings. Nonetheless, cases do exist in which the relative complexation abilities of donors can be interpreted in terms of charge transfer alone.[27,28] We thus consider the simple charge-transfer description to be useful in certain cases, occasionally providing good estimates of the bonding energies. Implicit in this view is the fact that the charge-transfer energy can be in line with the total bonding energy for structurally analogous complexes. If the contribution of the various other stabilizing factors happens to be counterbalanced by the intermolecular exchange repulsion, the role of charge transfer may even be regarded as a dominant factor of the bondings.

Despite the above complexity of the bonding character, the observed thermodynamics of complexation manifests a simple feature. The isokinetic relationship holding between ΔH° and ΔS° would imply an apparent thermodynamic uniformity of the complexation, irrespective of the precise nature of the bondings involved. This may not be quite a fortuitous result, if the spatial arrangements of the components are similar (*i.e.*, all parallel planes) for the various donors studied.

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[23] Both Eqs. (2) and (5) may be considered to be correct, only if $2C_2/(I_D-C_1)^2$ is small enough as compared with unity. For the sake of simplicity, we assume that this requirement is fulfilled here.

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[26] J. L. Lippert, M. W. Hanna, and P. J. Trotter, *J. Amer. Chem. Soc.*, **91**, 4035 (1969).

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