Formation of Charge-transfer Complexes by Solid State Reaction; Electronic Spectra and Relative Reactivity

Hiroyasu SATO and Tamiharu YASUNIWA
College of Liberal Arts, Kagoshima University, Kamoike, Kagoshima 890

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Formation of charge-transfer complexes by solid state reaction was studied for 16 donors and 10 acceptors. The relative reactivity of 160 pairs was determined by the presence or absence of the charge-transfer band on grinding the component pairs of the same concentration (diluted with sodium chloride) for the same length of time. Equilibrium was not reached within the grinding time. This relative reactivity was compared with and found to have a parallel relationship with the relative ease of formation of the charge-transfer complex on evaporating a mixture of the solutions of components, indicating that the relative reactivity is related to an apparent equilibrium established on the grain surface. Relative reactivity was found to be largely dependent on molecular size and geometry. Smaller molecules were more reactive. For molecules with the same number of rings, those with compact structure were more reactive. Most of the new bands given by the reaction were CT bands of microcrystals. They were very broad. A fairly good linear relationship was found between the transition energies of the CT bands and the ionization potentials of the donors or the electron affinities of the acceptors.

A considerable amount of information has been accumulated on the equilibria of charge-transfer (CT) complexes in solutions, but very little is known about those in solid phase. Hammick and Hutchison¹⁾ discussed the free energy of formation of solid CT complexes (from the solid components) from their solubility measurements of trinitrobenzene- or trinitrotoluene-aromatic hydrocarbon systems. Suzuki and Seki²⁾ calculated the heats of formation of crystalline CT complexes (from the crystalline components) on the basis of their measurements of heat of solution for trinitrobenzene-aromatic hydrocarbon systems. They noted that the relative magnitudes of the thermodynamic data differ from those in solutions. Braun and Kortüm³⁾ studied CT equilibria of some trinitrobenzene complexes formed by solid state reaction by means of diffuse reflection spectra (DRS). However, very little is known about the relative ease of CT complex formation by solid state reaction. We have carried out a qualitative study of relative reactivity choosing 16 donors and 10 acceptors.

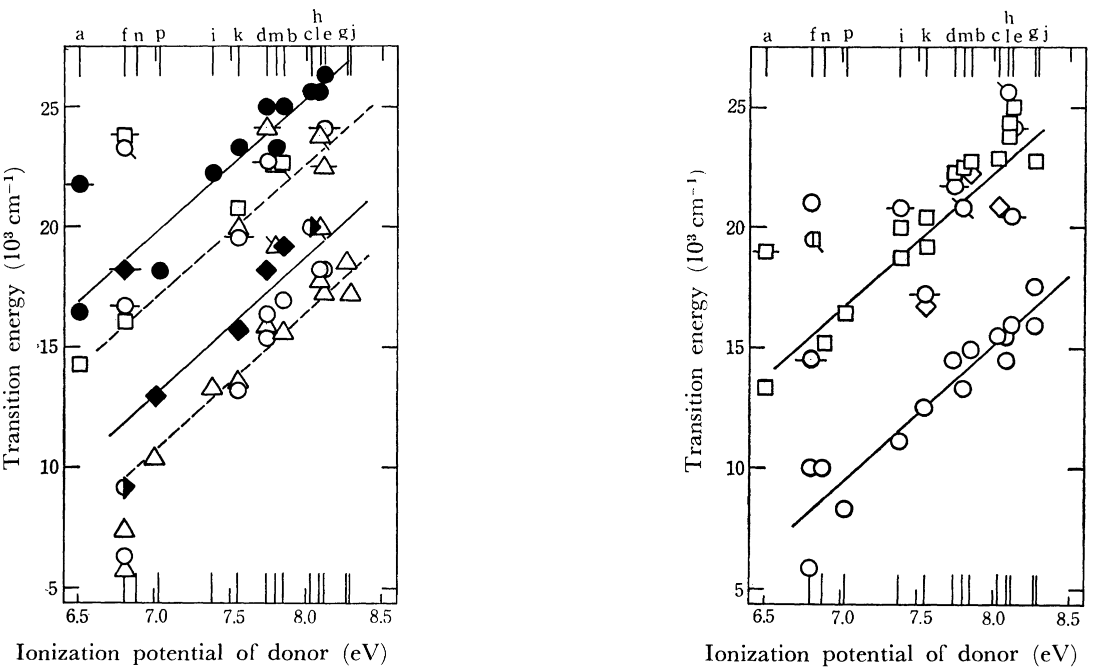
Experimental

Materials. The chemicals used are given in the following with their abbreviations and code numbers or symbols. Donors: (a) *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD), (b) hexamethylbenzene, (c) 1,2,4,5-tetramethylbenzene, (d) 1,5-dimethylnaphthalene, (e) naphthalene, (f) *N,N,N′,N′*-tetramethylbenzidine, (g) diphenyl, (h) phenanthrene, (i) anthracene, (j) *p*-terphenyl, (k) pyrene, (l) triphenylene, (m) chrysene, (n) tetracene, (o) *p*-quaterphenyl, (p) perylene. Acceptors: (**1**) tetracyanoethylene (TCNE), (**2**) 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), (**3**) 1,2-dichloro-4,5-dicyano-*p*-benzoquinone (DDQ), (**4**) *p*-chloranil, (**5**) 2,5-dichloro-*p*-benzoquinone, (**6**) *p*-benzoquinone, (**7**) α-naphthoquinone, (**8**) anthraquinone, (**9**) pyromellitic anhydride (PMDA), (**10**) tetrachlorophthalic anhydride (TCPA) All of these were commercial products. G.R. reagents (c, d, f, k, l, m, o, p, **4**, **5**, **6**, and **10**) were used without further purification. The others were purified by vacuum sublimation or recrystallization.

Procedure. *(I) Grinding Two Components Only (a preliminary test)*: Appropriate amounts (*ca.* 10 mg each) of two components were ground on a glass plate with a stainless spatula. The formation of CT complexes was monitored visually by color. In some cases (*e.g.* a-**1**, a-**3**) colored products appeared immediately after mixing (before any grinding) the two components together. In most cases (*e.g.* a-**4**), a few seconds of grinding was necessary for obtaining the colored products. In some cases (*e.g.* i-**4**), no color of CT complexes appeared even on prolonged grinding.⁴⁾

(II) Grinding Two Components with NaCl: The measurement of DRS was carried out to follow the CT complex formation.⁵⁾ In order to obtain good DRS by minimizing the effect of total reflection, it is necessary to disperse the sample in a white non-absorbing material used as a standard substance, which should neither react with the sample nor affect the CT equilibria. Braun and Kortüm³⁾ measured DRS of some CT complexes in sodium chloride, which was found not to cause dissociation of the complexes. Thus, sodium chloride was used as the white standard substance. Two components (10^{-4} mol each) and 5 g of sodium chloride were ground together manually in a porcelain mortar, 7.5 cm in diameter, for 30 s at room temperature. Sodium chloride was dried at 150 °C for 2 hours and stored in a desiccator.⁶⁾ Another 5 g of sodium chloride, ground in the same manner, was used as a reference. Measurement of DRS was then made quickly on a Shimadzu MPS-50 recording spectrophotometer with a reflection attachment. When a new DRS band or bands appeared, the measurement was repeated for some time to follow the spectral change after the sample was set in the reflection attachment. Values for $-\log R$ were measured rather than those for R. (For the definition of R, see footnote 7.) A very slight change in the spectra can thus be detected. The values for $f(R)$ in the Kubelka-Munk formula⁷⁾ were calculated from the measured values for $(-\log R)$, since the $f(R)$ value is proportional to absorbance on the assumption that the scattering coefficient is independent of wavelength. The value $-\log R=0.01$ was detectable in this measurement. This corresponds to $f(R)=2.65\times10^{-4}$. If no new band appeared, another sample was ground for 300 s at room temperature.⁸⁾

(III) Evaporating the Mixture of Dichloromethane Solutions of Each Component: Dichloromethane solutions (10^{-2} mol/l) of a donor and an acceptor were prepared separately. Dichloromethane (Wako, G.R. reagent) was used without further purification. An aliquot (0.1 ml) of the donor solution and that (0.1 ml) of the acceptor solution were mixed. The resulting mixture was then evaporated on a glass plate at room temperature. For sparingly soluble compounds (*i.e.* **9**, **10**, n, o, and p) solutions of smaller concentration were



1 a   1 b

Fig. 1. Transition energies of observed new bands *vs.* ionization potential of donors.[25] The symbols of donors are shown on the upper abscissa.

Acceptors: (a) ○ 1, △ 2, ◆ 4, □ 6, ● 10.
(b) ○ 3, ◇ 5, □ 9.

A short line (horizontal) shows that the band can be assigned to the second CT band.[26] A short oblique line shows that the assignment of the band is uncertain. Such a band was considered as due to "the other product" in the text. Long straight lines in the figure show the approximate linear relationship of the CT transition energies *vs* ionization potentials of the donors. For TMPD complexes, only those bands which can be assigned to outer-complexes are given. For TCNE complexes, those bands attributable to the 1,1,2,3,3-pentacyanopropenide ion are not given.

prepared. An aliquot including 10^{-6} mol of substance was used in one experiment. Whether the solid residue is mostly (a) a CT complex, or (b) a mixture of donor and acceptor crystals, was judged from the color of the residue after evaporation.

Results

Nature of the Product. The positions of observed new DRS bands are shown in Figs. 1 and 2. Most of these bands can be considered as CT bands of minute crystals of CT complex, since their positions essentially coincide with the data of 15 crystalline CT complexes,[9–17] and solution data.[18–20] A few remarks are given here.

(i) TMPD Complexes (Figs. 1 and 2.): For a-**1**, the spectrum of the ion-pair was obtained with a CT band at 850 nm. For a-**3**, the CT band at 800 nm decreased in intensity, with an increase in intensity of the ion-pair bands (at 400, 573, and 625 nm). For a-**2**, **4**, and **5**, the presence of a band in the near infrared can be related to the inner-complex nature of the complexes.[14,17] For a-**9** and a-**10**, the bands can be attributed to outer complexes (Fig. 1a, b.). For a-**6**, the band was very broad. The presence of an apparent peak at 620 nm and a broad shoulder at 1100 nm would be associated with an inner-complex (Fig. 2), while a smaller peak at *ca.* 700 nm indicates

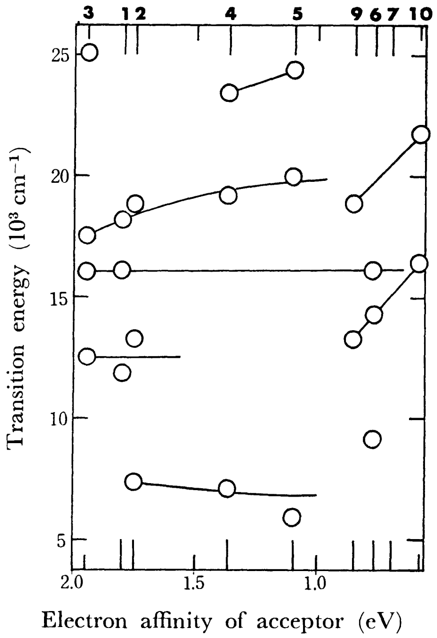


Fig. 2. Transition energy of observed new bands *vs.* electron affinity of acceptors,[27] for the TMPD-acceptor system. The code numbers of acceptors are shown on the abscissa.

TABLE 1. RELATIVE REACTIVITY IN SOLID STATE REACTION

Acceptor	Donor															
	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p
1	A	A	A	A	A	B	—	A	—	—	A	—	—	—	—	—
2	A	A	—	A	A	A	A	D	A	A	A	B	D	—	—	A
3	A	A	A	A	A	A	A	B	A	—	A	A	B	A	—	A
4	A	A	A	A	—	A	—	—	—	—	A	—	—	—	—	A
5	A	A	A	—	—	—	—	—	—	—	A	—	—	—	—	—
6	A	A	—	—	—	(A)	—	—	—	—	A	—	—	—	—	—
7	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
9	A	A	A	A	A	D	(A)	A	A	—	A	A	(A)	(A)	—	A
10	A	A	A	A	A	—	—	A	A	—	A	A	A	—	—	A

that an outer complex is also present (Fig. 1a).

(ii) N,N,N′,N′-Tetramethylbenzidine Complexes (Fig. 1): Most of the observed bands are found near those of single crystals.[13,16] Additional bands in the case of f-**3** (near 500 and 1000 nm) would be related to the cation of the donor, considering that benzidine cation has absorption bands near 450, 760, and 850 nm.[21,22] It is striking that no complex formation was found for f-**4** or f-**5** while the corresponding benzidine complexes were formed under the same conditions. Crystals of these two complexes can be formed by mixing the solutions of the components (experiment III, *cf.* Ref. 13.). These findings can be attributed to the smaller rate of complex formation due to the steric hindrance of the dimethylamino-groups.

Relative Reactivity in the Solid State. The results are summarized in Table 1. Symbols A, B, C, and D are given for those pairs which gave DRS bands not attributable to either parent molecule on 30 s grinding. The symbols A, B, C, and D denote new DRS bands as follows. (A) the CT complex only, (B) the CT complex with a small amount of another product, (C) a small amount of the CT complex and more of an other product, and (D) an other product only. The distinction was made on the criteria of CT bands given above. The symbols in parentheses are given for the pairs which gave such DRS bands not on 30 s grinding but on 300 s grinding. Those which gave no new DRS bands on 300 s grinding are denoted by the symbol — . The relative reactivity in experiment (I) showed similar features to the result given here, though comparison is possible only when the resulting CT complexes are colored, thus confirming that the presence of NaCl did not cause any change in, at least qualitatively, the relative reactivity of CT complex formation. Pairs C and D are excluded from the following discussion of relative reactivity.

Change in f(R) with Time. Although fast reaction was observed during the process of grinding, a very slow reaction continued to take place after grinding was stopped, for most component pairs studied. This is shown in Fig. 3, k-**4** being taken as an example.

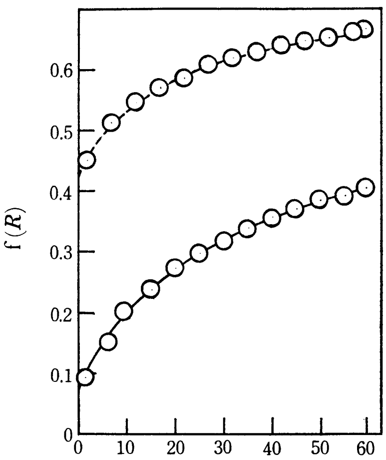


Fig. 3. The change of f(*R*) after grinding is ceased in the measurement of pyrene-*p*-chloranil (at 655 nm).
—— grinding for 30 s.
---- grinding for 300 s.

Time $t=0$ on the abscissa shows the time when the grinding (30 or 300 s) was stopped. Values for f(*R*) are plotted on the ordinate. The value of $[f(R)]_{t=0}$ corresponds to the total amount of the complex given in the process of grinding. Concentration-time curves could not be obtained due to the lack of information concerning (1) whether or not only one type of CT complex contributes, and (2) the molar extinction coefficient. Very few data are available so far on the molar extinction coefficients of solid CT complexes. When grinding was done for a longer time (*i.e.* 300 s), $[f(R)]_{t=0}$ became larger. Thus, the reaction is far from complete by grinding for 30 s. The leveling-off in the f(*R*)-*t* curve is only an apparent one. Only the region near the grain surface seems to have attained equilibrium. To bring the reaction completely up to true equilibrium, much more time will be needed. For a few component pairs, f(*R*) decreases with time because of a further reaction *via* the CT complex. This

TABLE 2. APPEARANCE OF COLORED PRODUCT ON EVAPORATING MIXTURE OF DICHLOROMETHANE SOLUTION

Acceptor	Donor															
	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p
1	+	+	−	+	−	+	−	+	−	−	+	+	−	−	−	+
2	+	+	−	+	−	+	+	+	+	+	+	+	+	+	−	+
3	+	+	+	+	+	+	+	+	+	−	+	+	+	+	−	+
4	+	+	+	+		+			−		+	−	−	−	−	+
5	+	+		−		+			−		+			−		−
6	+					+					+			−		−
7	−					+					+			−		−
8						+										
9	+					+			+		+			−		+
10	+					+								−		+

is the case for a-**1**, a-**3**, a-**5**, j-**1**, and k-**1**.

Evaporating the Dichloromethane Solution. The results are given in Table 2, in which the symbol + denotes the appearance of a new color. The color obtained for each pair was in line with that obtained in the solid state reaction with a few exceptions. The symbol − denotes only the color of parent compounds shown by the remaining solid. Since judgement was made only from color change, none can be made when little color change is expected on CT complex formation, *i.e.*, when the CT complex to be obtained (if any) for the given pair is either colorless or in a very close color to that of parent compounds (*i.e.* $\lambda_{CT}<500$ nm). No symbol is given in the Table for these cases.

Discussion

Shape and Position of CT Bands. Most of the new bands can be considered as CT bands of microcrystals. In crystal, the single band in solution splits into several bands, each of which has a peculiar polarization *vs.* crystal axes. In the microcrystalline sample, these bands are amalgamated into a very broad band. Most of the CT bands were very broad, making it sometimes very difficult to find absorption maxima. Nevertheless, a fairly good linear relationship was found between transition energy and ionization potential of the donor (I_D) or the electron affinity of the acceptor (E_A), in most of the cases (Figs. 1 and 2).

Relative Reactivity. The observed difference in chemical reactivity can be interpreted as resulting, mainly from the difference in (i) chemical equilibria or (ii) reaction rates. An important factor in the former is the difference in lattice energy, while in the latter it is the molecular diffusion through the grain boundary. The "relative reactivity" in this study is judged by whether or not the CT band is found on grinding for 30 (or 300) s. The reaction does not proceed to equilibrium for most of the component pairs. Experiment (III) was carried out to see what the relative order of chemical equilibria is like. The chemical equilibrium between complex and component molecules is established in the dichloromethane solution. On evaporating, crystals of DADA··· and/or DD··· plus AA··· were formed. The crystals thus obtained should give information on the equilibrium in solid phase, when the process of crystallization is assumed to be slow enough to establish the equilibrium. The assumption seems to be valid in this experiment. There is generally a good parallelism between the solid state reactivity and the formation of the CT complexes in evaporating the dichloromethane solution (Tables 1 and 2). This shows that an apparent (false) equilibrium was established on the grain surface. This is not the true equilibrium, since a slow reaction (probably by slow diffusion through the grain boundary) still continues.

The relative reactivity should be interpreted in terms of molecular and/or crystal structure (Table 1). Taking the molecular structure into consideration, we make the following qualitative conclusions. (1) The reactivity depends largely on molecular size and structure (Table 1). Smaller molecules are more reactive. (2) For the molecules with the same number of rings, those with compact structure are more reactive (*i.e.* h>i>j, k>l>m>n>o).
(3) For the molecules with similar molecular size and structure, the pairs which have smaller I_D-E_A values are more reactive.

The importance of molecular geometry in determining molecular properties in solid phase is sometimes mentioned. Matsunaga[23] has found the "size and shape effect" in the ionic character of solid molecular compounds. Such an effect will play an important role also in the chemical reactivity in solid phase. The higher selectivity in chemical reaction might thus be expected in solid state rather than in solution.

The observed order of reactivity in solid phase are not in line with that of equilibrium constants in fluid solution. Similar findings are also reported by Hammick and Hutchison,[1] and by Suzuki and Seki[2] for trinitrobenzene or trinitrotoluene complexes. For h-**4** and i-**4**, the former has greater reactivity in solid phase, though the equilibrium constant in fluid solution[24] is in the reverse order. This is also the case for k-**4** and l-**4**.

The origin of such a difference in reactivity cannot be understood only by means of molecular structure. The difference in crystal structure (space group and dimension of unit cell) undoubtedly plays an important role. In the solid state reaction in the system of mixed microcrystals, the reformation of the crystal on the grain boundary should occur during the course of reaction. If the crystal structure of the resulting CT complex is similar to that of at least one of the component molecules, the reformation will occur with a smaller activation energy. In order to confirm this hypothesis, however, the crystal data are necessary for the CT complex and for the parent molecules. Very few data of CT complexes are available at present to make such a discussion.

Thanks are due to Miss Yumiko Masumitsu and Mr. Shun-ichi Horai for their assistance in the measurement.

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4) A similar phenomenon was observed when the evaporated films of these components were prepared on glass plates and the compounds were pressed together. For i-**4**, the pressed plates showed only the absorption of components for days.

5) In Experiment (I), the absorption spectrum of the product could be measured by pressing it between two glass plates only when the product was very intensely colored (*e.g.* a-**1**). The positions of bands thus obtained were essentially in accordance with those given from DRS in Experiment (II).

6) This was taken as the standard procedure. Drying conditions gave no significant change on the qualitative feature of DRS in the visible region, except for TCNE complexes, for which a band attributable to 1,1,2,3,3-pentacyanopropenide ion appeared.

7) The Kubelka-Munk equation is given as

$$\mathrm{f}(R)=(1-R)^2/2R=k/s$$

where R is the relative diffuse reflectance of the sample referred to a non-absorbing standard substance (NaCl in this work), k is the absorption coefficient of the sample given by Lambert's law

$$I=I_0\exp(-kl),$$

s being the scattering coefficient: P. Kubelka and F. Munk, *Z. Techn. Phys.*, **12**, 593 (1931).

8) Although quantitative reproducibility in $\mathrm{f}(R)$ by this manual procedure was rather poor (by a factor of 1.2—1.4), qualitative reproducibility, *i.e.* whether or not the new band appears, was good.

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25) Ionization potentials are taken from: J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York (1970), Table 9.5. The ionization potential of a was assumed to be 6.5 eV after Briegleb (Ref. 18, p. 183). That of f was assumed to be 6.8 eV after Y. Matsunaga and G. Saito (Ref. 16).

26) Assignment to the second CT band was made according to Ref. 9, 13, 16, and 20 (for k-**1**, f-**4** and f-**6**, f-**1**, and d-**1**, respectively); compare the spacing between the band in question and the first CT band for a pair with that between the first and second CT bands for another pair composed of the same donor and a different acceptor, when both bands are reported for the latter pair and when the second CT band is associated with the second highest molecular orbital of the donor (for d-**2**, d-**3**. f-**3**, k-**2**, k-**3**); compare with d-**1**—d-**3** (for e-**1**—e-**3**). The band at 20800 cm^{-1} for i-**3** was assigned to the second CT band since the difference in transition energy of this band and that of the first CT band is close to the difference of the first and second ionization potentials of π-electron system in anthracene (P.A. Clark, F. Brogli and E. Heilbronner, *Helv. Chim. Acta*, **55**, 1415 (1972); See also, J. Aihara and H. Inokuchi, *Chem. Lett.*, **1973**, 421). For a-**9** and a-**10**, the bands at 18900 and 21700 cm^{-1}, respectively, were tentatively assigned to the second CT bands from the relationship shown in Fig. 2.

27) Electron affinities are taken from; G. Briegleb, *Angew., Chem.*, **76**, 326 (1964).