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Catalytic Activity and Reactivity of Aromatic Nitrile and Alkali Metal Ion Radical Salt. I. Homogeneous and Heterogeneous Catalysis of Benzonitrile-Cesium Ion Radical Salt

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Homogeneous and heterogeneous mechanisms of parahydrogen conversion and hydrogen-deuterium exchange reactions were investigated in the presence of benzonitrile–cesium ion radical salt. Studies of their activation energies and rate constants showed that the heterogeneous reaction on the solid-ion radical salt occurs mainly through the "chemisorption mechanism" and the "exchange mechanism", but the homogeneous reaction over the salt solution in benzonitrile takes place only through the "physical mechanism." According to these results, it was concluded that the catalytic activity and reactivity of the ion-radical salt must be due to the nature of its solid phase, not to that of its aromatic anion or free-ion radical pair.

Since tetracyanopyrene-cesium ion radical salt was found to catalyze the hydrogen-deuterium exchange reaction,[1] the catalytic activities for various aromatic–alkali metal ion radical salts[2–7] and charge-transfer complexes[8,9] have been studied. The results of these works may be summarized as follows: (1) the aromatic–aromatic charge-transfer complexes have only a weak catalytic activity for para-orthohydrogen conversion through the physical mechanism[8,10] (see Appendix 1); (2) the aromatic-halogen charge-transfer complexes, for instance, the violanthrene-iodine complex, catalyze the isomerization of 1-butene$\rightleftharpoons$2-butene, but no H_2-D_2 equilibration takes place over the complexes,[9] and (3) aromatic-alkali metal ion radical salts catalyze the hydrogen-deuterium equilibration. Further, over these ion radical salts it is found that deuterium exchanges with the hydrogen of the bulk aromatic anion.[1–7]

Recently, some assumptions about the catalytic mechanism on these ion salts were proposed, mainly on the basis of the electronic properties of the acceptor aromatic molecule, that is, the electron affinity,[7] the charge density of the lowest unoccupied orbitals,[4,7] the valency,[5] the reduction potential, and the effect of substitution on the aromatic skeleton,[4] but not on the basis of the properties of the bulk complex. Accordingly, no findings have been reported on whether the nature of isolated molecules or that of molecular aggregates is decisive in the catalytic activity.

In this paper, we will present the results of our study of homogeneous and heterogeneous catalyses over benzonitrile[*2]-alkali metal ion salts. Because the melting point of benzonitrile is fairly low (-13°C), the homogeneous reaction[*3] on the ion salts dissolved in a benzonitrile solution with hydrogen was observed satisfactorily.

Experimental

Purification of Samples. Commercial benzo-

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1) T. Kondow. H. Inokuchi and N. Wakayama, *J. Chem. Phys.*, **43**, 3766 (1965).

2) H. Inokuchi, N. Wakayama, T. Kondow and Y. Mori, *ibid.*, **46**, 837 (1967).

3) H. Inokuchi, Y. Mori and N. Wakayama, *J. Catal.*, **8**, 288 (1967).

4) N. Wakayama and H. Inokuchi, *ibid.*, **11**, 143 (1968).

5) N. Wakayama, Y. Mori and H. Inokuchi, *ibid.*, **12**, 15 (1968).

6) M. Tsuda, G. Inokuchi and H. Suzuki, *J. Phys. Chem.*, **73**, 1595 (1969).

7) M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, *ibid.*, **70**, 2069 (1966); *J. Catal.*, **6**, 336 (1966); *Trans. Faraday Soc.*, **63**, 997 (1967); *ibid.*, **63**, 2529 (1967); This Bulletin, **41**, 1739 (1968).

8) H. Inokuchi, M. Tsuda and T. Kondow, *J. Catal.*, **8**, 91 (1967).

9) M. Tsuda, T. Kondow, H. Inokuchi and H. Suzuki, *ibid.*, **11**, 81 (1968).

10) M. Tsuda, M. Sc. Thesis, Waseda University (1967).

[*2] The electronic spectra and also the ESR spectra show that only the mononegative anion (benzonitrile$^-$) in the ion salt is stable, though other aromatic anions have multivalencies.

[*3] We demonstrated a homogeneous catalysis for para–orthohydrogen conversion in the presence of a gaseous anthracene-*syn*-trinitrobenzene charge-transfer complex under illumination.[8] However, no ion-radical salts in the gaseous phase could be obtained.

nitrile was refluxed with diphosphorus pentoxide in a sealed glass vessel to eliminate a trace of water and was subsequently degassed by alternate boiling under a vacuum and repeated distillations. The cesium metal was prepared by reduction between its chloride and calcium metal, that is, $2CsCl+Ca=CaCl_2+2Cs$; it was distilled several times *in vacuo* in order to purify it.

Preparation of the Benzonitrile-Alkali Metal Ion Radical Salts. The benzonitrile-cesium ion radical salt used in this study was prepared as follows. A known amount of benzonitrile was placed in a glass vessel cooled with a dry ice-ethanol mixture, on which a measured volume of purified cesium metal had previously been evaporated. The vessel was then sealed off and heated at 60°C for 40 hr in order to complete the formation of the complex; a deep red-coloured ion radical salt solution was thus obtained. To separate the solid-phase salt aggregates from the solution, if any existed, the solution was passed through a fine glass filter. The solution was then submitted to a homogeneous catalytic reaction. The excess benzonitrile in the solution was completely evaporated at 60°C *in vacuo* in order to obtain the solid specimen.

Experimental Procedure. For the investigation of the homogeneous catalysis of the hydrogen conversion in the ion-radical salt solution, a cylindrical, thermostated glass vessel containing the solution was agitated with a magnetic stirrer arrangement, as is shown in shown in Fig. 1. A known amount of the salt solution was placed in the vessel and sealed off at the point indicated by the arrow ↓ in Fig. 1. Para-rich-hydrogen (80% p-H_2) was admitted into the vessel under a pressure of 100 Torr (at room temperature), and the system was sealed off by a greaseless stopcock. The temperature of the reaction system (surrounded by a broken line in Fig. 1) was controlled at temperatures between 33—90°C.

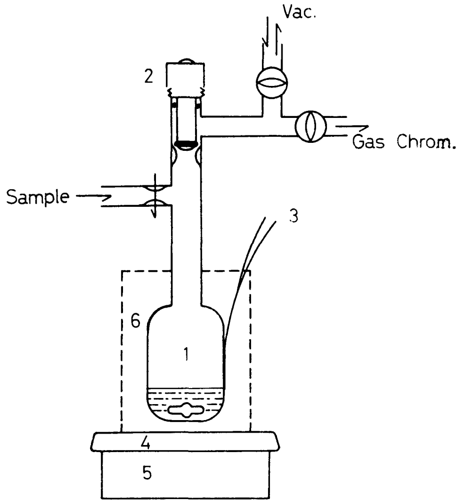

Fig. 1. The schematic diagram of the reaction system.
1. reaction vessel containing a piece of magnet, 2. greaseless stopcock, 3. chromel-alumel thermocouple, 4. electrical heater controlled at appropriated temperature, 5. magnetic stirrer and 6. air bath.

In order to keep the condition of the homogeneous catalytic reaction constant, after finishing each procedure the ion-salt solution was degassed in order to remove the converted hydrogen by alternate boiling under a vacuum.

In the heterogeneous reaction, the exchange of gaseous deterium with the hydrogen of the aromatic anion occurred. Therefore, after measuring the hydrogen-deuterium equilibration on the solid specimen, the hydrogen gas was admitted into the vessel to replace the deuterium in the aromatic ring of the anion and/or the chemisorbed deuterium of the salt at 70°C. This procedure was repeated until no D_2 (or HD) was detected in the gas phase. By this method, the solid specimen could be reproduced repeatedly.

The compositions of the various orthohydrogen–parahydrogen or hydrogen-deuterium mixtures were measured successfully by means of gaschromatography. A mixture was separated quantitatively by passing it through a heat-treated alumina column at the temperature of liquid nitrogen.[11,12] The electronic spectrum of the benzonitrile-cesium ion radical salt in a benzonitrile solution and that of the solid-ion salt film were measured with a Cary recording spectrophotometer, Model 14. The preparation of the radical anion and the measurement of the electronic absorption spectra were made in a vacuum system, as is shown in Fig. 2.

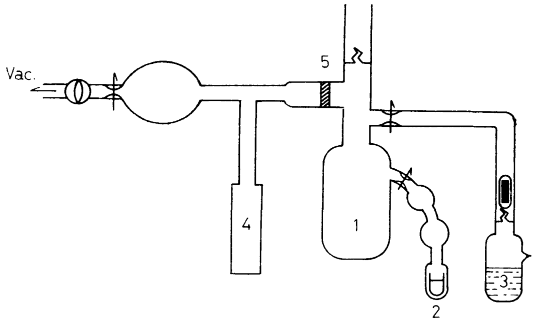

Fig. 2. The apparatus for preparation ion radical salt.
1. reaction vessel, 2. iron cell contained CsCl $+$Ca, 3. purified benzonitrile, 4. optical cell for electronic absorption spectra measurement and 5. glass filter.

Results

The kinetics of the heterogeneous and homogeneous reactions of the benzonitrile-cesium ion radical salt were investigated as a function of the hydrogen pressure and of the temperature. The experimental results on the heterogeneous reaction will first be shown, while those of the homogeneous reaction will be described later.

Heterogeneous Reaction. *Pressure Dependency.* The para-orthohydrogen conversion on

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[11] W. R. Moore and H. W. Ward, *J. Amer. Chem. Soc.*, **80**, 2909 (1958).

[12] S. Ohkoshi, Y. Fujita and T. Kwan, This Bulletin, **31**, 771 (1958).

the solid-ion radical salt was investigated as a function of the partial pressure of parahydrogen under a constant pressure (110 Torr) and at a constant temperature (87°C). Figure 3 shows the results, in which the rate was found to be a first-order reaction concerning the partial pressure of parahydrogen. Hence, the experimental rate constant, $k_e{}^{\mathrm{H}}$, was derived from the following equation:

$$k_e{}^{\mathrm{H}} = \frac{1}{t} \ln \frac{C_p(t) - C_p(\infty)}{C_p(0) - C_p(\infty)} \tag{1}$$

where $C_p(0)$, $C_p(\infty)$, and $C_p(t)$ are the concentration of parahydrogen at the initial point, in equilibrium, and after t min respectively.

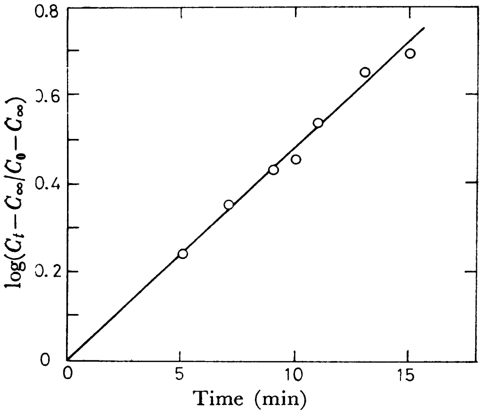

Fig. 3. The reaction velocity of ortho-para-hydrogen conversion under constant pressure for determining the order of rate constant.

Temperature Dependency. The kinetics of the hydrogen conversion were studied over the temperature range between 0°C and 100°C under a constant pressure of hydrogen. The experimental rate constant was also given by Eq. (1); the progression of the para-orthohydrogen conversion is plotted against the reaction time in Fig. 4.

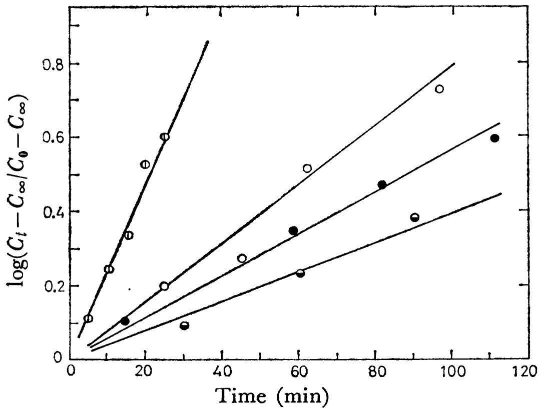

Fig. 4. The progression of the para-orthohydrogen conversion on the solid of the benzonitrile-cesium ion radical salt.
—⦶— at 80°C, —○— at 41°C,
—●— at 20°C, and —◒— at 0°C.

On the other hand, when deuterium gas was placed in contact with the benzonitrile-cesium solid film, it was found that exchange took place between the admitted deuterium and the hydrogen of the aromatic anion. In the reaction, denoted as the exchange mechanism, the decay of the concentration of deuterium in the gas phase obeyed the first-order law.[*4] The rate constant, $k_e{}^{\mathrm{D}}$ is:

$$k_e{}^{\mathrm{D}} = -\frac{1}{t} \ln \frac{D(t)}{D(0)} \tag{2}$$

where $D(0)$ and $D(t)$ represent, respectively,the concentrations of deuterium in the gas phase at the initial point and t min later. The experimentally-determined rate constants, $k_e{}^{\mathrm{H}}$ and $k_e{}^{\mathrm{D}}$, are shown in Fig. 5 as functions of the temperature. On the basis of the temperature dependence of the rate constant, we could determine an apparent activation energy, E^{D} or E^{H}, for these two reactions:

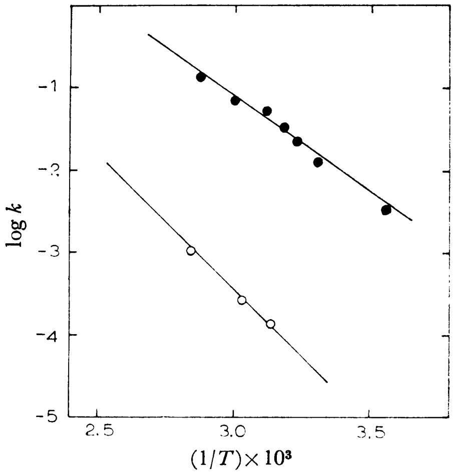

Fig. 5. The rate of the conversion at various temperatures for the solid of the benzonitrile-cesium ion radical salt.
-●- the rate of the para-othohydrogen conversion, -○- the rate of $D_2 + \varphi H \rightleftarrows HD + \varphi D$ reaction.

$$k_e{}^{\mathrm{H}} = S^{\mathrm{H}} A^{\mathrm{H}} \exp(-E^{\mathrm{H}}/\boldsymbol{k}T) \tag{3a}$$

$$k_e{}^{\mathrm{D}} = S^{\mathrm{D}} A^{\mathrm{D}} \exp(-E^{\mathrm{D}}/\boldsymbol{k}T) \tag{3b}$$

where S^{H} and S^{D} are the areas of the catalyst and where A^{H} and A^{D} are the factors which depend hardly at all upon the temperature. Experimentally, we obtained $E^{\mathrm{H}} = 10.2$ kcal/mol, and the value of E^{D} was 14.3 kcal/mol.

Homogeneous Reaction. The catalytic activity and the reactivity of benzonitrile-cesium ion salt dissolved in benzonitrile were also investigated by means of the para-orthohydrogen con-

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[*4] This reaction rate will be analyzed in Part II.

version and the hydrogen-deuterium exchange reaction. As was shown in the previous section, the solid film of the ion radical salt has a good catalytic activity. On the contrary, the hydrogen conversion with the salt solution occurred very slowly. Further, we could not detect any H_2-D_2 exchange reaction even after a long time, 1320 hr.[*5] These facts suggest that the hydrogen conversion in the homogeneous system is caused by the paramagnetic mechanism,[13] but not by the chemical mechanism.

The rate constant, $[k_e^H]_L$, which was found to be first order, as given by Eq. (1) for the solid system, was investigated at a series of temperatures between 33—90°C under a constant pressure of hydrogen (100 Torr).

The concentration of parahydrogen is plotted against the reaction time in Fig. 6. From these results, it seems that the apparent rate constant, $[k_e^H]_L$, is enhanced with the increase in the temperature. To obtain the intrinsic rate constant, k_L, however, we must eliminate the term of the temperature dependency of the solubility of hydrogen in the solution, as is described in the following equation:[14]

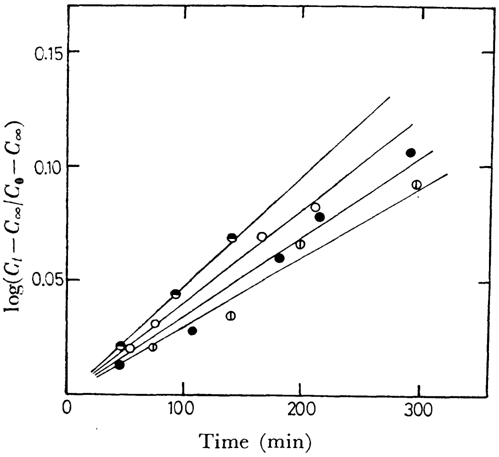

Fig. 6. The progression of the para-orthohydrogen conversion in the presence of the benzonitrile-cesium ion radical salt solution.
-◒- at 90°C, -○- at 70°C,
-●- at 40°C, and -⦶- at 33°C.

$$[k_e^H]_L = \frac{a(T)V_L}{V_G + a(T)V_L} k_L \qquad (4)$$

where $a(T)$ is the solubility[*6] and where V_G and V_L are the volumes of the gas and the solution in the reaction vessel. Figure 7 shows an Arrhenius plot for the k_L and $[k_e^H]_L$. The intrinsic activation energy, $[E^H]_L$, was found to be 0.1 kcal/mol though the apparent activation energy was 1.0 kcal/mol. When we compare these values with the value of $E^H = 10.2$ kcal/mol for the solid film, the mechanism of hydrogen conversion for these two systems may be assumed to be different.

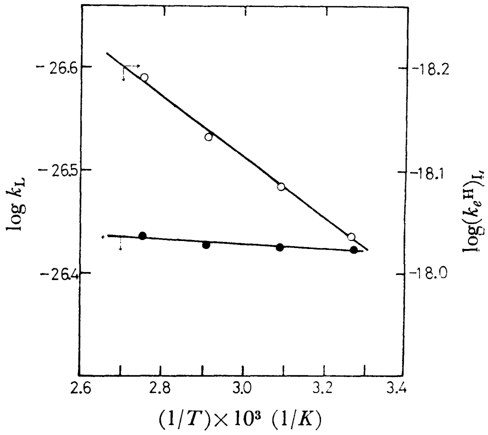

Fig. 7. The rate of the conversion at various temperatures for the benzonitrile-cesium ion radical solution.
-○- apparent rate, -●- intrinsic rate.

Discussion

In the last five years, the mechanism of the hydrogen conversion of the aromatic-alkali metal ion radical salt and the reaction of deuterium with the hydrogen of the aromatic anion have been investigated extensively, and some assumptions have been proposed based on the electronic structure of the aromatic *molecule* or the aromatic *anion*. However, the compounds used in those studies were in a solid state. Accordingly, the question was still left whether the nature of the isolated molecule or that of solid state is decisive in the catalytic activity.

The essential point is the fact that the isolated ion and/or ion pair shows no catalytic activity caused by the chemical mechanism; rather, a slow para-orthohydrogen conversion occurs in the presence of the ion and/or ion pair through the

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[*5] No apparent change in the activity for para-orthohydrogen conversion with the solution was found between before and after the long reaction; that is, the ion-radical salt solution was stable under these conditions.

13) L. G. Harrison and C. A. McDowell, *Proc. Roy. Soc.*, (London), **A220**, 77 (1953).

14) H. Sachsse, *Z. Phys. Chem.*, **B24**, 429 (1933).

[*6] Because of various experimental difficulties, the solubility, $a(T)$, of hydrogen in benzonitrile has not yet been measured, but the solubilities of hydrogen in benzene ($a = 5.8\times10^{-2} + 5\times10^{-4}T$) and in chlorobenzene ($a = 5.5\times10^{-2} + 3.5\times10^{-4}T$) have been observed.[15] For the present system, the solubility of hydrogen is assumed to be of the same order as that of benzene or chlorobenzene.

15) "Solubilities of Inorganic and Organic Compounds," Vol. 1, ed. by H. Stephen and T. Stephen, Pergamon Press, London (1963).

physical mechanism. This conclusion is supported by the following two reasons.

First, the ratio of the rate constant of the hydrogen conversion to that of the deuterium exchange reaction is very different in the cases of the solid film and the liquid phase at the same temperature. The empirically-determined rate constant of each case at 90°C is given as: $k_e^{\rm H}=2.6\times10^{-1}$/min and $k_e^{\rm D}=2.1\times10^{-3}$/min for the solid phase and $[k_e^{\rm H}]_{\rm L}=1.8\times10^{-5}$/min and $[k_e^{\rm D}]_{\rm L}\simeq0$ for the liquid phase. Assuming that the catalytic mechanism for hydrogen is the same for both states and that the large difference in the absolute value of $k_e^{\rm H}$ and $[k_e^{\rm H}]_{\rm L}$ originates only from the difference in collision efficiency in the two states, the following relation must be satisfied:

$$\frac{k_e^{\rm H}}{k_e^{\rm D}}=\frac{[k_e^{\rm H}]_{\rm L}}{[k_e^{\rm D}]_{\rm L}} \tag{5}$$

Equation (5) requires the value of 2.22×10^{-3} /min for $[k_e^{\rm D}]_{\rm L}$ instead of nearly zero, in view of the experimental results for $k_e^{\rm H}$, $k_e^{\rm D}$ and $[k_e^{\rm H}]_{\rm L}$; for instance, 4.8% of HD must be detected for a hydrogen-deuterium exchange reaction at 90°C after 1320 hr. However, we could not find any trace of HD content during that long period, as has been menitoned above.

Second, the catalytic mechanism is recognized from the activation energies of the para-ortho-hydrogen conversion for the two states. Figure 5 shows $E^{\rm H}=10.2$ kcal/mol; the hydrogen conversion on solid film occurs with the chemical mechanism. In the case of the molecular state, however, the activation energy is $[E^{\rm H}]_{\rm L}\simeq0$; this means that the hydrogen conversion occurs through the physical process.[13]

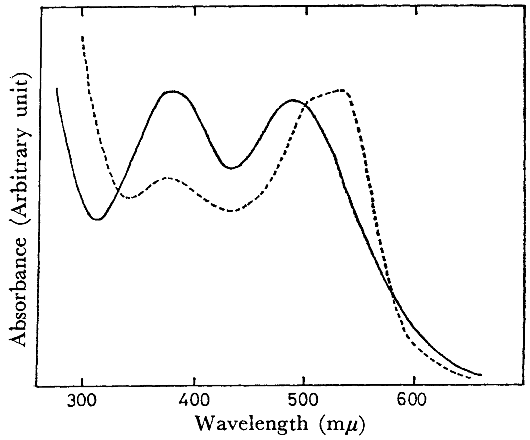

Fig. 8. The electronic spectra of the benzonitrile-cesium ion radical salt.
—— solid film, ---- solution.

The mechanism of the chemisorption of hydrogen on the aromatic-alkali metal ion radical salt is not clear at present. However, we may conclude that the mechanism can not be explained only in terms of the electronic structure of the isolated aromatic anion.

The electronic absorption spectra of the solid and liquid phases are both similar to the spectrum of the benzonitrile mononegative anion,[16] as is shown in Fig. 8. However, the wavelengths of the peaks are shifted from 375 mμ and 510 mμ in the solution to 380 mμ and 488 mμ in the solid, and the ratio of the extinction coefficients, ε, varies from $\varepsilon_{488\,{\rm m}\mu}/\varepsilon_{380\,{\rm m}\mu}=1.06$ in the solution to $\varepsilon_{510\,{\rm m}\mu}/\varepsilon_{375\,{\rm m}\mu}=2.01$ in the solid. These changes suggest that the benzonitrile anion in the solid-ion radical salt is strongly perturbed by the neighbouring cesium cations and the other benzonitrile anions. Therefore, in order to analyze the chemical mechanism of the hydrogen conversion on the ion salts, the structure of aromatic anion-alkali metal cation pairs perturbed strongly by neighbouring ions must be considered.

The authors wish to thank Drs. N. Wakayama and Y. Mori for their helpful discussion. One of us (M.T) also wishes to express his thanks to Professor S. Okamoto and Professor H. Suzuki of Waseda University for helpful discussion and for continuous encouragement. Thanks are due to Kawakami Foundation for financial support.

Appendix 1

The catalytic activity of a number of aromatic-aromatic charge transfer complexes, mentioned below, has been examined by means of the hydrogen-deuterium exchange reaction by us. (T. Kondow, N. Wakayama, Y. Mori, Y. Matsunaga and the authors) However, no exchange reaction occurred over these complexes.

Donor	Acceptor	Donor	Acceptor
DAD[a]	Chloranil (1 : 1)	TTN	TCNE (3 : 2)
DAD	9-Dicyanomethylene-2,4,7-Trinitrofluorene (1 : 1)	Dibenzo-Phenothiazine	DDQ[e] (2 : 1)
DAD	Dicyanonaphthoquinone (1 : 1)	Dibenzo-phenothiazine	DDQ (1 : 1)
DAD	TCNE[b] (1 : 1)	Tetramethylbenzidine	TCNE (1 : 1)
DAD	TCNQ[c] (1 : 1)	Tetramethylbenzidine	TCNQ (1 : 1)
TTN[d]	*o*-Chloranil (3 : 1)		

a) diaminodurene, b) tetracyanoethylene, c) tetracyanoquinodimethane, d) tetrathionaphthacene
e) dichlor-dicyano-*p*-benzoquinone

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[16] A. Ishitani and S. Nagakura, *Theor. Chem. Acta*, **4**, 236 (1966).