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Catalytic Activity and Reactivity of Aromatic Nitrile and Alkali Metal Ion Radical Salt. II. Hydrogen Exchange on Benzonitrile Ion Salt as a Function of Alkali Metals

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The para-orthohydrogen conversion (rate constant $k_e{}^H$ and the deuterium exchange reaction (rate constant $k_e{}^D$) over the benzonitrile-alkali metal ion radical salt were investigated as functions of the donor component—alkali metal. The sort of alkali metals in the ion radical salts greatly affected the catalytic activity and the reactivity. The activation energies obtained from the temperature dependence of $k_e{}^H$ and $k_e{}^D$, E^H and E^D, and the value of α(depending on the ratio of $k_e{}^H$ to $k_e{}^D$ monotonously decreased as Na→K→Rb, but those values showed an irregular trend for the Cs-complex. The results suggest that the catalytic activity cannot be understood only in terms of the nature of the components; must also be considered the structural nature of the solid phase of the ion radical salt.

In a previous paper,[1] we reported that the benzonitrile-cesium ion radical salt has a strong catalytic activity in the solid phase, but that the salt solution in a benzonitrile solvent does not possess any catalytic activity for hydrogen-deuterium equilibration. Thus, we concluded that the catalytic activity on the ion radical salts can be explained not by the electronic structure of the isolated aromatic anion, but by the structure of the solid ion radical salt which is perturbed strongly by neighbouring ions.

In this report, we wish to discuss mainly the catalytic activity on benzonitrile-alkali metal ion radical salts as a function of their donor metals in order to clarify the role of the metallic cations in the ion salt with regard to the catalytic activity. Further, we will discuss the mechanism of hydrogen-deuterium equilibration on the ion radical salt.

Experimental

The preparation of the benzonitrile-alkali metal ion radical salts has already been reported.[1] In this work, four sorts of alkali metals—Na, K, Rb and Cs— were used as electron-donor components. Their preparations and purifications were carried out carefully.[*2] The purified alkali metal was first evaporated onto the surface of a glass reaction vessel *in vacuo* and then the purified benzonitrile was introduced. A dark red-coloured ion radical salt solution was obtained immediately. The excess benzonitrile was completely evaporated from the salt solution by heating *in vacuo* about 8 hr, since no catalytic activity was found for the ion radical salt solution or the wet ion salt.

The hydrogen mixtures (p-H_2+o-H_2 and H_2+HD+D_2) were analyzed by gaschromatography using a heat-treated alumina column at the temperature of liquid nitrogen, as has been described in a previous paper.[2]

The electronic spectra of benzonitrile-alkali metal ion radical salt in a benzonitrile solvent and the solid film of the salt were observed with a Cary recording spectrophotometer, Model 14.

Results

As has been mentioned in the previous papers,[1-4] the aromatic-alkali metal ion radical salts show two chemical reactivities for hydrogen molecules; one is the "chemisorption mechanism", and the other is the "exchange mechanism."[*3] To make clear the mechanisms of these two reactions, the

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[*2] The sodium and potassium, obtained commercially, were purified by a distillation procedure under a vacuum free from hydrogen and carbohydrates. The rubidium and cesium were prepared from their chloride by reduction with calcium metal in an evacuated glass tube: $2MCl+Ca \rightarrow 2M+CaCl_2$

1) M. Tsuda, and H. Inokuchi, This Bulletin, **43**, 3410 (1970).

2) T. Kondow, H. Inokuchi and N. Wakayama, *J. Chem. Phys.*, **43**, 3766 (1965); H. Inokuchi, N. Wakayama, T. Kondow and Y. Mori, *ibid.*, **46**, 837 (1967).

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

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

[*3] The chemisorption mechanism and exchange mechanism proceed by way of a hydrogen-deuterium equilibration over the catalyst and by way of an exchange reaction between gaseous deuterium and the hydrogen atom of the aromatic anion respectively.

para-orthohydrogen conversion (p-$H_2 \rightleftarrows o$-H_2) and the deuterium-exchange reaction (D_2+H-$\phi \rightleftarrows$ HD+D-ϕ) were employed.

Hydrogen Conversion and Deuterium-Exchange Reaction. The kinetic analysis of these two reactions was done over the temperature range from 0°C to 80°C under a constant pressure of hydrogen (100 Torr). The rate constant, $k_e{}^H$, for the hydrogen conversion was found to obey a first-order law, as has been shown in Part I. The rate constant for the deuterium exchange reaction, $k_e{}^D$, obeys a first-order law for a fresh sample (curve a in Fig. 1), but the value of $k_e{}^D$ for the salt washed with hydrogen seems to deviate a first-order law (curve b in Fig. 1). In the Fig. 1, where the progression of the decay of deuterium on the ion radical salt is plotted against the reaction time, a sharp kink is found at the initial stage (region I of curve b) of the reaction. This behaviour suggests that both the two different mechanisms for hydrogen exchange occur on the hydrogen-exposed ion radical salt.*4

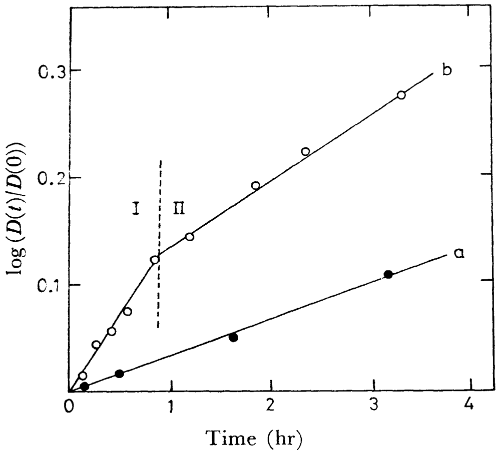

Fig. 1. The progression of deuterium exchange reaction with the benzonitrile-cesium ion radical salt.
—●— for fresh film
—○— for hydrogen exposed film

The progression of the reaction on the fresh salt was similar to that of the later stage (region II of curve b) of the reaction on hydrogen-exposed film. Therefore, the rate constant for the deuterium exchange reaction was obtained from the analysis of the reaction of region II of curve b at various temperatures, as is shown in Fig. 2 (see "Discussion").

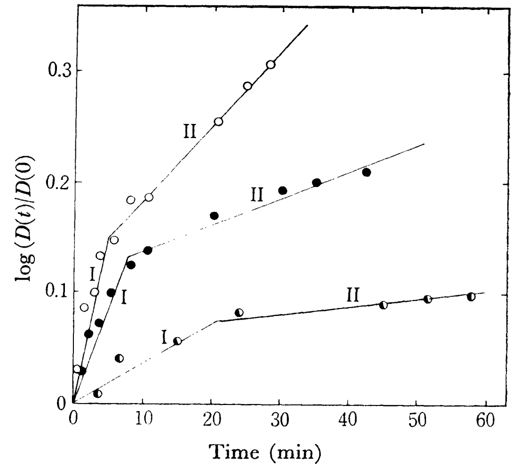

Fig. 2. The progression of deuterium exchange reaction with the benzonitrile-cesium metal film as a function of temperature.
—○— at 80°C
—●— at 60°C
—◐— at 40°C

TABLE 1. ACTIVATION ENERGY FOR BENZONITRILE-ALKALI-METAL ION RADICAL SALTS

Donor metal	E^H (kcal/mol)	E^D (kcal/mol)
Na	8.2	12.7
K	6.6	9.3
Rb	5.5	7.1
Cs	10.2	14.3

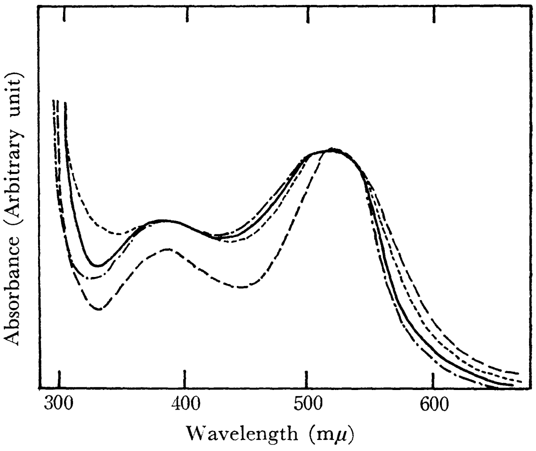

Fig. 3. Electronic spectra of benzonitrile-alkali metal ion radical salt in benzonitrile solvent as sorts of donor metals.
–·–·– Sodium salt
— — — Potassium salt
——— Rubidium salt
----- Cesium salt

From the temperature dependency (0°C—80°C) of $k_e{}^H$ and $k_e{}^D$ for the benzonitrile-alkali metal ion

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*4 Whenever the deuterium-exchange reaction was carried out over the salt, the species were washed with hydrogen gas completely in advance in order to eliminate the exchanged and/or chemisorbed deuterium of the proceeding reaction from the salt, and the hydrogen was evacuated for about 3 hr.

radical salts under a constant pressure (100 Torr), the activation energies for four alkali metal ion radical salts were obtained; they are summarized in Table 1.

Spectroscopic Survey. The results presented in the previous section show that the catalytic activity of the salt is greatly affected by a variation in the component—alkali metal. These findings suggest that the electronic state of the ion radical salt is influenced by the change in the donor metals. Figure 3 shows the electronic spectra of the benzonitrile solutions of the above four ion radical salts while Fig. 4 illustrates the patterns for their solid films. The spectral responses of the salt solutions resembled those of the benzonitrile mononegative ion reported by Ishitani and Nagakura.5) The sort of donor metals in the salt solution did not strongly affect the response curve. For the solid films, however, the positions of the absorption peaks and also their extinction coefficients changed as a function of the donor metals. As the atomic weight of the alkali metals increased, the 380 mμ absorption peak shifted to the longer-wavelength side and the 480 mμ absorption peak shifted to the shorter-wavelength side. Moreover, the ratio of the extinction coefficient of the 380 mμ-peak to that of the 480 mμ-peak decreased.

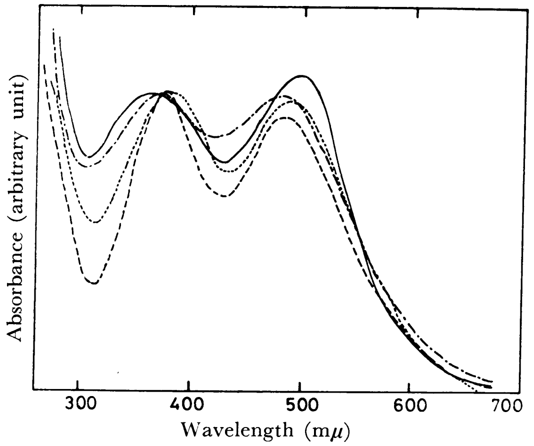

Fig. 4. Electronic spectra of solid film of benzonitrile-alkali metal ion radical salt as sorts of donor metals.
-·-·- Sodium salt
— — — Potassium salt
——— Rubidium salt
----- Cesium salt

Discussion

In the studies of the catalytic behaviour of the ion radical salts, the mechanism has often been interpreted in terms of the nature of the acceptor molecules6,7)—aromatics. Among the various types of aromatic complexes,8,9) however, only the aromatic-alkali metal (or alkali earth metal) ion radicals show catalytic activity in relation to hydrogen-deuterium equilibration. This suggests that the donor metal plays an important role in the reactivity of the ion radical salt. Therefore, we will discuss the relation between the catalytic activity and the sort of alkali metal in the salt.

First, the mechanism of the deuterium-exchange reaction on the hydrogen-exposed film will be discussed. Then, the role of the donor metal in the catalytic activity of the salt will be investigated. Finally, the electronic state of the salt is surveyed by means of the spectroscopical method.

Deuterium-Exchange Reaction. As has been mentioned in the section on "Results," two different mechanisms for deuterium exchange occur on the hydrogen-exposed ion radical salt. These mechanisms may be supposed to be as follows. One is that deuterium gas (D_2) exchanges with chemisorbed hydrogen ($\underset{*}{H}$) [Mechanism A]. The other is that deuterium gas chemisorbs on the salt surface ($D_2+2*\rightarrow 2\underset{*}{D}$), and that the chemisorbed deuterium ($\underset{*}{D}$) exchanges with the hydrogen of the aromatic anion (H-ϕ) and that the chemisorbed hydrogen thus produced reacts with D_2 ($\underset{*}{D}+\text{H-}\phi\rightarrow\underset{*}{H}+\text{D-}\phi$; $D_2+\underset{*}{H}\rightarrow HD+\underset{*}{D}$) [Mechanism B]. The procedures are illustrated as:

$$D_2+\underset{*}{H}\rightarrow HD+\underset{*}{D} \qquad \text{[Mechanism A]}^{*5}$$

$$\left.\begin{array}{l} D_2+2*\rightarrow 2\underset{*}{D} \\ \underset{*}{D}+\text{H-}\phi\rightarrow\underset{*}{H}+\text{D-}\phi \\ D_2+\underset{*}{H}\rightarrow HD+\underset{*}{D} \end{array}\right\} \qquad \text{[Mechanism B]}^{*5}$$

It is assumed that the rate-determining process for the initial stage (region I of curve b in Fig. 1) of the exchange reaction is "Mechanism A," and that for the later stage (region II of curve b in Fig. 1) is the chemisorption of deuterium on the complex salt ($D_2+2*\rightarrow 2\underset{*}{D}$) of "Mechanism B." The above assumptions require that the deuterium exchange on the fresh sample occur through Mechanism B (curve a in Fig. 1). The fact that the region II of curve b (Fig. 1) has a similar inclination to that of curve a for the fresh sample supports this assumption. Therefore, in order to obtain

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5) A. Ishitani and S. Nagakura, *Theoret. Chem. Acta*, **4**, 236 (1966).

6) M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, *Trans. Faraday Soc.*, **63**, 997, 2528 (1967).

7) N. Wakayama and H. Inokuchi, *J. Catalysis*, **11**, 143 (1968).

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

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

[*5] Here, * indicates a site of salt for chemisorption.

the rate constant for deuterium exchange with the hydrogen of the aromatic anion over the hydrogen-exposed salt film, the behaviour in the region II must be adopted.

The Role of the Donor Metal in the Catalytic Activity. As has been described in previous papers,[1-4] there are two processes which occur over the complexes: the chemisorption mechanism and the exchange mechanism. The para-ortho-hydrogen conversion (its rate constant: k_e^{H}) takes place through both these mechanisms,[*6] but the deuterium-exchange reaction (the rate constant: k_e^{D}) takes place only through the exchange mechanism. The ratio $k_e^{\mathrm{H}}/k_e^{\mathrm{D}}$,[*7] therefore, indicates the quantity of the contribution of the chemisorption mechanism to the hydrogen conversion. When we introduce the value of $\alpha(k_e^{\mathrm{H}}/k_e^{\mathrm{D}}=\alpha I_{\mathrm{HD}}$, where I_{HD} is as described in the Appendix), we can eliminate the hydrogen-deuterium isotope effect on the exchange reaction. Accordingly, the value of α is unity when the hydrogen conversion takes place through only the exchange mechanism, and the increasing value of α shows the increasing contribution of the chemisorption mechanism to the hydrogen conversion. The experimentally-determined values were about 1—10^2. The α-values are plotted against the reciprocal of the temperature for each alkali metal ion radical salt in Fig. 5. This behaviour shows that the contribution of the chemisorption mechanism to the hydrogen conversion increases as the temperature decreases.

From Table 1 and Fig. 5, two parameters for the reactivity of the salt—the activation energy, E^{H} and E^{D}, and the α-value—seem to be influenced by the sort of donor metal in the salt. In this section, therefore, the catalytic activity (E and α) of the ion radical salt will be discussed as a function of alkali metals—Na, K, Rb and Cs. The nature of the alkali metals—the ionization potential, the electron affinity, the ion radius and so on—changes monotonously with their atomic numbers. Among these characteristics, the cation radius of the alkali metal is adopted as a parameter for the reactivity for two reasons. An ESR study of the ion radical salt has shown that the cation radius correlates with the magnitude of the alkali metal splittings and with that of the spin density at the carbon of the aromatic anion.[10] Further, the location of the metal cation in the salt crystal or the interionic separation depends on the metal ion radius.

The activation energies, E^{H} and E^{D}, are first compared with the cation radius. Figure 6 shows the values of E^{H} and E^{D} plotted as functions of the cation radius. There is a regular trend for the E^{H} and E^{D} values to decrease with an increase in the size of the metal cations with the exception of cesium-benzonitrile ion radical salt. Similar phenomena are observed in the relation between the value of α and the ion radius, as is illustrated in Fig. 7. The value of α decreases in this order: Na→K→Rb, but for the Cs salt the value shows an irregular tendency.

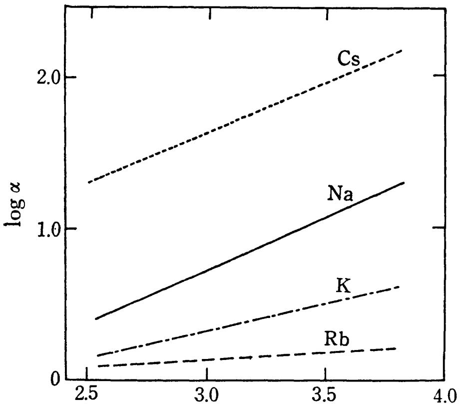

Fig. 5. log α is ploted as a function of temperature.

——— for benzonitrile-Na complex

— — — for benzonitrile-K complex

——— for benzonitrile-Rb

----- for benzonitrile-Cs

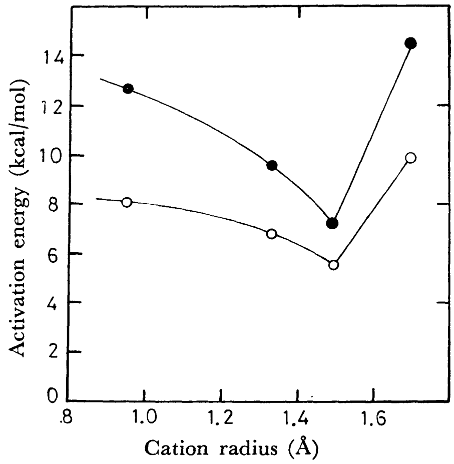

Fig. 6. Activation energies E^{H} for para-ortho-hydrogen conversion and E^{D} for deuterium exchange reaction plotted against the size of ion radius of donor metals.

—○— for E^{H}

—●— for E^{D}

[*6] The contribution of the paramegnetic mechanism to the ortho-parahydrogen conversion is negligible.

[*7] As the rate constants, k_e^{H} and k_e^{D}, are studied with relation to the same specimen, the two surface areas, S^{H} and S^{D}, may be assumed to be equivalent (see Eq. (3a) and (3b) in Part I). Therefore, the ratio ($k_e^{\mathrm{H}}/k_e^{\mathrm{D}}$) includes only A (enthropy factor) and E (activation energy) belongs to the nature of the catalyst.

10) N. Hirota, *J. Amer. Chem. Soc.*, **90**, 3603 (1968); N. Hirota, R. Carraway and W. Schook, *ibid.*, **90**, 3611 (1968).

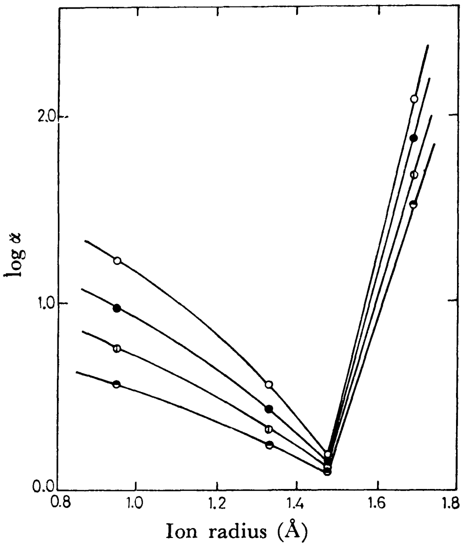

Fig. 7. log α ploted against the size of ion radius of donor metals at a various temperature.
—○— 0°C
—●— 30°C
—⦶— 60°C
—◒— 90°C

Mori *et al.*[11] proposed that the reactivity of the ion radical salt could be understood from the ionization potential of the donor metals. The present result does not, however, support their assumption.

As the activation energy and the α-value show a monotonous tendency to change in the orders: Na→K→Rb, the reactivity of the ion radical salt seems to be influenced by the metal-cation field. However, the irregularity in the cesium ion radical salt suggests that the reactivity of the salt can not be understood only in terms of the nature of the donor metals; also, the nature of the salt in the solid phase must be taken into consideration. To analyze the nature of the salt in the solid phase, the crystal structure must be considered, but the structure of the benzonitrile-alkali metal ion radical salt has not yet been reported.

Sometimes, the crystal structure of ion radical salts changes with the kind of their donor metal; for instance, the structure of *p*-chloranil-alkali metal salt shows a difference between the Li (or Na)-salt and the K (or Rb)-salt.[12] Accordingly, the crystal structure of the benzonitrile ion radical salt must be studied in order to ascertain the mechanism of the catalytic reaction.

Spectroscopical Analysis

Figure 3 illustrates that the patterns of the spectral response of the ion radical salt solutions scarcely change at all with the kind of metal cation. In the solution, the salt is stable as a free-anion or a loose-ion pair, as has been established by Carrington and Todd.[13] Therefore, the spectra of the ion radical salt in a solution is almost the same as that of a free anion. On the other hand, the spectral response curves of the solid film (illustrated as Fig. 4) vary with the kind of alkali metal. The interionic separation in the solid ion radical salt would be smaller than that in solution, and the perturbation of the neighbouring ionic field seems to affect the electronic state of the aromatic anion strongly. Figure 6 shows that the metal dependency of the parturbation increases monotonously in this order: Na<K<Rb, and the Cs salt seems to be tremendously perturbed compared with the other three metal salts. As a tentative explanation for these irregularities, it is assumed that the Cs-benzonitrile ion radical salt has a unique structure, because the cesium ion, Cs^+, has an enormously large ion radius as comparison with those of the other alkali metal cations.

The author wishes to express his thanks to Professor H. Inokuchi for his valuable advice, his many stimulating discussion, and his reading of the manuscript. He also wishes to express his thanks to Dr. N. Wakayama and Dr. Y. Mori for their helpful discussion.

Appendix

As shown in Part I, the rate constant, $k_e{}^{\mathrm{H}}$, for the hydrogen conversion and that, $k_e{}^{\mathrm{D}}$, for the deuterium-exchange reaction are expressed as:

$$k_e{}^{\mathrm{H}} = S^{\mathrm{H}}A^{\mathrm{H}}\exp(-E^{\mathrm{H}}/\boldsymbol{k}T) \tag{A1}$$

$$k_e{}^{\mathrm{D}} = S^{\mathrm{D}}A^{\mathrm{D}}\exp(-E^{\mathrm{D}}/\boldsymbol{k}T) \tag{A2}$$

The ratio between $k_e{}^{\mathrm{H}}$ and $k_e{}^{\mathrm{D}}$ can be described as:

$$\frac{k_e{}^{\mathrm{H}}}{k_e{}^{\mathrm{D}}} = \alpha I_{\mathrm{HD}} \tag{A3}$$

where I_{HD} is the kinetic isotope effect in the activated complex and is given as a function of the temperature:

$$I_{\mathrm{HD}} = I_0\exp(-\varepsilon/\boldsymbol{k}T) \tag{A4}$$

I_0 and ε have the following values:[14,15] Theoretically $I_0=1.15$ and $\varepsilon=1.08$ kcal/mol, and experimentally $I_0=1.10$ and $\varepsilon=1.3$ kcal/mol. From Eqs. (A1)—(A4), α is given as;

$$\alpha = \frac{1}{I_0}\frac{A^{\mathrm{H}}}{A^{\mathrm{D}}}\exp\left(-\frac{E^{\mathrm{H}}-E^{\mathrm{D}}-\varepsilon}{\boldsymbol{k}T}\right), \tag{A5}$$

assuming that the surface areas, S^{H} and S^{D}, are equivalent. Thus, the value of α of Eq. (A5) can be estimated experimentally.

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[11] Y. Mori, N. Wakayama and H. Inokuchi, *J. Catalysis*, **14**, 1 (1969).

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[13] A. Carrington and P. F. Todd, *Mol. Phys.*, **6**, 161 (1963).

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[15] W. K. Wilmarth Jr., and C. F. Baes, *J. Chem. Phys.*, **20**, 116 (1952).