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NOTES

Hydrogen–Deuterium Exchange with Anthracene–potassium and Anthracene–sodium Complexes

Heterogeneous catalysis by electron-donor–acceptor (EDA) complexes has been extensively studied since Kondow *et al.* (*1*) found that the hydrogen–deuterium equilibration reaction was catalyzed by a tetracyano-pyrene–cesium complex. The exchange reaction between deuterium in the gas phase and the hydrogen of the EDA complex has also been studied (*2*).

Klier *et al.* (*3*) have shown that for the exchange of oxygen isotopes between gaseous oxygen and a solid oxide, three possible reactions can be distinguished kinetically. It would be expected that in the system gaseous hydrogen and EDA complex, the same three reaction types would be discernible. These three mechanisms may be described by the following scheme where the symbols for reaction rates R', R'', and R have analogous meanings to those applying in Ref. (*3*) for the corresponding oxidation exchange reactions:

$$\begin{array}{ll}
\left.\begin{array}{l}
D_2(g) + H(s) \rightleftarrows HD(g) + D(s) \\
HD(g) + H(s) \rightleftarrows H_2(g) + D(s)
\end{array}\right\} & R', \\
\left.\begin{array}{l}
D_2(g) + 2H(s) \rightleftarrows H_2(g) + 2D(s) \\
HD(g) + 2H(s) \rightleftarrows H_2(g) + D(s) + H(s) \\
HD(g) + 2D(s) \rightleftarrows D_2(g) + D(s) + H(s)
\end{array}\right\} & R'', \\
D_2(g) + H_2(g) \rightleftarrows 2HD(g) & R.
\end{array}$$

[$H(s)$ or $D(s)$ means hydrogen of the catalysts; index (g) relates to the gas phase].

The molecule either exchanges one (R') or two (R'') of its hydrogen atoms per reactive collision with the EDA complex or exchanges between gaseous molecules take place without detectable participation of hydrogen atoms of the EDA-complex (R). In order to measure the value of R'' for an actual system where all three reactions might simultaneously take place, it is useful to study the exchange between a pre-equilibrated gas mixture of H_2, D_2, and HD and an EDA complex which, initially, contains exclusively the H isotope. If we call $(HD)^2/(H_2)(D_2) = \psi$, it can easily be shown that for such a system $d\psi/dt = 0$ if only the R and the R' reactions operate, but

$$\frac{1}{\psi}\left(\frac{d\psi}{dt_3}\right)_{t=0} = -\frac{R''}{z}, \tag{1}$$

with z = number of H_2 molecules, if also the R'' reaction takes place. The initial deviation of ψ from ψ_{eq} is, therefore, a reliable experimental criterion for the occurrence of the R'' reaction with a nonnegligible rate. Other methods have been suggested by the authors of the theory (*3*).

In our experiments the reaction was followed using a mercury-free closed system with a U-shaped glass tube reactor carrying an appendix in which purified anthracene (ca. 0.6 g) or alkali metal (ca. 0.3 g) was contained. The anthracene was first sublimed onto the glass vessel and was then exposed to alkali metal vapor to form the EDA complex. Highly colored complexes, bluish violet for anthracene–potassium and greenish violet for anthracene–sodium, were respectively formed and were heated at 160°C with evacuation for a day after the alkali metal reservoir had been sealed off. The number of EDA-complex molecules formed was not determined. The isotopic mixture of "hydrogen" (H_2, HD, and D_2) was analyzed by a mass spectrometer connected to the reaction system via a liquid

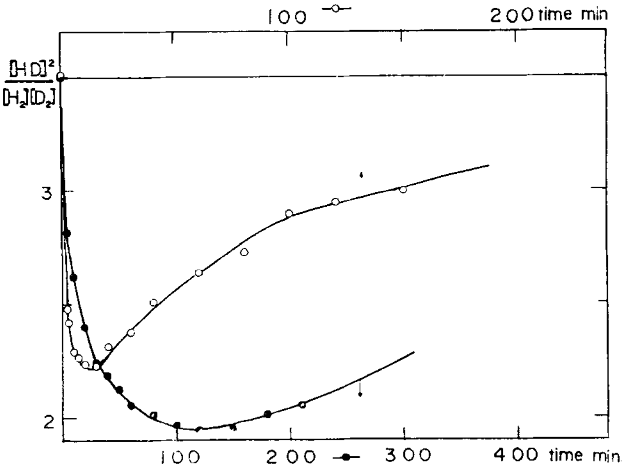

FIG. 1. $(HD)^2/(H_2)(D_2)$ vs time: (●) anthracene–sodium, at 147°C, total pressure, 0.220 Torr; (○) anthracene–potassium, at 156°C, total pressure 0.200 Torr; (horizontal line) equilibrium value.

nitrogen trap which was used to condense any "hydrogen"-containing organic vapors, (anthracene, EDA-complex) which might contribute to the mass spectrometer signals.

Figure 1 shows typical results for the hydrogen–deuterium exchange reaction on anthracene–potassium and –sodium EDA complexes, equilibrated mixture being used as the initial gas phase. The $(HD)^2/(H_2)(D_2)$ decreases from the initial equilibrium value and passes through a minimum before returning, finally, to the equilibrium value again. When applying Eq. (1) to the initial slope of the curve in Fig. 1, it is immediately clear that the contribution of R'' in the total exchange is important, i.e., in many reactive collisions both atoms of one hydrogen molecule are exchanged with two hydrogen atoms of the EDA complex.

In order to obtain numerical values for R, R', and R'', the number of exchangeable hydrogen atoms m is needed [for the definition of symbols see Ref. (*3*)]. This was calculated from the material balance: $m = 2a(c/w_\infty - 1)$, where w_∞ was estimated by extrapolation and best fit as described in

TABLE 1
THE RATES AND THE RATE CONSTANTS OF THE REACTIONS

Catalyst	Anthracene–potassium	Anthracene–sodium	
Reaction temp (°C)	156	147	147[a]
m(molecules)	1.15×10^{19}	1.56×10^{19}	
Rate[b] (molec/min) R	$\simeq 0$	$\simeq 0$	
R'	3.5×10^{16}	1.4×10^{16}	
R''	1.2×10^{16}	0.2×10^{16}	
Equilibration rate const. k[c] (min^{-1})	1.0×10^{-2}	4.0×10^{-3}	6.2×10^{-3}[d]
k for: $D_2(g)$ + EDA	1.0×10^{-2}	4.0×10^{-3}	6.1×10^{-3}[d]
Rate[e] (molec/min)	4.6×10^{16}	1.5×10^{16}	

[a] The rate constant at 80°C was reported by Ichikawa *et al.* (*4*).

[b] Total pressure of hydrogen 0.200 Torr.

[c] Derived from $\ln \{[(HD)_{t=\infty} - (HD)_t]/[(HD)_{t=\infty} - (HD)_{t=0}]\} = (-k/a)t$, where (HD) means mole fraction of HD.

[d] Estimated from the rate constant and the activation energy reported by Ichikawa *et al.* (*4*).

[e] Calculated from k and number of gaseous molecules in the system.

(*3*). The values for the rates R', R'', and R found in this manner are shown in Table 1. They confirm the significant contribution of R'' and show that the homomolecular R-mechanism is negligible. The value of R'' calculated by Eq. (1) is significantly higher (by one order of magnitude) than the values resulting from the best fit method. The difference is much higher than could be explained by isotopic effects only. Evidently a small number of hydrogen atoms is exchanged at a higher rate than the majority of the exchangeable atoms; consequently the initial slope used in Eq. (1) is steeper than the average slope of the integrated rate curve.

The first order rate constants for the hydrogen–deuterium equilibration reaction and for the exchange reaction between deuterium gas and the hydrogen of the EDA complexes were also measured (see Table 1). At 156°C for anthracene–potassium and at 147°C for anthracene–sodium the rate constants of both the equilibration and exchange reactions are equal. It supports the conclusion that no R-mechanism is involved, i.e., the equilibration proceeds via a heterophase exchange mechanism.

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REFERENCES

1. KONDOW, T., INOKUCHI, H., AND WAKAYAMA, N., *J. Chem. Phys.* **43**, 3766 (1965).
2. TAMARU, K., *Advan. Catal. Relat. Subj.* **20**, 327 (1969).
3. KLIER, K., NOVÁKOVÁ, J., JÍRŮ, P., *J. Catal.* **2**, 479 (1963).
4. ICHIKAWA, M., SOMA, M. M., ONISHI, T. M., AND TAMARU, K., *Bull. Chem. Soc. Jap.* **40**, 1015, 1294 (1967).

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Surface Diffusion and Reaction at Widely Separated Sites

A recent note by Moffat, Johnson, and Clark (*1*), calling attention to the failure of the classical analysis of diffusion and reaction when the sites of reaction are widely separated on a surface and transport to the surface is limited by the mass transfer resistance, has suggested that the following considerations on surface diffusion and reaction may be worth adumbrating. We shall consider the effective reaction rate at an isolated reaction site which "draws" reactant from the surrounding surface by surface diffusion, the surface itself being replenished by mass transfer or adsorption from the reactant above it. In the corresponding problem in three dimensions there is of course no replenishment from without, since this would involve a fourth dimension, but a steady-state solution can be found in which the concentration of reactant far from the site of reaction is constant and the reaction site is fed by diffusion in the space. This has been discussed by Bak and Fisher (*2*). In two dimensions, however, there is no steady-state solution for which the concentration remains constant far from the reaction site unless the surface is replenished by adsorption.

The problem to be solved is as follows.