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LETTERS TO THE EDITORS

A Theoretical Model of the Ethane/Deuterium Exchange Reaction Catalysed by Platinum and the Law of Microscopic Reversibility

The initial distributions for the exchange of ethane with D_2 on several forms of Pt catalyst show maxima in the d_1 and d_6 deuteroisomers (*1–3*). This has been explained by Anderson and Kemball (*1*) in terms of two types of active independent sites and the operation on both of the $\alpha\beta$ exchange processes, namely, the interconversion of monoadsorbed alkyl and 1,2-diadsorbed alkene. A low chance of alkyl reversal is postulated for sites A, but a high chance for sites B. The U-shaped distributions are then well-modelled by a statistical analysis using three arbitrary parameters, one for each of the two $\alpha\beta$ processes, and the third, q, for the percentage of the total reaction on each type of site.

The fact that virtually the same U-shaped distribution is obtained (*2*) using a Pt single crystal face (111) at the high temperature of 550 K, i.e., approx. 100 K higher than that for polycrystalline films (*1*), led us to reexamine this mechanism. Close inspection shows that the Anderson and Kemball scheme does not rule out minor amounts of intersite transfer of C_2X_5 and/or C_2X_4 ($X =$ H or D) species. The statistical contribution of such transfer is then also minor and can be regarded as zero to a good approximation, so this potential but minor kinetic event is simply ignored. What is left, total independence of A and B sites of each other, is kinetically perfectly valid but is it real, especially at 550 K for a single crystal face?

We therefore set up some more sophisticated models which investigated the possibility that intersite transfer is significant and tested these statistically, showing that under certain constraints the U-shaped distributions are well reproduced (*4*). However, Burwell and co-workers (*5*) now claim that our mechanism is a violation of the law of microscopic reversibility and must therefore be rejected. We show here that this assertion is incorrect and that the confusion has arisen apparently from placing a wrong kinetic construction on schemes and equations in our paper (*4*) which are designed (p. 1864) *to illustrate the details of the statistical analyses*. Our mechanism consists of predominant activation of ethane on A sites, significant reversible transfer to B sites, where much of the incorporation of deuterium takes place by the extensive $\alpha\beta$ process, and then elimination of C_2X_5 off the surface as C_2X_6 from both A and B. Intersite transfer from A to B is kinetically and statistically significant, whereas intersite transfer from B to A is kinetically significant but statistically minor.

This is readily understood using the following general scheme:

$$\begin{tikzcd}
& \Sigma C_2X_6 \arrow[dl, shift left] \arrow[dr, shift left] & \\
\Sigma C_2X_5A \arrow[ur, shift left] \arrow[rr, shift left, "k_A"] \arrow[d, shift left] & & \Sigma C_2X_5B \arrow[ll, shift left, "k_B"] \arrow[ul, shift left] \arrow[d, shift left] \\
\Sigma C_2X_4A \arrow[u, shift left] \arrow[rr, shift left, "k'_A"] & & \Sigma C_2X_4B \arrow[ll, shift left, "k'_B"] \arrow[u, shift left]
\end{tikzcd}$$

Assuming indistinguishability of the labels H and D and no isotopic effect on the energetics, everything is at equilibrium as the free energy change $\Delta G = 0–0$ for each reversible reaction. The constant concentrations P_{X_2} and Θ_X are incorporated into the

0021-9517/92 $5.00

rate constants for the appropriate steps. It is clear that the following equalities must hold from $t = 0$ to $T = \infty$, but only at $t = \infty$, when the label is fully scrambled, are these equations valid for each individual deutero-isomeric species:

$$k_A \Sigma C_2X_5A = k_B \Sigma C_2X_5B$$

$$k'_A \Sigma C_2X_4A = k'_B \Sigma C_2X_4B.$$

However, between $t = 0$ and $t = \infty$ there is no true equilibrium and $\Delta G = 0 - T\Delta S$ is negative because the entropy is increasing as the label is scrambled in a spontaneous event at constant temperature and total pressure. Now according to the defined behaviour of A and B sites,

$$k_AC_2H_5A > k_BC_2H_5B$$

$$k'_AC_2H_4A > k'_BC_2H_4B$$

but

$$k_AC_2D_5A < k_BC_2D_5B$$

$$k'_AC_2D_4A < k'_BC_2D_4B,$$

since most of the C_2X_5 and/or C_2X_4 returning from B to A is C_2D_5 and/or C_2D_4, so this step and second trips A → B, etc., are largely statistically redundant. However, the return step, B → A, is kinetically significant and much of the more deuterated C_2X_5 species finally exits off the surface from A sites.

In like fashion, direct adsorption of C_2X_6 on B sites is kinetically and statistically of minor importance and is statistically ignored to a good approximation. The alkyl reversal parameter for the B sites also incorporates elimination of C_2X_5 from both A and B sites because second and subsequent trips A → B, are regarded statistically as nonexistent. These simplifications reduce the number of arbitrary parameters from five to three, but even then the analyses are much more formidable than that of Anderson and Kemball (*1*). Fortunately the key parameter, q, which is now the fraction of C_2X_5 and/or C_2X_4 formed on A and transferring to B, is not very sensitive to these approximations.

Our schemes are, in fact, spillover mechanisms with adsorption mainly on A sites, spillover of intermediates onto B sites, reaction there, and return to the gas phase mainly via A sites. When C_2X_4 is the transferring species this mechanism is exactly analogous to that for dual-functional reforming of oil. Here paraffin is activated on metal to generate alkenes which then transfer to acidic sites (H^+) on the support and react. New alkenes are released, transfer back to the metal, and hydrogenate. Direct reactions of paraffins with H^+ and the reverse are regarded as kinetically very minor:

$$RH + H^+ \cdots S^- \rightleftarrows R^+ \cdots S^- + H_2.$$

The exchange reaction, $H_2 + D_2 \rightleftarrows 2HD$ with spillover on metal/SiO_2 catalysts, is another well known, very simple analogue of the present model.

However, the general idea of mobility of transients from one type of site to another on single metallic and nonmetallic phases in heterogeneous catalysts has not been discussed much.

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JOHN J. ROONEY

School of Chemistry
The Queen's University of Belfast
Belfast BT9 5AG
Northern Ireland

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