(*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.

ACKNOWLEDGMENTS

The investigations were supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organisation for the Advancement of Pure Research (Z.W.O.). The authors are also grateful to the Z.W.O. for a grant given to one of us (S.T.).

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Received September 9, 1970

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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.

An irreversible first-order reaction takes place at the boundary of an isolated reaction site in the plane. For simplicity, this reaction site is taken to be a circle of radius a, and its wide separation from other sites is modelled by considering it in isolation. The surface concentration of the reactant at a distance r from the center of the reaction site is $c(r)$, and the net rate of adsorption per unit area

$$k_aC\{c_0 - c(r)\} - k_dc(r),$$

where c_0 is the surface concentration at saturation and C the concentration of reactant above the surface. At equilibrium

$$c = c_e = c_0KC/(1 + KC), \tag{1}$$

where

$$K = k_a/k_d. \tag{2}$$

If the surface coverage is small, i.e. $c \ll c_0$ or $KC \ll 1$, then the rate of transfer to the surface may be written in the mass transfer form $k_c(C - c)$, where $k_c = k_ac_0 = k_d$. If D_s is the surface diffusion coefficient, $c(r)$ obeys the equation,

$$D_s\frac{1}{r}\frac{d}{dr}\left(r\frac{dc}{dr}\right) + k_ac_0C - (k_aC + k_d)c = 0, \tag{3}$$

in the region $r > a$. Far from the site of reaction the adsorption–desorption process will be at equilibrium so

$$c(r) \rightarrow c_e \text{ as } r \rightarrow \infty. \tag{4}$$

At the site of reaction $r = a$, the flux to the boundary of the reactive area just balances the rate of consumption of the reactant, i.e.,

$$D_s\frac{dc}{dr} = k_rc \text{ at } r = a, \tag{5}$$

where k_r is the rate constant for reaction at the boundary of the site. Thus if there are n sites per unit area of catalyst, the rate constant (per unit catalyst area) will be $n\ 2\pi ak_r$. Equations (3–5) can be solved in the standard way and give

$$c(r) = c_e\left\{\frac{\lambda K_1(\lambda) + \mu[K_0(\lambda) - K_0(\lambda r/a)]}{\lambda K_1(\lambda) + \mu K_0(\lambda)}\right\}, \tag{6}$$

where

$$\lambda = a\{(k_d + k_aC)/D_s\}^{1/2},\ \mu = ak_r/D_s, \tag{7}$$

and K_0 and K_1 are the second kind of modified Bessel functions of orders zero and one (*3*).

If there were no diffusional resistance or limitation of mass transfer to the surface, the concentration would everywhere be c_e, and so the rate of reaction at the site would be $2\pi ak_rc_e$. In the presence of these finite rate processes it is $2\pi ak_rc(a)$, and we may write this as $2\pi ak_rc_e\eta$, where η is the effectiveness factor for such a site. Clearly

$$\eta = \frac{c(a)}{c_e} = \frac{\lambda K_1(\lambda)}{\lambda K_1(\lambda) + \mu K_0(\lambda)}, \tag{8}$$

or

$$\frac{1}{\eta} = 1 + \mu\frac{K_0(\lambda)}{\lambda K_1(\lambda)}. \tag{9}$$

For small λ,

$$\frac{1}{\eta} \sim 1 - \mu \ln \lambda, \tag{10}$$

and for large λ

$$\frac{1}{\eta} \sim 1 + \frac{2\mu}{2\lambda + 1}. \tag{11}$$

The figure gives contours of constant η in the plane of λ and μ.

We note the following points in connection with this form of effectiveness factor.

(1) If the mass transfer interpretation is given to the rate of adsorption terms (i.e., $k_ac_0 = k_d = k_c$, $KC \ll 1$), then k_c merely replaces k_d in the modulus λ and KC is neglected: the expression for the effectiveness factor still holds, see Fig. 1.

(2) In this case the rate of reaction might still be markedly temperature dependent at high flow rates in spite of the relative constancy k_c, for λ being large, $\eta \simeq \lambda/\mu$ or the rate of reaction $\eta k_r \simeq (k_cD_s)^{1/2}$, and surface diffusion coefficients can have an appreciable activation energy. The flow rate will only affect the parameter λ.

(3) The assumption of isolation can be weakened by considering the circle to be at the center of a square or hexagon

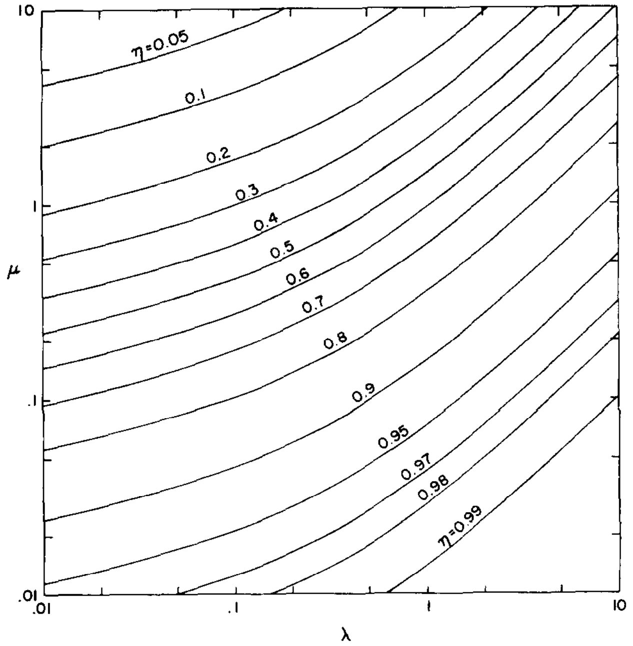

Fig. 1. Contours of constant effectiveness in the plane of the parameters λ and μ.

across whose boundary there is no diffusive flux in the surface. This analysis is being carried out in an ongoing program of research into the theory of diffusion and reaction. A hierarchy of problems involving interactions between adsorbed reactants, heterogeneous surfaces, etc. can easily be envisioned. A range of problems involving finite rates of adsorption and diffusion have been investigated by Amundson and Empie (*4*).

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Received December 8, 1970

The Unique Double-Bond Isomerization Properties of a Ruthenium Oxide–Silica Catalyst

An unique stereospecific double-bond isomerization activity has been observed for ruthenium oxide supported on silica gel. Results reported for other heterogeneous catalysts show that in the double-bond isomerization of 1-butene the initial product contains more *cis*-2-butene than *trans*-2-butene, although *trans*-2-butene is thermo-