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NOTE

The Conditions of Validity of Some Kinetic Models for Catalytic Dehydration of Alcohols

Recently, the kinetics of catalytic dehydration of *tert*-butanol, methanol, and ethanol on alumosilicates was described by Figueras *et al.* (*1*), Nohl *et al.* (*2*), and Figueras, De Mourges and Trambouze (*3*) by a rate equation which contained the square root of the partial pressure of the alcohol. In more general form it can be written in the following way.

$$r = ka(p_A)^{1/2}/(1 + a(p_A)^{1/2} + bp_W). \quad (1)$$

An equation of similar type has earlier been found by Knözinger and co-workers (*4–8*) for dehydration of these and other alcohols on alumina. Being the result of formal kinetic treatment, expression (1) can be regarded as a correlation equation which, from the considered set, best describes the experimental data. Figueras *et al.* (*1*), however, regard this equation as having a physical meaning and suggest a reaction mechanism which, they believe, is in accordance with this relation. The aim of this comment is to show that mechanistic interpretation of Eq. (1) is not so simple and that it agrees with the proposed mechanism only under certain assumptions which are not mentioned by Figueras *et al.* (*1*).

For dehydration of *tert*-butanol to isobutylene Figueras *et al.* (*1*) suggest the reaction scheme

$$\mathrm{Me_3C{-}OH} + l_B + l_A \overset{\text{fast}}{\rightleftarrows} \mathrm{Me_3C^+{-}}l_B + \mathrm{OH^-{-}}l_A, \quad \text{(I)}$$

$$\mathrm{Me_3C^+{-}}l_B \xrightarrow{\text{slow}} \mathrm{Me_2C{=}CH_2} + \mathrm{H^+{-}}l_B, \quad \text{(II)}$$

where l_B is the basic and l_A the acidic active center. The rate-determining step (II) must inevitably be followed by the formation of water from adsorbed hydrogen ion and hydroxyl [step (III)]. The overall reaction rate is given by the rate of the second step

$$r = k[\mathrm{Me_3C^+{-}}l_B], \quad (2)$$

and adsorption equilibrium of the first step is expressed by Eq. (3)

$$K_A = [\mathrm{Me_3C^+{-}}l_B][\mathrm{OH^-{-}}l_A]/p_A[l_B][l_A], \quad (3)$$

where p_A is the partial pressure of the alcohol and K_A is its adsorption coefficient. To obtain a rate equation of type (1) from the relations (2) and (3), it is necessary that: (a) The surface concentrations of the adsorbed carbonium ion and hydroxyl formed in step (I) must be the same, i.e.,

$$[\mathrm{Me_3C^+{-}}l_B] = [\mathrm{OH^-{-}}l_A]. \quad (4)$$

Generally, in mechanisms of the above type (adsorption of starting compound with dissociation and participation of only one fragment in the rate-determining step) this assumption does not have to be necessarily the correct one, since both fragments can react independently of each other and with different rate constants, so that their surface concentrations would not be the same even in the steady state. In the case of the suggested scheme of dehydration of *tert*-butanol they can be equal, since the hydroxyl does not react by a path which would be independent of the carbonium ion, but it reacts with the adsorbed proton which is the product of transformation of the carbonium ion. To fulfill condition (4), however, it is necessary that step (III) be fast enough and practically irreversible. This has been already stated by Kochloefl and Knözinger (*9*) in their scheme of dehydration of *tert*-butanol. Hence, step (III) cannot involve desorption of water, by combination of the particles H^+ and OH^-, since under this condition the observed strong rate-retarding effect of water (*1*) cannot be satisfactorily explained. This effect can be understood, however, under the assumption that, besides adsorbed particles of H^+ and OH^-, adsorbed molecules of water also are present. Then, step (III) has to be written as follows:

$$H^+\text{–}l_B + OH^-\text{–}l_A \rightarrow Wl_B + l_A, \tag{IIIa}$$

$$H^+\text{–}l_B + OH^-\text{–}l_A \rightarrow Wl_A + l_B, \tag{IIIb}$$

$$Wl_B \rightleftarrows W + l_B, \tag{IVa}$$

$$Wl_A \rightleftarrows W + l_A, \tag{IVb}$$

where W is the molecule of water. (b) It must be all the time present the same number of acidic and basic centers

$$[l_B] = [l_A] = [l], \tag{5}$$

so that from the relation (3), with the use of relations (4) and (5), the surface concentration of adsorbed carbonium ions can be expressed as

$$[Me_3C^+\text{–}l_B] = \sqrt{K_A p_A}\,[l]. \tag{6}$$

According to (IIIa,b) and (IVa,b) the molecular adsorption of water must be considered as occurring on one center (and that, in view of condition (5), to the same extent on centers of types l_B and l_A). The assumption of molecular adsorption of water on two centers would lead to a different denominator than in Eq. (1).

In the expression of the adsorption equilibrium of step (I) by relation (3) the assumption is included that the acidic and basic centers are located on the surface of a catalyst in such a way that each center of one type "communicates" with more than one center of the other type (the formation of separate couples of centers of the type l_B–l_A is precluded). This assumption, together with the requirement of equivalency of concentrations of centers of both types, is, however, impossible to verify. Equation (3) further implies that also the adsorbed fragments (carbonium ion and hydroxyl) must be mutually independent, (i.e., that the independent formations $M_3C^+\text{–}l_B$ and $OH^-\text{–}l_A$ must be present) and these can migrate over the surface. However, all these assumptions, which cannot be verified, weaken greatly the conclusions on the mechanism by Figueras *et al.* (*1*).

It is worthy of note that the species formed by dissociative adsorption of alcohol in the scheme I–IV could be also other fragments than carbonium ion and hydroxyl. For instance, Kochloefl and Knözinger (*9*) reason about the formation on alumina of the alkoxy group (bonded to the acidic center of Lewis type, represented by coordinatively unsaturated aluminium ion) and hydrogen (bonded to the basic center, the oxygen ion). This assumption may lead to the same kinetic scheme as (I–IV) and thus to the same rate Eq. (1), of course, under the same restrictive assumptions as were cited in the foregoing analysis.

In the dehydration of methanol to dimethyl ether the experimentally found (*1, 2, 5*) Eq. (1) was accounted for (*1*) by a scheme which involves two kinds of dissociative adsorption of methanol. One, reversible, leads to the formation of a methyl group and a hydroxy group and the other leads to the formation of a very strongly adsorbed methoxy group and hydrogen

$$CH_3OH + l_B + l_A \rightleftarrows CH_3^+\text{–}l_B + OH^-\text{–}l_A, \tag{I-M}$$

$$CH_3OH + l_B + l_A \rightarrow H^+\text{–}l_B + CH_3O^-\text{–}l_A. \tag{II-M}$$

The authors assume that the rate-determining step of the formation of dimethyl ether is the surface reaction between the species adsorbed according to scheme (I-M) and (II-M). This means that the following processes, both or either one of them, must be rate-determining.

$$CH_3^+\text{–}l_B + CH_3O^-\text{–}l_A \rightarrow CH_3\text{–}O\text{–}CH_3 + l_B + l_A, \tag{III-M}$$

$$OH^-\text{–}l_A + H^+\text{–}l_B \rightarrow H_2O + l_B + l_A. \tag{IV-M}$$

This does not exclude that the water remains adsorbed as a molecule.

In deriving Eq. (1) from the rates of processes (III-M) and (IV-M) and adsorption equilibria (I-M) and (II-M), given by relations (7) and (8),

$$K_{A,I} = [CH_3^+\text{–}l_B][OH^-\text{–}l_A]/p_A[l_A][l_B], \quad (7)$$

$$K_{A,II} = [CH_3O^-\text{–}l_A][H^+\text{–}l_B]/p_A[l_A][l_B], \quad (8)$$

it is necessary to make first the same restrictive assumption concerning concentration and location of the acidic and basic centers and adsorbed fragments as in the case of dehydration of *tert*-butanol. However, scheme (I-M)–(IV-M) leads to Eq. (1) only if it is further assumed that strongly adsorbed methoxy groups are formed by dissociative adsorption of the alcohol on the basic and acidic centers (Eq. II-M) of a different kind (l'_A, l'_B) to those on which the reversible formation of methyl ions according to Eq. (I-M) is taking place (l_A, l_B), i.e., that the adsorption is noncompetitive. The assumption of two different types of basic centers (l_B, l'_B) and two different types of acidic centers (l_A, l'_A), which, furthermore, should not form separate couples and should be freely distributed on the surface of the catalyst is, however, even more speculative than the previous assumptions for the dehydration of *tert*-butanol and it cannot be obviously fulfilled.

In contrast to the dehydration of *tert*-butanol, with the dehydration of methanol another important assumption is not obviously fulfilled, namely, the equivalence of the surface concentrations of the fragments formed by dissociative adsorption of methanol according to (I-M) and (II-M). This means that the equalities (9) and (10) are no longer valid.

$$[CH_3^+\text{–}l_B] = [OH^-\text{–}l_A], \quad (9)$$

$$[CH_3O^-\text{–}l_A] = [H^+\text{–}l_B]. \quad (10)$$

The reason can be found in that transformations of the adsorbed species according to (III-M) and (IV-M) proceed independently and generally with different rate constants ($k_{III} \neq k_{IV}$). In the steady state surface concentrations of the adsorbed species will be established such that, in addition to relations (7) and (8), there will also be the steady-state condition (11):

$$r = k_{III}[CH_3^+\text{–}l_B][CH_3O^-\text{–}l_A] = k_{IV}[OH^-\text{–}l_A][H^+\text{–}l_B], \quad (11)$$

so that the equalities (9) and (10) will not be attained. For this reason the solution of the kinetics of the reaction scheme (I-M)–(IV-M) of the dehydration of methanol is far more complex than is represented by Eq. (1). The expression for reaction rate as a function of partial pressure of methanol will then have the form

$$r = (k_{III}k_{IV}K_{A,I}p_A[l_A][l_B])^{1/2} \quad (12a)$$

where

$$[l_A][l_B] = \frac{L^2}{2(1-a)^2}\{a(b + b^{-1}) + 2 - a^{0.5}(b^{0.5} + b^{-0.5})[a(b^{0.5} - b^{-0.5})^2 + 4]^{1/2}\} \quad (12b)$$

and $a = K_{A,I}p_A$, $b = k_{IV}/k_{III}$ and L is the total concentration of active centers of the corresponding type ($L = L_A = L_B$).

In the special case $k_{IV}/k_{III} = 1$ Eqs. (12a) and (12b) become

$$r = k(K_{A,I}p_A)^{1/2}/[1 + (K_{A,I}p_A)^{1/2}], \quad (13)$$

which is the form of Eq. (1) for the initial reaction rate, when $p_W = 0$. By contrast, if $k_{IV}/k_{III} \ll 1$ or $k_{IV}/k_{III} \gg 1$, the value of the expression (12b) for $[l_A][l_B]$, and hence also the value of the reaction rate according to (12a), becomes close to zero. The assumption that $k_{III} = k_{IV}$ is however very improbable with reactions of such different species as methyl group and methoxy group on the one hand, and hydrogen and hydroxyl on the other.

From the above analysis it follows that Eq. (1) can accord with the suggested reaction schemes (*1*) only under a number of speculative assumptions which are, especially in the case of methanol dehydration, very improbable. Furthermore, it is not at all certain that Eq. (1) best describes the experimental data, since in the works (*1–3*) only a very limited set of kinetic equations has been tested and the procedure used to distinguish them (graphical linearization) is not sufficiently reliable from the statistical point of view. However, even when in kinetic studies the selection of the best equation is quite reliable it is necessary to bear in mind that the so-called best equation can be only an approximation of the equation which does correspond to the reaction mechanism. Therefore, one has to be very cautious in its mechanistic interpretation.

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