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Kinetics of the Bimolecular Ether Formation from Alcohols over Alumina*

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The derivation of some kinetic equations from mechanistic models is given for the bimolecular ether formation from alcohols on alumina. It is shown by means of a statistical analysis (nonlinear regression method) that these kinetic equations do not fit the experimental data for the reaction of ethanol on alumina, whereas there are five formal kinetic equations which describe the data equally well and which cannot be distinguished. These results are discussed. It is concluded that kinetic analysis is not a useful tool for the elucidation of the mechanism of this reaction. Mechanistic models appear to lead to complex multiparameter equations; a discrimination between such rival models is not possible.

A	Acidic surface site
B, B'	Basic surface sites
C	Normalized surface concentration, the subscript indicating the adsorbed species or the type of adsorption site
K	Adsorption equilibrium constant, the subscript indicating the number of the respective adsorption step
k	Rate constant, subscripts indicating the respective step of the reaction scheme
L, M	Unspecified adsorption sites
P	Partial pressure of reactants or products being indicated by the subscripts
Pr, Q, R, S, T	Unspecified chemical species
r	Reaction rate

INTRODUCTION

Kinetic data on ether formation from various alcohols over alumina and silica–alumina catalysts have been described satisfactorily by a pseudomonomolecular rate equation of the form

$$r = k_4\{(P_{\mathrm{ROH}})^{1/2}/[(P_{\mathrm{ROH}})^{1/2} + bP_{\mathrm{H_2O}}]\} \quad (1)$$

as shown by graphical inspection of the linearized equation (1) (*1–6*). In a recent publication Padmanabhan and Eastburn (*6*) present a kinetic model from which they derive Eq. (1). The scheme on which their kinetic treatment is based can be written in a somewhat modified manner as follows:

$$\mathrm{ROH} + \mathrm{A} \rightleftharpoons \mathrm{ROH{\cdot}A}; \quad (2)$$

$$\mathrm{ROH} + 2\mathrm{B} \rightleftharpoons \mathrm{RO^-{\cdot}B} + \mathrm{H^+{\cdot}B}; \quad (3)$$

$$\mathrm{ROH{\cdot}A} + \mathrm{RO^-{\cdot}B} \overset{\text{slow}}{\rightleftharpoons} \mathrm{R_2O} + \mathrm{OH^-{\cdot}A}; \quad (4)$$

$$\mathrm{H^+{\cdot}B} + \mathrm{OH^-{\cdot}A} \overset{\text{fast}}{\rightleftharpoons} \mathrm{H_2O{\cdot}B} + \mathrm{A}; \quad (5)$$

$$\mathrm{H_2O{\cdot}B} \rightleftharpoons \mathrm{H_2O} + \mathrm{B}. \quad (6)$$

This model differs from the one of Padmanabhan and Eastburn in two respects. First, the ether is assumed to desorb in-

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stantaneously. Second, the surface reaction [step (4)], which is assumed to be rate-determining, and the recombination of the elements of water [step (5)] are irreversible ($k_4 \gg k_{-4}$ and $k_5 \gg k_{-5}$). This assumption, as well as the postulate that step (5) be fast as compared to step (4), are necessary constraints for step (4) to be rate-determining. These constraints are generally necessary in cases where reactive intermediates are formed by dissociative adsorption, if only one dissociation product is taking part in the rate-determining step e.g., [see Refs. (*7–9*)]. These assumptions lead to the following relationships between the surface concentrations of $RO^-\cdot B$, $H^+\cdot B$, and $OH^-\cdot A$ and of the respective sites:

$$C_{RO^-\cdot B} = C_{H^+\cdot B}, \tag{7}$$

and

$$C_{OH^-\cdot A} \ll C_A + C_{ROH\cdot A}. \tag{8}$$

Under such conditions, the above-mentioned reaction scheme [Eqs. (2)–(6)] leads indeed to the pseudomonomolecular equation (1), if saturation of the A sites by the $ROH\cdot A$ species is assumed. An alternative reaction scheme proposed by Trambouze and coworkers (*4*, *5*), suggesting dissociation of one alcohol molecule on two different sites leads to Eq. (1) only with very restrictive assumptions, as shown by Beránek (*8*). It seems therefore very improbable.

An important proposal for Eq. (1) to be derived from Eqs. (2)–(6) is the assumption of the dissociation step (3) involving two equal basic sites B for the formation of the species $RO^-\cdot B$ and $H^+\cdot B$. This seems, however, unlikely from a chemical point of view. It must alternatively be postulated that dissociation of an alcohol molecule occurs on an acid–base pair-site A + B. The respective kinetic equations will be derived subsequently.

DERIVATION OF KINETIC EQUATIONS*

The following derivation of kinetic equations is based on suggestions of the molecular mechanism of the ether formation involving detectable intermediates of the reaction. It seems to be proved that a surface alkoxide species RO^- which is formed by dissociative adsorption of an alcohol molecule takes part in the bimolecular surface reaction (*10*). The second reaction partner is most probably a molecularly adsorbed alcohol molecule. It is known, furthermore, that the ether formation is a zero-order reaction at sufficiently high alcohol pressures and low conversions (*1–3*). The kinetic equations must therefore show this feature for the respective limiting conditions.

(1) *Four-parameter Equations*

Let us consider the following scheme to describe the reaction:

$$ROH + B \rightleftharpoons ROH\cdot B; \tag{9}$$

$$ROH + A + B \rightleftharpoons RO^-\cdot A + H^+B; \tag{10}$$

$$ROH\cdot B + RO^-\cdot A \overset{\text{slow}}{\rightleftharpoons} R_2O + OH^-\cdot A + B; \tag{11}$$

$$H^+\cdot B + OH^-\cdot A \overset{\text{fast}}{\rightleftharpoons} H_2O\cdot A + B \quad (\text{or } H_2O\cdot B + A). \tag{12}$$

The dissociation of an alcohol molecule is assumed to occur on an acid–base pair-site A + B [step (10)]. If molecular adsorption is suggested to take place on the B sites, the surface reaction (11) is assumed to be rate-determining (*10*, *12*, *13*), and the recombination of the elements of water [step (12)] is fast as compared to step (11) and both are irreversible ($k_{11} \gg k_{-11}$ and $k_{12} \gg k_{-12}$), equations analogous to (7) and (8) are valid ($C_{RO^-\cdot A} = C_{H^+\cdot B}$ and $C_{OH^-\cdot A} \ll C_A + C_{RO^-\cdot A}$).

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* The following terminology will be used throughout this paper:

Mechanistic model: A reaction scheme which can be interpreted as a possible molecular mechanism, the intermediate species and active sites of which can be observed directly or must be postulated on the grounds of experimental evidence.

Kinetic equation: A rate equation that is deduced for a given mechanistic model.

Kinetic model: A purely formal reaction scheme whose intermediates and active sites are not interpreted as any real chemical species.

Formal kinetic equation: A rate equation that is deduced for a given kinetic model.

Molecular and dissociative adsorption steps (9) and (10) compete for the B sites in this case. It is assumed for simplicity that the total number of A and B sites be equal. If the adsorption of molecular water occurs on the A sites

$$H_2O + A \rightleftharpoons H_2O{\cdot}A, \tag{13a}$$

the reaction rate r is given by

$$r = k_{11}\left(\frac{K_9P_{\mathrm{ROH}}}{1 + K_9P_{\mathrm{ROH}}}\right)\frac{[K_{10}P_{\mathrm{ROH}}(1 + K_9P_{\mathrm{ROH}})(1 + K_{13a}P_{\mathrm{H_2O}})]^{1/2}}{\{(K_{10}P_{\mathrm{ROH}})^{1/2} + [(1 + K_9P_{\mathrm{ROH}})(1 + K_{13a}P_{\mathrm{H_2O}})]^{1/2}\}^2}. \tag{14a}$$

Assuming the adsorption of water to occur on the B sites

$$H_2O + B \rightleftharpoons H_2O{\cdot}B, \tag{13b}$$

the reaction rate is

$$r = k_{11}\left(\frac{K_9P_{\mathrm{ROH}}}{1 + K_9P_{\mathrm{ROH}} + K_{13b}P_{\mathrm{H_2O}}}\right)\frac{[K_{10}P_{\mathrm{ROH}}(1 + K_9P_{\mathrm{ROH}} + K_{13b}P_{\mathrm{H_2O}})]^{1/2}}{[(1 + K_9P_{\mathrm{ROH}} + K_{13b}P_{\mathrm{H_2O}})^{1/2} + (K_{10}P_{\mathrm{ROH}})^{1/2}]^2}. \tag{14b}$$

Under the limiting conditions

$$K_{13a}P_{\mathrm{H_2O}} \quad \text{or} \quad K_{13b}P_{\mathrm{H_2O}} \ll 1;$$
$$K_9P_{\mathrm{ROH}} \gg 1,$$

which are experimentally realized for sufficiently high P_{ROH} and low conversions, both rate equations describe a zero-order reaction:

$$r = k_{11}\cdot\frac{(K_9\cdot K_{10})^{1/2}}{[(K_9)^{1/2} + (K_{10})^{1/2}]^2} = k'_{11}, \tag{14c}$$

as experimentally observed (*1–3*). The bimolecular rate equations (14a,b) are two examples out of a variety of possible four-parameter rate equations. Almost any experimental kinetic data will certainly be fitted to such equations; the results, however, have no physical meaning, since a discrimination between such rival models is usually not possible within the normal range of experimental errors.

(2) *Pseudomonomolecular Rate Equations*

It has been shown by Knözinger and Stolz (*10*) by means of poisoning experiments that the dissociative adsorption of alcohols which leads to the formation of alkoxide species $RO^-{\cdot}A$, only occurs on a small number of acid–base pair sites on the alumina surface. These pair sites involve strong Lewis acid sites A which were described on the basis of Peri's surface model (*11*) as triplet anion defects. These triplet vacancies are concentrated in the boundaries between regular surface domains according to Peri (*11*). The regular domains contain relatively basic oxygen ions (subsequently named B sites), whereas oxygen ions in the vicinity of the triplet vacancies should exhibit only lower basicity. They will be called B′ sites throughout. If this picture is adopted, the molecular adsorption of alcohol via H bonds occurs most probably on the B sites in the regular domains. Reaction between $RO^-{\cdot}A$ and $ROH{\cdot}B$ can therefore only proceed in the boundaries where A and B′ sites are located. It is assumed that the molecular species is only formed on B sites but not on B′ sites, because of the poorer H bond acceptor properties of the latter. The reaction scheme that describes this picture is as follows:

$$ROH + B \rightleftharpoons ROH{\cdot}B; \tag{15}$$

$$ROH + A + B' \rightleftharpoons RO^-{\cdot}A + H^+{\cdot}B'; \tag{16}$$

$$ROH{\cdot}B + RO^-{\cdot}A \overset{\text{slow}}{\rightleftharpoons} R_2O + OH^-{\cdot}A + B; \tag{17}$$

$$H^+{\cdot}B' + OH^-{\cdot}A \overset{\text{fast}}{\rightleftharpoons} H_2O{\cdot}A + B' \quad (\text{or } H_2O{\cdot}B' + A); \tag{18}$$

$$\left.\begin{array}{l} H_2O + A \rightleftharpoons H_2O{\cdot}A, \\ \text{or } H_2O + B' \rightleftharpoons H_2O{\cdot}B'; \end{array}\right\} \tag{19}$$

$$H_2O + B \rightleftharpoons H_2O{\cdot}B. \tag{20}$$

The following assumptions are made in the derivation of a kinetic equation:

(a) The adsorption steps (15), (16), (19), and (20) are at equilibrium;

(b) The surface reaction is irreversible (i.e., $k_{17} \gg k_{-17}$) and rate-determining;

(c) The recombination of the elements of water [step (19)] is irreversible ($k_{18} \gg k_{-18}$) and fast as compared to step (17). Consequently:

$$C_{H^+ \cdot B'} = C_{RO^- \cdot A},$$

and

$$C_{OH^- \cdot A} \ll C_{RO^- \cdot A} + C_A.$$

These relationships are necessary conditions for the adsorption equilibrium (16) to be undisturbed by the reaction;

(d) The total number of A and B sites is equal since they are pictured as acid–base pair-sites;

(e) Water is assumed to be adsorbed molecularly on the A or B′ sites in the boundaries [step (19)] and on the B sites in the regular domains [step (20)].

The reaction rate is then given by the five-parameter expression (21):

$$r = k_{17}\left(\frac{K_{15}P_{ROH}}{1 + K_{15}P_{ROH} + K_{20}P_{H_2O}}\right) \times \frac{(K_{16}P_{ROH})^{1/2}}{(1 + K_{19}P_{H_2O})^{1/2} + (K_{16} \cdot P_{ROH})^{1/2}}. \quad (21)$$

If the partial pressure of water is low (low conversions) so that

$$K_{20}P_{H_2O} \ll K_{15}P_{ROH},$$

and saturation of the B sites by the ROH·B species is assumed, Eq. (21) describes a pseudomonomolecular reaction. The resulting expression

$$r = k_{17} \cdot \frac{(K_{16} \cdot P_{ROH})^{1/2}}{(1 + K_{19}P_{H_2O})^{1/2} + (K_{16}P_{ROH})^{1/2}}, \quad (22)$$

however, differs from a type (1) equation. The zero-order range is described by Eq. (22) for sufficiently high P_{ROH} and low conversions.

The adsorption of water on the acid–base pair-sites can alternatively be described by a double-site adsorption representing a strongly polarized water molecule:

$$H^+ \cdot B' + OH^- \cdot A \rightleftharpoons H_2O \cdot (A - B'); \quad (19a)$$

$$H_2O + A + B' \rightleftharpoons H_2O(A - B'). \quad (23)$$

The respective rate equation in the pseudomonomolecular form is

$$r = k_{17} \cdot \frac{(K_{16}P_{ROH})^{1/2}}{2K_{23}P_{H_2O}} \times (\{4K_{23}P_{H_2O} + [1 + (K_{16}P_{ROH})^{1/2}]^2\}^{1/2} - [1 + (K_{16}P_{ROH})^{1/2}]), \quad (24)$$

which also reduces to a zero-order rate equation for sufficiently high alcohol pressures and low conversions.

Results of a Statistical Analysis of Kinetic Data

We have treated kinetic data of the ether formation from ethanol on η-alumina at temperatures between 174 and 193°C [the data were taken from Ref. (*1*)] by means of a nonlinear regression method (grid search method) (*7*). A series of 26 formal kinetic equations has been tested together with Eqs. (1), (22), and (24) using sets of experimental rate data with 30–77 individual values. The surface reaction was assumed to be rate determining in all models. This has previously been shown to be the case (*10, 12, 13*). The statistical analysis of the results using the criterion of Beale (*7, 14*) shows that the experimental data cannot be fitted satisfactorily by any of Eqs. (1), (22), or (24) which were derived in the previous section on the grounds of mechanistic models. Graphical inspection, which seemed to test the validity of Eq. (1) (*1–5*), is apparently not sufficient to discriminate between rival models. Even by means of the statistical analysis and despite the relatively large amount of experimental data there remain five indistinguishable and equally probable kinetic models. The necessary constraints with respect to the definition of a rate-determining step—especially in cases with formation of reactive intermediates by dissociation of the reactant—have certainly been applied in the derivation of the respective formal kinetic equations as described in the previous sections. The models are purely formal and the surface species are therefore not described by any real chemical species. The five models are characterized below:

(1) The reactant R is dissociatively adsorbed on sites L to form R′L and R″L. The R′L species react with each other and a free L site to form an adsorbed intermediate QL and a desorbed product P_r. QL recombines with R″L to a species S adsorbed on a double site L–L:

$$\mathrm{R + 2L \rightleftharpoons R'L + R''L,} \qquad (25)$$

$$\mathrm{R'L + R'L + L \overset{\text{slow}}{\rightleftharpoons} P_r + QL + 2L,} \qquad (26)$$

$$\mathrm{QL + R''L \overset{\text{fast}}{\rightleftharpoons} S(L\text{–}L),} \qquad (27)$$

$$\mathrm{S + 2L \rightleftharpoons S(L\text{–}L).} \qquad (28)$$

The resulting rate equation has the form

$$r = k_{26} \cdot \frac{K_{25} \cdot P_\mathrm{R}}{(4K_{28}P_\mathrm{S})^3} \times (\{[1 + (K_{25}P_\mathrm{R})^{1/2}]^2 + 8K_{28}P_\mathrm{S}\}^{1/2} - [1 + (K_{25}P_\mathrm{R})^{1/2}])^3. \qquad (29)$$

(2) Here steps (25) and (26) are valid. The adsorption of the second reaction product S, however, is assumed to be dissociative:

$$\mathrm{QL + R''L + R''L \overset{\text{fast}}{\rightleftharpoons} S'{\cdot}L + S''{\cdot}L,} \qquad (27a)$$

$$\mathrm{S + 2L \rightleftharpoons S'L + S''L;} \qquad (30)$$

$$r = k_{26} \cdot \frac{K_{25}P_\mathrm{R}}{[1 + (K_{25}P_\mathrm{R})^{1/2} + (K_{30}P_\mathrm{S})^{1/2}]^3}. \qquad (31)$$

(3) The reactant R is adsorbed on a site L; the rate-determining step involves reaction of two R·L species and a free site of type M, on which one of the reaction products P_r and Q is adsorbed:

$$\mathrm{R + L \rightleftharpoons RL,} \qquad (32)$$

$$\mathrm{RL + RL + M \overset{\text{slow}}{\rightleftharpoons} P_r + 2L + QM,} \qquad (33)$$

$$\mathrm{QM \rightleftharpoons Q + M.} \qquad (34)$$

The rate equation for this Langmuir–Hinshelwood type reaction is:

$$r = k_{33} \frac{(K_{32} \cdot P_\mathrm{R})^2}{(1 + K_{32}P_\mathrm{R})^2(1 + K_{34}P_\mathrm{Q})}. \qquad (35)$$

(4) An analogous equation describes the Eley–Rideal type reaction where one molecule R reacts from the gas phase with an adsorbed species R·L:

$$\mathrm{RL + R + M + L \rightleftharpoons P_r + 2L + QM;} \qquad (36)$$

and

$$r = k_{36} \cdot \frac{K_{32}P_\mathrm{R} \cdot P_\mathrm{R}}{(1 + K_{32}P_\mathrm{R})^2(1 + K_{34}P_\mathrm{Q})}. \qquad (37)$$

(5) Here dissociative adsorption of the reactant R on two different sites L and M is suggested; the surface reaction occurs between two equal surface species R′L and a free site M to form an adsorbed intermediate QL and a product P_r in the gas phase:

$$\mathrm{R + L + M \rightleftharpoons R'L + R''M,} \qquad (38)$$

$$\mathrm{R'L + R'L + M \overset{\text{slow}}{\rightleftharpoons} P_r + QL + M,} \qquad (39)$$

$$\mathrm{QL + R''M \overset{\text{fast}}{\rightleftharpoons} SM + L,} \qquad (40)$$

$$\mathrm{SM \rightleftharpoons S + M.} \qquad (41)$$

The rate equation resulting from this scheme with steps (39) and (40) being irreversible is:

$$r = k_{39} \cdot \frac{K_{38}P_\mathrm{R}(1 + K_{41}P_\mathrm{S})}{\{1 + K_{41}P_\mathrm{S} + [K_{38}P_\mathrm{R}(1 + K_{41}P_\mathrm{S})]^{1/2}\}^3}. \qquad (42)$$

CONCLUSIONS

These five kinetic models applied to ether formation from ethanol on η-alumina could not be distinguished from each other by the statistical analysis though they describe significantly different elementary adsorption and reaction steps. It is interesting to mention that the statistical mean error as calculated from the least-squares sums is identical with the mean experimental error as given by the uncertainty of all the factors determining the accuracy of the experimental reaction rate. Furthermore, the temperature dependence of the rate constants leads to reasonable activation energies for all of the five models. Within the error limits the calculated activation energies compare quite well with the directly determined value of 25–26 kcal/mol.

Similarly, physically reasonable heats of adsorption can be estimated from the temperature dependence of the adsorption coefficients K as calculated for the five models.

The rate data of the ether formation from ethanol cannot be unequivocally described by rate equations which are based on suggestions of a molecular mechanism. The most realistic (four-parameter) rate equations for different chemically meaningful mechanistic models are too similar from a mathematical point of view, so that a discrimination between them is not possible within the normal range of experimental error. It should be mentioned that even the four-parameter equations probably describe oversimplified models which do not take into consideration surface heterogeneity and possible interconversions of surface sites. Since one of the products of the reaction is water, and the elements of water are also elements of the surface layer of the oxide catalysts, interconversions of sites may well occur during the reaction. Furthermore, various forms of adsorbed and inhibiting water might be taken into account. Though possibly more realistic than the presently applied mechanistic models, the respective rate equations would become much more complex and thus intractable.

A further complication arises with the four-parameter equations (14a,b) insofar as certain geometric requirements with respect to the distribution of $ROH \cdot B$ and $RO^- \cdot A$ species have tacitly been adopted in the derivation. A regular two-dimensional lattice built up by A and B sites might be assumed as a model for the catalyst surface, so that each A site is four-coordinated by B sites and vice-versa. Thus, arrangements of $ROH \cdot B$ and $RO^- \cdot A$ species are possible which allow reaction between them. Since, however, adsorption and reaction are statistical processes the necessary molecular arrangements will only be formed with a certain probability less than unity and are by no means realized for any pair of reactive surface species $ROH \cdot B$ and $RO^- \cdot A$. This restriction is only removed if at least one of the reaction partners is free to move on the surface as already stated by Beránek (*8*) with respect to other kinetic models.

At least for the ether formation on alumina (and probably also on other oxide catalysts), it therefore seems unrealistic to use kinetic analysis for the elucidation of the molecular mechanism of the reaction. The only possible result is a purely formal description of the reaction rate as a function of the partial pressures of alcohol, ether, and water. We have decided therefore not to try a mechanistic interpretation of the five rate equations which describe the experimental data equally well.

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