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LETTERS TO THE EDITORS

Kinetic Studies on the Mechanism of Catalytic Ethene Oxidation

A recent comprehensive study of the mechanism of catalytic ethene oxidation was reported by Haul and Neubauer (*1*). Experimental measurements were evaluated by means of the Horiuti–Temkin procedure (*2*). Theoretical studies that we have made more recently (*3, 4*) present an improved method for evaluating possible reaction mechanisms that we believe could be applied advantageously here. A monograph by Happel (*5*) also discusses these concepts in the context of kinetic modeling using isotopic tracer techniques.

The relation given as Eq. (3) by Haul and Neubauer is used to establish possible reaction routes:

$$P = S + W - I,$$

where P, S, W, and I are the number of routes, elementary steps, balance equations, and surface intermediates, respectively (*2*). Thus P steady-state mechanisms can be chosen as a basis in terms of which all other mechanisms can be uniquely expressed. This gives a unique way to symbolize each steady-state mechanism and its overall reaction, but it does not provide a classification system for them that is valid from a chemical viewpoint, because the choice of a basis is arbitrary. In a chemical system there is a unique collection of mechanisms, called the "direct mechanisms" of the system, that can be shown to be the fundamental constituents of any mechanism, as discussed in our articles (*3, 4*).

A recent Russian publication also includes a comparison between our method and that of Temkin (Ostrovskii *et al.* (*6*)). This study is by investigators at the Karpov Institute with which Temkin is also associated. The authors suggest that in the study of heterogeneous catalytic reactions it may be advisable to form all direct mechanisms following our procedure and then to compare each of the direct mechanisms with experimental data on the kinetics of the reaction under consideration. They have written a computer program for the purpose of forming the direct mechanisms. We have also used computer programs for this purpose (*7*).

A comparison between our approach and that of Haul and Neubauer can be illustrated by a table similar to that given in their paper. The following table uses the same choice of elementary steps and numeration as theirs. m_1, m_2, and m_3 refer to the possible direct mechanisms obtained by our procedure without any a priori assumptions about the relative importance of individual mechanistic steps. ρ and σ are arbitrary degrees of advancement of the two overall reactions expressed by Haul and Neubauer's Eqs. (1) and (2). Other combinations of two independent overall reactions could be employed to obtain the same mechanisms:

Reaction step		1	2	3	4	5	5′	6	7	8	9	9′
m_1	ρ	0	0	0	1	−1	−1	0	0	1	1	1
	σ	0	0	0	0	0	0	0	0	1	1	1
m_2	ρ	$\frac{1}{2}$	$\frac{1}{2}$	1	1	0	0	0	0	0	0	0
	σ	$\frac{1}{2}$	$\frac{1}{2}$	1	0	1	1	0	0	0	0	0
m_3	ρ	$\frac{1}{2}$	$\frac{1}{2}$	1	1	0	0	0	0	0	0	0
	σ	0	0	0	0	0	0	0	0	1	1	1

Thus there are three direct mechanisms for consideration. If 5′ is assumed to be so rapid that it cannot proceed in the reverse direction, as assumed by Haul and Neubauer, then we are left with mechanisms m_2 and m_3. Their table is similar to ours but

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contains routes instead of mechanisms. The symbol "x" which appears in their table is not defined or explained, but by comparison with the table above "x" is identified as the fractional participation of m_3 of the total conversion. In agreement with Ostrovskii *et al.* we believe that it may be useful to first compare each of the direct mechanisms with experimental data on the kinetics. If neither m_2 or m_3 describes the experimental data, then it may be possible to combine them to determine whether better agreement can be obtained.

However, this is not what was done in Haul and Neubauer's treatment. Instead, it was assumed at the outset that a unique set of kinetic relationships can be obtained without the establishment of the extent to which each mechanism occurs. In fact, it does not appear that they computed the relative extent of these mechanisms. Either mechanism m_2 or m_3 could possibly model any selectivity obtained experimentally, but unless the extent to which each occurs is considered, it is not possible to draw conclusions about the relative importance of steps that are embedded in them, as they have done.

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