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The Determination of the Stoichiometric Number of the Oxidation of Sulfur Dioxide

By HIDEO ODANAKA
Utsunomiya University, Utsunomiya, Japan

The stoichiometric number of the rate-determining step of the catalyzed oxidation of SO_2

$$2SO_2 + O_2 = 2SO_3 \qquad (1)$$

in the presence of a Pt catalyst has been determined at 424°, 430°, and 440°C by following the reaction up to equilibrium by observing β-ray count of S^{35} in SO_2 and SO_3 and their partial pressures, and by determining the equilibrium constant.

The stoichiometric number, $\nu(r)$, was found to be 2. It follows from this finding that the rate-determining step is one of last two steps of the sequence:

$$O_2 \longrightarrow 2O(a) \qquad (1)$$
$$SO_2 \longrightarrow SO_2(a) \qquad (ii)$$
$$O(a) + SO_2(a) \rightarrow SO_3 \qquad (iii)$$

provided that the reaction follows the sequence at all.

The present finding is in agreement with, on the one hand, the $\nu(r)$ value derived from the data of Reiter incorporated with that of Knietsch at 600°C in equilibrium, and with, on the other hand, the conclusion arrived at previously by Boreskov.

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Role of Excited Particles in Branched Chain Reactions

N. N. S'YEM'YONOV AND A. E. SHEELOV
Institute of Chemical Physics of the Academy of Sciences of USSR

A mechanism of branching in chain reactions is proposed, including chemical reactions of excited molecules—the products of exothermal elementary chain evolution processes. To achieve branching, the excitation energy of oscillatory—and, at times, of rotational—type is required. Development of branches is most likely to take place when the excitation energy exceeds the dissociation energy of the weakest bond of the molecule being formed. Here, formation of wholly-branched chains may be anticipated as a result of monomolecular decomposition of the excited molecules. For example, interaction of fluorine molecules with certain compounds apparently occurs by this mechanism.

In some cases, bimolecular branching is also possible due to interaction of excited particles R′X* with molecules YR″, which are initially present in the reaction mixture. This reaction scheme is described by the following equation:

$$R'X^* + YR'' \rightarrow R'\cdot + XY + R''\cdot$$

Some of the known cases of branching reactions are explained in terms of the mechanism proposed. The latter constitutes a generalized treatment of the concepts in the field of branched chain reactions, including both the "material" and the "energy" aspects of these reactions.

The authors believe that the proposed mechanism represents the most advanced generalization in the field of branched chain reactions.