

LETTER TO THE EDITORS

On The Mechanism for Water Formation on Pt

The reaction of hydrogen and oxygen to form H_2O on Pt would appear to be one of the simplest catalytic reactions; however, as the recent literature illustrates, conventional models for this reaction seem inadequate. The advent of new experimental and theoretical tools has given us the power to examine such reactions on something approaching an atomic level and, at the same time, to control variables to a much higher degree than was possible previously. In this paper we emphasize a new model for the H_2O reaction on Pt developed on the basis of such tools and show that it may succeed where the previous models have not.

Two mechanisms have been widely considered (1-3) for the formation of water by the reaction of hydrogen and oxygen on Pt. They are in their simplest forms (i) the Eley-Rideal mechanism, in which the H_2 molecules incident from the gas phase react *directly* with adsorbed O atoms, and (ii) the Langmuir-Hinshelwood mechanism, in which the reaction is between adsorbed H and O atoms. The recent calculations of Weinberg and Merrill (2) support the former, whereas, the recent experiments of Pacia and Dumesic (3) have been interpreted to support the latter.

We would like to point out that Collins, Lee, and Spicer have proposed a third model (4) in which hydrogen in a precursor state, perhaps molecular in nature, reacts with adsorbed O atoms. It was necessary for Collins *et al.* (4) to develop their model in order to explain the high probability of reaction found (at room temperature) for

H_2 with O adsorbed on highly (111) oriented polycrystalline Pt foils. The reaction probability (defined as the number of adsorbed O atoms removed per incident H_2 molecule) was found to be on the order of unity and was independent of O coverage over the entire range of coverages studied (approximately 0.05 to 0.25 monolayers).

Note that: (i) the probability of a H_2 molecule directly encountering and reacting with an adsorbed O atom from the gas phase (the simplest form of the Eley-Rideal mechanism) is roughly proportional to the O coverage and therefore this mechanism is neither consistent with the near unity reaction probability nor the coverage independence of the reaction probability observed by Collins *et al.*; (ii) the sticking probability for dissociative hydrogen chemisorption (5) is lower than the reaction probabilities measured by Collins *et al.*, suggesting that a precursor state for hydrogen may be important rather than a simple Langmuir-Hinshelwood model involving atomically adsorbed H; and (iii) the present model only requires that an adsorbed hydrogen species have a "dwell" time of about 10^{-12} sec on the surface at room temperature, provided that it moves with thermal velocity and reacts with the first O atom which it encounters. Theoretical evidence for such weakly bound chemical and physical adsorption states for H_2 molecules on Pt has been given by Weinberg and Merrill (6).

Further, it should be noted that it was the problem of H_2 dissociation which ruled in favor of the Eley-Rideal mechanism in

the calculations of Weinberg and Merrill. Since dissociation is not necessary in the present model, it is consistent with their calculations.

It is more difficult to comment on the measurements and conclusions of Pacia and Dumesic because of the complexity of their experiment. (It covered a wide temperature range from ~ 300 to 1700 K, and involved simultaneous exposure to O_2 and H_2 .) This makes it difficult to be sure of the uniqueness of any model over the whole range of variables studied. However, one can conclude with surety that the explanations of their measurements require reaction of hydrogen and oxygen both of which are adsorbed on the Pt. It should be noted that the experiments of Collins *et al.* were performed at room temperature and that Pacia and Dumesic connect their work with the more straight forward experiments of Norton (?) carried out on polycrystalline Pt foils at 273 K and below. In a more detailed kinetic analysis than that of Collins *et al.*, Norton found the reduction of oxygen to follow a rate law of the form

$$\frac{d\theta_o}{dt} = \alpha\theta_o(1 - \theta_o),$$

where θ_o is the oxygen coverage normalized to unity at saturation coverage. This is consistent with the model of Collins *et al.* Pacia and Dumesic (3) indicate that this is consistent with a "pseudo-atomic" state for hydrogen or, as we would argue, a precursor state which may be molecular in nature. Pacia and Dumesic further argue that the work of Norton complements their work in that a "pseudo-atomic" state may play the important role below room temperature while an atomic adsorption state is important at higher temperature. In regard to this we raise the question as to whether

the experimental results of Pacia and Dumesic uniquely require the assumption that adsorbed H atoms react with the adsorbed O atoms or whether adsorbed H_2 molecules could explain the data over all or part of the temperature range studied, and thus we raise the possibility that these measurements also may be consistent with the present model.

The importance of this discussion transcends the water reaction on Pt. The general importance of the present model is that it emphasizes the importance of the transient adsorption state (the hydrogen momentarily adsorbed on Pt) which may be critical in certain catalytic reactions. As the reliance (in the literature) on the simplest forms of the Eley-Rideal and Langmuir-Hinshelwood mechanisms illustrates, there presently may be too much of a tendency to ignore the possibility of such adsorption states in catalytic reactions.

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REFERENCES

1. See, for example, References 2 and 3 and papers cited therein.
2. Weinberg, W. H., and Merrill, R. P., *J. Catal.* **40**, 268 (1975).
3. Pacia, N., and Dumesic, J. A., *J. Catal.* **41**, 155 (1976).
4. Collins, D. M., Lee, J. B., and Spicer, W. E., *Phys. Rev. Lett.* **35**, 592 (1975); Collins, D. M., Lee, J. B., and Spicer, W. E., *J. Vac. Sci. Technol.* **13**, 266 (1976).
5. Procop, M., and Völter, J., *Surface Sci.* **33**, 69 (1972); Lu, K. E., and Rye, R. R., *Surface Sci.* **45**, 677 (1974).
6. Weinberg, W. H., and Merrill, R. P., *Surface Sci.* **33**, 493 (1972).
7. Norton, P. R., *J. Catal.* **36**, 211 (1975).