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LETTER TO THE EDITORS

Volcano Plots and Cyclohexane Dehydrogenation

It has recently been suggested that a volcano relationship exists for the catalytic dehydrogenation of cyclohexane on oxides (*1*). The purpose of this letter is to suggest that the relationship suggested between activity and heat of formation is less valid than that originally proposed (*2*) between activity and *d* character (or position in the periodic table). Moreover, it is also questionable whether a thermodynamic function can be used for this reaction for the reasons discussed below.

Figure 1 compares the periodic trends of the catalytic dehydrogenation of cyclohexane on oxides plotted both as a function of actual rate constants and in rank order of rate constants as suggested by Wagh (*1*). Clearly there is a strong volcano correlation in both cases, as originally discussed by Richardson and Rossington (*2*). Now in Fig. 2 the plot is made in a similar manner but using heat of formation as Wagh proposed (*1*) rather than periodic position. Equally clearly there is little if any correlation between the two parameters; all that can be clearly stated is that the most stable oxides are inactive. These are the same oxides that are normally used

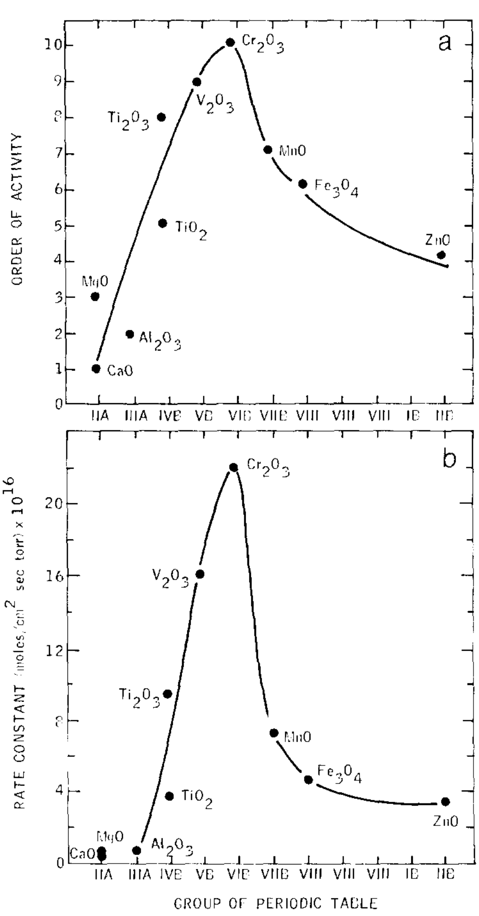

FIG. 1. Activity for the dehydrogenation of cyclohexane plotted as (a) order of activity and (b) rate constant versus position in the periodic table.

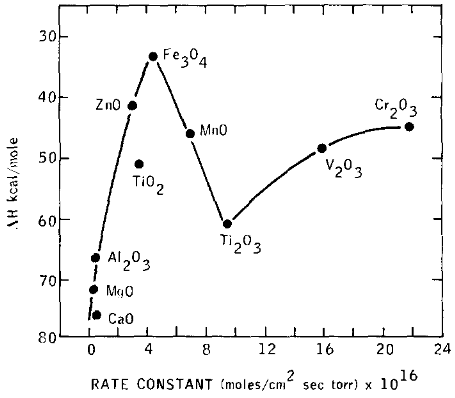

FIG. 2. Rate constant versus enthalpy of formation of the oxide.

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as catalyst supports for other reactions because of their chemical stability. The lack of any volcano behavior is emphasized by an inspection of the sesquioxides, which all have the corundum structure, where the activity increases almost linearly with decreasing ΔH.

The dehydrogenation of cyclohexane was performed in an oxygen-free flow of the nitrogen/cyclohexane feed (*2*) at 400–465°C. Therefore, the oxide could not be in thermodynamic equilibrium with its environment, otherwise it would have been reduced to a lower oxide and eventually to the metal. In such circumstances it is not appropriate to use a thermodynamic function, namely, the heat of formation, for the correlation. The use of ΔH implies that the energy of the metal–oxygen bond is important; if this bond were broken as an intermediate step in the reaction it is unlikely that it would be remade in the absence of an equilibrium oxygen environment. It is thus suggested that the activity of the oxides for this reaction is a function of their position in the periodic table and, therefore, probably of their *d* electron configuration, as originally proposed (*2*), and not of their heat of formation. Such periodic trends have been reviewed recently by Sinfelt (*3*) for a variety of reactions.

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