Some Considerations about the Selection of Kinetic Parameters in Order to Compare the Activity of Catalysts

Richardson and Rossington (1) studied the dehydrogenation of cyclohexane in an oxygen-free stream of nitrogen/cyclohexane as feed over a number of oxide catalysts in the temperature range 400 to 465°C. They showed that the reaction is first order with regard to cyclohexane pressure. The authors calculated the rate constants at 450°C and compared them with the $3d$ electron configuration of the metal ion (or position in the periodic table). They obtained the activity pattern shown in Fig. 1. Accordingly, they concluded that low activity is associated with the more stable d^0, d^5, and d^{10} configurations, while oxides with the $3d^1$, $3d^2$, and $3d^3$ configurations are progressively more active. The results were interpreted in terms of the application of crystal field theory to the formation of surface complexes, following Dowden and Wells (2).

Wagh (3) later ordered Richardson and Rossington's catalytic activity data by giving to each catalyst a correlative number that represents the order of increasing of the rate constants. These data were plotted against $-\Delta H_e$ (equivalent standard heat of formation of the oxides at 25°C), and a volcano relationship was obtained. Wagh (3) then reinterpreted the results of Richardson and Rossington (1) by considering that the catalytic activity of metal oxides toward the dehydrogenation of cyclohexane is connected with the magnitude of the M–O bond energy: Activity increases with increasing bond energy on

one arm of the volcano-shaped curve, whereas the opposite is true for the other arm.

Whittingham (4) has recently criticized Wagh's conclusions (3). It is shown in Ref. (4) that if we use the actual rate constants at 450°C reported by Richardson and Rossington (1), instead of the rank order of rate constants suggested by Wagh, there is little if any correlation between catalytic activity and ΔH_e, as Fig. 2 shows. Thus Whittingham (4) suggests that the activity of the oxides for the dehydrogenation of cyclohexane is a function of their position in the periodic table and, therefore, probably of their d electron configuration, as originally proposed by Richardson and Rossington (1).

The purpose of this Letter is to show that the rate constant at a single temperature, arbitrarily selected within the temperature range at which the kinetic data have been obtained, is not a proper parameter for representing catalytic activity patterns in order to draw conclusions about the reaction mechanism.

To prove the above statement we have calculated the values of the rate constants of dehydrogenation of cyclohexane on metal oxides at 400°C from the data of activation energy and rate constants at 450°C reported by Richardson and Rossington (1). The values obtained are plotted in Figs. 1 and 2b as a function of the periodic table position and the heat of formation of the oxides, respectively. We
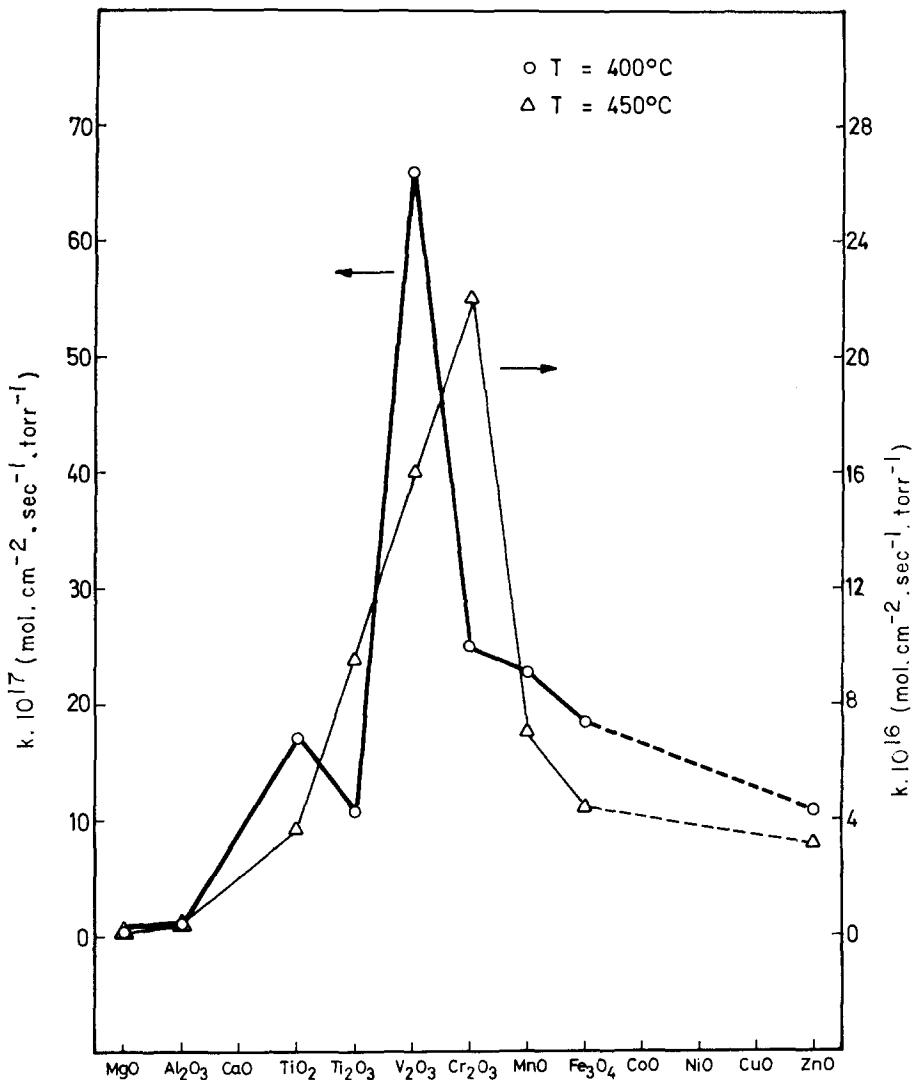
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Fig. 1. Activity of oxides in cyclohexane dehydrogenation at 400 and 450°C as a function of position in the periodic table [after Richardson and Rossington (*1*)].

can see that the plots are quite different from those ones obtained from the rate constants at 450°C. Moreover, whereas the most active catalyst at 450°C (Cr_2O_3) has a $3d^3$ configuration in agreement with what ligand field theory predicts (*3*), the most active catalyst at 400°C (V_2O_3) has a $3d^2$ configuration. At this lower temperature Cr_2O_3 with a $3d^3$ metal ion configuration shows a very poor catalytic activity indeed. This is true in spite of no change

in the reaction kinetics taking place in the temperature range 400 to 465°C.

Similar objection can be made to a large number of correlations found in the literature between various thermodynamic parameters of oxides and their catalytic activities. For instance, Roiter *et al.* (*5*) have correlated the values of the reaction rate of propene oxidation at 300°C, previously reported by Moro-oka and Ozaki (*6*), with the *enthalpy of change of stoi-*
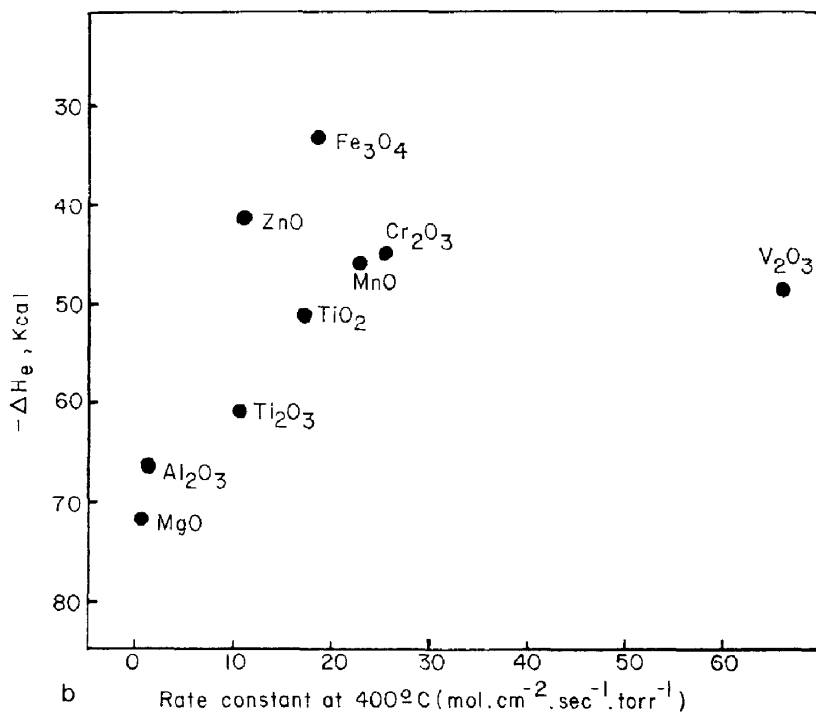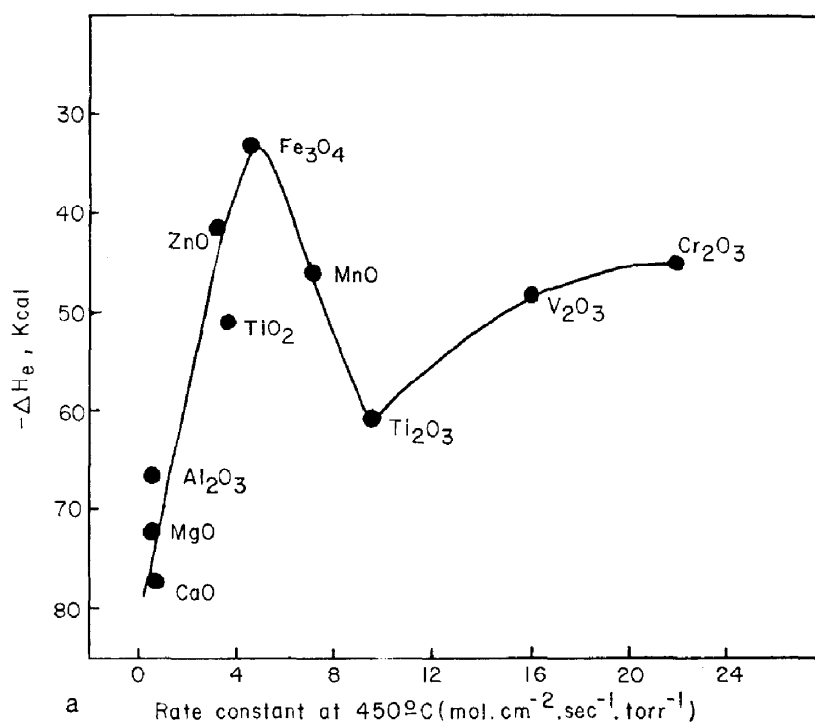
FIG. 2. Rate constant of cyclohexane dehydrogenation versus enthalpy of formation of the oxide. (a) Rate constant at 450°C; (b) at 400°C.
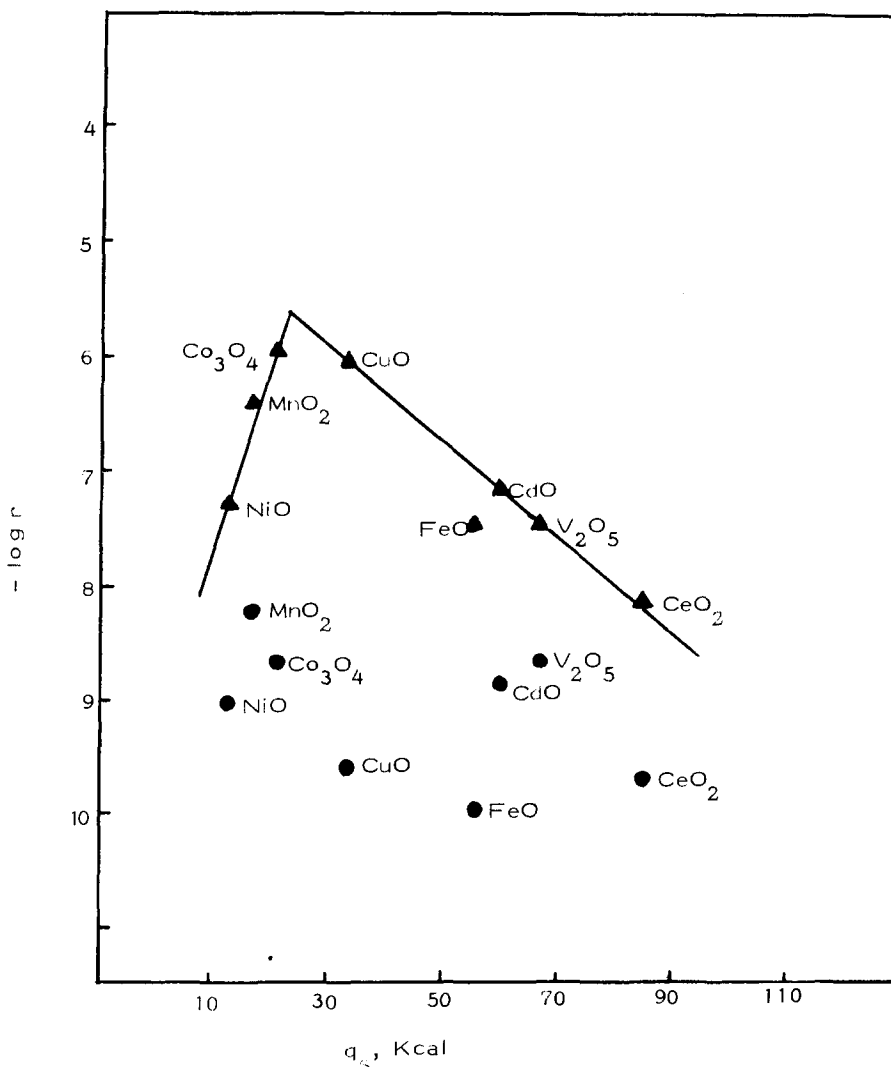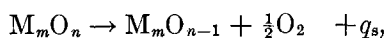
FIG. 3. Logarithm of rate constant of propene oxidation against energy of change of stoichiometry without change of phase of the oxide, q_s. ▲, rate constant at 450°C; ●, rate constant at 400°C.

chiometry *without change of phase*, q_s, corresponding to the reaction:

$$M_mO_n \rightarrow M_mO_{n-1} + \tfrac{1}{2}O_2 \quad +q_s,$$

and they have obtained the volcano-shaped curve that Fig. 3 shows. On the other hand, if we calculate the reaction rate at 200°C from the kinetic parameters reported by Moro-oka and Ozaki (*6*), no correlation is found, as Fig. 3 also shows. Again, no change of the reaction kinetics takes place between 200 and 300°C (*6*).

These considerations show rather clearly that it is very dangerous to draw conclusions with regard to the mechanism of catalytic reactions from rate constant (or reaction rate) trends obtained at a single temperature.

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