REDUCTION OF ALKENES BY HYDROGEN TRANSFER OVER A Pd/SEPIOLITE CATALYST. COMPENSATION EFFECT

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This paper shows the occurrence of a linear relationship between the activation energy ($E_A$) and the logarithm of the pre-exponential factor ($\ln A$) in the Arrhenius equation, and between the enthalpy increment ($\Delta H^*$) and the entropy increment ($\Delta S^*$) in the Eyring equation for the reduction of olefinic double bonds by hydrogen transfer over a Pd/sepiolite catalyst. Such a relationship is known as the "compensation effect" or "isokinetic relationship".

INTRODUCTION

The isokinetic relationship or compensation effect is a kinetic data correlation frequently reported in the literature [1-5], expressed mathematically by the following equation [1]:

$\Delta H^* = E_A - RT \ln A$

$\Delta S^* = R \ln \frac{A}{RT}$

where $E_A$, $R$, $T$, $A$, $\Delta H^*$, and $\Delta S^*$ have their usual meanings.
\[ \ln A = \ln \alpha + \left( \frac{E_A}{R\theta} \right) \]  \hspace{1cm} (1)

where \( R \) is the universal gas constant and \( \theta \) the isokinetic temperature at which identical values of the reaction rate constant \( k \) are obtained \( (k = \alpha) \). By plotting \( \ln A \) against \( E_A \), \( \alpha \) and \( \theta \) can be readily determined from the slope and intercept, respectively, of the resulting straight line.

An alternative equation for calculation of the isokinetic temperature, also considered to be the vibrational temperature of the reaction center (or core) of the adsorption complex, is

\[ \Delta G^* = -\theta R \ln k^* = \Delta H^* - \theta \Delta S^* \]  \hspace{1cm} (2)

By plotting \( \Delta S^* \) (the entropy of activation) as a function of \( \Delta H^* \) (enthalpy of the activated complex) one can calculate \( \theta \), \( \Delta G^* \) and \( k^* \) (equilibrium constant of the activated complex) from the slope and intercept of the straight line obtained.

According to Cremer, the compensation effect reflects the influence of the temperature on the distribution of active sites [6]. On the other hand, Sosnovski attributes this phenomenon to the occurrence of two types of active sites with different activation energies. Temperature changes the relative proportion of these sites, thereby compensating for the change in the average measured activation energy [7].

Galwey [4] reviewed the potential causes of the compensation effect and concluded that the most frequently used explanations were some type of surface heterogeneity and the occurrence of two or more concomitant reactions.

Catalytic hydrogenations by hydrogen transfer with different donors [8, 13] have been widely used in organic synthesis in the last few years, so much so that they have become a major alternative to conventional catalytic hydrogenations with gaseous hydrogen in some cases.

In this work we investigated the potential occurrence of a compensating effect in the reduction of variously substituted