

Investigations of Surface Reactions by Kinetic Isotope Effects

Raziskave reakcij na površinah s študijem kinetičnih izotopskih efektov

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The kinetic isotope effect is the phenomenon that in a chemical reaction in which two isotopic species of the same reacting molecule are involved, the rate constants of these two isotopic reactions differ, the value for the isotopically heavier reaction generally being smaller. Kinetic isotope effects can be obtained experimentally by analysing isotopic ratios in either the reactants or products at a given extent of the reaction. Applying Bigeleisen's formalism within the framework of absolute rate theory, kinetic isotope effects can be calculated if the geometry and force field of the transition state in the rate determining step of the reaction mechanism is postulated on the basis of chemical intuition and data are available on the chemical kinetics and the reaction mechanism. In this contribution, investigations of the kinetic isotope effects in the reduction of carbon monoxide and dioxide over Mg, and in its catalytic oxidation with oxygen over Pd, NiO and ZnO are presented. The results obtained give additional information about the reaction mechanisms of these reactions.

Key words: kinetic isotope effects, CO, Mg, Pd, NiO, ZnO

Izotopski efekt imenujemo pojav, da se konstanti hitrosti dveh izotopskih reakcij razlikujeta. V večini primerov poteka izotopsko težja reakcija počasneje. Kinetične izotopske efekte eksperimentalno določimo z izotopsko analizo bodisi preostalega reaktanta ali nastalega produkta reakcije. Če predpostavimo geometrijo in konstante sile aktiviranega kompleksa najpočasnejše stopnje v reakcijskem mehanizmu, lahko po metodologiji Bigeleisena, ki je osnovana na teoriji absolutnih reakcijskih hitrosti, izračunamo kinetične izotopske efekte. Če se eksperimentalne in teoretično izračunane vrednosti ujemajo, razumemo, da je bila predpostavka za aktivirani kompleks prava. V tem prispevku podajamo rezultate raziskav kinetičnih izotopskih efektov v redukcijo ogljikovega monoksida in dioksida na magneziju in v katalitični oksidaciji s kisikom na Pd, NiO in ZnO. Rezultati dajejo dodatne informacije o mehanizmih teh reakcij.

Ključne besede: kinetični izotopski efekti, CO, Mg, Pd, NiO, ZnO

1 Introduction

According to Bigeleisen^{1,2}, based on the Absolute Rate Theory of chemical reactions³, kinetic isotope effects, i.e. the ratio of the rate constants of two simultaneously running isotopic reactions, may be calculated applying the following equations:

$$\frac{k_1}{k_2} = \frac{v_{L1}^\ddagger}{v_{L2}^\ddagger} \prod_{i=1}^{3n-6} \frac{u_{2i} \sinh(u_{1i}/2)}{u_{1i} \sinh(u_{2i}/2)} \prod_{i=1}^{3n-7} \frac{u_{1i}^\ddagger \sinh(u_{2i}^\ddagger/2)}{u_{2i}^\ddagger \sinh(u_{1i}^\ddagger/2)}$$

$$\frac{v_{L1}^\ddagger}{v_{L2}^\ddagger} = \left(\frac{|G_1^\ddagger|}{|G_2^\ddagger|} \right)^{1/2} \prod_{i=1}^{3n-7} \frac{v_{2i}^\ddagger}{v_{1i}^\ddagger} \quad (1)$$

The meaning of the symbols is as follows: 1, 2 refer to the lighter and heavier isotope, respectively; \ddagger denotes the transition state of the rate determining step of the reaction mechanism; n , n^\ddagger - number of atoms in reactant molecule and transition state, respectively; T - temperature; k_b - Boltzmann's constant; h - Planck's constant; v - frequency; $u = hv/k_b T$; v_L - reaction-coordinate frequency.

The frequencies of the reactant molecules are usually taken from the literature, while those for the transition state are obtained by solving Wilson's matrix equation⁴:

$$GFL = LA$$

in which G is the Wilson's matrix comprising geometric parameters; F is the force constants matrix; L is the eigenvector matrix; A is a diagonal matrix of eigenvalues $\lambda_i = 4\pi^2 v_i^2$ with v_i equal to the frequency of the i th normal vibration.

For the transition state the above equation is to be solved under the condition⁵:

$$|F| = 0$$

in order to obtain for a $3n^\ddagger$ non-linear transition state $3n^\ddagger - 7$ real frequencies, the remaining frequency (referring to the reaction coordinate) being zero or imaginary (mainly the first case is used). When an agreement of the calculated kinetic isotope effects with the experimental values is achieved, the proposed transition state is accepted.

In our laboratory, kinetic isotope effects of carbon and oxygen in the reduction of CO and CO₂ over Mg, and in catalytic oxidation of CO over Pd, NiO and ZnO were investigated with the aim of obtaining additional understanding of the reaction mechanisms of these reactions. The experiments were carried out under steady state conditions in a reaction vessel connected to a vacuum system⁶. The reaction, run at a selected temperature, was stopped at the desired extent of reaction. The kinetic isotope effects were obtained from the extent of reaction, and the isotope enrichment factors⁶ measured by a mass

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spectrometer for the stable isotopes C-13, O-18, and by an ionisation chamber for C-14 in the residual reactant or the product formed. Due to isotopic exchange on the surface, we were not always able to determine oxygen effects experimentally. For the slowest step of the mechanism of the reactions studied, several geometries of the transition state, guessed by the chemical intuition and on the basis of information available for the reaction system, were considered in Wilson's analysis. In all the cases presented here the reactant molecule is CO for which the isotopic frequencies were taken from the literature⁷. Kinetic isotope effects (k_{12}/k_{13} , k_{12}/k_{14} , k_{16}/k_{18} , k being the rate constants) were calculated using Bigeleisen's equation as written above⁸ and an agreement with the experimental data was sought⁹.

2 Discussion

A. Reduction of CO over Mg¹⁰

Carbon kinetic isotope effects determined in the temperature range of 723-823 K were found to be practically temperature independent and amounted to 1.017 ± 0.001 and 1.035 ± 0.002 for C-13 (k_{12}/k_{13}) and C-14 (k_{12}/k_{14}), respectively. For the slowest step of the reaction mechanism the reaction of adsorbed CO with either one or two surface Mg atoms was assumed. Thus for the transition state different geometries of C-O-Mg and C-O-Mg₂ were taken into account. The first proposal may give effects close to the experimental ones but is not able to reproduce their temperature independence. For the second proposal different bond lengths and interbond angles were tried. The best agreement with experiment was found with the transition state shown in **Figure 1**.

These results confirm that in CO reduction over a Mg surface, one adsorbed CO molecule reacts with two metal surface atoms, and that among all the adsorbed CO molecules only those being adsorbed via the O atom to the surface at the moment of reaction are reactive.

B. Reduction of CO₂ over Mg¹¹

For this reaction the kinetic isotope effects determined in the temperature range of 773-873 K are: $k_{12}/k_{13} = 1.078 - 7.15 \times T \times 10^{-5}$ ($\pm 2.2 \times 10^{-3}$), $k_{12}/k_{14} = 1.156 - 1.42 \times T \times 10^{-5}$ ($\pm 3.2 \times 10^{-3}$), and $k_{16}/k_{18} = 0.909 + 1.12 \times T \times 10^{-4}$ ($\pm 3.6 \times 10^{-3}$).

In the slowest step of the reaction mechanism, the attachment of a CO₂ molecule to the surface, one CO bond is being weakened with simultaneous formation of a new Mg-O bond. Thus for this reaction a four-centre transition state O-C-O-Mg was proposed. Varying bond lengths and interbond angles, two bent structures with Mg and the terminal O atom either in cis or trans position all give three kinetic isotope effects in agreement with the experiment (**Figure 2**).

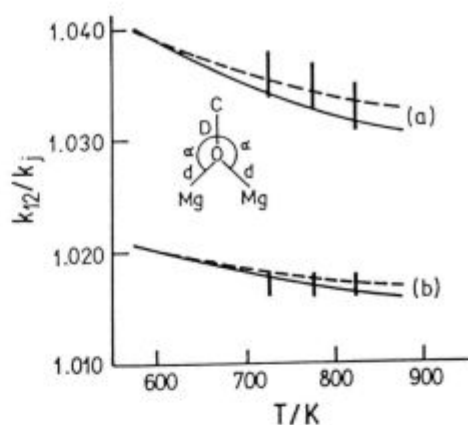


Figure 1: The agreement between the calculated and experimental kinetic isotope effects. $\alpha=140^\circ$, $\tau=0^\circ$, $F_{Dd}=0$, $F_{Oa}=0$, $F_{\alpha}=20 \text{ Nm}^{-1}$, $F_{\tau}=10 \text{ Nm}^{-1}$. (—) $F_D=1400 \text{ Nm}^{-1}$, $F_d=200 \text{ Nm}^{-1}$; (- - -) $F_D=1800 \text{ Nm}^{-1}$, $F_d=600 \text{ Nm}^{-1}$. (a) k_{12}/k_{14} , (b) k_{12}/k_{13} . Bars show experimental points

Slika 1: Ujemanje med eksperimentalnimi (stolpci) in teoretično izračunanimi (krivulje) kinetičnimi izotopskimi efekti. $\alpha=140^\circ$, $\tau=0^\circ$, $F_{Dd}=0$, $F_{Oa}=0$, $F_{\alpha}=20 \text{ Nm}^{-1}$, $F_{\tau}=10 \text{ Nm}^{-1}$. (—) $F_D=1400 \text{ Nm}^{-1}$, $F_d=200 \text{ Nm}^{-1}$; (- - -) $F_D=1800 \text{ Nm}^{-1}$, $F_d=600 \text{ Nm}^{-1}$. (a) k_{12}/k_{14} , (b) k_{12}/k_{13}

We may conclude that a CO₂ reacting molecule on a Mg surface is not linear. This could be due to its excitation or an interaction of the terminal O atom with the surface; this is especially evident for the D type transition state.

C. Catalytic oxidation of CO over Pd¹²

C-13 kinetic isotope effects in the oxidation of CO with oxygen over a Pd/Al₂O₃ catalyst were determined in the temperature range of 323-413 K and the following temperature dependence was found: $100 \ln(k_{12}/k_{13}) = 3.18 - 831/T$ (± 0.15). It has been widely accepted that the kinetics follow the Langmuir-Hinshelwood mechanism, and as the slowest step the reaction of adsorbed CO molecules with adsorbed O atoms was proposed¹³. For the transition state of this reaction both linear and bent O-C-O have been suggested^{14,15}. Thus, in our analysis we took a CO₂ molecule with interbond angles from 80 to 180°. The linear model was found never to give kinetic isotope effects in agreement with the experiment. The best agreement was obtained with a transition state having the interbond angle close to 90°. One of the best choices is a symmetric CO₂ with an interbond angle of about 80°, bond lengths of 123 pm, and 1080 and 200 Nm⁻¹ for the stretching and bending force constants, respectively. To save space the figure showing the agreement is omitted.

D. Catalytic oxidation of CO over NiO⁹

In the oxidation of CO with oxygen over a NiO catalyst, carbon kinetic isotope effects were determined in the temperature range of 523-773 K. They are practically temperature independent and amount to 1.0255 ± 0.0014

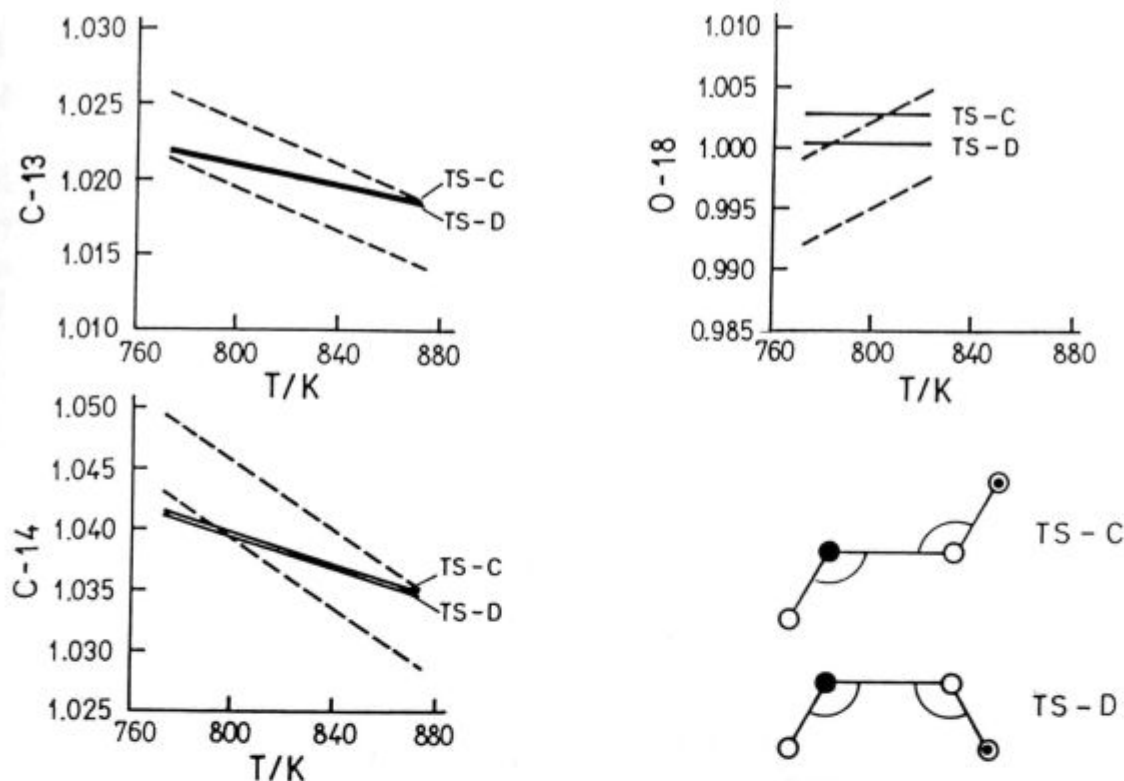


Figure 2: The agreement between the calculated and experimental kinetic isotope effects. The parameters Nm^{-1} for force constants, nm for bond length for TS-C and TS-D transition states, respectively; $F_{\text{CO}}=1700, 1700$; $F_{\text{CO}^*}=500, 300$; $F_{\text{MgO}^*}=150, 100$; $d_{\text{CO}}=113.6, 113.6$; $d_{\text{CO}^*}=140.3, 153.2$; $d_{\text{MgO}^*}=194.9, 225.0$; $\alpha=\beta=120^\circ$; $F_\alpha=100, 100$; $F_\beta=50, 30$; $F_\gamma=10, 20$

Slika 2: Ujemanje med eksperimentalnimi (območje med črtkanima premicama) in teoretično izračunanimi (za aktivirana kompleksa C in D) kinetičnimi izotopskimi efekti. Vrednosti parametrov (N/m^{-1} , d/nm): $F_{\text{CO}}=1700, 1700$; $F_{\text{CO}^*}=500, 300$; $F_{\text{MgO}^*}=150, 100$; $d_{\text{CO}}=113.6, 113.6$; $d_{\text{CO}^*}=140.3, 153.2$; $d_{\text{MgO}^*}=194.9, 225.0$; $\alpha=\beta=120^\circ$; $F_\alpha=100, 100$; $F_\beta=50, 30$; $F_\gamma=10, 20$

and 1.0493 ± 0.0013 for C-13 and C-14, respectively. Due to an isotopic exchange of oxygen on the surface, oxygen isotope effects could not be measured. For the rate determining and isotopic fractionation governing step of the reaction mechanism both CO_2 and CO_3 transition states may be taken into account¹⁶. With all selections of geometric parameters and force constants the CO_3 transition states gave kinetic isotope effects much lower than the experimental values. Thus only the CO_2 transition state may be considered as acceptable for this reaction. Best agreement was achieved with the following parameter values: interbond angle from 110 to 130° ; stretching force constants for both bonds 1600 - 1800 and 600 - 800 Nm^{-1} , respectively; bending force constant: 50 - 150 Nm^{-1} . To save space the agreement between the calculated and experimental values is omitted. This result supports the suggestion that in the slowest step a CO molecule, most probably adsorbed to the surface or maybe from the gas phase, interacts with one and not two adsorbed O atoms.

E. Catalytic oxidation of CO over ZnO ¹⁷

The temperature range investigated was 473 - 773 K . Also here the carbon kinetic isotope effects were found

to be temperature independent and amounted to 1.0101 ± 0.0010 and 1.0204 ± 0.0019 for k_{12}/k_{13} and k_{12}/k_{14} , respectively. Due to oxygen isotopic exchange reactions we were not able to determine the oxygen kinetic isotope effects. As on NiO, also here both CO_2 and CO_3 transition states may be considered as acceptable. In the contrast to NiO, we were not able here to distinguish between these two possibilities because both give a good agreement with experiment. In a symmetrical CO_2 transition state the following parameter values give the best agreement: interbond angle: 80 - 90° ; stretching force constants: 600 - 900 Nm^{-1} ; bending force constant: 200 - 300 Nm^{-1} . The CO_3 transition state is planar with all interbond angles of 120° and the following force constants in Nm^{-1} : 1700 - 1720 for one bond and 450 - 500 for the other two, 60 for two bending and 50 for out-of-plane bending. Again the graph presenting the agreement between the calculated and experimental values is not shown.

3 Conclusions

These examples have shown that investigation of kinetic isotope effects in a chemical reaction gives additional information about the transition state of that step

of the reaction mechanism which determines the overall rate and governs the isotopic fractionation. It often happens that the numerical values of the geometric parameters and force constants are obtained, but a selection of only one transition state out of several possibilities is impossible. In this case additional criteria should be introduced, for instance activation energy, or pre-exponentials¹⁸. A good support for a particular choice among various possible transition states can also be made by quantum chemical calculations¹⁹.

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