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^{13}C and ^{14}C Kinetic Isotope Effects in the Catalytic Oxidation of CO over NiO Catalyst

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For the reaction $CO + \frac{1}{2}O_2 \rightarrow CO_2$ over NiO catalyst, ^{13}C and ^{14}C kinetic isotope effects were determined in the temperature range from 250 to 500°C. The method used was the isotopic analysis of CO_2 formed during the reaction up to a known conversion. It was found that the kinetic isotope effects for both were temperature independent over the whole temperature range studied and were equal to 1.0255 ± 0.0014 for ^{13}C and 1.0493 ± 0.0013 for ^{14}C, respectively. Preliminary calculations show that these effects can be theoretically interpreted only when the CO_2 structure, not the CO_3 structure, is considered as the activated complex of the rate-determining and carbon isotope fractionation-governing step of the reaction mechanism.

INTRODUCTION

Catalytic oxidation of carbon monoxide over nickel oxide catalyst has been investigated extensively in the past. It has been known for a long time that the reaction mechanism is different at low and high temperatures (*1*). This has been well established and explained (*2–9*). The mechanism is governed (*5*) by the mobility of surface oxygen (*2, 4*) which depends on the physicochemical and electronic properties of the catalyst.

It is believed that the rate-determining step of the high-temperature mechanism is a reaction between CO and O_2, in which either both reactants are adsorbed or only oxygen is adsorbed (*1, 6, 10–12*). A reaction between adsorbed CO and gas-phase oxygen has been excluded (*13*). If both species are adsorbed, it is supposed that the reaction takes place between one molecule of reversibly adsorbed CO and either one or two oxygen ions (*5*).

In the great majority of investigations it was found that, in the high-temperature range, the reaction is first order with respect to the pressure of CO, zero order with respect to the pressure of oxygen, and either zero or first order with respect to the pressure of CO_2 (*14–16*). This is valid with undoped nickel oxide and a $CO:O_2$ mole ratio less than 1, whether or not CO_2 is removed from the reaction gas mixture (*17*). Under these conditions, the apparent activation energy was determined to be in the range from 5 to 17 kcal/mol (*3, 16–18*).

The aim of our work was to throw more light on the reaction mechanism by studying the ^{13}C and ^{14}C kinetic isotope effects in the reaction $CO + \frac{1}{2}O_2 \rightarrow CO_2$ on NiO. Kinetic isotope effects depend on the nature (geometry and force field) of the activated complex of the rate-determining and isotope effect-governing steps of the reaction mechanism and, thus, are a good tool for elucidation of reaction mechanisms.

First, the reaction kinetics were investigated under our chosen conditions; then, the absence of isotopic exchange reactions which might distort the pure kinetic isotopic fractionation was proven; and,

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finally, the enrichment in ^{13}C and ^{14}C of CO_2 formed during oxidation up to a known conversion was determined, and the rate constant ratios k_{12}/k_{13} and k_{12}/k_{14} were calculated for the simultaneous isotopic reactions:

$$^{12}CO + \tfrac{1}{2}\,O_2 \xrightarrow{k_{12}} {}^{12}CO_2,$$

$$^{13}CO + \tfrac{1}{2}\,O_2 \xrightarrow{k_{13}} {}^{13}CO_2,$$

$$^{14}CO + \tfrac{1}{2}\,O_2 \xrightarrow{k_{14}} {}^{14}CO_2.$$

METHODS

Apparatus. All experiments were performed in a Pyrex glass vacuum system (10^{-4}–10^{-5} Torr, 1 Torr = 133.3 N m^{-2}). The 250-ml cylindrical reaction vessel was maintained at the desired reaction temperature by means of an electrical kanthal furnace controlled by a special thermoregulator (within ± 1°C at 500°C) (*19*).

Materials. Oxygen was taken from a commercial cylinder and was purified by condensation with liquid nitrogen and subsequent distillation.

Carbon monoxide was prepared by mixing CO of natural isotopic composition (99.9%, L'Air Liquid, France) with ^{14}C-labeled CO to a final specific activity of $0.3 \cdot 10^{-3}$ Ci/liter (1 Ci = $3.7 \cdot 10^{10}$ s^{-1}). ^{14}C-labeled CO was prepared by decomposition of $Ba^{14}CO_3$ with H_2SO_4 and by reduction of the CO_2 formed to CO on Zn at 400°C.

The reaction gas mixture $CO + O_2$ was prepared by mixing carbon monoxide and oxygen (prepared by the procedures described above) in the mole ratio of 1:2, which was determined by gas chromatography. The gas mixture contained less than 0.3% impurities, mainly nitrogen, as revealed by mass spectrometry.

Nickel oxide was prepared by thermal decomposition of nickel nitrate (Kemika, Zagreb, Yugoslavia) in air at 950°C for 6 hr [similar to the method in Ref. (*5*)]. The specific surface area, as determined by the BET method, was found to be 2.0 ± 0.3 m^2/g and remained unchanged during oxidation runs.

Procedure. The reaction vessel was filled with NiO (0.2–1.4 g, depending on temperature) and was connected to the vacuum system. The catalyst was evacuated at 500°C for 2 hr and was then treated with oxygen (300 Torr) at 500°C for 12 hr. Before each oxidation run (the same charge of catalyst was used for all runs at one temperature), the catalyst was evaucated at 500°C for 30 min.

Reaction was started by transferring the $CO + O_2$ mixture from a vessel, in which its initial pressure was read on a mercury manometer, to the reaction vessel preheated to the reaction temperature. The reaction was terminated by removing the furnace and cooling the reaction vessel.

The kinetics of the reaction were studied by following the decrease of total pressure in the reaction vessel during oxidation. This was done on a capillary mercury manometer to which the reaction vessel was connected.

For kinetic isotope effect determinations, the reaction vessel was closed and disconnected from other parts of the system, after it was filled with reaction gas mixture. The time needed for a desired conversion was estimated roughly from preliminary oxidations which, at the same time, were used for conditioning the catalyst (*5*). At the end, CO_2 was isolated from the gas mixture which was made to circulate through a trap cooled with liquid nitrogen, then purified by several distillations between −196°C (liquid nitrogen) and −78°C (CCl_4–$CHCl_3$–liquid nitrogen mixture), and finally sealed into 5-ml glass ampoules for further isotopic analyses.

The conversion, *f*, was calculated from the pressure of the CO_2 formed and the initial total pressure of the $CO + O_2$ mixture. Each pressure was measured five times, and the mean value was taken; *f* was determined with an error of 1%.

The total initial pressures of the reaction gas mixture ranged from 200 to 300 Torr, reaction times from 5 to 20 min (in some exceptional cases, 200 min), conversions from 10 to 30%, and reaction temperatures from 250 to 500°C.

$S(^{13}_{12})$ factors for Eq. (5) (see below) were measured on a double-collector mass spectrometer (*20*, *21*) with an accuracy of 0.05%, and $S(^{14}_{12})$ factors for Eq. (6) were measured by means of a 30-ml stainless steel ionization chamber (*22*) connected to an electrometer (Vibrating Reed Electrometer, Cary, Model 31) with an accuracy of 0.2%.

RESULTS

Isotopic Exchange Reactions

Equations (3) and (4) (see below) can be used only if during the catalytic oxidation which governs ^{13}C and ^{14}C isotope fractionation, the isotopic exchange reactions

$$^{12}CO + {}^{13}CO_2 \rightleftharpoons {}^{13}CO + {}^{12}CO_2,$$

$$^{12}CO + {}^{14}CO_2 \rightleftharpoons {}^{14}CO + {}^{12}CO_2$$

do not take place on the NiO surface.

A gas mixture was prepared from oxygen and CO of natural isotopic composition, to which 10% ^{14}C-labeled CO_2 was added. Oxidation over NiO was initiated at 500°C and was stopped after 30% conversion. The radioactivity of the residual CO (determined by means of the 30-ml ionization chamber) was in the range of background, which proved the absence of the above isotopic exchange reactions.

Reaction Kinetics

For evaluation of reaction kinetics, we used the statistical computer program STEPREG 1 (*23*) which can be used to solve a sequence of one or more multiple linear regression equations by a stepwise application of the least-squares method. Experimental data were fitted into equations

$$\frac{V}{mA}\ln(P - P^{\infty}) = \frac{V}{mA}\ln(P^0 - P^{\infty}) - k_{\mathrm{abs}}t \qquad (1)$$

and

$$\frac{2V}{mA}(P^0 - P^{\infty})\ln\frac{P^0 - P^{\infty}}{P - P^{\infty}} - \frac{2V}{mA}(P^0 - P) = k_{\mathrm{abs}}t, \qquad (2)$$

which are the integrated forms of

$$dP_{\mathrm{CO}}/dt = -k_{\mathrm{abs}}(mA/V)P_{\mathrm{CO}} \qquad (1a)$$

and

$$dP_{\mathrm{CO}}/dt = -k_{\mathrm{abs}}(mA/V)(P_{\mathrm{CO}}/P_{\mathrm{CO_2}}), \qquad (2a)$$

respectively.

The symbols in the above equations are as follows: k_{abs}, absolute rate constant; V, effective reaction volume; m, mass of catalyst; A, surface of catalyst; t, time; P, total pressure of gas mixture at time t; P^0, initial total pressure $(t = 0)$; P^{∞}, final total pressure $(t = \infty$, 100% conversion). P_{CO}, $P_{\mathrm{CO_2}}$, and $P_{\mathrm{O_2}}$ are the partial pressures of CO, CO_2, and O_2, respectively, at time t expressed via the total pressure: $P_{\mathrm{CO}} = 2\,(P - P^{\infty})$; $P_{\mathrm{CO_2}} = 2\,(P^0 - P)$; $P_{\mathrm{O_2}} = P - 2\,(P^0 - P^{\infty})$. P^0 was calculated from P_{∞} (which can be better measured) by

$$P^0 = P^{\infty}/(1 + 0.5\,x_{\mathrm{CO}}),$$

where x_{CO} is the mole fraction of CO in the initial mixture (in our case, ca. 0.33).

As a criterion of the validity of Eqs, (1) and (2), the F test was adopted (*24*, *25*). The partial F value of the regression coefficients k_{abs} is defined as (*23*):

$$F = q^2/(1 - q^2)\,(N - 2),$$

with 1 and $N - 2$ degrees of freedom. In this equation, q is the partial correlation

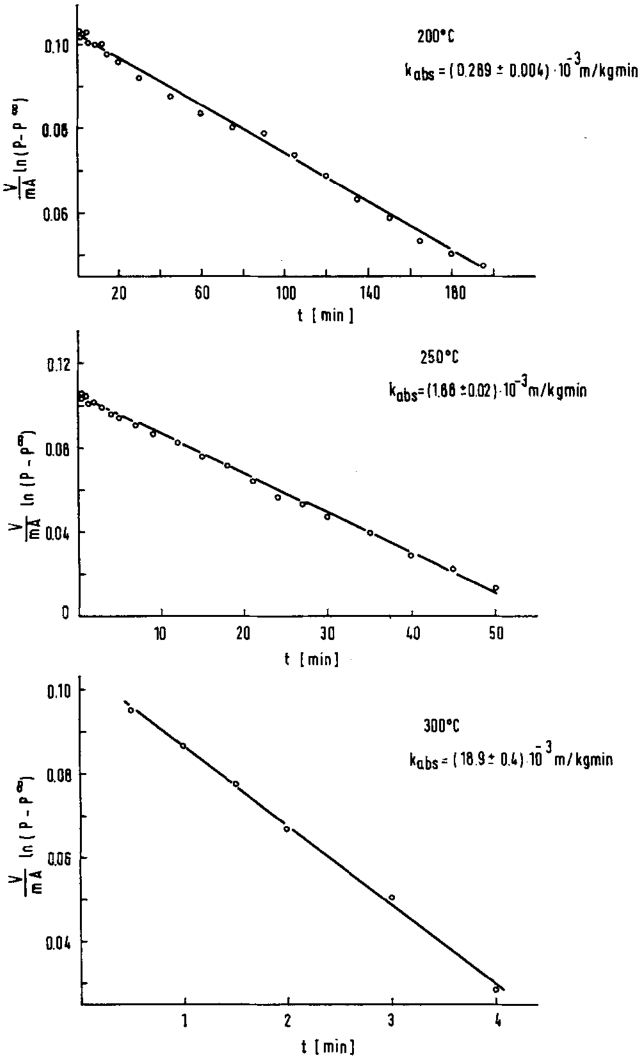

FIG. 1. Fitting experimental kinetic data into Eq. (1).

coefficient of k_{abs}, and N is the number of observations. Only when fitting Eq. (1), did we obtain significance levels of partial F values below 5%. Thus, we may say that, under our conditions, the reaction is of order 1 in P_{CO} and order 0 in P_{CO_2} and P_{O_2}. Some examples are presented in Fig. 1.

In Table 1 are shown the results, including the standard errors of this analysis together with the apparent activation energy. The activation energy was found from the Arrhenius plot in Fig. 2 using a statistical program (*23*).

Kinetic Isotope Effects

Absolute rate ratios (kinetic isotope effects) k_{12}/k_{13} and k_{12}/k_{14} were calculated using the following equations (*22*, *26*):

$$\frac{k_{12}}{k_{13}} = \frac{\ln(1 - f)}{\ln[1 - fS(\frac{13}{12})]} \tag{3}$$

and

$$\frac{k_{12}}{k_{14}} = \frac{\ln(1 - f)}{\ln[1 - fS(\frac{14}{12})]}, \tag{4}$$

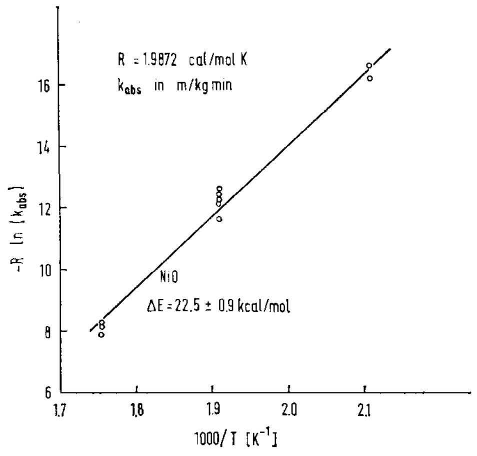

FIG. 2. Arrhenius plot.

where f is the conversion.

$$S\binom{13}{12} = ([^{13}CO_2]/[^{12}CO_2])_{sm} : ([^{13}CO_2]/[^{12}CO_2])_{st} \quad (5)$$

and

$$S\binom{14}{12} = ([^{14}CO_2]/[^{12}CO_2])_{sm} : ([^{14}CO_2]/[^{12}CO_2])_{st}, \quad (6)$$

where sm indicates a sample of CO_2 (which was formed up to a conversion f) and st, a CO_2 standard (which has the same isotopic composition as the initial CO) obtained by 100% conversion of CO. The results are collected in Table 2.

TABLE 1

Kinetic Data According to Equation (1)[a]

T (°C)	$k_{abs} \cdot 10^3$ (m/kg min)
200	0.237 ± 0.003
200	0.289 ± 0.004
250	1.88 ± 0.02
250	2.21 ± 0.05
250	1.75 ± 0.04
250	2.82 ± 0.06
250	1.99 ± 0.04
300	18.9 ± 0.4
300	15.7 ± 0.8
300	15.8 ± 0.4

$E = 22.5 \pm 0.9$ kcal/mole

[a] $V = 0.250 \cdot 10^{-3}$ m³; $m = 2.10^{-3}$ kg; $A = 4$ m².

TABLE 2

^{13}C and ^{14}C Kinetic Isotope Effects

No.	T (°C)	k_{12}/k_{13}	k_{12}/k_{14}
1	250	1.0254	
2	250	1.0242	
3	250	1.0262	
4	250	1.0213	
5	300	1.0277	
6	300	1.0253	1.048
7	300	1.0254	1.051
8	300	1.0285	1.047
9	300	1.0258	1.048
10	400	1.0251	1.050
11	400	1.0256	1.049
12	400	1.0251	1.051
13	400	1.0249	
14	450	1.0256	
15	450	1.0258	
16	450	1.0261	
17	450	1.0243	
18	500	1.0260	1.049
19	500	1.0256	1.050
20	500	1.0252	
21	500		1.049

The temperature dependence of kinetic isotope effects was tested (*27–29*) by the low-temperature approximations,

$$100 \ln (k_{12}/k_{13}) = A(13) + B(13)\,\theta \quad (7)$$

and

$$100 \ln (k_{12}/k_{14}) = A(14) + B(14)\,\theta, \quad (8)$$

and high-temperature approximations:

$$100 \ln (k_{12}/k_{13}) = C(13) + D(13)\,\theta^2 \quad (9)$$

and

$$100 \ln (k_{12}/k_{14}) = C(14) + D(14)\,\theta^2, \quad (10)$$

with $\theta = 1000/T$°K.

The above coefficients, evaluated by applying the statistical computer program (*23*), are listed in Table 3. It was found that, for A and C coefficients, the partial F values ranged from 100 to 700, with significance levels beyond 10^{-4}, but, for B and D coefficients, the partial F values were less than 1, with significance levels greater than 0.50.

TABLE 3

Coefficients of Equations (7)–(10)[a]

Coefficient	Value	Standard error	Partial F value	Significance level
$A(13)$	2.62	0.22	141	$<10^{-4}$
$A(14)$	5.06	0.36	200	$<10^{-4}$
$B(13)$	−0.067	0.138	0.23	0.64
$B(14)$	−0.16	0.23	0.47	0.52
$C(13)$	2.57	0.11	512	$<10^{-4}$
$C(14)$	4.94	0.18	734	$<10^{-4}$
$D(13)$	−0.024	0.043	0.30	0.58
$D(14)$	−0.056	0.077	0.52	0.49

[a] Reference (*23*).

Hence, there is a probability greater than 50% that the values of B and D coefficients arise purely by chance. This results in the conclusion that both ^{13}C and ^{14}C kinetic isotope effects, over the whole temperature range studied, can be considered to be temperature independent. In this case, we obtain (the mean value ± standard deviation) in the temperature range from 250 to 500°C:

$$k_{12}/k_{13} = 1.0255 \pm 0.0014$$

and

$$k_{12}/k_{14} = 1.0493 \pm 0.0013.$$

DISCUSSION

It has been shown that the reaction kinetics under our conditions agree with those found in the literature (first order with respect to P_{CO} and zero order with respect to P_{CO_2} and P_{O_2}), but the apparent activation energy is slightly higher (22.5 kcal/mole as compared with the range of 5–17 kcal/mol (*3*, *16–18*)). This could be due to simultaneous admission of CO and O_2 and not CO after O_2 (*18*), or because only a thin surface layer of catalyst is in thermodynamic equilibrium with the gas phase, which is often the case (*30*) and can result in an increase in the activation energy (*31*).

Pankrat'ev (*5*) has shown that, for a NiO catalyst with a specific surface area of 1.5 m^2/g, prepared by calcination in air at 950°C for 6 hr (as ours was), the high-temperature mechanism is predominant above 200°C. Thus, we may say that the ^{13}C and ^{14}C kinetic isotope effects determined experimentally in our work are relevant for the high-temperature mechanism. In the Introduction it was explained that the rate-determining step of the mechanism can be a reaction of a gas phase or adsorbed CO molecule with one or two adsorbed oxygen atoms (ions). In this reaction, a new C–O bond is being formed, and, hence, it governs the kinetic isotope fractionation. According to the transition-state theory of chemical reactions (*32*), the $(CO_2)^{\ddagger}$ and $(CO_3)^{\ddagger}$ structures can be considered as the activated complexes of this reaction.

The normal coordinate analysis of these two activated complexes was made by the *FG* matrix method of Wilson *et al.* (*33*) and the theoretical rate constant ratios k_{12}/k_{13} and k_{12}/k_{14} were calculated following the formalism of Bigeleisen and Goeppert-Mayer (*26*, *29*). We based the analysis of our computational results on the fact that the experimental kinetic isotope effects can be considered to be temperature independent, and, hence, the calculated rate constant ratio can be written (*27*) as a product of the temperature-independent factor (TIF) and the temperature-dependent factor (TDF). Thus a successful activated complex, in our case, is one in which the parameters give a value of TIF close (within experimental errors) to the experimental value of the rate constant ratio and a value of TDF equal to 1 or so near 1 that the product of both factors may be considered as temperature independent over the whole temperature range studied.

The preliminary results of our computations (*34*) show that only the $(CO_2)^{\ddagger}$-activated complex is able to give appropriate values of TIF and TDF compatible with the above-mentioned requirements, while the $(CO_3)^{\ddagger}$ structure gives TIF values far too low to be acceptable for the interpretation of the experimental results, This results in the conclusion that, in the high-temperature mechanism of the catalytic oxidation of CO over NiO catalyst, the rate-determining and isotope-fractionation governing step is a reaction of one gas phase or adsorbed molecule of CO with only one oxygen atom (ion) (*35–37*) and not with two, as has been suggested in reports on some other experimental techniques.

In our calculations, more complex structures, for example, two-carbon-activated complexes, have not been included, though they were proposed (*38*) for the mechanism at 180°C.

A detailed computational analysis dealing with $(CO_2)^{\ddagger}$- and $(CO_3)^{\ddagger}$-activated complexes in the catalytic oxidation of CO over NiO will be given in a separate paper.

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