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# <sup>13</sup>C and <sup>14</sup>C kinetic isotope effects in the catalytic oxidation of CO over ZnO

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<sup>13</sup>C and <sup>14</sup>C kinetic effects in the reaction  $CO + 1/2 O_2 \rightarrow CO_2$  over ZnO catalyst were experimentally determined. The k12/k13 and k12/k14 ratios were found to be temperature independent in the temperature range studied (200-500 °C) and amounted to 1.0101±0.0010 and 1.0204±0.0019, respectively. Interpretation of the experimental values, following Bigeleisen's formalism, reveals that  $(CO_2)^{\ddagger}$  with an interband angles of  $(90 \pm 10)^{\circ}$  and planar  $(CO_3)^{\ddagger}$  with two interband angles in the range of  $(120 \pm 10)^{\circ}$  may be considered as activated complexes of the rate determining and isotope effect fractionation governing step of the reaction mechanism.

## INTRODUCTION

Apart from NiO, ZnO has been frequently investigated in the past as a catalyst in the oxidation of CO to  $CO_2$ . It has been challenging many investigators to study its *n*-type semiconducting properties and related phenomena, among them surface reactions have a predominant position.<sup>1-26</sup> It was found that oxygen in contact with a ZnO surface reacted with interstitial Zn ions to form<sup>3-5,8,9,18</sup> O<sub>2</sub>, O<sup>-</sup>, and O<sup>2-</sup> adsorbed species (or probably an O<sub>3</sub> complex<sup>17</sup>). Calculations showed that the adsorption of oxygen on interstitial Zn atoms was rather improbable.<sup>13</sup> Of the above mentioned adsorbed forms of oxygen, the O<sub>2</sub> species is persistent only at room temperature and is converted to O<sup>-</sup> above 160 °C.<sup>9</sup>

CO from the gas phase can be adsorbed on ZnO surface reversibly (at room temperature) or irreversibly (at higher temperatures).<sup>5,14</sup>

 $CO_2$  at the surface of ZnO catalyst which is in contact with a CO- $O_2$  gas mixture can be formed as a product of the reaction of reversibly adsorbed  $CO^{14}$  or gas phase  $CO^4$  with the adsorbed oxygen. This reaction is believed to be the rate determining step<sup>8,9</sup> of a complex reaction mechanism. This step in which a new C-O bond is formed also governs the isotope fractionation during the reaction.

The question arises<sup>6,10,14</sup> whether in this step only one or two oxygen atoms (ions) are involved. Thus, from the view point of the transition state theory of chemical reactions,  $^{27,28}$  (CO<sub>2</sub>)<sup>‡</sup> or (CO<sub>3</sub>)<sup>‡</sup> structures could be considered as the activated complexes of this reaction step.

Encouraged by the results of similar investigations on NiO,  $^{29}$  we have investigated the kinetic isotope effects in the catalytic oxidation of CO over ZnO in order to answer this question.

First, the reaction kinetics were studied, then  $^{13}$ C and  $^{14}$ C kinetic isotope effects in the temperature range from 200 to 500 °C were experimentally determined by measuring carbon isotopic ratios in the CO<sub>2</sub> formed during the reaction. Following the formalism of Bigeleisen,  $^{50,31}$  such geometries and force fields of the activated complexes were sought as to furnish a satisfac-

tory agreement between experimental and theoretical values of the isotope effects.

## EXPERIMENTAL

#### Equipment, materials, and procedure

To perform the experimental part of our work we used the same equipment and procedures as in our previous work on NiO.<sup>32</sup>

The reaction gas mixture of  $CO+O_2$  (mole ratio 1:2) was obtained by mixing oxygen from a commercial cylinder and <sup>14</sup>C-labeled CO. The latter was prepared by decomposition of Ba<sup>14</sup>CO<sub>4</sub>, reduction of CO<sub>2</sub> to CO, and dilution with CO of natural isotope composition (99.9% purity L'Air Liquid France) to get a final activity of about 0.3 Ci/m<sup>3</sup>.

The ZnO catalyst (Riedel-de-Haën, p.a.) was put into a 250 cm<sup>3</sup> cylindrical Pyrex glass reaction vessel, evacuated at 500 °C for 2 h and stabilized with two catalytic oxidations with  $CO+O_2$  gas mixture at 500 °C. The specific surface area of ZnO, as determined by the BET method, amounted to  $2.8 \pm 0.3$  m<sup>3</sup>/g and remained unchanged during oxidations. The same charge of ZnO was used for all oxidations at one temperature. The masses of catalyst ranged from 35 mg (at 500 °C) to 2 g (at 200 °C) to enable a 10%-30% conversion in 5-50 min (only in a few cases was it longer). Before each oxidation the catalyst was evacuated at 500 °C for 30 min.

Reaction was started by enclosing a known amount of reaction gas mixture in the reaction vessel preheated to a desired reaction temperature, and was stopped by removing the furnace and cooling the vessel with air. The CO<sub>2</sub> formed during the reaction was separated from the gas mixture in a trap cooled with liquid nitrogen and purified by several distillations between a liquid nitrogen trap and a  $CCl_4: CHCl_3:$  liquid nitrogen (-78 °C) trap.

Conversion was calculated from the initial total pressure of the reaction gas mixture (ranging from 150 to 300 Torr) and the  $CO_2$  pressure measured in a special vessel by a mercury manometer. Thus only in kinetics studies, the reaction vessel was connected to the mercury manometer.

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| (*). |  |                                |                        |  |
|------|--|--------------------------------|------------------------|--|
|      | $k_{abs} (cm^3/m^2 min)$ $\left(\frac{dP_{CO}}{dt} = k_{abs} \times P_{CO} \times \frac{mA}{V}\right)$ |                                |                        |  |
| T    |  |                                |                        |  |
| (°C) | m = 2g,  | $A = 2.8 \text{ m}^2/\text{g}$ | $V = 250 \text{ cm}^3$ |  |
| 250  |  | $0.760 \pm 0.008$              |                        |  |
| 250  |  | $0.708 \pm 0.008$              |                        |  |
| 300  |  | $1.96 \pm 0.04$                |                        |  |
| 300  |  | $2.26 \pm 0.04$                |                        |  |
| 350  |  | $8.46 \pm 0.12$                |                        |  |
| 350  |  | $7.20 \pm 0.14$                |                        |  |
| 400  |  | $17.6 \pm 0.8$                 |                        |  |
|      | E  | $=(15.2\pm0.7)$ kca            | ul/mol                 |  |

TABLE I. Kinetic data according to Eqs.(1).

 $S^{(13)}_{(12)}$  and  $S^{(14)}_{(12)}$  factors for Eq. (6) (see below) were determined on a double collector mass spectrometer and with an ionization chamber, respectively.

#### **REACTION KINETICS**

To study reaction kinetics the total pressure of reaction gas mixture in the reaction vessel was followed during a reaction. The time and total pressure data were fitted into equations:

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

and

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

which are the integrated forms of equations

$$\frac{dP_{\rm co}}{dt} = -k_{\rm abs} \frac{mA}{V} P_{\rm co} \tag{3}$$

and

$$\frac{dP_{co}}{dt} = -k_{abs} \frac{mA}{V} \frac{P_{co}}{P_{co_2}},$$
(4)

respectively.

In the above equations  $k_{abs}$  is the absolute rate constant; V, effective reaction volume; m, mass of cata-



FIG. 1. Fitting experimental kinetic data for  $300 \,^{\circ}$ C into Eq. (1).



FIG. 2. Arrhenius plot.

lyst; A, specific surface area of catalyst; t, time; P, total pressure of gas mixture at time t;  $P^0$ , initial total pressure;  $P^{\infty}$ , total pressure at 100% conversion; and  $P_{\rm CO}$  and  $P_{\rm CO_2}$ , partial CO and CO<sub>2</sub> pressures at time t, respectively.

The fitting was made by applying a statistical computer program stepreg 1,  $^{33}$  and as a criterion the Ftest was considered.  $^{34}$  The partial F value is defined as $^{33}$ 

$$F = \frac{q^2}{1-q^2} \left(N-2\right)$$

where q is the partial correlation coefficient of  $k_{abs}$ , and N is the number of observations.

Only in case of Eq. (1) did significance level of partial F values fall below 0.05, confirming that under our experimental conditions the reaction was of order 1 in  $P_{\rm CO}$  and order 0 in  $P_{\rm CO_2}$  and  $P_{\rm O_2}$ .

The results of the kinetics investigations are collected in Table I. The reaction run at 300 °C is graphically represented in Fig. 1.

Using the same computer program, the apparent activation energy was calculated; its value is given at the bottom of Table I. The corresponding Arrhenius plot is drawn in Fig. 2.

#### **ISOTOPIC EXCHANGE REACTIONS**

It was proven that during the oxidation, isotopic exchange reactions

$${}^{12}\text{CO} + {}^{j}\text{CO}_2 \rightleftharpoons {}^{j}\text{CO} + {}^{12}\text{CO}_2, \quad j = 13, 14$$

do not take place, allowing us to use Eq. (5) (see below) for calculation of experimental kinetic isotope effects.

This was performed after an oxidation run with an initial gas mixture of oxygen and CO of natural isotopic composition to which about 10 vol. % of <sup>14</sup>C labeled CO<sub>2</sub> (specific activity about 1 Ci/m<sup>3</sup>) had been added. The reaction at 500 °C was stopped after about 30% conver-

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sion. The final activity of the residual CO was found to lie at background level.

On the other hand, reactions on the catalyst enriched with <sup>18</sup>O, showed isotopic exchange of oxygen between CO and CO<sub>2</sub> and the oxide surface. Hence, we did not determine the <sup>18</sup>O kinetic isotope effect.

## KINETIC ISOTOPE EFFECTS

Kinetic isotope effects, the absolute rate constant ratios  $k_{12}/k_{13}$  and  $k_{12}/k_{14}$  for the simultaneous isotopic reactions

 ${}^{12}CO + 1/2O_2 \stackrel{*_{12}}{-} {}^{12}CO_2,$ 

TABLE II. <sup>13</sup>C and <sup>14</sup>C kinetic isotope effects. From 200 to 500 °C:  $k_{12}/k_{13}=1.0108\pm0.0010$  and  $k_{12}/k_{14}=1.0204\pm0.0019$ .

|           | T    |      |                 |                    | <b>k</b> 12     | $k_{12}$            |
|-----------|------|------|-----------------|--------------------|-----------------|---------------------|
| No.       | (°C) | f    | $S(^{13}_{12})$ | $S(\frac{14}{12})$ | k <sub>13</sub> | $\overline{k_{14}}$ |
| 43        | 200  | 0.20 | 0,9925          | 0.984              | 1,0085          | 1.018               |
| 44        | 200  | 0.26 | 0.9915          | 0.984              | 1.0100          | 1.019               |
| 45        | 200  | 0.29 | 0.9913          | 0,981              | 1.0105          | 1.023               |
| 119       | 200  | 0.23 | 0.9905          |                    | 1.0110          |                     |
| 121       | 200  | 0.29 | 0.9902          | 0,985              | 1.0118          | 1.018               |
| 46        | 250  | 0.34 | 0.9911          | 0.984              | 1.0111          | 1.020               |
| 47        | 250  | 0.23 | 0.9916          | 0,982              | 1.0097          | 1.021               |
| 48        | 250  | 0.22 |                 | 0.983              |                 | 1.020               |
| 49        | 250  | 0.30 | 0.9911          | 0.983              | 1.0108          | 1.021               |
| 50        | 250  | 0.28 | 0.9908          | 0.981              | 1.0110          | 1.023               |
| 51        | 250  | 0.29 |                 | 0.983              |                 | 1.021               |
| 52        | 300  | 0.36 | 0.9916          | 0.984              | 1.0107          | 1,020               |
| 53        | 300  | 0.28 | 0.9916          | 0.982              | 1.0100          | 1.022               |
| 54        | 300  | 0.32 | 0,9903          | 0,981              | 1.0120          | 1.024               |
| 55        | 300  | 0.30 | 0.9905          | 0.985              | 1.0115          | 1.018               |
| 56        | 300  | 0.27 | 0.9901          | 0.981              | 1.0118          | 1.023               |
| 57        | 300  | 0.25 | 0.9928          | 0.985              | 1.0084          | 1.018               |
| 59        | 300  | 0.45 | 0.9913          | 0.985              | 1.0120          | 1.021               |
| 60        | 300  | 0.39 |                 | 0,985              |                 | 1.020               |
| 61        | 300  | 0.28 | 0.9913          | 0.982              | 1.0104          | 1,022               |
| 62        | 300  | 0.09 |                 | 0,985              |                 | 1.016               |
| 63        | 350  | 0.31 | 0.9905          | 0.982              | 1,0116          | 1.022               |
| 64        | 350  | 0.32 | 0.9908          | 0.983              | 1.0113          | 1.021               |
| 65        | 350  | 0.33 | 0.9905          | 0.986              | 1.0118          | 1.017               |
| 66        | 350  | 0.33 | 0.9913          | 0.984              | 1.0108          | 1.020               |
| 67        | 350  | 0.17 | 0.9896          | 0.981              | 1.0116          | 1.021               |
| 74        | 400  | 0.56 | 0.9933          | 0.987              | 1.0105          | 1.020               |
| 76        | 400  | 0.26 | 0.9918          | 0.983              | 1.0096          | 1.020               |
| 77        | 400  | 0.48 | 0,9925          | 0.986              | 1.0107          | 1.020               |
| 78        | 400  | 0.45 | 0,9913          | 0.985              | 1.0120          | 1.021               |
| 79        | 400  | 0.35 | 0.9915          | 0.985              | 1.0107          | 1.019               |
| 80        | 400  | 0.17 | 0,9905          | 0.981              | 1.0105          | 1.021               |
| 83        | 450  | 0.37 | 0.9933          |                    | 1.0086          |                     |
| 84        | 450  | 0.40 | 0,9919          |                    | 1.0107          |                     |
| 86        | 450  | 0.14 |                 | 0.982              |                 | 1.020               |
| 88        | 450  | 0.29 | 0,9910          | 0.982              | 1.0108          | 1.022               |
| 89        | 450  | 0.25 | 0,9915          |                    | 1.0099          |                     |
| 91        | 450  | 0.20 | 0,9889          | 0.981              | 1.0126          | 1.022               |
| 93        | 450  | 0.19 | 0.9895          | 0.985              | 1,0118          | 1.017               |
| 93        | 500  | 0.11 |                 | 0.989              |                 | 1.023               |
| 95<br>00  | 500  | 0.18 |                 | 0.984              |                 | 1.018               |
| 96        | 500  | 0.19 | 0,9907          | 0.980              | 1.0104          | 1.023               |
| 97        | 500  | 0.18 | 0.9902          | 0 001              | 1,0109          |                     |
| 98<br>00  | 500  | 0.24 | 0.9905          | 0.981              | 1,0110          | 1.022               |
| 99<br>100 | 500  | 0,20 | 0.9915          | 0.981              | 1,0099          | 1.022               |
| 101       | 500  | 0.10 | 0.9907          | 0.981              | 1,0104          | 1.021               |
| 102       | 500  | 0.18 |                 | 0.981              |                 | 1.021               |
| 104       | 900  | 0.19 |                 | 0,984              |                 | 1.018               |

TABLE III. Coefficients of Eqs. (5) and (6).

| Coefficient   | Value  | Standard<br>error | Partial<br>F value | Significance<br>level |
|---------------|--------|-------------------|--------------------|-----------------------|
| A (13)        | 1.014  | 0.099             | 124                | <10-4                 |
| A (14)        | 2.14   | 0.18              | 134                | < 10 <sup>-4</sup>    |
| <b>B</b> (13) | -0.021 | 0.060             | 0.12               | 0.72                  |
| B (14)        | -0.069 | 0.111             | 0.38               | 0.54                  |
| C (13)        | 1.09   | 0.05              | 462                | < 10 <sup>-4</sup>    |
| C (14)        | 2,080  | 0.095             | 476                | < 10-4                |
| D (13)        | -0.008 | 0.018             | 0.21               | 0.65                  |
| D (14)        | -0.021 | 0.033             | 0.38               | 0.54                  |

$${}^{13}\text{CO} + 1/2\text{O}_2 \stackrel{k_{13}}{+} {}^{13}\text{CO}_2,$$
  
 ${}^{14}\text{CO} + 1/2\text{O}_2 \stackrel{k_{14}}{+} {}^{14}\text{CO}_2,$ 

were calculated by the following equation<sup>30, 32</sup>:

$$\frac{k_{12}}{k_j} = \frac{1-f}{1-f \times S(\frac{j}{12})}; \quad j = 13, 14 .$$
(5)

In it, f is the conversion factor and

$$S(_{12}^{j}) = ([^{j}CO_{2}]/[^{12}CO_{2}])_{sm} : ([^{j}CO_{2}]/[^{12}CO_{2}])_{st} .$$
 (6)

The index "sm" refers to the isotopic ratio in  $CO_2$  formed up to a conversion f, while "st" refers to a  $CO_2$  standard, obtained by a 100% conversion of CO.

The experimental values of kinetic isotope effects are summarized in Table II.

In order to find the temperature dependence of kinetic isotope effects, the experimental values were fitted (using stepreg 1) to equation<sup>35</sup>

$$100\ln(k_{12}/k_i) = A(j) + B(j) \times \theta$$

for the low-temperature approximation, and into equation

$$100 \ln(k_{12}/k_{j}) = C(j) + D(j) \times \theta^{2}$$

with  $\theta = 1000/T$ , T temperature in K for the high temperature approximation.

Thus the coefficients for the above equations were obtained and are collected in Table III. Significance levels connected to partial F values of B and D coefficients are greater than 0.50. This means that their values arise by chance, with a probability greater than 50%.<sup>34,36</sup> Hence <sup>13</sup>C and <sup>14</sup>C kinetic isotope effects may be considered as practically temperature independent in the range from 200 to 500 °C having mean values (± a standard deviation):

 $k_{12}/k_{13} = 1.0108 \pm 0.0010$ ,

 $k_{12}/k_{14} = 1.0204 \pm 0.0019$ .

## DISCUSSION

Comparing our experimental data with those from the literature, we find good agreement. Thus it is well known (with the exception of Ref. 5) that the reaction is of first order in  $P_{\rm CO}$  and zeroth order in  $P_{\rm O_2}$ . In addition, some investigations<sup>4,8</sup> confirmed the inhibition of CO<sub>2</sub> and thus an order of -1 in  $P_{\rm CO_2}$ . In our experiments, CO<sub>2</sub> inhibition was not observed. The values of activation energies are very different; they range from  $9^{4_*6_*11}$  to  $24^4$  kcalmol<sup>-1</sup>. Our value of  $(15.2 \pm 0.7)$  kcalmol<sup>-1</sup> is somewhat inbetween.

On account of these similarities we may, with confidence, apply our experimental results for kinetic isotope effects to the interpretation of the reaction schemes previously postulated by other authors in order to obtain information about the activated complexes, at least in the rate determining and isotope effect governing step of the reaction mechanism.

We consider  $(CO_2)^{^{\uparrow}}$  and  $(CO_3)^{^{\ddagger}}$  structures as activated complexes, calculate theoretical values of isotopic rate constant ratios, and compare them with the experimental values.

The calculational basis is the same as in our former work.  $^{29}$ 

The normal frequences of an activated complex were calculated by the Wilson FG matrix method.<sup>37</sup>

The solution of the equation<sup>38</sup>

 $GFL=L\Lambda$ ,

where G is the Wilson matrix; F the force constant matrix; L, the eigenvector matrix;  $\Lambda$ , the diagonal matrix of eigenvalues, (with  $\lambda = 4\pi^2 \nu_i^2$  for the *i*th normal vibration) gives  $3n^2 - 7$  ( $n^2$  is the number of atoms in a non-linear activated complex) real frequencies and one frequency (referred to reaction coordinate) is given a real, zero, or imaginary value using the condition:

$$F| \stackrel{>}{=} 0 . \tag{7}$$

|F| is the determinant of the F matrix.

The thus obtained normal frequencies of an activated complex designated by  $\ddagger$  and the normal frequency of the reactant molecule CO furnish, when applying equations,  $^{29,39,40}$ 

$$HRR(j) = TIF(j) \times TDF(j) , \quad j = 13, 14 ,$$

$$TIF(j) = \nu_{12,L}^{\dagger} / \nu_{j,L}^{\dagger} = (|G_{12}| / |G_j|)^{1/2} \times \prod_{i=1}^{3n-7} \nu_{j,i}^{\dagger} / \nu_{12,i}^{\dagger} ,$$

$$TDF(j) = \prod_{i=1}^{3n-6} \frac{u_{1,i}}{u_{12,i}} \frac{\sinh(u_{12,i}/2)}{\sinh(u_{j,i}/2)} \times \prod_{i=1}^{3n^{1-7}} \frac{u_{12,i}^{\dagger}}{u_{j,i}^{\dagger}} \frac{\sinh(u_{12,i}/2)}{\sinh(u_{12,i}^{\dagger}/2)}$$
(8)

rate constant ratios  $k_{12}/k_{13}$  and  $k_{12}/k_{14}$  for two isotopic reactions.

The meaning of the symbols are as follows: HRR: harmonic rate constant ratio<sup>31</sup>; TIF: temperature independent factor; TDF: temperature dependent factor;  $v_L^{\ddagger}$ : reaction-coordinate frequency (in our case always zero: imaginary and real values are taken only for Figs. 10 and 11); *n*: number of atoms in the molecule; *u*:  $hc\omega/kT$  ( $\omega$  = wave number of a normal vibration, cm<sup>-1</sup>); *h*: Planck's constant; *k*: Boltzmann's constant; *T*: temperature.

In the interpretation of our experimental findings we proceed from the statement that carbon kinetic isotope



FIG. 3.  $(CO_2)^{\ddagger}$  activated complex.

effects were found to be temperature independent in the temperature range studied. We are thus looking for such activated complex models as will give TIF equal to experimental values of the appropriate rate constant ratio, and TDF very close to 1, in order to obtain the product TIF  $\times$  TDF over the whole temperature range within the limits of the experimental values; thus the conditions:

$$TIF(13) \approx 1.0108$$
,  $TDF(13) \approx 1$ ,  
 $TIF(14) \approx 1.0204$ ,  $TDF(14) \approx 1$ , (9)

were preliminaryly obeyed; but only as a first orientation.

To obtain acceptable values (giving satisfactory agreement between theory and experiment) of the parameters of the activated complexes (geometry and force constants), we follow the graphical method<sup>29</sup> previously introduced by Senegačnik, <sup>41</sup> taking into account all results of HRR obtained in the regions (11) and (14), respectively (see below).

## (CO<sub>2</sub>)<sup>‡</sup> activated complex

The definition of the  $\Delta D$ ,  $\Delta d$ , and  $\Delta \alpha$  internal coordinates are evident from Fig. 3. Of the F matrix elements (generalized valence bond field)  $F_D$ ,  $F_d$ , and  $F_{\alpha}$  are given physically reasonable values, while values of  $F_{Dd}$  are calculated from the condition

$$F_{Dd} = \pm (F_D \times F_d - \Delta_1)^{1/2}$$
 (10)

and the others are set to zero.  $\Delta_1$  stands for the determinant of the upper left  $2 \times 2$  block of the *F* matrix of the  $(CO_2)^{\ddagger}$  activated complex.

The values of parameters were varied over the following ranges:

 $F_{D}: 2-20 \text{ mdyn/Å} (\text{in steps of 2});$   $F_{d}: 2-20 \text{ mdyn/Å} (\text{in steps of 2});$   $F_{\alpha}: 0.5-3 \text{ mdyn/Å} (\text{in steps of 0.5});$   $F_{\alpha}: 70-180^{\circ} (\text{in steps of 10}).$ (11)

Bond lengths D and d are calculated from the formula<sup>42</sup>

$$F_{\star} = 35.5/\gamma^{5.79}, \quad r = D, d$$
 (12)

All the calculated TIF(13) for asymmetric  $(F_{Dd} > 0)$  and symmetric  $(F_{Dd} < 0)$  stretching vibration as reaction coordinate motion are comprised<sup>29</sup> in the two areas of Fig. 4. It is immediately clear, that only by taking into account the "-" sign in Eq. (10) and at small interbond angles  $\alpha$  may we expect conditions (9) to be realized.

By drawing graphs like those in Fig. 5 of Ref. 29 for the combinations of values in the ranges given under



FIG. 4. Ranges of TIF(13) values for the  $(CO_2)^{\ddagger}$  activated complexes with  $F_{Dd} \gtrsim 0$  and  $\Delta_1 = 0$ .

Eq. (11), we obtained intervals of acceptable values of  $F_D$  and  $F_d$  as represented in Figs. 5(a)-(c). We may conclude that the interbond angle in  $(CO_2)^{\ddagger}$  ought to be between 80 and 100° (approximately). Going from 100 to 80° of  $\alpha$ , intervals of acceptable values are pushed to smaller values of  $F_D$ ,  $F_d$ , and greater values of  $F_{\alpha}$ . With increasing  $F_{\alpha}$ , the intervals are shifted to smaller  $F_D$  and  $F_d$  values.

Figure 6 shows the agreement between experimental and theoretical kinetic isotope effects (calculated for a



FIG. 6. Agreement between experimental and calculated kinetic isotope effects as achieved with  $(CO_2)^{\ddagger}$  activated complex with  $F_{Dd} < 0$  and  $\Delta_1 = 0$  (reactant molecule: CO,  $F_{CO} = 19.338 \text{ mdyn}/\text{Å}^{49}$ ).

selected combination of values of activated complex parameters) for  $(CO_2)^{\dagger}$  as activated complex. For the complex of  $\alpha = 90^{\circ}$  the isotopic frequencies of its normal vibrations are collected in Table IV.

## $(CO_3)^{\ddagger}$ activated complex

For a better understanding of the definition of the internal coordinates  $\Delta D$ ,  $\Delta d$  (twice),  $\Delta \alpha$  (twice), and  $\Delta \tau$ , the shape of the (CO<sub>3</sub>)<sup>‡</sup> planar structure is drawn



FIG. 5. Ranges of acceptable values of parameters of  $(CO_2)^{\ddagger}$  activated complexes with  $F_{Dd} < 0$  and  $\Delta_1 = 0$ .

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FIG. 7.  $(CO_3)^{\ddagger}$  activated complex.

in Fig.7. For the F matrix elements  $F_D$ ,  $F_d$ ,  $F_{dd}$ ,  $F_{\alpha}$ , and  $F_{\tau}$  physically reasonable values are given;  $F_{Dd}$  values were calculated by the relation

$$F_{Dd} = \pm (1/2)^{1/2} x [F_D(F_d + F_{dd}) - \Delta_2 / (F_d - F_{dd})]^{1/2}$$
(13)

and all others were kept zero.  $\Delta_2$  stands for the determinant of the upper left  $3 \times 3$  sub matrix of the *F* matrix of the (CO<sub>3</sub>)<sup>1</sup> activated complex.



| $({}^{12}CO_2)^{\ddagger}$ | ( <sup>13</sup> CO <sub>2</sub> ) <sup>‡</sup> | ( <sup>14</sup> CO <sub>2</sub> ) <sup>‡</sup> |
|----------------------------|--|--|
| 1759.43                    | 1720.33  | 1686.12  |
| 737.26                     | 720.86   | 706.52   |
| 0.58 i                     | 0.57 <i>i</i>                                  | 0.57 i   |

The lengths of D and d were correlated to the appropriate force constants by Eq. (12). In Eq. (13) only "+" sign was taken into consideration on the basis of the assumption that only an asymmetric vibration of the  $(CO_3)^{\dagger}$  complex can lead to formation of a  $CO_2$  molecule.



FIG. 8. Ranges of acceptable values of parameters of  $(CO_3)^{\ddagger}$  activated complexes with  $F_{Dd} > 0$  and  $\Delta_2 = 0$ .





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FIG. 9. Agreement between experimental and calculated kinetic isotope effects as achieved with  $(CO_3)^{\ddagger}$  activated complex with  $F_{Dd} > 0$  and  $\Delta_2 = 0$  (reactant molecule: CO,  $F_{CO} = 19.338 \text{ mdyn}/\text{Å}^{29}$ ).

The values of the parameters were varied over the following ranges:

 $F_D$ : 2-20 mdyn/Å (in steps of 2);

 $F_d$ : 2-20 mdyn/Å (in steps of 2);

 $F_{dd}$ : 0 and 0.6-2.6 mdyn/Å (in steps of 1);

 $F_{\alpha}$ : 0.2-1 mdyn/Å (in steps of 0.4); (14)

- $F_{\tau}$ : 0.1-0.9 mdyn/Å (in steps of 0.4);
- $\alpha$ : 110-140° (in steps of 10);
- $\tau$ : 0°.

It was already known that TIF values obtained with  $(CO_3)^{\dagger}$  are much smaller than those with  $(CO_2)^{\ddagger}$  and fall in the range of the experimental kinetic isotope effect on ZnO.<sup>29</sup>

For all combinations of values of  $(CO_3)^7$  parameters given under Eq. (14) the calculated HRR (13) values were plotted in graphs like those in Fig. 5 of Ref. 29. The intervals of thus obtained acceptable values of parameters are represented in Figs. 8(a)-(p). It is seen that only values of 110 to 130° for  $\alpha$ 's are able to explain the experimental results. A glance at Figs. 8(a)-(i), and especially j, shows us that with increasing  $F_{dd}$  values, the intervals move to greater  $F_D$  and  $F_d$ values; the opposite is true for dependence on  $F_{\alpha}$  and  $F_{\tau}$ . One valence force constant  $(F_D)$  may take values

TABLE V. Isotopic normal frequencies (in cm<sup>-1</sup>) of the  $(CO_3)^{\ddagger}$  activated complex with the following parameter values:  $F_D = 17.2$  mdyn/Å,  $F_d = 4.5$  mdyn/Å,  $F_{dd} = 2.6$  mdyn/Å,  $F_{\alpha} = 0.6$  mdyn/Å,  $F_{\tau} = 0.5$  mdyn/Å,  $\alpha = 120^{\circ}$ ,  $\tau = 0^{\circ}$ ,  $F_{Dd} > 0$ ,  $\Delta_{\tau} = 0$ 

| $\Delta_2 = 0.$                                |  |  |
|--|--|--|
| ( <sup>12</sup> CO <sub>3</sub> ) <sup>‡</sup> | ( <sup>13</sup> CO <sub>3</sub> ) <sup>‡</sup> | ( <sup>14</sup> CO <sub>3</sub> ) <sup>‡</sup> |
| 1821.37  | 1805.56  | 1791.96  |
| 914.76   | 886.60   | 861.75   |
| 679.80   | 658,41   | 639.69   |
| 395.45   | 395.26   | 395.09   |
| 282,07   | 276.84   | 272.14   |
| 0.18 i   | 0.18 i   | 0.18 i   |

up to 20 mdyn/Å, while the force constants of the other two of the three C-O bonds never exceed values of about 10 mdyn/Å.

The agreement between experiment and theory (for a selected combination of parameter values) is graphically represented on Fig. 9. For the complex of  $\alpha = 120^{\circ}$ , the isotopic frequencies of its normal vibrations are collected in Table V.

#### CONCLUSIONS

The aim stated at the beginning of our work, (i.e., whether the activated complex in the rate determining and isotope effects governing step of the reaction mechanism corresponds to a  $(CO_2)^{\dagger}$  or  $(CO_3)^{\dagger}$  structure) was only partially achieved. In contrast to studies on NiO



FIG. 10. Dependences of kinetic isotope effects on  $\Delta_1$  [Eq. (10)] for  $(CO_2)^{\ddagger}$  activated complex.

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FIG. 11. Dependence of kinetic isotope effects on  $\Delta_2$  [Eq. (13)] for  $(CO_3)^{\ddagger}$  activated complex.

catalyst where we were able to confirm the  $(CO_2)^{\dagger}$  as the only activated complex,  $[(CO_3)^{\dagger}$  was not acceptable], in the case of ZnO the study of kinetic isotope effects was not selective enough to confirm one and reject the other of the structures.

Nevertheless, as a successful result of our investigations on <sup>13</sup>C and <sup>14</sup>C kinetic isotope effects in the catalytic oxidation of CO over ZnO, we obtained information about geometry and force constants of the acceptable activated complex models conceived as physically reasonable on the basis of reaction schemes.

We found that a  $(CO_2)^{\dagger}$  activated complex could explain the experimental isotopic rate constant ratios. In this case the interbond angle ought to be in the range  $(90 \pm 10)^{\circ}$ . A symmetric stretching normal vibration  $(F_{dd} < 0)$  of a loose  $(CO_2)^{\dagger}$  complex (a simultaneous strengthening of both C-O bonds) leads to formation of a  $CO_2$  molecule.

The CO<sub>2</sub> molecule could also be formed by decomposition of the  $(CO_3)^{\dagger}$  activated complex if the movement along the reaction coordinate is described by an asymmetric stretching normal mode.  $(CO_3)^{\dagger}$  is planar with interbond angles  $\alpha$  in the range  $(120 \pm 10)^{\circ}$ .

By comparing the results of kinetic isotope effect investigations in the reaction  $CO + 1/2O_2 - CO_2$  over NiO and ZnO catalysts we may conclude that the rate determining step of the reaction mechanism which also governs isotopic fractionation is in the two cases different. On NiO it takes place via  $(CO_2)^{\dagger}$  activated complex with an asymmetric stretching normal vibration describing the movement along the reaction coordinate.  $(CO_2)^{\dagger}$  can be also considered as activated complex on ZnO, when a symmetric normal vibration is taken as reaction coordinate motion.

Catalytic oxidation of CO on both oxides proceeds over such reaction mechanism steps as to give temperature independence (within experimental errors) of the carbon kinetic isotope effects in the temperature range studied. This situation seems to be somehow anomalous but it can be explained by the phenomenon of the so called crossovers.<sup>31,43,44,45</sup> A small temperature dependence of a kinetic isotope effect, at least in a limited temperature range, can be obtained by two-element reaction coordinate (one nonzero off-diagonal force constant element) of the activated complex. This was confirmed on NiO. The probability of occurrance of crossovers, and hence temperature independence, is greater for symmetric reaction coordinate vibration and with increasing the complexity of reaction coordinate (more than one nonzero off-diagonal force constant). This can be applied for the activated complexes on ZnO.

All the above calculations are based on zero reaction coordinate frequencies. We have also made calculations using different values of  $\Delta_1$  [Eq. (10)] and  $\Delta_2$  [Eq. (13)]. Results for two typical activated complex models are graphically shown in Figs. 10 and 11. The dependence of TIF on  $\Delta$  (and thus indirectly on reaction coordinate frequencies) is in the case of  $(CO_3)^{\ddagger}$  complex very large at negative  $\Delta$  values, but TDF dependence on  $\Delta$  for  $(CO_2)^{\ddagger}$  and  $(CO_3)^{\ddagger}$  complexes becomes important at positive values. This obliges us to strictly use the interpretation of the kinetic isotope effects in this paper with a limitation to zero reaction coordinate frequencies. Further calculations are still in progress and will be elaborated separately.

Activated complexes comprising two or more carbon atoms, though these structures were found as intermediates in some chemical reactions, <sup>46,47</sup> have until now not been taken into consideration.

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