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Isotope Effects in Isotope-Exchange Reactions: Evidence for a Large $^{12}C/^{13}C$ Kinetic Isotope Effect in the Gas Phase

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The O-exchange reaction between CO_2^+ and CO is triggered by two different entrance channels in ^{13}C-labeled systems. The unimolecular dissociation of the $C^{13}CO_3^+$ reactive intermediate is investigated at varying energies by mass spectrometric techniques. An almost "one-way" O-exchange at energies close to the dissociation threshold discloses a remarkably large intramolecular $^{12}C/^{13}C$ kinetic isotope effect ranging from 6.0 to 7.3 ± 0.5.

Introduction

Isotope effects are key to understanding reaction mechanisms because isotopic substitution affects reaction rates and equilibrium constants.[1] In the past decade, the study of isotope variations in nature has shown that anomalous fractionations might be key to better understanding isotope effects.[2] In this context, carbon oxides are the focus of great interest; mass-dependent and -independent isotope effects have been studied in neutral and ionic reactions involving either CO_2 or CO, relevant to isotopic fractionation in planetary atmospheres.[2,3] We report herein an unusually large $^{12}C/^{13}C$ kinetic isotope effect (KIE) measured in the ion−molecule reaction between CO_2^+ and CO.

We have previously reported that the CO_2^+ ion reacts with CO, undergoing O-exchange.[4] A possible approach to isotope effects in isotope-exchange reactions is the study of intramolecular effects in the unimolecular dissociation of the reactive intermediate.[5,6] This allows investigation of reaction rates under identical conditions for light and heavy elements because one reactant with a given density of quantum states is involved.[5,7] Competitive reaction channels have also to be considered as they can modify the magnitude of these kinetic isotope effects.[8] The large $^{12}C/^{13}C$ KIE, associated with the O-exchange reaction between CO_2^+ and CO, is devoid of any contribution from other superimposed isotope effects, and to the best of our knowledge, it is unprecedented.

Experimental Section

A. Mass Spectrometric Methods. All experiments were performed using a modified ZABSpec oa-TOF instrument (VG Micromass) of EBE-TOF configuration, where E and B stand for electric and magnetic sectors, respectively, and TOF stands for an orthogonal time-of-flight mass spectrometer.[9] Mixtures containing labeled and unlabeled carbon oxides were preliminarily prepared in a vacuum line in CO/CO_2 ratios ranging from 10:1 to 20:1. They were introduced into the ion source under the pressure of 0.1−0.2 Torr, as read inside the source block by a Magnehelic differential pressure gauge. The MIKE (mass-analyzed ion kinetic energy) spectra were recorded at 8 keV, averaged over 150 acquisitions, and repeated over an extended time period to average ~20 spectra. The same spectra were obtained in the whole range of investigated CO/CO_2 ratios. The CAD (collisionally activated dissociation) spectra were recorded using helium as the target gas; it was admitted into the collision cell at such a pressure to achieve 80% transmittance. The MIKE and CAD spectra of the natural ^{13}C isotopomer of $C_2O_3^+$ were recorded under the same conditions using the unlabeled CO/CO_2 mixture (10:1). The MIKE and CAD abundances were measured by peaks areas.

In ^{13}C-labeled systems, any contribution from ^{17}O was excluded by the elemental analysis of the parent ion and its fragments in the TOF sector of the instrument. These CAD/TOF spectra were recorded at 0.8 keV after mass and energy selection of the ion. In these systems, a possible source of $C_2{}^{17}OO_2^+$ was the ^{17}O isotopomer of $C_2O_3^+$. A peak at m/z 72 ($C_2O_3^+$) was however observed only in the $^{13}CO_2/CO$ mixture (from subsequent reaction of the exchanged CO_2^+ ion with CO). The ^{17}O contribution to m/z 73 was evaluated to be vanishingly small (≤0.023%), consistent with the elemental analysis. In the unlabeled system (CO/CO_2), the ^{17}O contribution to m/z 73 was evaluated to be 5%.

B. Materials. The CO_2 and CO carbon oxides utilized in this study were ^{13}C-depleted (Isotec), with a stated purity in excess of 99.95 mol %. The following labeled compounds were used: ^{13}CO (Isotec, 99.0 ^{13}C atom %), $^{13}CO_2$ (Isotec, 99.0 ^{13}C atom %), $C^{18}O$ (Euriso-Top, 99.58 ^{18}O atom %), and $C^{18}O_2$ (CIL, 95.0 ^{18}O atom %). CO_2 and CO research-grade products were used to study the ^{13}C isotopomer of $C_2O_3^+$ (99.95 mol %).

Results and Discussion

In a previous extensive study performed on various ^{13}C- and ^{18}O-labeled ions at varying pressure and energy, we have

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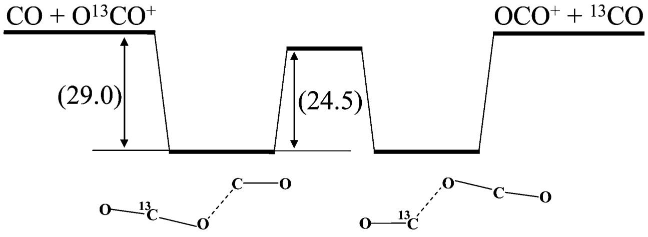
SCHEME 1: Simplified Energy Profile of the O-Exchange Reaction between CO_2^+ and CO[a]



[a] The energy values refer to unlabeled species (kcal mol^{-1}, $\Delta H°$, 298 K, from ref 4, re-evaluated at the B3LYP//CCSD(T) aug-cc-pVTZ level of theory).

showed that the O-exchange between CO_2^+ and CO occurs via $[OCO-CO]^+$ ion−molecule complexes[4]

$$^{13}CO_2^+ + CO \rightleftarrows [O^{13}CO\cdots CO]^+ \rightleftarrows [O^{13}C\cdots OCO]^+ \rightleftarrows CO_2^+ + {}^{13}CO \quad (1)$$

The main features of reaction 1 are summarized as follows (see also the simplified Scheme 1): (i) the O-exchange critically depends on the energy content of the $C^{13}CO_3^+$ intermediates; it is less effective at increasing energy, when significant back dissociation occurs; (ii) the $C^{13}CO_3^+$ ions unimolecularly dissociate into CO_2^+ (exchanged and original); in addition, CO^+ fragments are observed at increasing energy; (iii) according to electronic structure calculations at different levels of theory, ions of different structure are the highest-energy species or not stable minima.[4,10,11]

The aim of this study is the measurement of the $^{12}C/^{13}C$ KIE associated with the isotope-exchange reaction. The experimental conditions were hence optimized to ensure formation of low-energy CO_2^+ reactant ions that more effectively undergo O-exchange. These conditions are reached using preformed mixtures containing labeled and unlabeled (^{13}C-depleted) carbon oxides, with CO/CO_2 ratios as high as 10−20:1. In such case, the CO_2^+ reactant ion is formed softly by a slightly exothermic ($\Delta H° = -5.5$ kcal mol^{-1}) and very efficient ($k = 10^{-9}$ cm^3 molecule^{-1} s^{-1}) charge transfer from CO^+.[12]

The dissociation of the $C^{13}CO_3^+$ intermediates was studied by MIKE spectrometry,[5] which samples the metastable fraction having a narrow energy range close to the dissociation limit. This fraction unimolecularly decomposes, with rate constants typically ranging from 5 to 10×10^6 s^{-1}. The only product observed is the CO_2^+ ion (exchanged and original), whereas CO^+ is nearly negligible, which indicates that the metastable ions have a small energy excess (<0.24 eV).[12a]

The $C^{13}CO_3^+$ intermediates were prepared using two different routes; they were generated by ionization of $CO/^{13}CO_2$ and $^{13}CO/CO_2$ mixtures from reactions 1a and 1b, respectively

$$^{13}CO_2^+ + CO \rightarrow \underset{\mathbf{1}^+}{[O^{13}CO\cdots CO]^+} \quad (1a)$$

$$CO_2^+ + {}^{13}CO \rightarrow \underset{\mathbf{2}^+}{[OCO\cdots {}^{13}CO]^+} \quad (1b)$$

The two reactions differ for the initially formed complexes $[O^{13}CO\cdots CO]^+$ and $[OCO\cdots {}^{13}CO]^+$, henceforth denoted as $\mathbf{1}^+$ and $\mathbf{2}^+$, respectively. They hence differ for the entrance channel of the process (Scheme 1); $^{13}CO_2^+$ and CO_2^+ are the original and exchanged CO_2^+ ions for reaction 1a, whereas the opposite is true for reaction 1b.

If reversible atom exchange occurs prior to dissociation, partial or complete randomization are typically observed. Accordingly, orig/exch CO_2^+ ratios ≥ statistical would be expected. Table 1 shows that the metastable population formed by reaction 1a only partially undergoes O-exchange, whereas that formed by reaction 1b surprisingly shows an extent of O-exchange even higher than that expected from statistics. In summary, the metastable $C^{13}CO_3^+$ ions formed by both reactions 1a and 1b predominantly dissociate into $^{13}CO_2^+$, which is the original CO_2^+ for reaction 1a and the exchanged CO_2^+ for reaction 1b (Figure 1A,B).

A rationale for these results can be found in the isomerization−dissociation sequences that characterize the whole process. Two isomerization−dissociation routes can be identified: $\mathbf{a} = \mathbf{1}^{+*} \rightarrow \mathbf{2}^{+*} \rightarrow CO_2^+$ and $\mathbf{b} = \mathbf{2}^{+*} \rightarrow \mathbf{1}^{+*} \rightarrow {}^{13}CO_2^+$, where $\mathbf{1}^{+*}$ and $\mathbf{2}^{+*}$ are the vibrationally excited ions sampled by MIKE

$$^{13}CO_2^+ + CO \xleftarrow{k_{d1}} \underset{\mathbf{1}^{+*}}{[O^{13}CO\cdots CO]^+} \underset{k_{i2}}{\overset{k_{i1}}{\rightleftarrows}} \underset{\mathbf{2}^{+*}}{[O^{13}C\cdots OCO]^+} \xrightarrow{k_{d2}} CO_2^+ + {}^{13}CO \quad (2)$$

Reactions 1a and 1b allow us to see one route at a time (**a** or **b**, respectively). The evidence from reaction 1b is particularly telling; the significant O-exchange of the $[O^{13}C\cdots OCO]^+$ complexes $\mathbf{2}^{+*}$ by route **b** is an almost "one-way" process, pointing to an isomerization−dissociation sequence that is much faster than the reverse one. Consistent with this, the ions directly formed as the $[O^{13}CO\cdots CO]^+$ complexes $\mathbf{1}^{+*}$ by reaction 1a are reluctant to go by route **a**, giving only 12% of the exchanged CO_2^+. This amount is less than that observed by high-energy CAD and from the high-energy fraction decomposing in the source (Table 1). Here, simple-bond cleavage reactions are largely favored with respect to isomerizations due to the steep rise of their rate constant with the ion energy.[13] All of these findings point to a primary isotope effect that decreases at increasing energy[5,7] and privileges one direction of the process.

The comparison of routes **a** and **b** shows that their isomerization steps are mirror-like with regard to the $^{13}C-O$ and $C-O$ bonds made or broken through the symmetrical saddle point.[4] The dissociation steps instead differ because only that of **a** has the ^{13}C atom involved in the fragmentation. Intramolecular KIE only reflect the transition-state properties of the relevant processes; however here, two reactive intermediates are distinguished. Thus, their properties and reactions at the central barrier may play a role in the process, as discussed in the last paragraph.

It is evident from the above that two conditions must be met to observe the statistical ratios of Table 1, (1) randomization prior to dissociation and (2) no isotope effect. The two factors may be interlinked. For instance, the competition of the back dissociation with isomerization is known to reduce the efficiency of bimolecular processes occurring through double-well energy surfaces. [14a] This effect increases with energy and may be reduced in unimolecular dissociations of activated intermediates with a given internal energy distribution (e.g., between the isomerization and dissociation barriers).[14b−d] As anticipated, the sampled $C^{13}CO_3^+$ ions have a narrow energy excess, and the back dissociation significantly occurs under conditions where an intense CO^+ fragment is also observed in the MIKE spectrum.[4] Nonetheless the question arises whether the dissociation into the original CO_2^+ can entirely be traced to the isotope effect in these experiments. The following experiments help to disentangle these factors.

TABLE 1: Original/Exchanged CO_2^+ Ratios from Dissociation of $C^{13}CO_3^+$ Ions

reactants	precursor ions	orig./exch. CO_2^+fragments	*m/z*	MIKE[a]	CAD[a]	source[b]	statistical
$^{13}CO_2/CO$	$C^{13}CO_3^+$ (**1**$^+$)	$^{13}CO_2^+/CO_2^+$	45/44	88/12	69/31	63/37	50/50
$CO_2/^{13}CO$	$C^{13}CO_3^+$ (**2**$^+$)	$CO_2^+/^{13}CO_2^+$	44/45	28/72	70/30	65/35	50/50
CO_2/CO	$C^{13}CO_3^{+c}$		44/45	19/81[d]	50/50		50/50

[a] Intensities derived from peak areas. Uncertainty ≤ ±5%. [b] Uncertainty ±10%. [c] Natural isotopomer of $C_2O_3^+$. [d] The low abundance of the precursor ion prevents an accurate measurement. Uncertainty (*m/z* 44) ±20%.

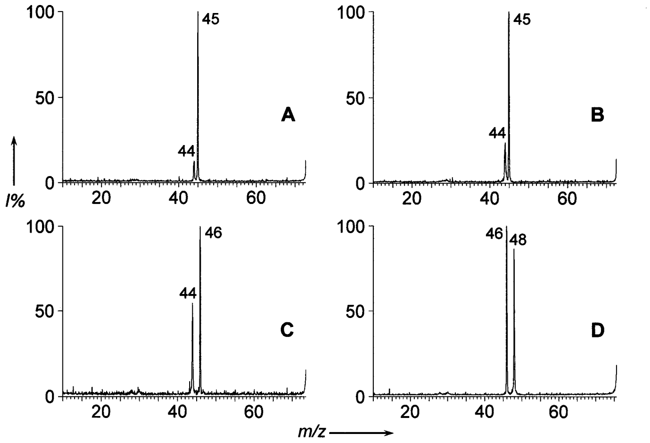


Figure 1. MIKE spectra of $C^{13}CO_3^+$ ions (*m/z* 73) from (A) a 10:1 $CO/^{13}CO_2$ mixture (precursor ion **1**$^+$) and (B) a 10:1 $^{13}CO/CO_2$ mixture (precursor ion **2**$^+$). MIKE spectra of (C) $C_2O_2{}^{18}O^+$ ions (*m/z* 74) from a 10:1 $C^{18}O/CO_2$ mixture and (D) $C_2O^{18}O_2^+$ ions (*m/z* 76) from a 10:1 $CO/C^{18}O_2$ mixture.

The first one examines the dissociation of a randomized population, typically represented by the natural ^{13}C isotopomer of $C_2O_3^+$ (Table 1).[15] Although no orig/exch CO_2^+ ratio can be measured in such a case, a high metastable $^{13}CO_2^+/CO_2^+$ ratio is observed. The result is due to the isotope effect that kinetically favors route **b** to $^{13}CO_2^+$ by the underlying mechanism clearly evidenced in reactions 1a and 1b. Conversely, the statistical ratio is observed by CAD, where both of the required conditions are met.

The second experiment involves $C_2O_2{}^{18}O^+$ ions, prepared from the reaction of CO_2^+ and $C^{18}O$. Here, the metastable orig/exch CO_2^+ ratio approaches statistics, whereas the back dissociation remains competitive in the high-energy CAD (Table 2; Figure 1C). This system proves to be a good approximation to the pure competition between isomerization and back dissociation at varying energies, consistent with the fact that both processes do not directly involve ^{18}O in the initially formed $[OCO\cdots C^{18}O]^+$ and "exchanged" $[OC\cdots OC^{18}O]^+$ complexes. We exclude that the MIKE ratio reflects a secondary isotope effect, based on the following evidence. It was previously shown that multilabeled ions undergo scrambling prior to dissociation (particularly at high CO/CO_2 pressure ratios).[4] The nature of this scrambling denotes intracomplex rotations leading to different arrangements of the same CO and CO_2 moieties (for instance, $[OC\cdots O{*}C{*}O]^+ \rightarrow [OC\cdots{*}O{*}CO]^+$).[16] Accordingly, the MIKE ratio can be attributed to the contribution of $[OC\cdots{}^{18}OCO]^+$ ions, which likely accounts for the nearly statistical value as well. Consistent with this, metastable $C_2O^{18}O_2^+$ ions (from the reaction between $C^{18}O_2^+$ and CO) do not reach the statistical ratio in the time available (Figure 1D). Here, all processes including rotations involve ^{18}O in the initially formed $[^{18}OC^{18}O\cdots CO]^+$ and "exchanged" $[^{18}OC\cdots{}^{18}OCO]^+$ complexes.

As a whole, these results show that, under the experimental conditions used in this study, the isomerization effectively occurs until randomization in the metastable time window. Different results can be traced to isotope effects, as demonstrated by the MIKE dissociation of the natural isotopomer of $C_2O_3^+$. The primary isotope effect associated with the O-exchange can hence be measured in ^{13}C complexes when the reaction is triggered by two different entrance channels. Importantly, the different metastable $^{13}CO_2^+/CO_2^+$ ratios, recorded in reactions 1a and 1b, show that the decomposing ions $\mathbf{1}^{+*}$ and $\mathbf{2}^{+*}$ do not equilibrate. This key result indicates that the intermediates have different k_i/k_d branching ratios, which affect the consecutive process in a different manner depending on the entrance channel.

The abundance of the exchanged CO_2^+ ions, exclusively formed by processes **a** and **b** under the constraint of the direct dissociation, makes allowance for all factors, giving $^{12}C/^{13}C$ KIE $= 6.0 \pm 0.3$. The maximum $^{12}C/^{13}C$ KIE effect of 7.3 ± 0.5 is measured in reaction 1a, where dissociation and isomerization−dissociation processes are involved. Notably, the effect could vary depending on the observation time window that affects the metastable dissociations.[5,6g]

The magnitude of this effect is actually surprising, given the tiny ZPE differences. It is well-known that H/D intramolecular KIE are magnified in gaseous ions that fragment at the threshold by simple-bond cleavage;[5,7] yet, large heavy-atom KIE are less common. Recently, Cooks has reported a very large, inverse $^{35}Cl/^{37}Cl$ KIE (0.026 near the threshold), pointing out the role of rotational energy in the dissociation at the threshold of ion−molecule complexes.[6a] A $^{12}C/^{13}C$ effect of ∼3 has been observed with exceptionally high H/D effects,[6d] whereas mass-independent isotopic fractionations have been observed in the ion−molecule reaction between CO_2^+ and CO_2.[3d] Strong unconventional mass-dependent effects have also been found in some asymmetric ozone formation reactions under the pressure of 200 Torr.[17] Following the seminal work by Marcus and co-workers, many theoretical models have been developed based on recombination−dissociation (isotope-exchange) reactions, excited ozone lifetime, and other properties at the threshold of ozone metastable states or van der Waals-type states.[2c−e,18]

Despite this great effort, a unified theory that explains unconventional heavy-atom KIE is still awaited. In our experiments, the negligible fragmentation into CO^+ suggests that the ions populate a narrow energy range near the threshold for dissociation. Only one limit may be evaluated, <0.24 eV, though

TABLE 2: Original/Exchanged CO_2^+ Ratios from Dissociation of ^{18}O-Labeled $C_2O_3^+$ Ions

Reactants	precursor ions	orig./exch. CO_2^+ fragments	*m/z*	MIKE[a]	CAD[a]	source[b]	statistical
$CO_2/C^{18}O$	$C_2O_2{}^{18}O^+$	$CO_2^+/OC^{18}O^+$	44/46	39/61	59/41	65/35	33/67
$C^{18}O_2/CO$	$C_2O^{18}O_2^+$	$C^{18}O_2^+/OC^{18}O^+$	48/46	49/51	60/40	62/38	33/67

[a] Intensities derived from peak areas. Uncertainty ≤ ±5%. [b] Uncertainty ±10%.

the excitation internal energy could be lower. As a possible hypothesis for our results, we suggest that the KIE reflects the combined effect of the low-energy excess and the competitive, isotopically specific reactions that occur in a consecutive process involving two intermediates. It is well-known that kinetic isotope effects are dramatically magnified by competitive reactions occurring with one intermediate.[8] Here, the different branching ratios of the two intermediates combine in the repeated consecutive process, and the different bottleneck at the central barrier may contribute to magnify the effect, eventually favoring the $\mathbf{2}^{+*} \rightarrow \mathbf{1}^{+*} \rightarrow {}^{13}CO_2^+$ route **b**. Moreover, a nonstatistical behavior of the "exchanged" complex may affect its lifetime (by prompt dissociation) and further enhance the difference in favor of route **b**. In this light, the density of states of the two intermediates could play non-negligible roles near the threshold. These and other aspects (e.g., centrifugal potentials), relevant to the microscopic pathways in the two directions, would be worthy of further investigation to elucidate this unusual enrichment of ${}^{13}CO_2^+$.

In conclusion, the O-exchange reaction between CO_2^+ and CO has been performed under conditions where the fine balance between equilibration and dissociation provides a magnifying lens on the two directions of the process, allowing a large ${}^{12}C/{}^{13}C$ KIE to be measured. This unconventional ${}^{12}C/{}^{13}C$ KIE indicates that similar effects might operate in laboratory studies, and in atmospheric phenomena evolving from nonequilibrated species that populate a narrow energy range.

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