Experimental Evidence for Oxygen Isotope Exchange between CO_2 Molecules, Adsorbed in an NaY Zeolite at 0 °C

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Summary When natural CO_2, to which a known proportion of ^{13}C and ^{18}O enriched CO_2 has been added is adsorbed on an NaY zeolite at 0 °C, differences in isotopic composition before and after adsorption, determined by mass spectrometry, indicate that oxygen exchange between CO_2 molecules has occurred during adsorption.

WHEN two gases are mixed, the mass spectrum of the blend gas can be predicted from the mixing ratio and the mass spectrum of the components. In this study, mixtures were prepared by volumetrically mixing CO_2 with natural and artificial isotopic compositions (Table 1) and their mass spectra were recorded both before and after the mixtures had been adsorbed overnight on an NaY zeolite at 0 °C. The differences between the mass spectra before and after adsorption yield evidence for oxygen exchange between adsorbed CO_2 molecules.

TABLE 1. Measured fractions of the different isotopic CO_2^+ ions in the CO_2 used.

Species	Symbol	Fraction in natural CO_2	Fraction in tracer CO_2
$^{12}C^{16}O_2$	^{44}A	0·9846	0·0725
$^{13}C^{16}O^{17}O$ $^{13}C^{16}O_2$	^{45}A	0·0114	0·8609
$^{12}C^{16}O^{18}O$ $^{13}C^{16}O^{17}O$	^{46}A	0·0040	0·0064
$^{12}C^{17}O^{18}O$ $^{13}C^{16}O^{18}O$	^{47}A	—	0·0592
$^{12}C^{18}O_2$	^{48}A	—	0·0001
$^{13}C^{18}O_2$	^{49}A	—	0·0010

As can be seen in Table 2, the CO_2 tracer sample is not only enriched in ^{13}C, but also in ^{18}O (from the natural 0·2% to 3·3%). Therefore, when tracer and natural CO_2 are mixed, the CO_2 molecules in the blend which contain ^{12}C have an average oxygen isotopic composition different from that of the CO_2 molecules containing ^{13}C.

TABLE 2. Isotopic compositions of C and O in CO_2 used.

Symbol	Fraction in natural CO_2	Fraction in tracer CO_2
^{12}A	0·9896	0·0776
^{13}A	0·0107	0·9224
^{16}A	0·9976	0·9661
^{17}A	0·0004	0·0007
^{18}A	0·0020	0·0332

In the blend, the ratio R_1 of CO_2 molecules with mass 45 to those with mass 44 can be written as in equation (1)

$$R_1 = \frac{^{45}A_b}{^{44}A_b} = \frac{^{45}A_nF_n + {}^{45}A_tF_t}{^{44}A_nF_n + {}^{44}A_tF_t} = \frac{^{45}A_n + M.{}^{45}A_t}{^{44}A_n + M.{}^{44}A_t} \quad (1)$$

where n, t, and b denote the natural, tracer, and blend CO_2 respectively. M stands for the mixing ratio, *i.e.* the ratio of tracer CO_2 molecules to those with natural isotopic composition. F denotes a mixing fraction, so that $F_n = 1/(M + 1)$ and $F_t = M(M + 1)$. The different molecular ions which a CO_2 molecule can generate (masses 44—49) are a result of different combinations of C and O isotopes. For reasons of convenience, however, molecular ions with mass 44—49 from a CO_2 molecule can formally be treated as 'isotopic ions' of one 'element.' ^{m}A stands for the abundance of the isotopic ion with mass m, defined as the number of 'isotopes' m compared with the total number of atoms of the 'element' concerned. The abundances of ^{12}C, ^{13}C, ^{16}O, ^{17}O, ^{18}O, $^{44}(CO_2)$ ... $^{49}(CO_2)$ may be written as ^{12}A, ^{13}A, ^{16}A, ^{17}A, ^{18}A, ^{44}A ... ^{49}A.

If, however, isotopic equilibration can take place, *i.e.*, if oxygen exchange between the CO_2 molecules of the blend is possible, then a uniform oxygen isotopic composition is reached, valid for all CO_2 molecules, regardless of the mass of the C atom. In that case, the ^{18}O atoms, initially found mainly on $^{13}CO_2$ molecules, are distributed equally among all CO_2 molecules. This means that part of the $^{13}C^{18}O^{16}O$ molecules have exchanged their ^{18}O for an ^{16}O, whereas part

of the $^{12}C^{16}O^{16}O$ have received an ^{18}O for an ^{16}O. Therefore, after equilibration, there will be more molecules with masses 45 and 46, and fewer with masses 44 and 47 (the changes in the number of molecules with mass 48 and 49 are unimportant here). Moreover, the number of $^{12}C^{16}O^{17}O$ molecules is much smaller than the number of $^{13}C^{16}O^{16}O$ molecules, so that the 45:44 ratio can be approximated by equation (2). The ratio $R_1:R_2$ can be written as a function

$$R_2 = \frac{F_n{}^{13}A_n + F_t{}^{13}A_t}{F_n{}^{12}A_n + F_t{}^{12}A_t} = \frac{{}^{13}A_n + M.{}^{13}A_t}{{}^{12}A_n + M.{}^{12}A_t} \qquad (2)$$

of the mixing ratio M by combining equations (1) and (2) as equation (3). The Figure (a) shows the α vs. M curve

$$\alpha(M) = \frac{R_1}{R_2} = \frac{({}^{45}A_n + M.{}^{45}A_t)\ ({}^{12}A_n + M.{}^{12}A_t)}{({}^{44}A_n + M.{}^{44}A_t)\ ({}^{13}A_n + M.{}^{13}A_t)} \qquad (3)$$

expected when complete isotopic equilibration takes place.

The ratios R_1 and R_2 can be measured mass spectrometrically as the ratio of the peak heights at m/e 45 and 44, before and after the prepared CO_2 mixture is passed over the NaY zeolite sample. In the Figure (a) a number of experimental α values at different mixing ratios are shown. As can be seen, the experimentally observed difference in the 45:44 ratio before and after adsorption can be quantitatively explained assuming exchange of oxygen atoms between adsorbed CO_2 molecules.

Analogous experiments have been carried out with CO present in the CO_2 mixtures. The Figure (b) shows the relative difference $\Delta\alpha$ between measured α values (α_{meas}) and α values calculated assuming complete isotopic equilibration ($\alpha_{is.eq}$), as a function of the total CO_2 content (natural + tracer CO_2) of the mixture before adsorption. When the CO_2 content is $> 13\%$ (CO content $< 87\%$) isotopic equilibration is apparently complete ($\Delta\alpha = 0$). Below this value, the presence of CO molecules in the adsorbed phase makes oxygen exchange between CO_2 molecules more difficult, thus increasing $\Delta\alpha$. This increase appears not to be influenced by the adsorption time.

After adsorption, the zeolite sample holder can be cut off and the remaining gas evacuated. This gas is depleted in CO_2, since it is well known that NaY zeolite preferentially adsorbs CO_2 from $CO-CO_2$ mixtures.[1] The gas inside the sample holder (consisting of the adsorbed phase and a smaller gas phase) is then expanded into the system. Owing to the selective properties of the NaY zeolite, this will considerably increase the CO_2 content of the adsorbed phase. As a result, isotopic equilibration will proceed further ($\Delta\alpha$ approaches 0) as can be seen in the Figure (b). After a third adsorption step, $\Delta\alpha$ will again become smaller. Complete isotopic equilibration ($\Delta\alpha = 0$) will, however, not be reached by this procedure of repeated adsorption, because
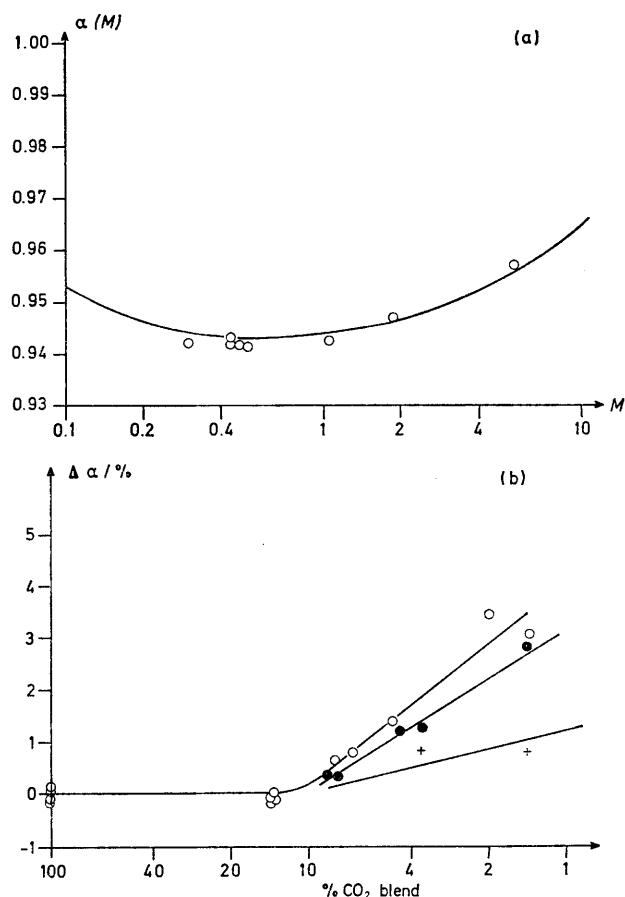

FIGURE. (a) Calculated $\alpha(M)$ vs. M curve on the basis of equation (3) assuming complete isotopic equilibration and experimentally observed points. (b) $\Delta\alpha = 100\ (\alpha_{meas} - \alpha_{is.eq})/\alpha_{is.eq}$ as a function of the total CO_2 content of the blend before adsorption. $\bigcirc$: after 1 adsorption; $\bullet$: after 2 adsorptions; $+$: after 3 adsorptions.

every step not only increases the CO_2 content of the adsorbed phase, but at the same time strongly decreases the total number of adsorbed molecules, thus enlarging the average distance between the adsorbed CO_2 molecules. Further investigation is necessary in order to reach a conclusion about the possible mechanism for the observed isotopic exchange. Indeed, there is no evident explanation for an O atom of CO_2 being so loosely bound to the C atom that exchange with an O atom of another CO_2 molecule can take place.

[1] E. F. Vansant, G. Peeters, and I. Michelena, J. Chem. Research, 1978, (S), 90; (M), 1165.