Oxygen Exchange in Chemisorbed Carbon Monoxide[1]

BY A. N. WEBB AND R. P. EISCHENS

The exchange of oxygen between molecules of carbon monoxide chemisorbed on iron is appreciable (20% of completion) at $-78°$. The extent of exchange appears to increase with temperature. Portions of carbon monoxide pumped off at 160° show almost complete exchange. Oxygen and carbon dioxide have little effect on the exchange of oxygen between carbon monoxide molecules. The exchange is influenced by the presence of gaseous CO. There is no detectable oxygen exchange between CO and CO_2 over iron at 25°.

Introduction

The conventional theory of the nature of chemisorbed carbon monoxide has been strongly influenced by analogy with the structure of metal carbonyls. According to this analogy carbon monoxide is chemisorbed as a molecule bonded to the metal through the carbon atom. The theory that carbon monoxide is chemisorbed as a molecule rather than as separate carbon and oxygen atoms is supported by adsorption work in which it was found that chemisorbed carbon monoxide appears to occupy only one site on nickel and iron surfaces.[2,3]

On the basis of the simple molecular theory of chemisorption it would be expected that an oxygen atom would remain bonded to the same carbon atom during the adsorption–desorption cycle. The present work was undertaken to study the exchange of oxygen atoms between molecules of chemisorbed carbon monoxide. The general procedure was to chemisorb a mixture of carbon monoxide highly enriched with $C^{13}O$ and CO^{18} and then measure the amount of $C^{13}O^{18}$ in the desorbed gas. The presence of $C^{13}O^{18}$ in amounts greater than expected from normal abundance ratios is proof that intermolecular oxygen exchange occurs while carbon monoxide is chemisorbed on iron.[4]

The fact that oxygen exchange occurs indicates that the nature of chemisorbed carbon monoxide is more complicated than expected from the simple analogy with the structure of metal carbonyls. However, the fact that exchange occurs is not proof that chemisorbed carbon monoxide is dissociated into atoms. The possibility of associative exchange mechanisms must be considered. Because of this an attempt was made to obtain information on the mechanism of the oxygen exchange by studying the effect of oxygen, carbon dioxide and gaseous carbon monoxide.

Experimental

Apparatus.—The apparatus consisted of a conventional volumetric adsorption system equipped with a combination mercury diffusion-Sprengel pump to collect gas pumped off at low pressures.[5] The gas analyses and isotope species determinations were made with a Consolidated Engineering Type 21-101 mass spectrometer.

Materials.—The iron was prepared from the oxide by hydrogen reduction. A hydrated oxide precipitated from nitrate solution with ammonium hydroxide was formed in $1/4''$ pellets, calcined 6 hours at 540° and reduced in flowing hydrogen for six days at 400°. After this treatment the specific surface area by the BET nitrogen adsorption method was 4 m.^{2}/g. After the BET determination the iron was again reduced at 400° with flowing hydrogen for six days. The hydrogen was purified over copper at 400° and then passed through a charcoal filled trap immersed in liquid nitrogen. Experience shows that the second reduction would not decrease the surface area of the iron by more than 10%. After the final reduction the iron was pumped at 400° until the pressure was 10^{-4} mm. or less. Pumping was continued while the sample was cooled to the temperature of adsorption and the final pressure was about 10^{-6} mm. Chemicals of C.P. grade were used in preparation of the iron. Spectrographic analysis showed trace quantities of Cu and Si. The over-all purity was 99.9%.

The carbon labeled carbon monoxide, which will be referred to as $C^{13}O$, contains 38.2% $C^{13}O$. The O^{18} concentration of the oxygen in this material is the natural abundance, 0.20%. The $C^{13}O$ was prepared by reducing $C^{13}O_2$ over zinc at 425°. The $C^{13}O_2$ was obtained by addition of perchloric acid to $BaC^{13}O_3$ which was purchased from the Eastman Kodak Company. The carbon monoxide prepared in this manner was contaminated with 0.1% H_2 and 0.2% CH_4.

The O^{18} abundance in the CO^{18} was 14.4%.[6] The C^{13} concentration in the CO^{18} is the natural abundance of 1.1%. As received this gas contained 1.6% N_2, 0.4% O_2, 6.0% CO_2 and 1.4% H_2. The O^{18} abundances in the O_2 and CO_2 were the same as in the CO. Oxygen and CO_2 were removed by circulation over Cu at 500° and through a liquid nitrogen trap. Following this treatment the gas was 86.6% carbon monoxide and contained no detectable amount of O_2, $<0.1\%$ CO_2, 12.8% N_2 and 0.6% H_2. The O^{18} abundance was reduced to 13.0%.

Procedure.—In run A a mixture of 39.6 cc. of $C^{13}O$ and 51.9 cc. of unpurified CO^{18} was brought into contact with 91.1 g. of iron at $-78°$. After standing overnight the unadsorbed gas (15.8 cc.) was removed by pumping down to a pressure of less than 0.1 mm. with a Toepler pump. In run B a mixture of 34.8 cc. of $C^{13}O$ and 37.2 cc. of purified CO^{18} gas was exposed to 79.8 g. of the iron at $-196°$. After 30 minutes the residual pressure was less than 0.1 mm. and no appreciable amount of gas could be removed by the Toepler pump

The gas remaining on the iron sample after pumping with the Toepler pump was considered to be chemisorbed. The removal of the chemisorbed gas was started at the temperature of adsorption by pumping with the mercury diffusion-Sprengel pump. At the start of pumping at a given temperature the gas is removed at a rate of about 0.5 cc. per hour. After several hours the rate decreases to 1 or 2 cc. per day. When the pump-off rate became too low to be practical the collected batch was measured and transferred to a bulb for mass spectrometric analysis. The temperature of the adsorbent was then raised and pump-off of a new batch was started.

Experimental Results

Effect of Oxygen and Carbon Dioxide.—The oxygen exchange in the absence of gaseous CO was studied in two experiments. In run A unpurified CO^{18} was used while run B was conducted with purified CO^{18}. The important contaminants in the unpurified CO^{18} were the 0.4% O_2 and the 6.0% CO_2,

(1) Part of this paper was presented before the Petroleum Division of the American Chemical Society at Los Angeles in March, 1953.

(2) O. Beeck, A. E. Smith and A. Wheeler, *Proc. Roy. Soc., London*, **A177**, 62 (1940).

(3) S. Brunauer and P. H. Emmett, THIS JOURNAL, **62**, 1732 (1940).

(4) R. P. Eischens and A. N. Webb, *J. Chem. Phys.*, **20**, 1048 (1952).

(5) I. E. Puddington, *Ind. Eng. Chem., Anal. Ed.*, **16**, 592 (1944).

(6) The CO^{18} was obtained from A. D. Kirshenbaum, Research Institute of Temple University.

since these impurities might act as intermediates in the exchange of oxygen between molecules of chemisorbed CO. This type of mechanism would be possible if chemisorbed CO and CO_2 reacted with oxygen to form a dissociable complex as has been postulated for the chemisorption of CO on Cu and on Ni.[7,8]

The amounts of CO and CO_2 recovered by pumping at successively higher temperatures are shown in Table I. In run B the amounts of CO that could be pumped off before the rate of removal became negligible were considerably less than expected on the basis of Run A except at $-78°$. This indicates that the CO is more strongly chemisorbed when O_2 and CO_2 are not present. The nitrogen in the mixture used for run B was recovered in the batch pumped off at $-196°$. In run A it was more difficult to determine when the nitrogen in the original mixture was removed from the iron because air leaked into the bulbs containing the unadsorbed gas and the samples collected at -78 and $0°$. However, the oxygen–nitrogen ratio in the gas which was unadsorbed at $-78°$ indicates that practically all of the original nitrogen was in this portion.

TABLE I

RECOVERY OF CARBON MONOXIDE AND CARBON DIOXIDE

	Pump-off temp., °C.	Pumping time, hr.	CO, cc., S.T.P.	CO₂, cc., S.T.P.
Run A	Vol. added	..	86.5	3.1
	Unadsorbed[a]	..	14.4	0.6
	−78	28	12.1	1.6
	−33[a]	90	12.1	0.4
	0[a]	46	15.7	0.4
	25	72	13.8	0.1
	60	48	11.8	0.2
	120–160	52	2.4	2.2
	Not pumped off	..	4.2	−(2.4)
Run B	Vol. added	..	66.7	0
	−196	23	0.9	0
	−78	24	14.5	0
	−33	44	6.0	0
	0	47	8.7	0
	25	29	4.5	0
	60	42	5.1	0.1
	120–160	23	2.3	.8
	Not pumped off	..	24.7	−(.9)

In run A, where the original gas mixture contained CO_2 as an impurity, the CO_2 concentration in the pumped-off gas falls to a minimum at $25°$ and then starts to increase as the temperature is raised. In run B there is no CO_2 in the pumped-off gas until the temperature reached $60°$. The CO_2 in the batches collected at $60°$ and $120-160°$ is probably a product of the carbiding reaction
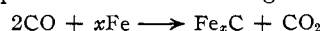
$$2CO + xFe \longrightarrow Fe_xC + CO_2$$

Table II shows the concentration of $C^{13}O^{18}$ in the carbon monoxide pumped off at the various temperatures. The mass spectrometric analyses are accurate to 5% of the reported value. In run A the analyses for the unadsorbed gas and the fractions

(7) W. E. Garner, T. J. Gray and F. S. Stone, *Faraday Soc. Discs.*, No. 8, 246 (1950).

(8) R. M. Dell and F. S. Stone, *Trans. Faraday Soc.*, **50**, 501 (1954).

collected at -78 and $0°$ were not successful because of air leakage into the sample bulbs prior to the mass spectrometric analysis determinations. This lowered the carbon monoxide concentration to levels so low that the isotopic composition could not be accurately measured.

In both runs there is a theoretical blank of 0.1% due to the natural abundance of C^{13} and O^{18}. A blank run was made to be certain that the chemisorption was the important factor in producing the exchange. For this blank a mixture of gases similar to those used for runs A and B was prepared and passed through the apparatus with no iron present. Analyses of the mixture before and after pumping showed the concentrations of $C^{13}O^{18}$ to be the 0.1% expected from the natural abundances of C^{13} and O^{18}.

The value of 0.1% $C^{13}O^{18}$ at $-196°$ in run B indicates that no exchange occurs at this temperature. In both runs there is a steady increase of $C^{13}O^{18}$ content as the pump-off temperature is increased. The maximum in run A is close to the 1.4% calculated for complex mixing. In run B, with purified CO^{18}, there is a greater exchange at lower temperatures but at $120-160°$ the equilibrium value, 1.3%, is not as closely approached as in run A.

TABLE II

$C^{13}O^{18}$ CONCENTRATION IN THE DESORBED CARBON MONOXIDE, %

Desorption temp., °C.	Run A	Run B
−196	..	0.1
−33	..	.4
−33	0.3	.5
0	..	.6
25	.4	.7
60	.6	.8
120–160	1.3	1.0
Complete exchange (calcd.)	1.4	1.3

In run B all of the CO_2 pumped off appears to stem from the carbiding reaction. The observed concentration of $C^{13}O^{16}O^{18}$ was 2.1% in the CO_2 removed at $60°$ and 2.3% in the $120-160°$ sample. These values agree closely with 2.05% and 2.27%, respectively, calculated on the basis of the $C^{13}O^{18}$ concentration. This agreement between the calculated and observed values shows that the CO_2 formed during carbiding is in isotopic equilibrium with the CO removed in the same batch.

Exchange between CO and CO_2.—In order to determine whether there is any formation of CO_2 from CO or CO from CO_2 over iron under conditions where there is no carbide formation a mixture of 20 cc. of $C^{13}O$ and 20 cc. of normal CO_2 was exposed to a 35-g. sample of reduced iron. The pressure of gas over the iron after this addition was 20 cm. After 60 hours at $25°$ there was no detectable increase of C^{13} in the CO_2. A second run was made using a mixture of 6.3 cc. of $C^{13}O^{18}$ (6.5% O^{18}, 20.2% C^{13}) and 10 cc. of normal CO_2. This mixture was exposed to 15 g. of reduced iron at $-78°$. This second experiment was designed to determine whether there is any oxygen exchange between CO and CO_2 during which the molecules maintained their original chemical form. No evidence for oxygen exchange between CO and CO_2

was found after 19 hours at $-78°$ and 3 hours at $25°$. There was some O^{18} in the CO_2 after the temperature was increased to $125°$. However this O^{18} in the CO_2 could be accounted for as a product of carbide formation using a material balance which shows that the C^{13} loss is in agreement with the amount of O^{18} appearing in the CO_2. The conclusion from this experiment is that there is no autooxidation–reduction of CO and CO_2 or oxygen exchange between CO and CO_2 over iron at temperatures where carbide formation does not occur.

Effect of Gaseous Phase.—The experimental procedure used in runs A and B in which the CO is desorbed at successively higher temperatures is in part dictated by the fact that chemisorbed CO cannot be removed by pumping unless the temperature is increased. This complicates the interpretation of results because the temperature and surface coverage variables are being changed simultaneously. It has been found that CO, chemisorbed on the type of iron used in the present experiments, can be exchanged with gaseous CO under conditions where it cannot be removed by pumping.[9] In order to determine how the exchange between molecules of gaseous and chemisorbed CO affects the oxygen exchange an experiment was conducted in which both types of exchange reaction were carried out at the same time.

A monolayer of 15.0 cc. of $C^{13}O$ was chemisorbed on 20.7 g. of reduced iron at $-78°$ then 16.5 cc. of CO^{18} was added to give a gaseous phase at a pressure of 30 cm.[10] The system was allowed to stand for one hour at $25°$. It was known that under these conditions there would be complete mixing of the gaseous and chemisorbed molecules.[9] Part of the gaseous phase was then removed and analyzed for $C^{13}O^{18}$ to determine the extent of oxygen exchange.

Complete mixing of all oxygen atoms in the system would increase the $C^{13}O^{18}$ from 0.07% (due to natural abundance) to 0.54%. The observed concentration was 0.5% showing that practically complete mixing has been obtained. The data in Table II show that the oxygen exchange was only half complete in the portions removed at $25°$. It is evident that deliberate inclusion of a gaseous phase has markedly increased the extent of the exchange.

Discussion

Four questions will be considered in the discussion of the results of the oxygen exchange experiments.

(1) Is CO chemisorbed as a molecular unit or does it dissociate into separate oxygen and carbon atoms?

(2) Can the exchange take place if only CO is present or is it necessary to have extra oxygen in order to form a complex such as $[CO_3]$?

(3) If exchange mechanisms based on dissociation of the chemisorbed CO or formation of oxygen-rich complex are not indicated, what alternative mechanism is reasonable?

(4) Does the oxygen exchange proceed at the same rate on all parts of the iron surface?

It is reasonable to assume that oxygen exchange would occur if chemisorbed CO is dissociated into

(9) R. P. Eischens, This Journal., **74**, 6167 (1952).
(10) In this case the C^{13} abundance in $C^{13}O$ was 38.5% and the O^{18} abundance in CO^{18} was 5.3%.

atoms. However, it is not possible to conclude that the converse is true and that oxygen exchange is proof of dissociation. Other evidence against dissociation is exceptionally strong. The most conclusive evidence that CO is chemisorbed as a molecule is provided by infrared studies.[11] The fact that CO appears to occupy only a single site when chemisorbed on nickel and iron is also convincing.[2,3] The conclusion that CO is not dissociated is substantiated by the fact that very little oxygen exchange is observed in the gas removed at the low temperatures, since random recombination of dissociated molecules would result in at least half complete exchange.[12] These three lines of evidence lead to the conclusion that a mechanism other than dissociation into atoms must be used to explain the oxygen exchange in chemisorbed CO.

The evidence that chemisorbed CO can form a complex of the type $[CO_3]$ on Cu and Ni when oxygen is available appears to be conclusive.[7,8] A complex of this type could provide a path for oxygen if all of the oxygens in the complex are equivalent and if CO in the complex is in equilibrium with uncomplexed CO. The amount of complex present would be a direct function of the amount of oxygen available. The oxygen present as an impurity in run A should produce a marked increase in the amount of complex if complex formation occurs on iron. This would be expected to facilitate the oxygen exchange. Actually it is found that the impurity oxygen has not increased the extent of the oxygen exchange. This indicates that oxygen-rich complexes are not important factors in the mechanism of the exchange. This conclusion is strengthened by the fact that there is no exchange between CO and CO_2 since the oxygen-rich complex formation could also provide a path for this exchange.

If the evidence against mechanisms based on dissociation into atoms or oxygen-rich complexes is accepted one is forced to consider that the oxygen exchange takes place directly between carbon monoxide molecules. The exchange complex could involve only two CO molecules at one time,

$$\begin{bmatrix} O & O \\ \| & \times & \| \\ C & C \\ \wedge & \wedge \end{bmatrix},$$
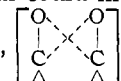
or it could extend over an entire crystal face

$$\begin{bmatrix} C & O & C & O & C & O & C \\ \wedge & & \wedge & & \wedge & & \wedge \end{bmatrix}.$$ This type of exchange complex differs from the oxygen-rich complex previously discussed because it has only one oxygen for each carbon. In the exchange complex an oxygen atom becomes bonded to two carbon atoms at the same time and it never exists as a separate atom even though it finally becomes bonded to a different carbon than the one it was bonded to prior to chemisorption.

The increase in $C^{13}O^{18}$ concentration in the gas pumped off in runs A or B could be attributed either to the effect of increasing temperature or to the fact that the exchange does not proceed to the same extent on all parts of the surfaces. If the latter were

(11) R. P. Eischens, W. A. Pliskin and S. A. Francis, *J. Chem. Phys.*, **22**, 1786 (1954).
(12) This minimum exchange would occur if recombination were confined to adjacent immobile pairs. Complete mixing would be approached as recombination occurred randomly among larger numbers of molecules.

correct the increase in the $C^{13}O^{18}$ concentration would be explained if the extent of the exchange is greatest on the portions of the surface where the CO is most strongly bonded. In this case the $C^{13}O^{18}$ concentration in the desorbed gas would not be the same as in the gas remaining on the surface.

If the exchange proceeds uniformly over the entire surface and the increase in $C^{13}O^{18}$ concentration is due to the increases in temperature, the $C^{13}O^{18}$ concentration in the desorbed gas would represent the concentration in the gas remaining on the surface. Since the CO_2 formed during carbiding is in isotopic equilibrium with the carbon monoxide pumped off simultaneously, it appears that at 60° or above, the $C^{13}O^{18}$ concentration in the desorbed carbon monoxide is the same as that in the gas remaining on the surface. This is based on the assumption that the oxygen exchange and carbide formation are independent processes so that one would not expect them to be in isotopic equilibrium unless the CO_2 was formed from carbon monoxide which had the same $C^{13}O^{18}$ concentration as the carbon monoxide pumped off.

The effect of a gas phase in markedly increasing the extent of exchange could be due to two factors. The gaseous phase could simply provide a means of transporting chemisorbed carbon monoxide from inactive to active parts of the surface. It is known that under these conditions exchange of CO molecules between the gaseous and chemisorbed phases is rapid and complete.[9] The second factor is the maintenance of a fully covered surface by the gaseous phase. On a sparsely populated surface there are few pairs of adjacent molecules and exchange depends upon surface migration. According to this concept the apparent exchange rate would become slower as coverage decreased even on a uniform surface. By increasing the gas phase pressure the full coverage rate is maintained at the higher temperatures. At present there are not enough data to clearly differentiate between the transport and full coverage mechanism. The full coverage mechanism appears more plausible because it is consistent with the uniform surface concept indicated by the formation of CO_2 in isotopic equilibrium with the CO.

It is apparent that the discovery that oxygen exchange occurs in chemisorbed CO poses more questions than it answers. Despite the difficulties found in trying to arrive at unreserved conclusions it appears that the oxygen exchange will prove to be valuable in the study of how the nature of CO is modified by chemisorption.

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Low Temperature Heat Capacity of Ceylon Graphite

By Warren DeSorbo

Low-temperature specific heat data are presented in the temperature region 17 to 300°K. for a Ceylon natural graphite. The data and the thermodynamic functions derived therefrom are compared with those previously reported for a graphite sample having a smaller crystallite size.

Introduction

There can be a considerable difference in particle size between natural and artificial graphites.[1] What influence this variation in crystallite size has on the specific heat has not been reported. The problem is complicated by the fact that the specific heat of graphite is very small at low temperatures, and the substance can easily become contaminated by various gaseous adsorbates. Furthermore, lattice irregularities (presence of turbostatic structures, faulting, twinning, edge effects on the crystallites, lattice strain, etc.) and the presence of intergranular, non-graphitic carbon can also influence a graphite's thermal properties. Discrepancies in the low temperature specific heat[2] and thermal conductivity[3] of graphite have been reported recently. The theoretical aspects of specific heat of graphite have recently been summarized by Newell.[4]

(1) J. P. Howe, *J. Am. Ceramic Soc.*, **35**, 275 (1952) (contains bibliography on structure of graphite).

(2) U. Bergenlid, R. W. Hill, F. J. Webb and J. Wilks, *Philosophical Mag.*, **45**, 851 (1954).

(3) A. W. Smith, *Phys. Rev.*, **95**, 1095 (1954).

(4) G. F. Newell, "Specific Heats of Lamellar Crystals," Technical Report Contract No. Nonr-562 (08), Brown University, December 15, 1954.

The present experiment was undertaken to find out if a particle-size effect on the specific heat of graphite could be measured. The specific heat of a Ceylon natural graphite is reported and compared with the results obtained earlier[5] on an Acheson graphite, CS grade. These two samples differed in their crystallite size, as evidenced by X-ray analysis. Both samples had been purified earlier by an identical method.

Experimental

The high-purity Ceylon natural graphite studied in this investigation was obtained from the Great Lakes Corporation.[6] Approximately 84 g. (6.974 gram-atoms) of large "foliated" crystals were selected and sealed in the copper calorimeter. The calorimeter cryostat and accessory equipment used in this work have been described previously.[7] Identical techniques were employed, as in the study on the CS grade sample.[5]

Between liquid hydrogen temperature and the ice point the accuracy of the measurements is about 0.5%. In the liquid hydrogen temperature region, the data are accurate to approximately 4 to 5%. Higher drift rates than those

(5) W. DeSorbo and W. W. Tyler, *J. Chem. Phys.*, **21**, 1660 (1953).

(6) Sample loaned to the writer by Dr. W. W. Tyler, Knolls Atomic Power Laboratory, now with the General Electric Research Laboratory.

(7) W. DeSorbo, This Journal, **75**, 1825 (1953).