Carbon Dioxide, Carbonyl Sulfide, and Carbon Disulfide Insertion Reactions on a Manganese Surface

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Abstract: The adsorption of CO_2 on an evaporated Mn surface that contains preadsorbed methanol or ethanol as an alkoxide produces a number of infrared bands in the 800–1700-cm^{-1} region which are not produced when either CO_2 or alcohol is adsorbed alone. These bands indicate the formation of an organic carbonate on the surface by the insertion of CO_2 into the Mn–O bond of the surface alkoxide formed by alcohol adsorption. Upon heating in a vacuum the reaction is reversed to desorb CO_2 and give the infrared bands for the surface alkoxide in their original intensity. The mechanism of the insertion is discussed. Addition of COS or CS_2 to the surface alkoxide produces the analogous sulfur-substituted compounds.

The detailed understanding of surface processes lags other areas of chemical knowledge partly because of a lack of knowledge about the structure of surface species and their reactivity. In most studies of catalysis and surface reactions, the nature of the chemical changes that occur while molecules are actually on the surface is inferred from an analysis of gas-phase reactants and products and the kinetics of their interaction. In order to gain a satisfactory detailed understanding of surface processes, data which are directly interpretable in terms of surface structure and reactions are necessary. In attacking this problem we have looked for surface reactions which were direct counterparts to homogeneous complex reactions so that comparisons of heterogeneous and homogeneous processes could be made more explicit. Here infrared spectroscopy is used to determine the structure of a surface complex and its reaction product on the surface. Thus a reaction is traced on the surface from one known surface structure to another.

In the course of work to produce data to allow a direct comparison of heterogeneous and homogeneous reactions we discovered a CO insertion reaction in a metal–carbon bond on an iron surface.[2] Here a new reaction, which may be termed a CO_2 insertion reaction, is reported, where one of the reactants is an alkoxide structure on a Mn surface produced by the adsorption of an alcohol.[3] While the adsorption of CO_2 alone on a Mn surface produces a carbonate complex,[4] adsorption on a surface containing a methoxide or ethoxide group results in the insertion of the CO_2 in the Mn–O bond. The only other CO_2 insertion reaction we are aware of is the addition of CO_2 to the Mg–C bond of Grignard reagent to produce organic acids.

Since the CO_2 insertion reaction for transition metal compounds has not been previously reported, it is desirable to examine the generality of this reaction for structurally similar compounds such as COS and CS_2. Sulfur compounds are of interest on their own because of their roles in catalyst poisoning and air pollution. The extent of reaction and bond rupture of sulfur compounds upon interaction with metal surfaces is variable depending upon the specific compounds and conditions. SO_2 reacts with itself to produce surface SO_4 groups[5] while mercaptans can adsorb on Fe and Ni without rupturing C–S bonds.[5,6] COS and CS_2 have been found to dissociate upon interaction with a Mn surface[4] and not to produce structures analogous to the carbonate structure produced by CO_2.

Experimental Section

Manganese metal was evaporated into a cell shown schematically in Figure 1 and is of such design that the reaction could be carried out *in situ*. It is basically a 6-cm gas cell equipped with a 4-mm high-vacuum stopcock on a side arm for attaching the cell to the vacuum system. The body of the cell was constructed from O-ring joints of 25-mm inside diameter. An advantage of using O-rings is that the cell can be heated to 200° without damaging the salt window seal. All spectra were obtained with a Perkin-Elmer Model 21.

After the cell had been outgassed by evacuation at 10^{-6} Torr for 16 hr, the metal was evaporated as described previously[7] with a thin film of hydrocarbon oil on the salt windows and a background infrared spectrum was taken immediately. Either methanol, ethanol, or ethanol-d_6 (40 Torr) was then added and left in the cell for a period of from 1 to 4 hr to ensure maximum chemisorption. The cell was evacuated 30 min and a second infrared spectrum was taken to record the positions of the chemisorbed alkoxide bands. It was found in general that approximately 10 min of pumping on a cell removed most of the gaseous and dissolved components. Therefore 30 min of pumping was used to ensure that only the chemisorbed species would be left to react with incoming gases.

A spectrum was taken immediately after the introduction of CO_2 or COS or CS_2; at various times during the reaction until a sufficient amount of reaction had occurred to give intense, well-defined bands which usually required about 5 hr of reaction time at room temperature; after the cell was pumped for a period of 30 min; and after the cell had been heated at approximately 100° for a period of about 2 hr in order to investigate the stability of the reaction product. A spectrum was recorded immediately after heating and the changes from the previous spectrum were noted. The gases produced by the heat treatment were trapped by means of a cold finger cooled with liquid air and introduced into a clean cell and an infrared spectrum was taken of these. A mass spectrum was also taken of these gas residuals.

Carbonyl sulfide was obtained from K and K Laboratories, Inc., and further purified by distilling three times from liquid air-cooled traps and discarding the first and last portion of each distillation by pumping on the system. Carbon disulfide was obtained from Fischer Scientific Co. as reagent grade liquid and used without further purification other than standard degassing procedures. Carbon dioxide was distilled four times from liquid air-cooled traps.

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(1) Author to whom correspondence should be addressed.
(2) A. J. Goodsel and G. Blyholder, *J. Catal.*, **23**, 374 (1971).
(3) G. Blyholder and M. Allen, *ibid.*, **16**, 189 (1970).
(4) A. J. Goodsel and G. Blyholder, *ibid.*, accepted for publication.
(5) G. Blyholder and G. Cagle, *Environ. Sci. Technol.*, **5**, 158 (1971).
(6) G. Blyholder and D. Bowen, *J. Phys. Chem.*, **66**, 1288 (1962).
(7) G. Blyholder, *J. Chem. Phys.*, **36**, 2036 (1962).

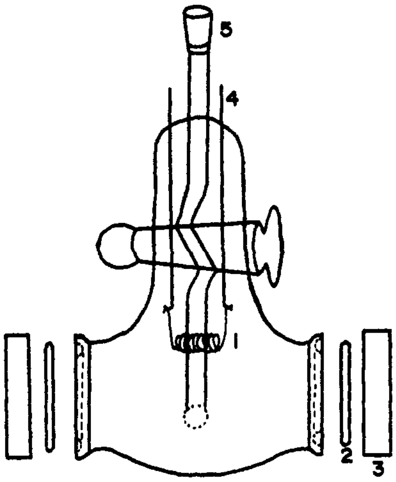


Figure 1. Vacuum cell: 1, filament for evaporating metal; 2, O-ring; 3, KBr windows; 4, tungsten leads; 5, ground glass joint.

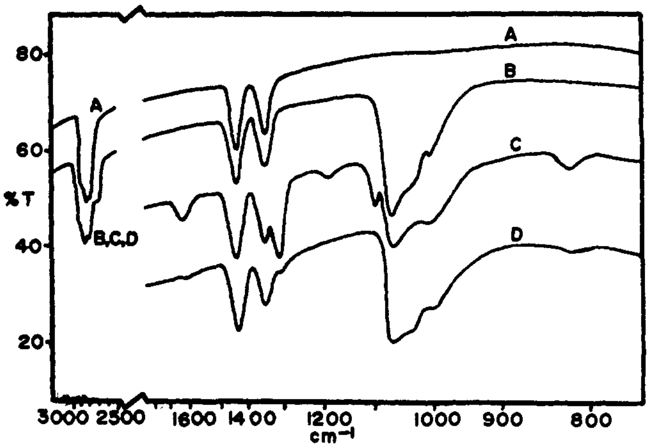


Figure 3. A, Mn evaporated into oil; B, chemisorbed methanol; C, CO_2 added and reacted for 5 hr at room temperature; D, cell heated 2 hr at 100°. Ordinate is displaced to prevent overlap.

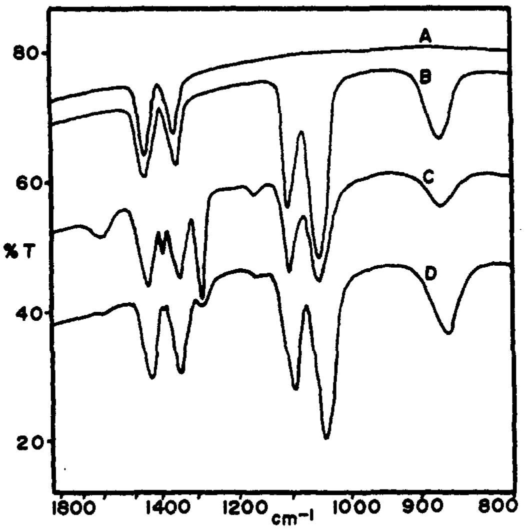


Figure 2. A, Mn evaporated into oil; B, chemisorbed ethanol; C, CO_2 added and reacted 5 hr at room temperature, then cell pumped 30 min; D, cell heated 2 hr at 100°. Ordinate is displaced to prevent overlap.

Results

Ethanol chemisorbed on manganese produces bands at 1095, 1052, 878, and 540 cm^{-1} which are stable to extended periods of evacuation and to heating at 150° for periods of up to 2 hr. It is not possible to determine the positions of the CH_2 and CH_3 deformation bands because of the oil support bands which block out the region in which these bands occur. The results of ethanol chemisorbed on manganese can be seen in trace B of Figure 2, trace A representing the background before adding ethanol. These results are in accord with those reported previously for ethanol on manganese.[3]

Ethanol-d_6 chemisorbed on manganese shows the following frequencies: 2230, 2145, 2075, 1160, 1103, 1056, 990, and 732 cm^{-1}.

Methanol chemisorbed on manganese produces bands at 2820, 1072, 1043, and 1015 cm^{-1}. These bands are not removed by pumping on the cell for up to 12 hr. Heating the cell to 150° for periods of several hours also had little or no effect on the bands. The results are shown as trace B in Figure 3, trace A representing the background before adding methanol.

The bands produced by chemisorbed methanol and ethanol have been previously attributed to methoxide and ethoxide species, respectively.[3] Ethanol-d_6 was chemisorbed on manganese to investigate the portions of the spectra which were obscured by the background oil bands. This information was used in evaluating structures of the interaction product.

When carbon dioxide is introduced into a cell containing a manganese surface pretreated with ethanol, additional bands appear, as shown in trace C of Figure 2. Heating the cell for 2 hr at 100° produces the effect shown in trace D of Figure 2. The gases produced by the heat treatment were trapped and an infrared spectrum was taken. An insufficient amount of material was desorbed from the manganese surface to produce a spectrum with ordinate scale expansion of 5, when the desorbed gases were trapped and introduced into a clean evacuated cell.

Mass spectra indicated that only small amounts of ethanol and carbon dioxide were desorbed by the heat treatment.

Adding ethanol to a manganese surface with chemisorbed carbon dioxide produces a spectrum which indicates both the chemisorbed ethanol and the chemisorbed CO_3 species[4] are present but the additional bands which appeared upon the addition of CO_2 to chemisorbed ethanol (trace D, Figure 2) did not appear. However, upon subsequent introduction of CO_2, the additional bands noted above do appear.

Adding carbon dioxide to a manganese sample with chemisorbed methanol produces additional bands as shown in trace C of Figure 3. Heating the cell for 2 hr at 110° produces the effect shown in trace D of Figure 3. Only small amounts of gaseous materials were detected in the cell after the heat treatment. The band positions and assignments of the chemisorbed interaction products of CO_2 and adsorbed alcohols are listed in Table I.

The new infrared bands produced by adding COS or CS_2 to a cell at room temperature with the alkoxide structure already on the surface are shown in trace C of Figures 4–7. The band assignments for the new

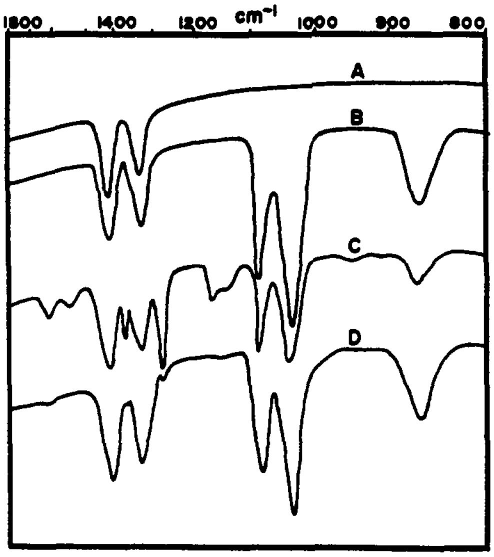


Figure 4. A, Mn evaporated into oil; B, chemisorbed ethanol; C, COS added and reacted 3 hr at room temperature, then cell pumped 30 min; D, cell heated 1.5 hr at 100°. Ordinate is displaced to prevent overlap.

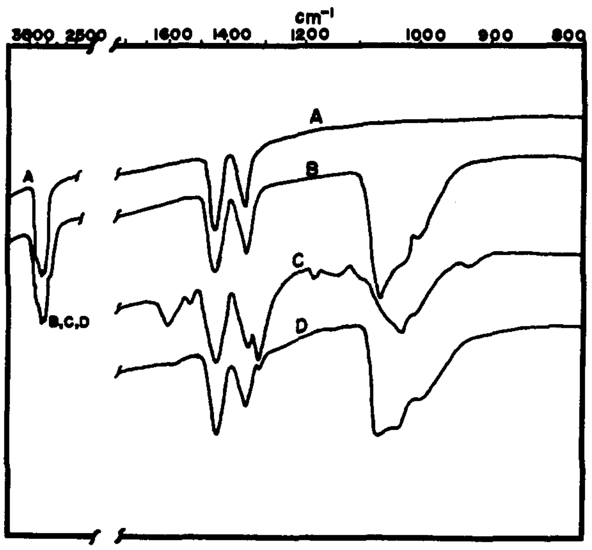


Figure 5. A, Mn evaporated into oil; B, chemisorbed methanol; C, COS added and reacted 3 hr at room temperature, then cell pumped 30 min; D, cell heated 1.5 hr at 100°. Ordinate is displaced to prevent overlap.

Table I. Infrared Bands (cm^{-1}) Formed by CO_2 and Alcohols on Mn[a]

CH_3CO_3–Mn	$C_2H_5CO_3$–Mn	Assignment
2820		C–H stretching of OCH_3
1610*	1615*	CO_3 str
	1405*	CH_2 def
1330*	1320*	CH_3 def
1184*	1165*	CO_3 str
1090*		CH_3 rock
1072	1095	CH_3 rock
1043		Skeletal str
1015	1052	Skeletal str
	878	Skeletal str
809*	805*	CO_3 out of plane

[a] The starred bands are those which develop upon CO_2 addition.

structures produced by COS addition are shown in Table II while those for CS_2 addition are in Table III.

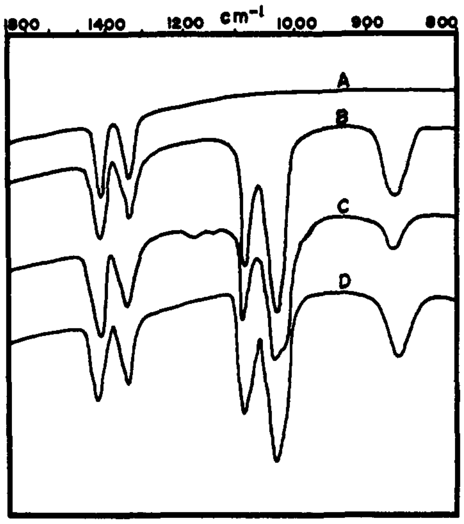


Figure 6. A, Mn evaporated into oil; B, chemisorbed ethanol; C, CS_2 added and reacted for 5 hr, then cell pumped 30 min; D, cell heated 2 hr at 100°. Ordinate is displaced to prevent overlap.

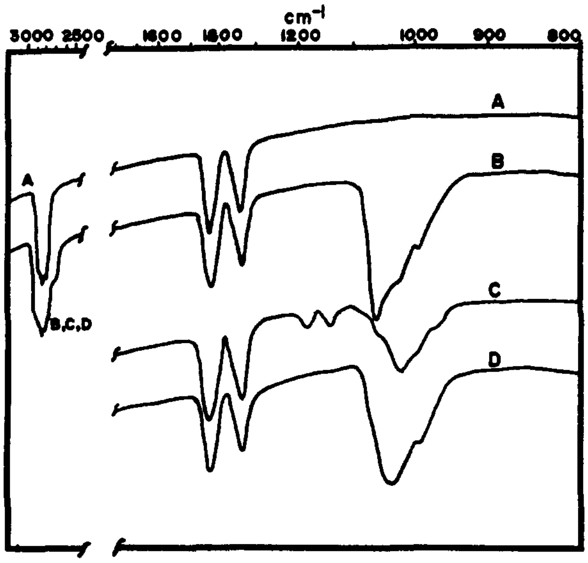


Figure 7. A, Mn evaporated into oil; B, chemisorbed methanol; C, CS_2 added and reacted for 5 hr, then pumped 30 min; D, cell heated 2 hr at 100°. Ordinate displaced to prevent overlap.

Table II. Infrared Bands (cm^{-1}) for the Interaction Product of COS and a Surface Alkoxide on Mn

$MnOCSOCH_3$	$MnOCSOCH_2CH_3$	Assignments
2820 w		O–CH_3 str
1620 m	1615 m	C=O str
1540 w	1545 m	C=O str
	1405 s	CH_2 def
1335 s	1320 s	CH_3 def
1185 w	1170 m	Thiocarbonate group str
1145 w	1145 m	Thiocarbonate group str
1072 sh	1095 m	Skeletal str
1043 m		Skeletal str
1015 sh	1052 m	Skeletal str
925 w	960 w	C–S str
	878 m	Skeletal str

Heating and evacuating the cell at 100° for 1.5 hr after formation of one of the reaction products produces

Table III. Infrared Bands (cm^{-1}) for the Interaction Product of CS_2 and a Surface Alkoxide on Mn

$MnSCSOCH_3$	$MnSCSOC_2H_5$	Xanthates[a]	Assignments
2820 w			O–CH_3 str
1205 m	1190 w	1200 ± 20	Xanthate group str
1155 m	1140 w	1120 ± 35	Xanthate group str
1072 sh	1095 m		Skeletal str
1035 m			C=S str
1015 sh	1052 m		Skeletal str
	1020 sh	1050 ± 35	C=S str
990 sh	995 sh	800–950	C–S str
	878 m		Skeletal str

[a] See ref 12.

the effect shown as trace D of Figures 4–7. The spectra indicate that the products produced by the introduction of COS or CS_2 revert almost completely to the original surface structures during the heat treatment.

The addition of COS to a sample containing chemisorbed ethanol-d_6 gave no bands in the vicinity of 1405 and 1320 cm^{-1} as would have been the case if these bands were due primarily to C–S or C–O structures.

The gases formed in the cell by the heat treatment of the interaction product of COS and ethanol were trapped using a liquid air-cooled trap. Infrared and mass spectra were taken of these residuals. The infrared results indicated that a small amount of a carbonyl species was formed as evidenced by a band at 1755 cm^{-1}. Analysis of the mass spectrum of the trapped gases revealed that several species were present. The most abundant species was found with a mass number of 60, which is probably due to COS driven from the surface along with some ethanol. Also observed were some compounds of higher mass numbers (76 and 95), both of which were present in low concentrations as compared to COS.

The infrared spectrum of the trapped residuals after heating the interaction product of COS and methanol shows a relatively intense band at approximately 1790 cm^{-1}, with other weak bands observed at 1465, 1450, 1300, and 970 cm^{-1}. The mass spectrum of this gas shows a peak at mass number 60 along with peaks characteristic of methanol.

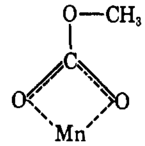
An infrared spectrum and a mass spectrum of the residuals trapped after the heat treatment of the interaction product of CS_2 and ethanol showed only CS_2 and trace quantities of other gases which were not in sufficient quantity to identify.

Discussion

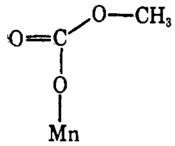
The band assignments for the adsorption of methanol and ethanol as methoxide and ethoxide structures are already well established.[3] The infrared bands for the CO_3 complex formed by adding CO_2 to Mn[4] are quite distinctively different from the bands observed here. The evidence seems to us to indicate the formation of a single surface complex made up from CO_2 and the surface alkoxide.

When the CO_2 is added to a surface containing the alkoxide species, a number of spectral changes occur simultaneously. The starred bands in Table I develop and the alkoxide bands change in intensity and exact position. This indicates that the alkoxide structure is modified but not destroyed. This conclusion is further supported by the fact that the spectral changes are reversed by heating. Except for bands specifically due to methoxide and ethoxide structures the same new bands are produced. If there were just physical, *i.e.*, van der Waal's type, interactions producing the intensity changes for the alkoxide groups, it seems unlikely that methyl and ethyl groups would be so similar. It should be noted that the new carbon and oxygen structure is not produced when CO_2 is added to a surface containing adsorbed CO_3 complexes but is only produced when the alkoxide structure is present. This indicates that the alkoxide is necessary to form the new structure. That sites to produce the new structure are available even on a surface with CO_3 complexes is shown by the fact that alcohols can be adsorbed to produce the alkoxide structure on a surface already having CO_3 complexes on it and subsequent addition of CO_2 produces the new structure.

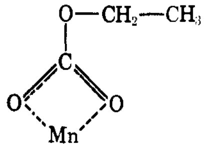
Organic carbonate type of structures, indicated in structures I–III, are consistent with the spectral data.



I



II



III

The data do not clearly distinguish between the mono- and bidentate structures II and I, respectively. A convenient reference to carbonate bands is found in Figures 26 and 29 of Little.[8] From these figures it is seen that a free C=O on an organic carbonate is expected to have a band in the vicinity of 1800 cm^{-1}. However, in the bidentate carbonate the band is down to around 1600 cm^{-1}. On the other hand, the asymmetric stretch of the CO_2 group in a bidentate metal–organic acid complex has a band in the vicinity of 1600 cm^{-1}.[9] On the basis of our experience with adsorbed CO_3 complexes[10] and adsorbed organic acids,[11] the bidentate structure seems more likely.

In general, four infrared bands are expected to be associated with a CO_3 structural unit.[8] The bands around 1610 and 1180 cm^{-1} fit the range for the high-frequency stretches. The band near 810 cm^{-1} falls nicely in the region for an out-of-plane bend. Also expected is a symmetric stretch at about 1000 ± 100 cm^{-1}. Since this band is usually somewhat weaker in intensity than the asymmetric stretches and this region is partially obscured by alkoxide bands, it is not surprising that this band has not been found.

The bands at 1402 and 1320 cm^{-1} are assigned as CH_2 and CH_3 deformations on the basis of the spectra using COS and ethanol-d_6 clearly showing these bands not to be carbon–oxygen or carbon–sulfur stretching frequencies.[4] For the methyl carbonate structure the band at 1090 cm^{-1} is thought to be a methyl rock that has been shifted from 1072 cm^{-1} by the changing environment. Likewise the CH_2 deformation is shifted a little from its usual frequency.

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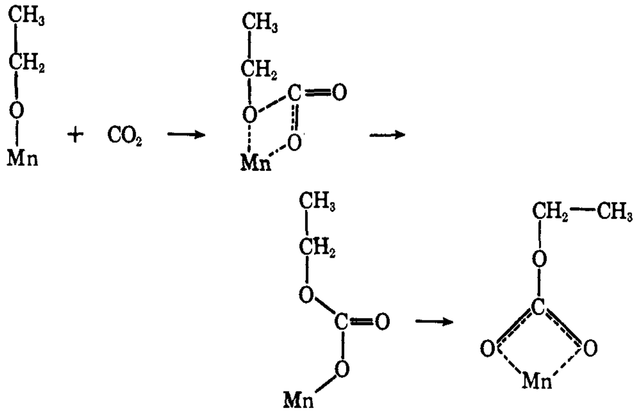
(8) L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press, New York, N. Y., 1966.

(9) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

(10) G. Blyholder, *Proc. Int. Congr. Catal., 3rd*, 657 (1965).

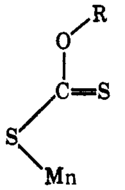
(11) G. Blyholder, unpublished data.

A mechanism similar to that suggested for the CO_2–Grignard reaction may be proposed in which the Mn–oxygen group adds across the C–O double bond of adsorbed CO_2 as illustrated below.



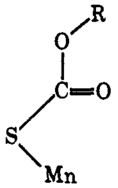
As presented here the adsorption of CO_2 and addition across the double bond occur simultaneously. Alternatively both oxygen atoms of CO_2 could be interacting with the Mn during adsorption with reaction proceeding as above or the CO_2 could adsorb and then the alkoxide group migrate onto the carbon atom. Since the carbonate structure is not formed when alcohol is adsorbed on a surface with existing CO_3 complexes, the mechanism probably does not involve formation of CO_3 groups followed by carbon atom migration.

The adsorption of COS or CS_2 alone on Mn produces no infrared bands detectable by our technique in the spectral range covered.[4] The close correspondence between the infrared bands for the interaction product of CS_2 and adsorbed alkoxide with the bands for xanthates leaves little doubt that a xanthate structure IV is formed. Previous infrared work[12] has indicated that, based on the appearance of a C=S stretching frequency in the neighborhood of 1040 cm^{-1}, metal xanthates have monodentate attachment to the metal and seem to have no tendency toward bidentate attachment. Thus, the insertion of CS_2 follows the same pattern as that reported for CO_2, including the reversibility of the reaction by heating to 100°. The mechanism for the CS_2 insertion is presumed to be similar to that presented for the CO_2 insertion reaction. While in the case of the ethyl xanthate formation the appearance of a C=S stretching band at 1020 cm^{-1} shows up clearly in the infrared spectrum, this region is so obscured with changes in the methoxide bands that the positive identification of a C=S stretching frequency cannot be made when methanol is a reactant. Nonetheless, there seems to be no reason to believe methanol behaves differently from ethanol.

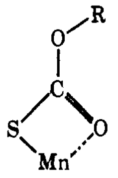


IV

The infrared spectrum of the interaction product of COS and alkoxide structures strongly suggests that COS behaves similarly to CO_2 and CS_2. However, one unique feature is the appearance of two bands in the carbonyl stretching region at 1545 and 1615 cm^{-1}. Since a survey of the infrared spectra of esters, carbonates, and organic acids reveals that none have two strong bands in the carbonyl region above 1400 cm^{-1}, the COS interaction apparently produces two distinguishable structures, which we propose are those given as V and VI. The band assignments listed in Table II for these structures are made by analogy to the surface carbonate and xanthate structures produced by CO_2 and CS_2. The high frequency band at 1615 cm^{-1} would then be associated with structure V and the lower frequency band at 1545 cm^{-1} with the bidentate structure VI.



V



VI

The similarity of behavior of COS and CS_2 to CO_2 is remarkable both with respect to the insertion reactions to form structurally similar surface complexes and their reversibility at mild heating to give the surface alkoxide back. The changes in spectra as oxygen is progressively replaced by sulfur in the series CO_2, COS, CS_2 leave little doubt as to the validity of the structural assignments. The behavior of COS and CS_2 in reacting without dissociation on the alkoxide covered surface is in marked contrast to their behavior on a bare Mn surface where dissociation and sulfiding of the surface occur.

While in all previous cases of heterogeneous–homogenous comparisons, surface reactions have been proposed by analogy to coordination complex reactions; on the basis of this work, a CO_2 insertion reaction for homogenous alkoxide transition metal coordination complexes is proposed as a possible reaction.

Acknowledgment. This investigation was supported in part by Research Grant AP 00818 from the Air Pollution Control Office, Environmental Protection Agency.

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(12) L. H. Little, G. W. Poling, and J. Leja, *Can. J. Chem.*, **39**, 745 (1961).