CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ARKANSAS, FAYETTEVILLE, ARKANSAS 72701

Infrared Spectra of Vanadium Surface Complexes Formed with Oxygen-Containing Molecules

BY GEORGE BLYHOLDER AND MARVIN C. ALLEN

Received July 8, 1969

Infrared spectra of the stable surface species formed at 25° by the interaction with a vanadium surface of menthanol, ethanol, 1-propanol, 1-butanol, isobutyl alcohol, 2-propanol, 2-butanol, *t*-butyl alcohol, diethyl ether, tetrahydrofuran, acetaldehyde, acetone, methyl ethyl ketone, allyl alcohol, methyl vinyl ether, ethylene oxide, propylene oxide, and oxygen have been obtained. From the spectra it is concluded that: (1) alkoxides are quite stable surface species, (2) a coordinate covalent bond of oxygen to the surface is not stable, (3) the O—H bond of the original alcohol is readily broken, (4) the degree of surface coverage by alkoxide structures is in the order primary > secondary > tertiary, (5) the C═C bond does not strongly add to the surface when in competition with OH in the same molecule, (6) the C—H bond does not readily break at 25° to form dissociatively adsorbed hydrocarbons, and (7) oxygen chemisorption produces a V═O species. It is suggested that attachment of a reacting complex to the V surface is more likely to be through an oxygen atom than a carbon atom.

Introduction

The structure and reactions of coordination complexes have been suggested by a number of authors[1-5] as models for catalytic reactions occurring on metal surfaces. In considering the reactions of coordination complexes, reaction mechanisms and transition states are firmly based on a large body of good structural data. In strong contrast, however, very few data directly interpretable in terms of structure exist for surface species. Most mechanisms and proposed transition states for heterogeneous reactions are based on kinetic data which do not support unambiguous mechanistic interpretations. Recently, infrared techniques have been developed that give data interpretable in terms of definite surface structures. If surface reactions are to be treated with the same assurance as other inorganic reactions, then structural data about surface species are necessary. In order to apply concepts about the reactivity of different inorganic structures to surface chemistry, the structures of surface species being dealt with must be determined.

In this paper the structure of a variety of surface species formed on a vanadium surface are examined by infrared spectroscopy and the results are compared to known structures of V complexes. In particular the infrared spectra produced by the interaction with a V surface of a variety of alcohols, aldehydes, ketones, ethers, epoxides, and olefins are reported. Our technique is best suited to revealing major surface species that cover a reasonable fraction of the surface. Thus, the aim here is at determining the structure of the majority of surface species which may or may not be particularly reactive for catalytic processes. Clearly reactive intermediates for catalytic processes proposed in the light of a knowledge of stable surface structures will be more meaningful than those proposed in the absence of such knowledge.

Experimental Section

The wide spectral range experimental technique, which has been described in detail elsewhere,[6] consists of evaporating V from an electrically heated tungsten filament in the presence of a small pressure of helium. The metal particles formed in the gas phase deposit in a hydrocarbon oil film on the salt windows of an infrared cell. The gas to be studied is then admitted to the cell, and the spectrum of the chemisorbed species is obtained. Spectra are recorded before and after admission of the gas to the cell. Five minutes of pumping has been found sufficient to remove all spectra due to gas-phase molecules. For three- and four-carbon-atom molecules 30 min of pumping may be required to remove molecules dissolved in the oil film.

The spectra were obtained using Perkin-Elmer Models 21 and 337 spectrophotometers. The Model 21 is equipped with CsBr optics which permit scanning from 715 to 250 cm^{-1}. The Model 337, which is a grating instrument, is used to scan the region from 4000 to 400 cm^{-1}.

The adsorbates were obtained as reagent grade chemicals from commercial sources. They were degassed by repeated freeze–thaw cycles in the vacuum system. The CO was passed through an activated charcoal trap cooled with liquid air.

The vanadium was obtained as 10-mil wire and 5-mil foil from A. D. MacKay, Inc., and the United Mineral and Chemical Co. Both the wire and foil are labeled 99.8% pure. The vanadium was used directly without further treatment until just before evaporation, at which time it was briefly reduced in a hydrogen atmosphere at about 1200°.

This technique has the advantage that a wide infrared spectral region is available for study. It has the disadvantage that the metal surface is covered with oil. This oil is apparently only weakly adsorbed since many gases have been found to chemisorb readily on the metal. Essentially the oil is regarded as a solvent which has weak interactions with the systems of interest. Having a wide spectral range available aids greatly in attempts to determine structure.

Spectra and Interpretation

The spectral bands for primary alcohols chemisorbed on V at 25° are listed in Table I. The primary alcohols studied are methanol, ethanol, 1-propanol, 1-butanol, and isobutyl alcohol. A typical spectrum, that for 1-

---

(1) H. W. Sternberg and I. Wender, "International Conference on Coordination Chemistry, London, 1959," Special Publication No. 13, The Chemical Socieity, London, 1959, p 35.

(2) R. S. Nyholm, "Proceedings of the Third International Congress on Catalysis," North-Holland Publishing Co., Amsterdam, 1965, p 25.

(3) J. Halpern, "Proceedings of the Third International Congress on Catalysis," North-Holland Publishing Co., Amsterdam, 1965, p 146.

(4) M. Orchin, *Advan. Catalysis*, **16**, 1 (1966).

(5) G. C. Bond, *Discussions Faraday Soc.*, **41**, 200 (1966).

(6) G. Blyholder, *J. Chem. Phys.*, **36**, 2036 (1962).

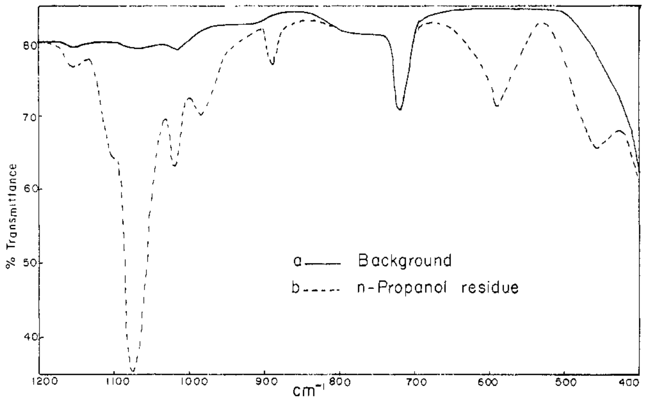

Figure 1.—Spectrum of 1-propanol adsorbed on vanadium at 25°. (The solid line is the background.)

propanol, is shown in Figure 1. All of the spectra are for the stable surface species at 25° which remain after the cell has been evacuated for more than 0.5 hr.

TABLE I

INFRARED SPECTRA OF PRIMARY ALCOHOLS ADSORBED ON VANADIUM AT 25°

Methanol on V	Liquid methanol[a]	Ethanol on V	Liquid ethanol[a]	1-Propanol on V	Liquid 1-propanol[b]	1-Butanol on V	Liquid 1-butanol[c]	Isobutyl alcohol on V	Liquid isobutyl alcohol[d]	Assignments[a]
2820 sh	2820 s									O–CH_3 str
			1273 m							CH_2 twist
			1149 w		1140 w	1114 w	1114 m	1150 w	1140 w	CH_3 rock
1085 s	1112 s	1105 s	1089 s	1105 m	1100 m	1075 s	1070 vs	1128 w	1118 m	CH_3 rock
							1057 sh			
1045 sh	1030 s	1062 s	1050 s	1075 s	1075–1060 s	1050 sh	1043 s	1075 sh	1048 sh	Skel str
				1020 m	1020 s	1035 sh	1021 sh	1040 s	1032 s	CH_3 rock
				980 m	990 m	1000 w	997 m	950 w	967 m	CH_3 rock
					972 w	965 w	954 m			
					918 w			935 w	942 m	CH_3 rock
					908 w	900 w	905 w	900 w	908 m	
		900 m	880 s	888 m	890 w	850 w	853 m			Skel str
					860 w			885 w	878 m	
			802 w					820 w	821 w	
540 sh		540 m		590 m		585 m		590 m		M–O str
475 m	470 w	430 w	433 m	465 m	460 w	465 m	460 w	465 m	480 m	Skel bend

[a] C. Tanaka, *Nippon Kagaku Zasshi*, **83**, 792 (1962). [b] American Petroleum Institute, Project 44, Spectrum No. 427. [c] American Petroleum Institute, Project 44, Spectrum No. 429. [d] American Petroleum Institute, Project 44, Spectrum No. 430.

In all cases the assignments in Table I lead to principal stable surface species which have an alkoxide structure. This conclusion is drawn on the basis of the similarity of the spectra for the adsorbed species to the spectra of the alcohols. In some cases detailed assignments were not available in the literature, but even here the spectrum of the adsorbed species is in good agreement with that of the alcohol. This agreement is due to both the H and the metal having little effect on the skeletal vibrations due to mass and force constant effects.[7] This agreement between alkoxide spectra and free alcohol spectra has also been found in the few infrared spectra that have been reported for Al and Ti alkoxides.[8–11]

In the case of methanol adsorption an alkoxide structure is further supported by the presence of the band at 2820 cm^{-1} because a band in this region is indicative of a methyl group attached to an oxygen atom.[12] In all of these spectra a medium-intensity band occurs in the region from 540 to 590 cm^{-1}. There are no alcohol skeletal vibrations within 70 cm^{-1} of this band. The one new feature expected in these spectra would be a band due primarily to a metal–oxygen stretching mode, which band would be expected to be in this region.[11] Therefore, the band in the region from 540 to 590 cm^{-1} in each spectrum has been tentatively assigned to the metal–oxygen stretch.

The possibilities of some other structures were considered and discarded for a variety of reasons. Structures containing hydrogen atoms attached to unsaturated carbon atoms were eliminated because of the absence of C–H stretching vibrations above 3000 cm^{-1}. While the oil blocks out the saturated C–H stretching region, bands for unsaturated C–H groups which usually occur near 3100 cm^{-1} should be clearly visible. Structures containing O–H groups were eliminated because of the absence of O–H stretching and bending vibrations which are clearly evident when gas-phase alcohol is in the cell. The intensity of OH bands for free alcohols is near enough to that of the other bands so that, if the surface structures contain OH groups, their bands should have been observable. Likewise, structures containing carbon–oxygen double bonds were eliminated because of the absence of a band around 1700 cm^{-1}. Even π-complexed double bonds are only shifted within about 100 cm^{-1} so these too are presumed absent. Two-point (or more) attachment to the surface, in which both a carbon–metal and an oxygen–metal bond are present, is eliminated in the case of methyl alcohol adsorption because of the presence of the CH_3 rocking band at 1085 cm^{-1} and in the other cases

---

(7) E. G. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(8) J. V. Bell, J. Heisler, H. Tannenbaum, and J. Goldenson, *Anal. Chem.*, **25**, 1720 (1953).

(9) D. L. Guertin, S. E. Wiberley, W. H. Bauer, and J. Goldenson, *J. Phys. Chem.*, **60**, 1018 (1956).

(10) R. C. Wilhoit, J. R. Burton, F. Kuo, S. Huang, and A. Viguesnel, *J. Inorg. Nucl. Chem.*, **24**, 851 (1962).

(11) V. H. Kriegsmann and K. Licht, *Z. Elektrochem.*, **62**, 1163 (1958).

(12) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962.

TABLE II

INFRARED SPECTRA OF SECONDARY AND TERTIARY ALCOHOLS ADSORBED ON VANADIUM AT 25°

2-Propanol on V	Liquid 2-propanol[a]	2-Butanol on V	Liquid 2-butanol[b]	*t*-Butyl alcohol on V	Liquid *t*-butyl alcohol[c]	Assignments[a,d]
	1250 s					OH bend
1155 m	1162 s	1160 w	1150 m		1242 m	Skel str
1125 m	1130 sh	1130 sh	1135 sh	1178 m	1201–1185 s	Skel str
	1113 vw	1110 m	1112 s			CH_3 rock
990 m		1030 m	1030 s			CH_3 rock
960 m	950 s	990 m	990 s	990 m	1023 m	CH_3 rock
		918 m	912 s	918 vw	915 s	Skel str + CH_3 rock
835 w	818 w	825 vw	820 m	780 w	750 m	Skel str
600 m		610 m		600 w, b		M–O str
	485 m		490 vw		465 m	Skel bend
	420 m					Skel bend

[a] C. Tanaka, *Nippon Kagaku Zasshi*, **83**, 521, 657 (1962). [b] American Petroleum Institute, Project 44, Spectrum No. 431. [c] American Petroleum Institute, Project 44, Spectrum No. 432. [d] C. Tanaka, *Nippon Kagaku Zasshi*, **83**, 398 (1962).

because multiple attachment is expected to perturb the skeletal vibrations more than is observed. When it is stated that these structures are eliminated, it is not meant that they cannot exist in small concentrations on the surface but only that they do not exist in sufficient concentration to be observed in our spectra.

The spectral bands for the secondary alcohols 2-propanol and 2-butanol together with the tertiary *t*-butyl alcohol are listed in Table II. As in the case of the primary alcohols, the correspondence of the spectra of the adsorbed species to the liquid alcohols leads to the conclusion that an alkoxide structure predominates on the surface for the secondary and tertiary alcohols. The intensity of the spectra suggests that less secondary than primary alcohol is adsorbed on the surface and that still less tertiary alcohol is adsorbed. This is presumed to be due to steric factors. There is a pronounced broadening of the band near 600 cm^{-1}, which has been assigned as the metal–oxygen stretch, for the secondary and tertiary alcohols in comparison to the primary alcohols. This again suggests increased steric interactions.

The ethers diethyl ether and tetrahydrofuran gave no infrared evidence of adsorbing. The V samples chemisorbed CO in a normal manner after exposure to the ethers, thereby showing that the surfaces had not become contaminated. These experiments are taken as indicating that the often proposed mode of a gas adsorbing by a lone pair of electrons on an oxygen atom coordinating with a surface metal atom is not a strong enough interaction to produce stable surface species at room temperature.

The behavior of acetaldehyde was investigated and the results are shown in Table III. The most intense bands correspond closely to those produced by adsorption of ethanol, which has been concluded to be an alkoxide structure. These bands at 1095, 1060, 930, and 580 cm^{-1} are quite far removed from any bands for liquid acetaldehyde. Again the band at 580 cm^{-1} is tentatively ascribed to the metal–oxygen bond holding the complex to the surface. The weak band at 1740 cm^{-1} is presumed to be due to an acyl structure on the surface. Since the C=O stretch normally produces a very intense band and the 1740-cm^{-1} band is very weak, there seems to be relatively little acyl structure on the surface. In order to form an alkoxide structure from an aldehyde, a hydrogen atom must be added. The hydrogen can come from either some of the oil matrix or some of the acetaldehyde cracking on the metal surface. The fact that a surface alkoxide structure forms from the adsorption of an aldehyde is taken as an indication of the stability of an alkoxide structure on the surface.

The results of adsorbing two ketones, acetone and methyl ethyl ketone, are also given in Table III. The bands for the adsorbed species from acetone are seen in Table III to correspond to the bands from adsorbed 2-propanol which forms an alkoxide structure. The isopropoxide surface structure can form from acetone by the addition of a hydrogen atom without any rearrangement of the carbon–oxygen skeleton. The bands for the adsorbed species produced from methyl ethyl ketone correspond well with those for the alkoxide structure produced by 2-butanol. Again this structure can form from the ketone with only the addition of a hydrogen atom and without any skeletal rearrangement. As before the extra hydrogen for these structures can come from either cracking of the oil matrix or some of the ketone on the V surface. The weakness of the bands suggests that the number of recognizable surface species is relatively small. Thus, the stability of the surface alkoxide structure is demonstrated here by its formation from aldehyde and ketones.

Because of the interest in the behavior of unsaturated compounds on metal surfaces, the adsorption of allyl alcohol was investigated. The infrared bands for the surface species formed and for liquid allyl alcohol are listed in Table IV. The close correspondence of these two spectra strongly suggests the formation of an alkoxide surface species with the carbon–oxygen skeletal chain from allyl alcohol unchanged. While it has often been suggested that a carbon–carbon double bond may readily interact with a metal surface by either associative adsorption or π complexing, we see in this case on V the competition between the double bond and the alcohol group to interact with the surface results in interaction of the alcohol function. Again, the stability of the alkoxide structure is demonstrated.

To define further the behavior of unsaturated compounds, the infrared spectrum resulting from exposure of the vanadium surface to methyl vinyl ether was obtained. Having previously determined that ethers do not produce stable surface species, if methyl vinyl ether is to interact with the surface, it must do so through the double bond. The spectrum in Table V indicates only a small fraction of the surface is covered. The weak band at 1070 cm^{-1} suggests that a methoxide surface species is formed by breaking the carbon–oxygen bond adjacent to the carbon–carbon double bond. Apparently the double bond provides enough of an interaction with the surface to allow time for some dissociation to occur.

Continuing the investigation of the behavior of oxygen-containing molecules, the adsorption of the epoxides ethylene oxide and propylene oxide was examined. The results are given in Table V. The infrared bands for the surface species formed from ethylene oxide agree well with the ethoxide structure formed from adsorbed ethanol. The low intensity of the infrared bands indicates that the fractional surface coverage is low. The formation of an ethoxide structure requires the acquisition of a hydrogen atom, but as already indicated in the cases of aldehyde and ketone adsorption, this does occur. In addition to the surface species, medium-intensity infrared bands for gas-phase ethylene are formed. This process presumably leaves the surface partially oxidized which would account for the low number of stable surface species formed.

In the case of propylene oxide the infrared bands correlate well with those of an *n*-propoxide structure as formed by 1-propanol. The infrared spectra gave no evidence of gas-phase propylene formation, and medium-intensity bands were observed for the surface species. Breaking either carbon–oxygen bond of ethylene oxide forms identically the same surface ethoxide structure. However, for propylene oxide rupture of one bond leads to *n*-propoxide formation while the other gives isopropoxide. The propylene oxide surface species does not have bands at 1125 and 1155 cm^{-1}, which are the most intense bands for isopropoxide, and does have a broad band at 1065 cm^{-1}, covering the region of the most intense adsorption at 1075 and 1020 cm^{-1} of *n*-propoxide. This indicates that the carbon–oxygen bond to the middle carbon atom preferentially breaks in the surface interaction.

Because of the possibility of some of the adsorbed compounds producing metal oxide on the surface, the interaction of 13 mm of molecular oxygen with the surface was obtained. A medium-intensity band at 1015 cm^{-1} and a very broad medium-intensity band extending from 900 to 500 cm^{-1} are observed. The band at 1015 cm^{-1} is assigned to a vanadium–oxygen double bond similar to that found in vanadyl species, which is reported[13] to have a band in the 980–1020-cm^{-1} region in a number of vanadyl complexes and vanadium

TABLE III

INFRARED SPECTRA OF ALDEHYDES AND KETONES ADSORBED ON VANADIUM AT 25°

Acetaldehyde on V	Ethanol on V	Liquid acetaldehyde[a]	Assignments[a]	Acetone on V	2-Propanol on V	Liquid acetone[b,c]	Assignments[b,c]	Methyl ethyl ketone on V	2-Butanol on V	Liquid methyl ethyl ketone[d]	Assignments
1740 w		1745 vs	Acyl CO str			1725 vs	CO str			1740 vs	C–O str
1660 w						1221 m	CH_3 rock			1265 w	
1575 vw			C=C str		1155 m		CH_3 rock + skel str			1220 w	CH_3 rock
		1258 m	CH_3 rock + C–H def	1135 m, b	1125 m	1100	C–C–C asym str			1170 vs	Skel str
1240 w		1241 m	CH_3 rock + C–H def		990 m	990 m	CH_3 rock		1160 w	1155 sh	Skel str
1150 sh				960 m	960 m		CH_3 rock	1135 w	1130 sh		Skel str
1095 m	1105 s		CH_3 rock	890 w		885 m		1100 w	1110 m	1090 w	CH_3 def
1060 m	1062 s		Skel str		835 w		Skel str	1020 w	1030 m		CH_3 rock
930 w	900 m	917 w	Sym C–C str			781 w		990 w	990 m	993 m	Skel str
890 w		890 w	CH_3 rock	620 w	600 m		M–O str			945	
580 w	540 m		M–O str					918 w	918 m		CH_3 rock
	430 w		Skel bend						825 vw		
								600 w	610 m		M–O str

[a] C. Tanaka, *Nippon Kagaku Zasshi*, **83**, 398 (1962). [b] Corin, *J. Chem. Phys.*, **32**, 241 (1935). [c] P. Cossee and J. H. Schachtschneider, *ibid.*, **44**, 97 (1966). [d] American Petroleum Institute, Project 44, Spectrum No. 1226.

---

(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963.

TABLE IV

INFRARED SPECTRA OF UNSATURATED COMPOUNDS ADSORBED ON VANADIUM AT 25°

Allyl alcohol on V	Liquid allyl alcohol[a]	Assignments[a]	Methyl vinyl ether on V	Methanol on V	Assignments
3070 w	3105 m	$CH_2=$		2820 sh	$O-CH_3$ str
1640 w	1650 m	C=C str	1070 w	1085 s	CH_3 rock
1820 vw	1830 w	Overtone		1045 sh	C–O str
1425 w	1420 m	CH_2 def		540 sh	M–O str
1355 w	1350 m	CH def		475 m	Skel bend
1110 w	1105 s	$=CH_2$ rock			
1060 m	1030 vs	CO str			
995 w	995 vs	CH def			
960 vw					
912 m	920 vs	CH_2 def			
885 vw	880 w	Skel str			
670 w	640 w				
530 w	550 m	Skel bend			
460 w		M–O str			

[a] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day Inc., San Francisco, Calif., 1962.

TABLE V

INFRARED SPECTRA OF EPOXIDES CHEMISORBED ON VANADIUM AT 25°

Ethylene oxide on V	Ethanol on V	Propylene oxide on V	1-Propanol on V	Assignments
1090 w	1105 s	1110 m	1105 m	CH_3 rock
1055 w	1062 s	1065 m, b	1075 s	Skel str
			1020 m	CH_3 rock
		975 m	980 m	CH_3 rock
890 vw	900 m	850 w	888 m	Skel str
540 w, b	540 m	600 m	590 m	M–O str
	430 w		465 m	Skel bend

oxides.[14] The ease of formation of the V=O structure is of interest because of its importance in catalytic processes.[15]

Discussion and Conclusions

The most striking feature of the work here on the structure of oxygen-containing molecules adsorbed on vanadium is the overwhelming appearance of the alkoxide structure. This does fit in well with the inorganic chemistry of vanadium in which alkoxides are quite stable species. Considerable data exist concerning vanadium alkoxides.[16–19] Some vanadium alkoxides have been found to be polymeric, presumably with oxygen forming bridges between vanadium atoms. Our spectra do not readily reveal whether the oxygen of the surface alkoxide is bridging between more than one vanadium atom or not. Bridging requires the formation of a coordinate covalent bond between an oxygen and a vanadium atom. Since ethers were found not to form stable surface species, this type of bond does not appear to be stable at room temperature. While a bridging bond is not identical with an ether coordinate bond to the surface, this does suggest that bridging bonds may not be formed as readily on the surface as in coordination complexes. Another factor leading in this same direction is that the surface consists of V(0), whereas the coordination complexes consist of V(III) and V(IV) where because of the positive charge on the metal a coordinate bond to an oxygen atom would be more stable than for V(0).

Thermochemical studies of metal alkoxides indicate a decreasing stability in the series Ti, V, Cr.[19] The stability of the alkoxide structure on metallic surfaces has also been found to decrease in going from left to right across the first-row transition metals in that the alkoxide structure has been found to be stable on V and Fe[20] but not on Ni.[21] On Ni primary alcohols and acetaldehyde decompose at room temperature to produce chemisorbed CO while secondary and tertiary alcohols, ketones, and ethers do not produce stable surface species detectable by infrared techniques.[21,22]

While there have been few previous structural studies of oxygen-containing molecules adsorbed on metals, there have been several infrared studies of oxygen-containing molecules adsorbed on other substrates. Adsorption of alcohols on the oxides silica, alumina, and magnesia near room temperature produces largely physically adsorbed alcohols and an alkoxide structure.[23–25] Aldehydes and ketones give physically adsorbed molecules at room temperature on silica with the aldehyde producing some condensation products at 120°.[26]

The behavior of the alcohols, aldehydes, ketones, ethers, epoxides, unsaturated compounds, and oxygen detailed above leads to the following conclusions concerning a vanadium surface. (1) A coordinate covalent bond of oxygen to the surface is not stable. (2) The O—H bond of the original alcohol is readily broken. (3) Alkoxides are quite stable surface species. (4) The degree of surface coverage by alkoxide structures is in the order primary > secondary > tertiary. (5) The C=C bond does not strongly add to the surface

---

[14] L. D. Frederickson, Jr., and D. M. Hausen, *Anal. Chem.*, **35**, 818 (1963).

[15] K. Tarama, S. Teranishi, S. Yoshida, and H. Tamura, "Proceedings of the Third International Congress on Catalysis," North-Holland Publishing Co., Amsterdam, 1965, p 282.

[16] D. C. Bradley and M. L. Mehta, *Can. J. Chem.*, **40**, 1183 (1962).

[17] D. C. Bradley and M. L. Mehta, *ibid.*, **40**, 1710 (1962).

[18] C. N. Caughlan, H. M. Smith, and K. Watenpaugh, *Inorg. Chem.*, **5**, 2131 (1966).

[19] D. C. Bradley and M. J. Hillyer, *Trans. Faraday Soc.*, **62**, 2382 (1966).

[20] G. Blyholder and L. D. Neff, *J. Phys. Chem.*, **70**, 893 (1966).

[21] G. Blyholder and L. D. Neff, *ibid.*, **70**, 1738 (1966).

[22] R. P. Young and N. Sheppard, *J. Catalysis*, **7**, 223 (1967).

[23] L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press, New York, N. Y., 1966.

[24] M. L. Hair, "Infrared Spectroscopy in Surface Chemistry," Marcel Dekker, Inc., New York, N. Y., 1967.

[25] R. O. Kagel and R. G. Greenler, *J. Chem. Phys.*, **49**, 1638 (1968).

[26] R. P. Young and N. Sheppard, *Trans. Faraday Soc.*, **63**, 2291 (1967).

when in competition with OH in the same molecule. (6) The C—H bond does not readily break at room temperature to form dissociatively adsorbed hydrocarbons. (7) Chemisorption of oxygen does produce the V═O species.

This behavior pattern suggests that in the catalytic interaction of alcohols, aldehydes, or ketones with vanadium surfaces attachment of the reacting complex to the surface is more likely to be through an oxygen atom than a carbon atom.

CONTRIBUTION FROM OAK RIDGE NATIONAL LABORATORY,
OAK RIDGE, TENNESSEE 37830

Solubility of Cerium Trifluoride in Molten Mixtures of Lithium, Beryllium, and Thorium Fluorides[1,2]

BY CHARLES J. BARTON, MAX A. BREDIG, L. O. GILPATRICK, AND JUDY A. FREDRICKSEN[3]

Received July 28, 1969

The solubility of CeF_3 in eight $LiF-BeF_2-ThF_4$ and four $LiF-ThF_4$ mixtures was determined between 600 and 800° by radiochemical and wet chemical methods. Sintered copper filter sticks were used to remove filtered samples of the molten fluoride mixtures that were saturated with CeF_3 tagged with ^{144}Ce. The data are represented by straight lines in log (solubility) *vs.* $1/T$ plots, the slopes of which gave heats of solution. These data, together with published values for the solubility of CeF_3 in $LiF-BeF_2$ mixtures, permitted formulation of relationships between solubility and solvent composition that could be rationalized in terms of charge and size of the ions involved.

Introduction

The molten salt reactor experiment has been in operation at Oak Ridge National Laboratory for several years and has fully demonstrated the feasibility of the molten fluoride reactor concept. The initial fuel loading for the reactor had the composition 65 mol % LiF-29 mol % BeF_2-5 mol % ZrF_4-0.9 mol % UF_4. Attention is now being directed to development of molten salt breeder reactors. Although the fuel composition for these reactors has not been fixed, the solvent for the fissionable species is expected to be a mixture of LiF, BeF_2, and ThF_4. A phase diagram for this system[4] was developed at ORNL about 10 years ago. Interest in the solubility of CeF_3 in such mixtures results, in part, from the fact that rare earth trifluorides will be produced by the fission process. In a molten salt breeder reactor the concentration of these fission products is expected to be maintained far below their solubility limit by continuously processing the fuel. The principal reason for the present interest in CeF_3 solubility is that PuF_3 may be one of the fissionable species used for the initial fueling of molten salt breeder reactors. A comparison of data on the solubility of CeF_3[5] and PuF_3[6] in $LiF-BeF_2$ mixtures (Figure 1) suggests that CeF_3 can serve as a convenient stand-in for PuF_3 in a systematic study of solubility behavior in the system $LiF-BeF_2-ThF_4$. A limited number of PuF_3 solubility measurements may be made in the future to confirm predictions based on the CeF_3 results. A description of the technique used in this investigation and part of the data reported here were included in an ORNL report.[7]

Experimental Section

The reaction vessel used (Figure 2) was a welded cylindrical nickel container with an internal diameter of 1.5 in. and a depth of 6.5 in. A 7-in. secion of 0.5-in. i.d. nickel pipe was welded to the lid and was closed at the top with a stainless steel ball valve having an internal clearance of 0.5 in. An additional opening in the lid accommodated a thermocouple well of 0.25-in. thin-wall nickel tubing closed at the lower end which extended to within 0.125 in. of the bottom. The remaining lid opening held a 0.25-in. dip leg of heavy-wall nickel tubing extending to within 0.25 in. of the vessel bottom to facilitate agitation and purification of the melt by admitting gases beneath the melt surface.

The vessel was mounted vertically in a 3-in. tube furnace whose temperature was regulated by means of a chromel–alumel thermocouple placed between the furnace wall and the vessel and by a high-sensitivity bucking-circuit controller. Melt temperatures were determined by means of a second chromel–alumel thermocouple in the thermocouple well and a Leeds and Northrup Type K-2 potentiometer.

Copper filter sticks of the type shown in Figure 2 were used to take filtered samples of the molten fluoride mixtures. The sintered copper filter material had a nominal pore size of 0.0004 in. The 0.125-in. tubing of these filter sticks slipped through a Teflon gland made to fit a 0.5-in. Swagelok tubing connector. A length of soft rubber tubing which fitted over the free end of

---

[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

[2] Paper presented before the Division of Nuclear Chemistry and Technology at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

[3] Oak Ridge Associated Universities summer participant from St. Cloud State College, St. Cloud, Minn.

[4] R. E. Thoma, H. Insley, H. A. Friedman, and C. F. Weaver, *J. Phys. Chem.*, **64**, 865 (1960).

[5] W. T. Ward, R. A. Strehlow, W. R. Grimes, and G. M. Watson, "Solubility Relations among Rare Earth Fluorides in Selected Molten Fluoride Solvents," Report ORNL-2749, Oak Ridge National Laboratory, Oak Ridge, Tenn., Oct 1959.

[6] C. J. Barton, *J. Phys. Chem.*, **64**, 306 (1960).

[7] J. A. Fredricksen, L. O. Gilpatrick, and C. J. Barton, "Solubility of Cerium Trifluoride in Molten Mixtures of LiF, BeF_2, and ThF_4," Report ORNL-TM-2335, Oak Ridge National Laboratory, Oak Ridge, Tenn., Jan 1969.