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Magic-Angle-Spinning Carbon-13 NMR Spectroscopy of Molybdenum and Tungsten Carbonyls Supported on X- and Y-Type Zeolites

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Carbon-13 NMR spectra using magic-angle spinning (MAS) have been obtained for samples prepared from $Mo(CO)_6$ or $W(CO)_6$ and Na-X, Na-Y, or H-Y zeolite. The preparations in which the carbonyls were decomposed on the Na-X and Na-Y zeolites at 393 K gave surface CO/metal ratios of approximately 3. Samples prepared from $Mo(CO)_6$ and Na-X or Na-Y zeolite have NMR spectra showing an isotropic peak at 239 ppm with a corresponding powder pattern about 100 ppm wide. Two broad powder patterns superimposed on this relatively narrow powder pattern were identified in the nonspinning spectrum of an $Mo(CO)_6$/Na-X sample. The samples prepared with $W(CO)_6$ have spectra similar to those of the molybdenum samples, with isotropic resonances at 233 and 231 ppm for Na-X and Na-Y, respectively. Additional isotropic resonances at 218 and 201 ppm are present in the spectrum of the sample prepared from $W(CO)_6$ and Na-X. A sample with molybdenum carbonyl supported on H-Y zeolite gave a resonance at 219 ppm and may be a surface pentacarbonyl.

Introduction

The reactions between group VI metal carbonyls and zeolites produce surface metal subcarbonyls which have been only partially characterized. Surface metal subcarbonyls formed are relevant to the design of catalysts, since materials produced by the decomposition of a surface subcarbonyl should have the properties of a molecular sieve combined with the catalytic activity of a supported metal. Catalytic activity in several reactions has been reported for catalysts prepared from a group VI metal carbonyl and a zeolite.[1-4] Recent interest in these systems has also arisen because they provide a way to obtain oxide semiconductor structures within the confines of zeolite cages.[5,6]

A number of techniques have been used to investigate the nature of group VI surface subcarbonyls. Temperature-programmed decompositions (TPDE's) have been useful in detecting the presence of subcarbonyls and indicating their thermal stabilities.[3,7,8] A stable subcarbonyl with an overall CO/metal ratio of 3 seems to be a common result when group VI metal carbonyls are decomposed on a zeolite or alumina at 393 K.[7,9,10] Infrared spectra of samples prepared from $Mo(CO)_6$ and Na-X or Na-Y zeolite were used by Okamoto et al. to propose that a mononuclear $Mo(CO)_3$ subcarbonyl is attached to three oxygens of the zeolite framework with a significantly distorted octahedral symmetry.[7,11] This picture has been substantially confirmed with more recent IR and EXAFS studies of the group VI carbonyls on various Y zeolites.[6,12] TPDE, IR, and EPR studies have shown that the decomposition of $Mo(CO)_6$ or $W(CO)_6$ on H-Y zeolite involves oxidation of the metal and the production of hydrogen.[13-15] Carbon-13 NMR spectroscopy with magic-angle spinning (MAS) indicated that a highly mobile subcarbonyl is produced when $Cr(CO)_6$ is decomposed on Na-X zeolite at 393 K.[9] Along with a highly mobile species, an almost immobile subcarbonyl was identified in the static ^{13}C and ^{17}O NMR powder patterns of samples prepared with $Mo(CO)_6$ and Na-X zeolite at 393 K.[16]

This investigation uses carbon-13 NMR spectroscopy, with MAS to study molybdenum and tungsten subcarbonyls on Na-X, Na-Y, and H-Y zeolites.

Experimental Section

Some details of the sample preparation have been discussed elsewhere.[9,16] The three types of zeolites used were Na-X (Davison Grade 542, 4-8-mesh beads, Type 13X), Na-Y (Linde LZY-52, $^1/_{16}$-in. pellets), and H-Y (Linde LZY-72, $^1/_{16}$-in. pellets). Before use, the zeolites were crushed, sieved (60-80 mesh), and calcined (780 K for 1 h in an oxygen flow and 30 min under vacuum). The dry-mixing procedure involved mixing the solid $Mo(CO)_6$ or $W(CO)_6$ (Aldrich) with the zeolite and gradually increasing the temperature in a flow of helium. An alternate procedure was to add a pentane solution of the hexacarbonyl to the zeolite and allow the pentane to evaporate in a helium flow before increasing the temperature. Sample heating at 393 K in a 30 mL/min helium flow was continued until the evolution of CO had nearly stopped. Gas chromatography was used to monitor the carbon monoxide. Samples were enriched with ^{13}C by exposing the supported subcarbonyl to enriched carbon monoxide at 373 K for 30 min and then repeating the decomposition at 393 K. Isotope percentages in the samples were calculated with the assumption of rapid CO exchange as indicated by observations with similar samples.[6,17] A decomposition temperature of 348 K was used to prepare one sample with H-Y zeolite. Air was strictly excluded in the preparations. The samples were sealed in NMR tubes under reduced helium pressure while the tubes were attached directly to the reactor.

The spectra shown were obtained on either a Nicolet NT-150 (3.5 T) or an NT-200 (4.7 T) NMR spectrometer. Both spectrometers were equipped with MAS probes designed to spin samples in sealed 8-mm glass NMR tubes.[18] A modified single-pulse method alternately adding the free induction decay (fid) resulting from a 90° flip and subtracting the fid following a composite 270° pulse (180°-50 μs-90°-acquire) was used to cancel instrumental artifacts.[19] The spectra were obtained at room temperature, and the chemical shifts (reported relative to TMS) have an uncertainty of ±1 ppm. Some preliminary spectra were run without MAS on a Varian XL-300 NMR spectrometer (7.05 T).

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Table I. Samples Prepared from Mo(CO)$_6$ or W(CO)$_6$ and a Zeolite

sample	metal	zeolite	loading,[a] g of metal/g of zeolite	initial CO/metal ratio on surface[b]	^{13}C isotope %[c]	prepn method	color
A	Mo	Na-X	0.0166	3.36	56	pentane	yellow
B	Mo	Na-X	0.0170	3.10	54	dry	orange
C	W	Na-X	0.0360	3.47	49	dry	orange-brown
D	Mo	Na-Y	0.0149	3.34	52	pentane	light brown
E	Mo	Na-Y	0.0172	3.25	53	pentane	light brown
F	Mo	Na-Y	0.0142	3.06	54	dry	yellow-brown
G	W	Na-Y	0.0141	3.38	73	dry	yellow-green
H	W	Na-Y	0.0155	3.21	70	dry	yellow-green
I	Mo	H-Y	0.0075	3.48	69	pentane	light yellow

[a] The zeolites were weighed before calcination (12 ± 1% water based on four Na-X samples). [b] Estimated uncertainties are ±0.15. [c] Estimated uncertainties are ±5% of the given percentages.

Results

Details of the sample preparations are given in Table I. The reactions of Cr(CO)$_6$,[9] Mo(CO)$_6$, and W(CO)$_6$ with Na-X zeolite and of Mo(CO)$_6$ with Na-Y zeolite are similar in that a surface CO/metal ratio of nearly 3 is obtained on heating the sample at 393 K from 2 to 5 h with the loadings (g of metal/g of zeolite) indicated in the table. The loadings are much smaller than the maximum loading of about 0.13 (g of Mo/g of zeolite) reported by Yong and Howe for the adsorption of Mo(CO)$_6$ on Na-Y zeolite.[11] The decomposition at 393 K during preparation of the samples (G, H) made with W(CO)$_6$ and Na-Y zeolite required about 15 h. When sample H was heated to 420 K in a 5-mm NMR tube, a narrow (3 ppm) resonance at 193 ppm appeared in the carbon-13 NMR spectrum made at 7.05 T without MAS. Carbon monoxide evolution at 393 K from samples prepared with H-Y zeolite and either Mo(CO)$_6$ or W(CO)$_6$ continued until the surface CO/metal ratio approached 1. Almost 2 days was required to obtain the CO/metal ratio of 3.48 reported in Table I for the sample (I) prepared with Mo(CO)$_6$ and H-Y zeolite, since a low temperature (348 K) was used in the decomposition. After the ^{13}C enrichment and subsequent decomposition, the final CO/metal ratios were close to the initial values indicated in the table despite the higher uncertainty in the final values. Final ratios for samples A-I, respectively, were 3.38, 3.16, 3.48, 3.48, 3.32, 2.97, 3.78, 2.86, and 4.02 (estimated uncertainties ±0.25).

As previously noted,[16] samples prepared with Mo(CO)$_6$ and Na-X zeolite have a striking difference in color when different preparation methods are used. The sample (B) prepared by dry-mixing was a homogeneous orange color; however, most samples prepared by dry-mixing had grains ranging from yellow to orange in color.[16] The color change due to the preparation method was not as striking for samples prepared from Mo(CO)$_6$ and Na-Y zeolite, and the methods were not compared for the other samples. All the samples listed in Table I had a homogeneous appearance.

Carbon-13 MAS NMR spectra of samples A and B prepared from Mo(CO)$_6$ and Na-X zeolite by different methods are shown in Figure 1. The largest isotropic peak in both spectra is at 239 ppm. A value of about 1.5 s was found for the spin-lattice relaxation time, T_1, of this isotropic peak by varying the delay times between pulses. A small isotropic peak at 171 ppm probably represents a trace of carbon monoxide gas.[17] The sidebands in Figure 1b are doubled, as is best seen around 300 ppm. The sideband at 300 ppm with a spinning rate of 2.3 kHz arises from the main isotropic peak at 239 ppm. Thus the sideband at 289 ppm arises from an isotropic peak at 228 ppm, which is barely visible as a shoulder in Figure 1b. Another small isotropic peak in Figure 1b was identified at 251 ppm when the spinning rate was varied to confirm sideband identification.

The molybdenum samples D and I made with Na-Y and H-Y zeolites gave the spectra shown in Figure 2. One isotropic peak at 239 ppm is definitely identified in Figure 2a. However, a shoulder on this peak is a possible second isotropic resonance. Air contamination of another Mo(CO)$_6$/Na-Y sample (E) caused the loss of the 239 ppm resonance and the appearance of a large resonance at 202 ppm. This new resonance is undoubtedly due to physisorbed Mo(CO)$_6$ and is also seen in the Figure 2b spectrum of Mo(CO)$_6$ on H-Y sample (I). When a spectrum of sample I was obtained at 7.05 T without MAS, this resonance had a line width of 4 ppm, and another resonance centered near 215 ppm was 40 ppm wide. This second resonance corresponds to the second peak in Figure 2b at 219 ppm with no noticeable sidebands. The T_1 values found by inversion-recovery with MAS were 1.9 ± 0.1

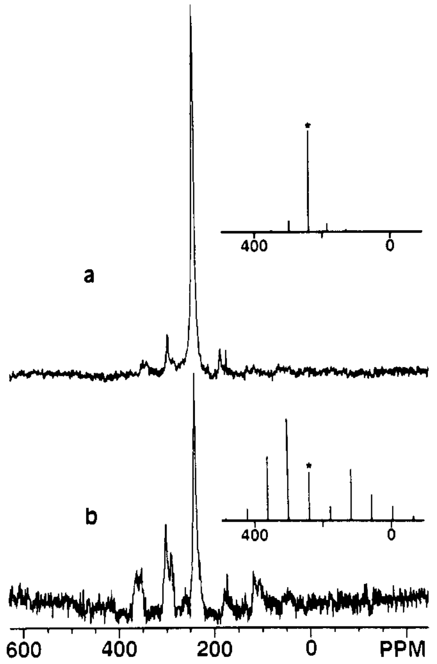

Figure 1. NMR spectra of samples prepared from Mo(CO)$_6$ and Na-X zeolite: (a) sample A prepared by pentane impregnation (2000 transients); (b) sample B prepared by dry-mixing (4000 transients). A 5-s delay, a line-broadening factor (LB) of 20 Hz, and a 37.7-MHz radio frequency were used.

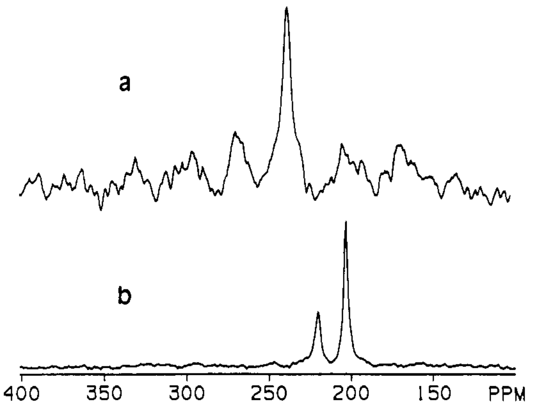

Figure 2. (a) NMR spectrum of sample D prepared from Mo(CO)$_6$ and Na-Y zeolite (50.3 MHz, 25 000 transients, 0.5-s delay, LB = 50 Hz). (b) NMR spectrum of sample I prepared from Mo(CO)$_6$ and H-Y zeolite (37.7 MHz, 18 000 transients, 1-s delay, LB = 20 Hz).

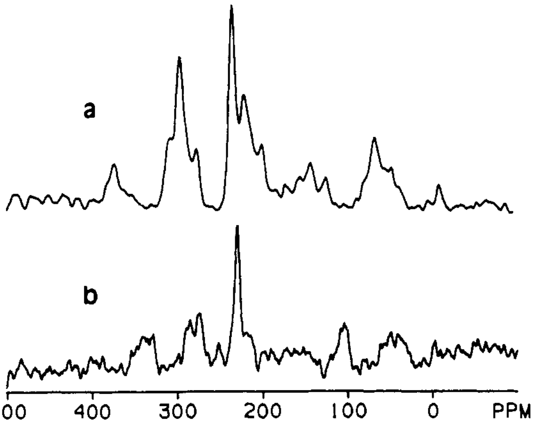

Figure 3. (a) NMR spectrum of sample C prepared from $W(CO)_6$ and Na–X zeolite (37.7 MHz, 10 000 transients, 1-s delay, LB = 100 Hz). (b) NMR spectrum of sample G prepared from $W(CO)_6$ and Na–Y zeolite (37.7 MHz, 2600 transients, 5-s delay, LB = 100 Hz).

s for the 219 ppm peak and 0.39 ± 0.01 s for the 202 ppm peak. The effect of proton decoupling on the spectrum of the H–Y sample was not significant.

Spectra from the tungsten samples C and G are shown in Figure 3. Three major isotropic peaks in Figure 3a are at 233, 218, and 201 ppm for $W(CO)_6$ on Na–X sample (C). The relative intensities of these three isotropic resonances are very different from the relative intensities of corresponding sidebands, indicating significant differences in chemical shift anisotropy. The resonance at 233 ppm was found to disappear sooner than the other resonances when a small amount of air was admitted into a sample similar to sample C. An isotropic peak at 231 ppm is the main feature in the Figure 3b spectrum of $W(CO)_6$ on Na–Y sample (G). A second isotropic peak at 219 ppm is a shoulder on the main resonance. The doubled sidebands at 287 and 275 ppm confirm the chemical shift values for the isotropic peaks.

Discussion

The results of this work appear consistent with prior IR, TPDE, and stoichiometry investigations of molybdenum subcarbonyls on Na–X, Na–Y, and H–Y zeolites.[6,7,11-14] The overall CO/Mo ratios of about 3 in the Na–X and Na–Y samples confirm work by Okamoto et al.[7,15] However, the CO/Mo ratio of 3.48 in the H–Y sample (I) is not the ratio for a subcarbonyl, since this sample is a mixture of physisorbed $Mo(CO)_6$ and at least one subcarbonyl. Unlike the Na–X and Na–Y zeolites, an H–Y zeolite has hydrogen atoms which can oxidize the molybdenum during the decomposition of the hexacarbonyl at 393 K.[13-15] Because sample I was prepared at 348 K, the oxidation that occurs at 393 K was avoided. While a peak at 393 K in the TPDE of $W(CO)_6$ on Na–X zeolite indicates that subcarbonyls form and do not decompose significantly below 570 K,[8] tungsten subcarbonyls on Na–Y zeolite begin to decompose below 420 K. This decomposition was indicated by the appearance of the physisorbed $W(CO)_6$ NMR peak at 193 ppm when sample H was heated. The CO released when a subcarbonyl complex decomposes apparently is captured by neighboring subcarbonyls to eventually produce a hexacarbonyl. This also explains the appearance of physisorbed $Mo(CO)_6$ when sample E was exposed to air and the appearance of physisorbed $Cr(CO)_6$ in a previous study.[9]

The IR spectrum of a sample prepared by the thermal decomposition of $Mo(CO)_6$ on Na–Y zeolite under vacuum at 403 K has bands at 1923, 1795, and 1754 cm^{-1}.[6] Okamoto et al. assigned the spectrum to a $Mo(CO)_3$(ads) species with distortion to a symmetry lower than C_{3v} and Ozkar et al. further identified the point group as C_s.[6,7] The NMR spectrum in Figure 2a apparently shows the same main subcarbonyl as the IR spectrum of the Na–Y sample. Three strong IR bands were found at 1916, 1896, and 1763 cm^{-1} when an orange sample of $Mo(CO)_6$ on Na–X zeolite was evacuated at 373 K for 20 min.[7] Again, the IR spectrum indicates distortion to a symmetry lower than C_{3v}. The presence of two NMR isotropic resonances for sample B in Figure 1b indicates that more than one type of surface complex is involved. Abdo and Howe obtained a complicated IR spectrum with three types of IR bands for a sample made with $Mo(CO)_6$ on H–Y zeolite evacuated for 30 min at 348 K.[13] The NMR spectrum of a similar sample (I) in Figure 2b shows only two resonances. While the NMR resonance at 202 ppm and a set of IR bands are assigned to $Mo(CO)_6$, the second NMR resonance may correspond to the other IR bands previously assigned to two binuclear species. However, another possible source of this resonance at 219 ppm is a pentacarbonyl much like the molybdenum pentacarbonyl thought to form on an alumina surface.[17,20,21]

Table II. Carbon-13 Chemical Shifts (ppm) of Group VI Metal Subcarbonyls on Supports

metal	probable CO/metal ratio	support				
		none[a,b]	γ-alumina[c]	Na–X	Na–Y	H–Y
Cr	3	236.3		247[d]		
Mo	3	225.9	225	239	239	
Mo	5		205			219
W	3	215.7	219	233	231	
W	5		200			

[a] (π-hexamethylbenzene)$M(CO)_3$ (M = Cr, Mo, W) in CH_2Cl_2. [b] Reference 22 (±0.1 ppm). [c] References 17 and 20 (±1 ppm). [d] Reference 9 (±1 ppm).

The isotropic chemical shifts of the most prominent subcarbonyl resonances from the zeolite samples form a consistent set. They are compared in Table II to shifts of subcarbonyls on γ-alumina and of organometallic tricarbonyl model compounds. The peak assigned to molybdenum pentacarbonyl on alumina is 20 ppm downfield of the tricarbonyl, the same change is found between the peak assigned to the pentacarbonyl on H–Y and the tricarbonyl on Na–Y. Both Na–X and Na–Y zeolites have the same chemical shift at 239 ppm for the presumed $Mo(CO)_3$(ads) species whereas the $W(CO)_3$(ads) chemical shift changes slightly from 233 to 231 ppm. Okamoto et al. interpreted their TPDE spectra of $Mo(CO)_6$ on various zeolites according to the base strength of the lattice oxygens.[3,7] They suggested that $Mo(CO)_3$(ads) forms at a lower temperature on Na–X than Na–Y because the Na–X zeolite oxygens are more basic than those of the Na–Y zeolite, as shown by XPS.[7] Electron-donating ligands on a metal carbonyl are known to shift the ^{13}C resonance downfield;[23] it is not clear whether this effect explains the 10–15 ppm change in the chemical shift between a metal subcarbonyl on γ-alumina and a metal subcarbonyl on the negatively charged zeolite framework. It is apparent from Table II that the change in base strength between Na–X and Na–Y is not large enough to cause very significant changes in the carbon-13 chemical shifts.

The temperature dependences of the NMR line shapes from samples prepared with $Mo(CO)_6$ and Na–X were previously studied without MAS.[16] The carbon-13 powder pattern from a sample similar to sample A was reported to have chemical shift tensor elements equal to 286, 258, and 181 ppm. These tensor values and graphs by Herzfeld and Berger[24] were used to estimate the relative spinning sideband intensities of the MAS spectrum of sample A, as shown in the insert of Figure 1a. These calculated sidebands match the observed sidebands rather well. Thus, the line shape found in the static NMR experiments is consistent with the MAS spectrum of the yellow sample (A) prepared by pentane impregnation. At high temperature without MAS, the powder pattern narrowed to a single isotropic peak at 235 ± 1 ppm (4 ppm lower than the room-temperature MAS isotropic peak).[16] One source of this temperature dependence could be a contribution to the high-temperature chemical shift from a resonance upfield

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of 235 ppm. Previously, no chemical shift change was detected under similar circumstances for a sample prepared from $Cr(CO)_6$ and Na–X zeolite.[9,16]

The sidebands in the spectrum (Figure 1b) for the orange sample (B) prepared from $Mo(CO)_6$ and Na–X by dry-mixing are quite different from those found in Figure 1a. In the static NMR investigation,[16] evidence for a broad powder pattern was found for the molybdenum subcarbonyl samples prepared by dry-mixing as well as for samples prepared by pentane impregnation. Assuming axial symmetry and a chemical shift anisotropy ($\delta_{33} - \delta_{11}$) of 400 ppm for this powder pattern, the relative MAS sideband intensities shown in the insert of Figure 1b were found. There are similarities between the calculated sideband intensities and the intensities of the sidebands corresponding to the 228 ppm isotropic resonance. The largest peak is the first downfield sideband and not the isotropic peak at 228 ppm. Clearly, sideband intensities of the isotropic peak at 239 ppm in Figure 1b fit neither of the calculated sets of sidebands. Perhaps both a broad powder pattern and a narrow powder pattern have isotropic peaks superimposed at 239 ppm. While the yellow sample (A) is mainly a single molybdenum subcarbonyl, the orange sample (B) is a mixture of this subcarbonyl and two less mobile subcarbonyls. It is possible that the only difference between the two subcarbonyls with isotropic peaks at 239 ppm is in their mobilities.

In contrast to the conclusion of the investigation by static NMR spectroscopy,[16] the presence of at least one of the molybdenum subcarbonyls with a broad powder pattern appears to give the dry-mixed sample (B) its orange color. The spectra in the earlier study were not of sufficient quality to compare the intensity of the broad component from the dry-mixed sample to the intensity from the pentane-impregnation sample.

Rapid mobility in a metal carbonyl with terminally bound CO groups is indicated whenever the ^{13}C chemical shift anisotropy is much less than 400 ppm. Therefore, the main isotropic resonances of zeolite-supported subcarbonyls listed in Table II all represent mobile subcarbonyl species. The sample prepared from $W(CO)_6$ and Na–X has an MAS spectrum (Figure 3a) with three isotropic resonances coming from one mobile subcarbonyl and two subcarbonyls that appear immobile. Chemical shift anisotropies of 200 ± 50 and 360 ± 50 ppm were estimated for the isotropic peaks at 233 and 218 ppm, respectively, by assuming axial symmetry and using Herzfeld and Berger graphs to analyze the sidebands.[24] The spectrum in Figure 2a for the molybdenum sample with Na–Y zeolite has a low signal-to-noise ratio, which makes the spectrum difficult to interpret. The isotropic peaks in this spectrum probably correspond to a narrow powder pattern and at least one broad pattern, as was the case for the spectrum in Figure 1b for the Na–X sample (B). Sidebands from the narrow powder pattern contribute more in Figure 2a than in Figure 1b because a higher field and a lower spinning rate were used to obtain Figure 2a.

The zeolite-supported tricarbonyls listed in Table II almost certainly are mononuclear complexes attached to the zeolite through the oxygen atoms of the zeolite framework. Recent EXAFS and IR analyses of the tricarbonyls on X and Y zeolites have shown that more complicated structures are unlikely.[6,12] The present NMR spectra give another perspective on the nature of the samples. The main tricarbonyls are in rapid motion, and their chemical shifts show little difference between species on the Na–X and Na–Y supports. Secondary species on the Na–X support do not move rapidly, and their presence can be controlled by the preparation technique. Molecular modeling studies now underway should provide more structural and motional details.

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Facile α/β Diastereomerism in Organocobalt Corrins. Evidence for Thermodynamic Control in the Synthesis of Alkylcobamides

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Reductive alkylation of aquacobalamin with certain alkyl halides is known to produce a mixture of diastereomeric β-alkylcobalamins (with the organic ligand in the "upper" axial ligand position) and α-alkylcobalamins (with the organic ligand in the "lower" axial ligand position) when the reducing agent is zinc/acetic acid. However, reduction with sodium borohydride followed by alkylation produces only β-alkylcobalamins. This difference has now been shown to be a pH effect, and the pH dependence of the relative proportions of α- and β-diastereomers produced upon reductive alkylation of aquacobalamin with CF_3CH_2I, CF_3I, and $NCCH_2Br$ has been studied. In each case, the fraction of the alkylcobalamin as the α-diastereomer increases with increasing acidity, following a typical titration curve. The apparent pK_a's obtained from these data (3.04 ± 0.03, 2.69 ± 0.02, and 2.25 ± 0.02 for R = CF_3CH_2, CF_3, and $NCCH_2$, respectively) are shown to be consistent with the hypothesis that the products are under equilibrium control and that the pH dependence is due to the base-on/base-off equilibrium of the product β-alkylcobalamin. The alternative of kinetically controlled products requires that the species being alkylated in zinc/acid reducing systems is cob(II)alamin, since cob(I)alamin is base-off at all pH's. The pK_a for the base-on/base-off reaction of cob(II)alamin has been determined spectrophotometrically to be 3.10 ± 0.01. However, interpretation of the apparent pK_a's for the pH dependence of the diastereomeric outcome of the reductive alkylation of aquacobalamin assuming kinetic control leads to relative reactivities of the base-off and base-on species of cob(II)alamin which are not consistent with the observed rates of product formation or with literature data on the reaction of cob(II)alamin with alkyl halides. Studies of the temperature dependence of the diastereomer ratio in the analogous alkylcobinamides show that the apparent equilibrium between diastereomers is entropically controlled.

Introduction

In recent publications[1,2] the facile formation of diastereomeric α- and β-alkylcobinamides[3] (RCbi's) and alkylcobalamins (RCbl's) (Figure 1) upon reductive alkylation of factor B[4] or H_2OCbl with various alkyl halides has been described. Interestingly, in the case of cobinamides, α- and β-RCbi's were formed in similar ratios regardless of whether factor B was reduced with sodium borohydride or with Zn/10% acetic acid, although the

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(3) α is the "lower" and β the "upper" axial ligand position.

(4) Factor B is a mixture of the diastereomers of cyanoaquacobinamide,[5] α-(CN)-β-(H_2O)Cbi and α-(H_2O)-β-(CN)Cbi.

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