used in this study. Although there may be a fairly large error associated with the quantitative calculations, one may see a good qualitative description of the bonding involved in these actinide β-diketone complexes. The f orbitals which have been considered to be inert as far as bonding is concerned have now been shown to be involved in bonding schemes.

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Spectroscopic Studies on Coordinated Acetylene

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The structure and bonding of acetylene in $CH\equiv CHCo_2(CO)_6$ was studied by means of spectroscopic methods. The assignments of the infrared absorption bands were established unequivocally by the use of some isotope-substituted molecules: $CH\equiv CDCo_2(CO)_6$, $CD\equiv CDCo_2(CO)_6$, and $^{13}CH\equiv CHCo_2(CO)_6$. The frequency of the $C\equiv C$ stretching vibration of coordinated acetylene was found to be lower than that of free acetylene by about 570 cm^{-1}, and such a marked change in the vibrational frequency implies a large distortion of the coordinated acetylene from its free state. A structure with the C_{2v} symmetry of coordinated acetylene can well explain the observed infrared and nmr spectra. The similarity of the vibrational spectrum of coordinated acetylene to the electronically excited molecule is suggested, and the nature of the bond between acetylene and cobalt is discussed.

Introduction

The reaction of acetylene with cobalt carbonyl has been studied by many investigators.[1,2] In these reactions, $CH\equiv CHCo_2(CO)_6$ is one of the most frequently encountered complexes. In the present study, we attempted to obtain information on the molecular structure of the acetylene molecule in such a complex. Greenfield and his coworkers[3] observed infrared spectra of $CH\equiv CHCo_2(CO)_6$ and discussed the possible structures. This assignment of the absorption bands, however, was not conclusive. Sly[4] showed that the diphenylacetylene of $C_2(C_6H_5)_2Co_2(CO)_6$ has a nonlinear structure from X-ray analysis. However, information on the structure of acetylene itself, instead of diphenylacetylene, is still wanted.

We have observed not only the infrared and nmr spectra of the complex $CH\equiv CHCo_2(CO)_6$ itself, but also those of $CH\equiv CDCo_2(CO)_6$, $C\ \equiv CDCo_2(CO)_6$, $^{13}CH\equiv CHCo_2(CO)_6$, and $CH\equiv CHCo_2(CO)_5P(C_6H_5)_3$. On the basis of these observations, unequivocal assignments of the absorption bands of the acetylene molecule have been established. A number of definite conclusions on the structure of the acetylene molecule are now drawn from such assignments. Comparison of the vibrational frequencies in the coordinated state with those in the electronically excited state seems to be very interesting.

Results and Discussion

Assignment of Infrared Spectra.—Figure 1 illustrates the infrared spectrum of $CH\equiv CHCo_2(CO)_6$ from 4000 to 200 cm^{-1}. The five strong bands observed at 2097.8, 2058.5, 2033.7, 2028.1, and 2016.6 cm^{-1} can be assigned to the $C\equiv O$ stretching mode,[3] a series of bands in the far-infrared region to metal–ligand vibrations, and progressions from 2300 to 2600 cm^{-1} to their combination bands. A comparison of $CH\equiv CHCo_2(CO)_6$, $CH\equiv CDCo_2(CO)_6$, and $CD\equiv CDCo_2(CO)_6$ (Figure 2) shows that the bands at 3116.0 (m), 3086.0 (m), 1402.5 (s), 894.0 (s), and 768.0 (s) cm^{-1} are due to the coordinated acetylene. Judging from isotope shifts given in Table I, 3116.0 (m) and 3086.0 (m) cm^{-1} can be assigned to CH stretching modes, the band at 1402.5 (s) cm^{-1} is almost a pure $C\equiv C$ stretching mode (Figure 3), and the bands at 894.0 (s) and 768.0 (s) cm^{-1} can be assigned to CH bending modes (Figure 4), respectively. In the far-infrared region (Figure 4), two absorptions at 605.0 and 551.0 cm^{-1} must be due to the acetylene–cobalt bond on the basis of their shifts.

Broad 1530-cm^{-1} bands may be tentatively assignable to difference bands between $C\equiv O$ stretching bands and metal–ligand bands since the above-mentioned combination bands from 2300 to 2600 cm^{-1} show considerable intensity.

Symmetry of the Coordinated Acetylene Molecule.—The appearance of two CH stretching modes and one $C\equiv C$ stretching mode in the infrared spectrum suggests that the symmetry of the coordinated acetylene is lower than that of free acetylene, that is, C_{2v}, C_{2h}, C_2 (Figure 5), or asymmetric. In the nmr spectrum of the complex, the acetylene protons show a singlet signal at δ -4.0 ppm; therefore the possibility of the asymmetric structure can be eliminated.

Furthermore, infrared and nmr spectra of the monotriphenylphosphine-substituted complex $CH\equiv CHCo_2(CO)_5P(C_6H_5)_3$ were examined. In the infrared spec-

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(1) U. Krüerke, C. Hoogzand, and W. Hübel, *Chem. Ber.*, **94**, 2817 (1961).

(2) R. Markby, I. Wender, R. A. Friedel, F. A. Cotton, and H. W. Sternberg, *J. Am. Chem. Soc.*, **80**, 6529 (1958).

(3) H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, R. Markby, and I. Wender, *ibid.*, **76**, 1457 (1954); **78**, 120 (1956).

(4) W. G. Sly, *ibid.*, **81**, 18 (1959).

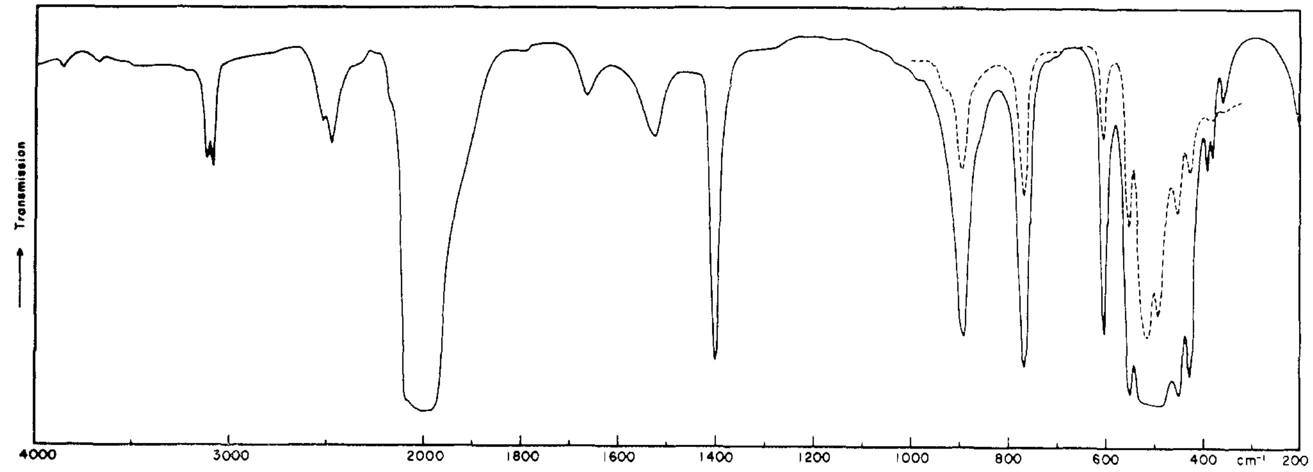

Figure 1.—Infrared spectrum of $CH{\equiv}CHCo_2(CO)_6$: solid line, 0.025 mm; broken line, capillary.

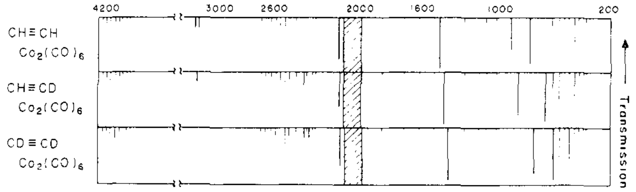

Figure 2.—Infrared spectra of $CH{\equiv}CHCo_2(CO)_6$, $CH{\equiv}CDCo_2(CO)_6$, and $CD{\equiv}CDCo_2(CO)_6$.

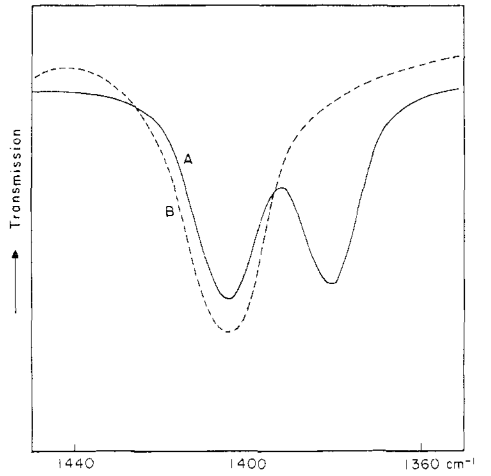

Figure 3.—The ^{13}C isotope shift of the C≡C stretching mode: broken line, $CH{\equiv}CHCo_2(CO)_6$; solid line, 1:1 mixture of $CH{\equiv}CHCo_2(CO)_6$ and $^{13}CH{\equiv}CHCo_2(CO)_6$.

trum, the coordinated acetylene shows bands at almost the same frequencies as $CH{\equiv}CHCo_2(CO)_6$, but in the nmr spectrum, it shows a doublet signal at δ −5.25 ppm, instead of a singlet. The nmr spectra were examined not only at 60 MHz but also at 100 MHz and from a comparison of these nmr spectra, this doublet was concluded to be due to the P–H spin–spin coupling through cobalt atoms (J_{PH} = 2.9 Hz). Thus it has been established that the two protons of the acetylene molecules are equivalent in $CH{\equiv}CHCo_2(CO)_5P(C_6H_5)_3$, and hence the possibility of the C_2 structure of the coordinated acetylene of $CH{\equiv}CHCo_2(CO)_6$ has been excluded, unless a rapid exchange of positions of acetylene protons takes place through a torsional motion. The coordinated acetylene molecule is now considered to have most probably the C_{2v} symmetry, and five strong infrared-active bands seem to support this (Table II). There are marked changes observed in the vibrational frequencies of the acetylene molecule on bringing it from its free state into the complex. Therefore, the lowering of the symmetry ($D_{\infty h} \rightarrow C_{2v}$) is considered to be caused mostly by a distortion of the acetylene molecule itself rather than by a mere change of its environment.

Physical Nature of Coordinated Acetylene.—Chatt and his coworkers[5,6] have reported that the C≡C stretching vibration of platinum–acetylene complexes appears between 1700 and 2000 cm⁻¹. However, in our case the C≡C stretching vibration of the coordinated acetylenes (1402.5 cm⁻¹) is about 570 cm⁻¹ lower than that of free acetylenes of the normal state[7] $^1\Sigma_g{}^+$ (1973.8 cm⁻¹), while two CH bending modes (894.0, 768.0 cm⁻¹) are both about 150 cm⁻¹ higher than those of the free molecule (729.1, 611.8 cm⁻¹) (Table III). These changes imply that the physical nature of coordinated acetylene is considerably different from that of normal-state acetylene ($^1\Sigma_g{}^+$).

A comparison of the vibrational frequencies of coordinated acetylene with those of the first electronically excited state[8] (^1A_u) is shown in Table III. The excited acetylenes show the C≡C stretching vibration at 1380 cm⁻¹ (C_2H_2) and 1310 cm⁻¹ (C_2D_2), with CH bending vibration at 1049 cm⁻¹ (C_2H_2) and 844 cm⁻¹ (C_2D_2). On the other hand, the coordinated acetylenes give corresponding vibrations at 1402.5 cm⁻¹ (C_2H_2) and 1346 cm⁻¹ (C_2D_2) and 894.0 cm⁻¹ (C_2H_2) and 751.4 cm⁻¹ (C_2D_2), respectively. This means that the force constants, the normal vibration treatment now in progress, and therefore the electronic structure of the coordinated acetylene are similar to those of the excited state (^1A_u). Ingold and King[8] have concluded that the first excited state of acetylene is a *trans*-bent state, showing a completed change of σ-bond hybridization from sp to plane-trigonal sp². In the coordinated state, there must be

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[5] J. Chatt, R. G. Guy, and L. A. Duncanson, *J. Chem. Soc.*, 827 (1961).

[6] J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957).

[7] G. Hertzberg, "Infrared and Raman Spectra of Polyatomic Molecules," 1st ed, D. Van Nostrand Co., Princeton, N. J., 1945, p 288.

[8] C. K. Ingold and G. W. King, *J. Chem. Soc.*, 2702 (1953).

TABLE I

INFRARED SPECTRA OF $C_2H_2Co_2(CO)_6$ AND ITS ISOTOPIC DERIVATIVES[a]

$CH{\equiv}CHCo_2(CO)_6$	$CH{\equiv}CDCo_2(CO)_6$	$CD{\equiv}CDCo_2(CO)_6$	$^{13}CH{\equiv}CHCo_2(CO)_6$	Assignment
4199.0 vw	...[b]	...	...	Overtones of C≡O stretching vibrations
4152.0 w	...	...	...	
4119.0 w	...	...	...	
4060.0 w	...	...	...	
4013.0 w	...	...	...	
3868.0 vw	...	...	...	
3116.0 m	3113.0 m	2359.0 m	4.0[d]	CH stretching vibrations
3086.0 m	2328.0 m	2297.0 m	5.1[d]	
2585.0 vw[c]	...	...	...	Combination tones of C≡O and cobalt ligand vibrations
2548.0 w[c]	...	...	...	
2525.0 m[c]	...	...	...	
2487.0 m[c]	...	...	...	
2452.0 m[c]	...	...	...	
2425.0 w[c]	...	...	...	
2395.0 vw[c]	...	...	...	
2097.8 s[c]	...	2097.8 s	0[d]	C≡O stretching vibrations
2058.5 vs[c]	...	2058.5 vs	0[d]	
2033.7 vs[c]	...	2033.7 vs	0[d]	
2028.1 vs[c]	...	2027.8 vs	0[d]	
2016.6 m[c]	...	2016.5 m	0[d]	
1985.1 w[c]	...	1985.9 w	0[d]	
1668.6 w	1668.0 w	1668.0 w	0[d]	
1530.8 b	1530.5 w	1530.5 w	0[d]	
1402.5 s	1381.0 s	1346.5 s	23.5[d]	C≡C stretching vibration
894.0 s	861.5 s	751.4 s	3.5[d]	CH bending vibrations
768.0 s	657.2 s	602.0 s	1.2[d]	
605.0 w	...	586.7 w	8.0[d]	Cobalt–acetylene stretching vibrations
551.0 m	...	561.0 m	5.0[d]	
515.0 s	...	520.0 s	0[d]	Cobalt–carbonyl stretching and bending vibrations
492.0 s	...	491.8 s	0[d]	
450.0 m	...	450.8 m	0[d]	
424.0 w	...	421.5 w	0[d]	
392.0 w	...	...	...	
385.0 w	...	...	...	
359.0 w	...	...	...	

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; b, broad. [b] Not observed. [c] *n*-Hexane solution. [d] $\nu(CH{\equiv}CHCo_2(CO)_6) - \nu(^{13}CH{\equiv}CHCo_2(CO)_6)$.

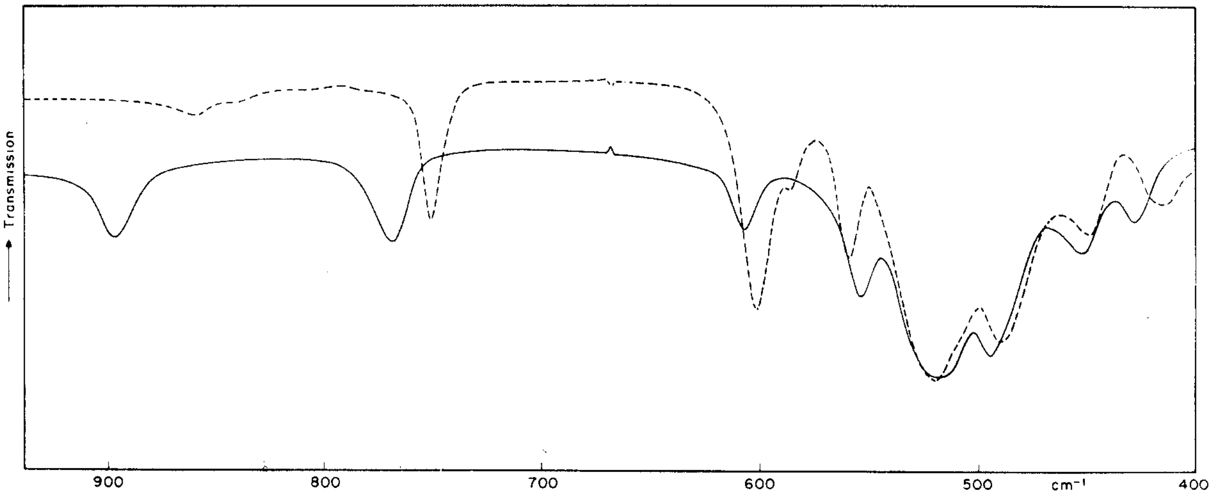

Figure 4.—Spectra of the far-infrared region of acetylene complexes: solid line, $CH{\equiv}CHCo_2(CO)_6$; broken line, $CD{\equiv}CDCo_2(CO)_6$.

much steric repulsion between the hydrogen in the *trans*-bent acetylene molecule and the cobalt carbonyl moiety. Faced with these difficulties, the acetylene molecule must take the *cis* form (C_{2v}), which should be of almost the same energy content as the *trans*-bent form (C_{2h}). Thus, the change of hybridization (sp → sp^2) in the coordinated acetylene molecule was confirmed with certainty. This is supported by the nmr spectrum of $^{13}CH{\equiv}CHCo_2(CO)_6$. The coupling constant of ^{13}CH, determined from the spin-perturbation

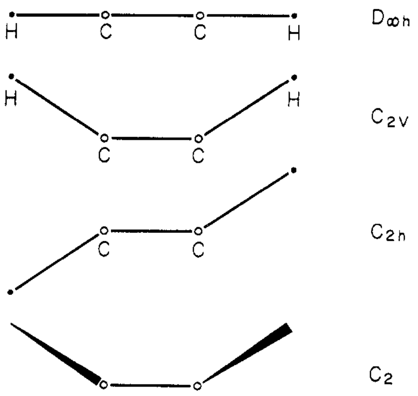

Figure 5.—Different conceivable models of the coordinated acetylene.

TABLE II

SYMMETRY TYPES AND NUMBER OF VIBRATIONS FOR C_{2v} AND C_2 MODELS

Species of vib	No. of vib	Activity
	C_2	
A	4	Ir, Raman
B	2	Ir, Raman
	C_{2v}	
A_1	3	Ir
A_2	1	Raman
B_1	2	Ir, Raman
B_2	0	Ir, Raman

TABLE III

INFRARED SPECTRA OF ACETYLENES IN NORMAL, EXCITED, AND COORDINATED STATES

State	Point group		ν_1	ν_2	ν_3	ν_4	ν_5
$^1\Sigma_g{}^+$	$D_{\infty h}$	C_2H_2	3373.7	1973.8	3287.0	611.8	729.1
		C_2D_2	2700.5	1762.4	2427	505	539.1
^1A_u	C_{2h}	C_2H_2		1380	3020		1049
		C_2D_2		1310	2215		844
Coordinated molecule	C_{2v}	C_2H_2	3116.0	1402.5	3086.0	768.0	894.0
		C_2D_2	2359.0	1346.5	2297.0	602.0	751.4

method,[9] has been observed to be between that of acetylene and ethylene. If this is the case, the coordinated acetylene takes the shape of ethylene in which the two *cis*-related sites are occupied by two hydrogen atoms, and another two empty *cis*-related sites (nonbonding orbital) are used for σ bonding to the cobalts. Two absorption bands at 605.0 and 551.0 cm^{-1} (Figure 4) may be assigned to the stretching modes of these cobalt–carbon bonds, judging from their large ^{13}C isotope shifts (Table I). The similarity of the coordinated state and electronically excited state of acetylene in vibrational frequencies and structures must come from the nature of Co–C bonds; that is, antibonding π orbitals of acetylene are occupied by σ electrons of cobalt–carbon bonds, just as in the electronic excited state. The proposed structure of the whole molecule is shown in Figure 6, where the C_{2v} symmetry is assumed from the above-described results.

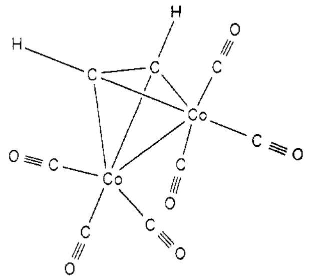

Figure 6.—The proposed structure of $CH\equiv CHCo_2(CO)_6$.

Experimental Section

Spectral Measurements.—The infrared spectra from 4000 to 200 cm^{-1} were observed using a Hitachi Perkin-Elmer 225 infrared spectrometer, and nmr spectra were obtained with Varian HA-100 and A-60 nmr spectrometers. The ir spectra were observed using mostly neat sample and partly *n*-hexane and CS_2 solution. The nmr spectra were obtained using CS_2 solution.

Preparation of Compounds. $CH\equiv CHCo_2(CO)_6$.—$Co_2(CO)_8$ (3.0 g) was dissolved in 100 ml of degassed *n*-pentane in a Shlenk tube, and purified $CH\equiv CH$ was admitted to the solution at 0°. The reaction mixture was condensed under vacuum and chromatographed on alumina gel. The complex was purified by sublimation at ice temperature *in vacuo*. This procedure was applied for the preparation of $CH\equiv CDCo_2(CO)_6$ and $CD\equiv CDCo_2(CO)_6$. Acetylene was prepared from water (or heavy water) and CaC_2 and purified by KCl solution (20%) dried by $CaCl_2$.

$CH\equiv CHCo_2(CO)_5P(C_6H_5)_3$.—Triphenylphosphine (3.0 g) was added to 100 ml of the above-described reaction mixture for $CH\equiv CHCo_2(CO)_6$ at −10°. The reaction mixture was chromatographed on alumina using *n*-hexane, and the violet layer was eluted and condensed under vacuum. The violet crystals thus obtained were purified by crystallization; mp 130° (uncor). The molecular weight was determined to be 537 with a Mechrolab vapor pressure osmometer, Model 301 (the calculated value for $CH\equiv CHCo_2(CO)_5P(C_6H_5)_3$ is 545). *Anal.* Calcd for $C_{25}H_{17}Co_2O_5P$: C, 54.97; H, 3.14; Co, 21.58; P, 5.66. Found: C, 55.29; H, 3.51; Co, 21.61; P, 5.49.

Infrared spectra in CS_2 solution showed the following frequencies (in cm^{-1}): 3143 (w), 3073 (m), 3058 (m), 3023 (w), 3005 (w), 2065 (v, s), 2011 (v, s), 2001 (v, s), 1966 (s), 1812 (w), 1780 (w), 1760 (w), 1665 (w), 1400 (m), 1331 (m), 1307 (w), 1286 (w), 1185 (m), 1156 (w), 1095 (m), 1070 (w), 1028 (m), 1000 (m), 967 (w), 899 (m), 738 (s), 698 (s), 688 (s).

The nmr spectra in CS_2 solution showed δ −7.3 ppm (multiplet), δ −5.25 ppm (doublet) (from TMS), and J_{PH} = 2.6 Hz.

Preparation of $^{13}CH\equiv CHCo_2(CO)_6$.—Barium carbonate containing 63 atom % of ^{13}C was purchased from Isotopes Inc., Westwood, N. J. From this $Ba^{13}CO_3$, acetylene-^{13}C was prepared *via* the steps

$$Ba^{13}CO_3 \longrightarrow {}^{13}CO_2 \longrightarrow CH_3{}^{13}COOH \longrightarrow CH_3{}^{13}CH_2OH \longrightarrow CH_2{=}{}^{13}CH_2 \longrightarrow CH_2Br^{13}CH_2Br \longrightarrow CH\equiv{}^{13}CH$$

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[9] M. Kainosho and Y. Iwashita, unpublished data.

From 10 g of Ba^{13}CO$_3$ and methylmagnesium iodide, acetic acid-^{13}C was prepared by the ordinary technique for the synthesis of ^{14}C-labeled carboxylic acids.[10] An aqueous solution of the acid was carefully neutralized by lithium hydroxide. After concentrating and thoroughly drying *in vacuo*, lithium acetate-^{13}C was reduced by lithium aluminum hydride (3.8 g) in dry diethylene glycol diethyl ether (150 ml) for 10 hr at 60°. The reaction mixture was treated with diethylene glycol monobutyl ether, and ethanol-1-^{13}C was distilled into a flask chilled with liquid nitrogen, under high vacuum at room temperature. It was converted into ethylene-1^{13}C by passing through a heated column of activated alumina at 400°,[11] with the aid of a nitrogen stream. The resulting gas mixture was introduced into a small excess of bromine chilled at $-78°$. After standing at room temperature for a while, ethylene-1-^{13}C bromide was purified by distillation *in vacuo*.

To an ether suspension of sodium amide (3.34 g) was added 9.68 g of aniline[12] at 0° for 20 min and ammonia was removed by a nitrogen stream. An ether solution of ethylene-1-^{13}C bromide was dropped into the sodium anilide solution prepared as described above, while stirring. Stirring was continued for an additional 2 hr. Acetylene-1-^{13}C was liberated from this mixture by adding 30 ml of water and then 30 ml of 2 *N* sulfuric acid, carried out with the aid of a helium stream, collected in a cold trap at $-195°$, and purified by repeated sublimation and degassing.

Acknowledgment.—The authors acknowledge helpful discussions with Professor M. Tsuboi, Dr. I. Kumashiro, and Dr. H. Wakamatsu. Also the authors thank Mr. M. Kainosho for his measurement of the nmr spectra and Mr. Y. Ozawa for his help in the preparation of acetylene-^{13}C.

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[10] The procedure has been described elsewhere; for example: B. M. Tolbert, *J. Biol. Chem.*, **173**, 205 (1948).

[11] D. S. Popplewell and R. G. Wilkings, *J. Chem. Soc.*, 2521 (1955).

[12] D. Bodroux and M. Delepine, *Compt. Rend.*, **208**, 1022 (1939).

Notes

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The Preparation of Bronzes by an Alkali Azide–Metal Oxide Reaction

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Metal bronzes, A_xBO_3 (where A is an alkali metal, B is W, Re, or Mo, and $0 < x < 1.0$), have been prepared in a variety of ways.[1-4] Standard methods include the reduction of alkali tungstate melts electrolytically or with H$_2$ or strong metallic and nonmetallic reducing agents. The most common route uses the appropriate metal. For example, tungsten bronzes may be prepared by the reaction

$$3x\text{Na}_2\text{WO}_4 + (6 - 4x)\text{WO}_3 + x\text{W} \rightleftharpoons 6\text{Na}_x\text{WO}_3$$

The products are always nonstoichiometric ($x < 1$) and are often contaminated with tungsten metal.

In the present investigation alkali bronzes were prepared by the reaction

$$x\text{AN}_3 + \text{MO}_3 \longrightarrow \text{A}_x\text{MO}_3 + (3x/2)\text{N}_2$$

with the application of external pressure. By this technique stoichiometric compositions, AMO$_3$, could also be prepared.

Variations of cell edges as a function of x in the cubic K$_x$WO$_3$ solid solution are described to aid in the characterization of members of this series in future studies.

Experimental Section

Preparation of Bronzes.—The alkali azide reactions were carried out in a pressure system to minimize detonation of the azide and to prevent the volatilization of the alkali metal at high temperature. Reactions of the intimately mixed, reagent grade alkali azides and transition metal oxides were performed in open but crimped gold tubes between 100 and 3000 atm pressure in a stainless steel pressure vessel or in sealed platinum capsules at 60–65 kbars in a calibrated[2] tetrahedral anvil apparatus.[5] The temperature of operation in the low-pressure apparatus was varied between 500 and 700° and in the anvil press between 500 and 1000°. The evolution of nitrogen during the decomposition of the azides always led to the formation of microcrystalline products.

X-Ray Characterization.—X-Ray powder diffraction data were obtained with either a Debye–Scherrer or Hägg–Guinier camera using copper radiation. The patterns were read on a Mann film reader and the powder data were refined by least squares. The Nelson–Riley function was used as a parameter in the Debye–Scherrer back-reflection data. The Guinier data were obtained with monochromatic Cu Kα_1 radiation and an internal KCl standard (a = 6.2931 Å) was used.

Analyses.—Compositions of the cubic sodium tungsten bronzes were calculated from the equation relating Na content to unit cell size as derived by Brown and Banks.[6] The potassium:tungsten ratios for the K$_x$WO$_3$ products were determined by X-ray fluorescence studies. The W^{5+} content was determined by the weight gain on oxidation in an O$_2$–Ar atmosphere utilizing a Du Pont tga apparatus. Flame-emission studies were also made on the oxidized products and on the original bronzes dissolved in H$_2$O$_2$–NH$_4$OH solution.

Results

Na$_x$WO$_3$.—The Na$_x$WO$_3$ system has been extensively studied by several groups, and the cell size *vs.* composition relationship derived by Brown and Banks[6] has been most useful in determining the composition of the products directly from accurate X-ray cell dimensions. This relation, $a(\text{Å}) = 0.0819x + 3.7846$,

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[1] L. E. Conroy and G. Podolsky, *Inorg. Chem.*, **7**, 614 (1968).

[2] T. A. Bither, J. L. Gillson, and H. S. Young, *ibid.*, **5**, 1559 (1966).

[3] A. W. Sleight and J. L. Gillson, *Solid State Commun.*, **21**, 601 (1966).

[4] T. E. Gier, D. C. Pease, A. W. Sleight, and T. A. Bither, *Inorg. Chem.*, **7**, 1646 (1968).

[5] E. C. Lloyd, U. O. Hutton, and D. P. Johnson, *J. Res. Natl. Bur. Std.*, **C63**, 59 (1959).

[6] B. W. Brown and E. Banks, *J. Am. Chem. Soc.*, **76**, 963 (1954).