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Derivatives of Technetium Carbonyl. Synthesis and Properties of the Carbonyl Halides and the Pentacarbonyl Hydride[1a]

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The carbonyl halides of technetium, $Tc(CO)_5X$ and $[Tc(CO)_4X]_2$ (X = Cl, Br, and I), have been synthesized by the action of the halogens on technetium carbonyl. The carbonyl chlorides also are formed in solutions of the carbonyl in carbon tetrachloride at room temperature. These reactions are analogous to those found for the carbonyls of manganese and rhenium. On the other hand, only traces of a volatile carbonyl hydride of technetium can be isolated from a reaction sequence known to afford the pentacarbonyl hydrides of manganese and rhenium in good yields (from the respective carbonyls). Recovery of technetium from reaction residues as the dioxide and direct conversion of the latter to the carbonyl are reported. The new derivatives have been characterized, and their infrared absorption spectra in the carbonyl region compared with improved spectra for the analogous compounds of manganese and rhenium.

Introduction

The syntheses, reported in this paper, of the carbonyl,[2] carbonyl halides, and carbonyl hydride of technetium permit systematic comparisons with the known analogs of manganese and rhenium.[3] Using spectroscopic techniques and experiments on a semimicro scale (20–200 mg.) we have studied the action of the halogens on $Tc_2(CO)_{10}$, to form the carbonyl halides. If $Tc_2(CO)_{10}$ is treated with sodium amalgam and the product is acidified, some evidence for $HTc(CO)_5$ is obtained. Infrared spectra are presented.

Experimental

Reagents.—Technetium, consisting principally of the isotope Tc-99 (β^-, 0.29-Mev., $t_{1/2} = 2.1 \times 10^5$ years), was obtained in the form of NH_4TcO_4 from the Oak Ridge National Laboratories, Oak Ridge, Tennessee. $Tc_2(CO)_{10}$ was prepared from Tc_2O_7,[2] or in equally good yields from TcO_2, which is conveniently obtained either from the first step of the pyrolysis of NH_4TcO_4 or in the recovery of technetium from reaction residues (see below). CO was research grade, from the Matheson Co.

$Mn_2(CO)_{10}$ was obtained from the Ethyl Corporation. $Re_2(CO)_{10}$ was prepared by the method of Hieber and Fuchs[4] from Re_2O_7, purchased from the Chemistry Department, University of Tennessee. The carbonyl halides of manganese[5,6] and rhenium[7] were prepared from the respective carbonyls using methods which closely paralleled those described below for the corresponding derivatives of technetium.

The halogens and sodium metal were commercial items of reagent grade. The solvents used were of spectrophotometric grade, cyclohexane and tetrahydrofuran were dried and distilled from $LiAlH_4$ before use. CCl_4 was dried by storing over alumina.

Infrared Spectroscopic Measurements.—Absorptions were obtained using a Beckman IR-4 spectrophotometer equipped with LiF optics. The spectral slit width was close to 1 cm.$^{-1}$, in the region of interest (1800 to 2200 cm.$^{-1}$). Each spectrum was calibrated against the bands at 1847.7 and 1988.5 cm.$^{-1}$, in the ν_2 fundamental of water vapor.[8] The values reported are reproducible within 1 cm.$^{-1}$, on calibrated spectra.

Analyses.—Technetium was determined by the Schwarzkopf Microanalytical Laboratories, Woodside, New York, using the spectrophotometric method of Howard and Weber.[9] The non-condensable gases were analyzed through a special gas manipulation technique. The quantity of gas was displaced with mercury, from the calibrated compartment of the vacuum line where it had been measured, into a previously well-evacuated bulb. The bulb was of special construction, fitted with two stopcocks at diametrically opposed extremes. The bulb next was attached through one of its stopcocks into the receiving end of a standard analytical microcombustion apparatus.

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(2) For a preliminary account of the synthesis of technetium carbonyl, see J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 2953 (1961). Shortly thereafter, an independent study was reported: W. Hieber and C. Herget, *Angew. Chem.*, **73**, 579 (1961).

(3) J. Chatt, P. L. Pauson, and L. M. Venanzi, A.C.S. Monograph 147, "Organometallic Chemistry" (Editor, H. Zeiss), Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 10.

(4) W. Hieber and H. Fuchs, *Z. anorg. allgem. Chem.*, **248**, 256 (1941).

(5) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

(6) E. O. Brimm, M. A. Lynch, Jr., and W. J. Sesny, *J. Am. Chem. Soc.*, **76**, 3831 (1954).

(7) E. W. Abel, G. B. Hargreaves, and G. Wilkinson, *J. Chem. Soc.*, 3149 (1958).

(8) Bands 44 and 50, respectively, Table 5, E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidwell, *J. Res. Natl. Bur. Std.*, **64A**, 1 (1960).

(9) O. H. Howard and C. W. Weber, *Anal. Chem.*, **34**, 530 (1962).

The gas was displaced slowly into the oxygen stream by introducing mercury into the bulb through the second stopcock. The carbon and hydrogen content of the trapped gas was determined by the standard analytical method.

Technetium Carbonyl Chlorides and Bromides.—$Tc_2(CO)_{10}$ (15 mg.) was added to CCl_4 (10 ml.) previously saturated with Cl_2 gas at 25°. To prepare the bromide, 1.0 ml. of Br_2 replaced the Cl_2. Colorless crystals began to precipitate from solution after about 1 hr. Spectra of the chloride solution at this point showed absorptions of $Tc(CO)_5Cl$ and some $[Tc(CO)_4Cl]_2$. The bromide showed practically pure $Tc(CO)_5Br$. Solvent was removed by evaporation, and the solids of the chlorides were treated with CO at 1000 p.s.i. in a Grosse[10] flask of 10 ml. volume. During the pressurization, the flask was held at 100° for 40 hr. by insertion in a copper-plated steel autoclave of 250 ml. volume. The mixture of $Tc(CO)_5Cl$ and $[Tc(CO)_4Cl]_2$ was converted entirely to the colorless crystals of the monomer.

Heating the pentacarbonyl halides to 100° in air resulted in complete conversion to the tetracarbonyl halide dimers within 24 hr.; monomer also was observed to lose CO slowly, on standing in solution at room temperature.

Anal. Calcd. for $Tc(CO)_5Br$: C, 18.83; Tc, 31.04; Br, 25.08. Found: C, 18.98; Tc, 31.0; Br, 25.25.

Technetium Carbonyl Iodides.—The action of I_2 on $Tc_2(CO)_{10}$ in CCl_4 solution is extremely slow. Direct action of I_2 on $Tc_2(CO)_{10}$ at 100°, in sealed ampoules, yielded $[Tc(CO)_4I]_2$. This was converted to $Tc(CO)_5I$ by high-pressure carbonylation in a Grosse tube, as reported for the chloride above. Attempts to obtain a melting point of $Tc(CO)_5I$ or $[Tc(CO)_4I]_2$ in a sealed tube led solely to decomposition to other products, before any fusion of the solids was observed.

The carbonyl iodides proved to be the most soluble of the halogen derivatives, and the magnetic properties of these were determined for toluene solutions, using the nuclear magnetic resonance method of Evans[11] adapted to organometallic compounds as previously described.[2] A solution of 10.7 mg. of $Tc(CO)_5I$ in 442 mg. of toluene (0.076 molal) was placed in the inner tube of a set of coaxial sample tubes. The resonance of the methyl protons of the solvent was separated by 13.6 c.p.s. (at 40 Mc.p.s., 31°) from the resonance of protons of cyclohexane in the annular space. The separation found for pure toluene (in the inner tube) was 13.3 c.p.s., indicating diamagnetic character for $Tc(CO)_5I$. A similar experiment for $[Tc(CO)_4I]_2$ also demonstrated diamagnetic character.

The infrared absorptions in the CO stretching region for comparable carbonyl halides of Mn, Tc, and Re are entirely analogous. Typical absorption patterns are shown in Fig. 1 for representative compounds of technetium. High resolution data for the entire series of compounds are given in Tables I and II.

A comparison of the infrared spectra of the compounds of technetium with data for the previously known compounds of manganese and rhenium indicates comparable carbonyl halides of Mn, Tc, and Re possess the same structure. In the case of the simple carbonyls, this is further corroborated by comparison of crystallographic parameters (see below).

TABLE I

CARBONYL STRETCHING BANDS (CM.$^{-1}$) FOR THE COMPOUNDS $M_2(CO)_{10}$, M = Mn, Tc, and Re[a]

M	Band designation[b] A	B	(C)	D
Mn	2044(50%)	2013(100%)	2002(5%)	1983(35%)
Tc	2064(65%)	2017(100%)	2005(5%)	1984(75%)
Re	2070(35%)	2014(100%)	2003(5%)	1976(60%)

[a] Measured for solutions in cyclohexane (relative % absorption given in parentheses, the most intense peak adjusted to full scale). These are close to the band positions observed in carbon tetrachloride, reported previously.[2] The bands are much narrower in cyclohexane, and it was possible to resolve a small shoulder (near 2000 cm.$^{-1}$) on the most intense peak (band C). [b] Band designation refers to the labeled bands shown for technetium carbonyl in Fig. 1.

The Action of CCl_4 on the Group VII-B Metal Carbonyls.—In using CCl_4 as a solvent for $Mn_2(CO)_{10}$, it was found that the carbonyl reacts rapidly with CCl_4 as indicated by the general equation

$$M_2(CO)_{10} \rightarrow M(CO)_5Cl \rightarrow [M(CO)_4Cl]_2 \rightarrow \text{insol. residue with no infrared carbonyl absorptions}$$

The analogous reactions occurred with the carbonyls of technetium and rhenium, though much less rapidly than in the case of manganese. The data for this series of reactions are summarized in Table III.

Recovery of Technetium as the Dioxide; Conversion to the Carbonyl.—On account of the rarity of technetium it was necessary to recover the metal from the residues of reaction mixtures. All residues were washed into a solution of about 6 *M* HNO_3, in which the technetium would be oxidized to TcO_4^-. This solution was evaporated almost to dryness (care is required here as $HTcO_4$ is volatile) and the HNO_3 displaced with H_2SO_4. The concentrated H_2SO_4 solution then was diluted with NaOH solution (1 *M*) until a pH of 8 or 9 was obtained. Acetaldehyde (20 g.) then was added, and the solution gently warmed for a period of 2 or 3 days. If the nitrate had not been completely removed in the earlier step, it was found that additional quantities of acetaldehyde were required. A flocculent black precipitate of TcO_2 slowly formed; this was collected and dried over $CaSO_4$. In a representative experiment it was found that 0.5 g. (3.8 mmoles) of TcO_2 was recovered from the residues resulting from the use of 1.0 g. of NH_4TcO_4 to form 0.250 g. of $Tc_2(CO)_{10}$. This represents approximately 85% recovery of the metal.

As the dioxide is more convenient to handle than the heptoxide, direct conversion of TcO_2 to the carbonyl was attempted. In a typical preparation, 0.502 g. (3.83 mmoles) of the dioxide was treated at 250° with CO in a 250-ml. autoclave for 24 hr.; the resulting 0.50-g. sample of the carbonyl corresponds to a yield of 55% based on the metal. The value was comparable to the best yields that had been obtained from the heptoxide. *Anal.* Calcd. for $[Tc(CO)_5]_n$: C, 25.12; Tc, 41.41. Found: C, 25.21; Tc, 41.86.

Crystallographic Parameters for the Unit Cell of Technetium Carbonyl.—Mr. D. Wallach, in association with

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[10] L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1955, p. 249.

[11] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

TABLE II

CO STRETCHING BANDS OF THE GROUP VII-B METAL CARBONYL HALIDES[a]

		Pentacarbonyl monomer[b] $M(CO)_5X$				Tetracarbonyl dimer[b] $[M(CO)_4X]_2$			
		Band designation[c]				Band designation[c]			
M	X	A	B	(C)	D	A	B	C	D
Mn	Cl	2138 w	2054 s	2022 w	1999 m	2104 w	2045 s	2012 m	1977 m
	Br	2133 w	2050 s	2019 w	2001 m	2099 w	2042 s	2011 m	1975 m
	I	2125 w	2044 s	2016 w	2003 m	2087 w	2033 s	2009 m	1976 m
Tc	Cl	2153 w	2057 s	2028 w	1991 m	2119 w	2048 s	2011 m	1972 m
	Br	2150 w	2056 s	2027 w	1995 m	2116 w	2046 s	2012 m	1973 m
	I	2146 w	2055 s	2024 w	2000 m	2108 w	2042 s	2012 m	1975 m
Re	Cl	2156 w	2045 s	2016 w	1982 m	2114 w	2032 s	2000 m	1959 m
	Br	2150 w	2045 s	2016 w	1984 m	2113 w	2031 s	2000 m	1964 m
	I	2145 w	2042 s	2013 w	1987 m	2106 w	2029 s	2001 m	1965 m

[a] CCl_4 solution; LiF optics. [b] Relative intensities: weak, (w); moderate, (m); strong, (s). [c] Band designation refers to the labeled bands shown for $Tc(CO)_5I$ and $[Tc(CO)_4I]_2$, respectively, in Fig. 1.

TABLE III

THE ACTION OF CARBON TETRACHLORIDE ON THE GROUP VII-B METAL CARBONYLS[a]

	Approx. time for appearance of		
M	$M(CO)_5Cl$	$[M(CO)_4Cl]_2$	Insoluble residue
Mn	5 min.	2 days	1 week
Tc	6 days	2 weeks	2 months
Re	3 months	(4 months)	(4 months)

[a] About 2 mg. $M_2(CO)_{10}$ per ml. CCl_4 at 25 to 30°.

Professor K. N. Trueblood of this Department, has obtained the X-ray diffraction pattern for a single crystal of $Tc_2(CO)_{10}$. The data are compared with those of its congeners in Table IV.

TABLE IV

SINGLE CRYSTAL X-RAY DIFFRACTION PARAMETERS FOR THE CARBONYL OF TECHNETIUM AND THOSE OF ITS CONGENERS

				Unit cell parameters			
$M_2(CO)_{10}$	Class	Density, g./cc.	Molecules/ unit cell	a, Å.	b, Å.	c, Å.	β, deg.
Mn[a]	Monoclinic	1.81	4	14.16	7.11	14.67	105
Tc[b]	Monoclinic	2.08	4	14.73	7.22	14.90	104.6
Re[c]	Monoclinic	2.87	4	14.70	7.15	14.91	106

[a] L. F. Dahl and R. E. Rundle, *Acta Cryst.*, in press (1962). [b] The authors are indebted to M. D. Wallach of this Department for making his results available to us preliminary to publication, *cf. Acta Cryst.*, in press (1962). [c] L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, 26, 1750 (1957).

Technetium Pentacarbonyl Hydride.—A number of attempts to isolate a volatile carbonyl hydride of technetium by the method known to give high yields of the pentacarbonyl hydrides of manganese and rhenium[12] have resulted only in traces of the corresponding derivative of technetium. Standard vacuum line techniques were used. In a typical preparation, freshly sublimed $Tc_2(CO)_{10}$ (110 mg.) was inserted into a 50-ml. reaction vessel on the vacuum line; the vessel was equipped with a magnetic stirring bar and a bent-tube side arm for addition of nonvolatile reagents after evacuation.[13] An excess of 1% Na-amalgam (1.5 g., containing 0.65 mg.-atom of Na) was placed in the side arm and the apparatus evacuated. A quantity (15 ml.) of dry tetrahydrofuran was distilled into the vessel at −78°. After the reaction system had warmed nearly to 0°, Na-amalgam was added slowly to the solution. The tetrahydrofuran would always take on a reddish coloration, with the visible evolution of CO (identified by infrared) from the interface of the amalgam and solution. The coloration and evolution of gas occurred rapidly and seemed to go to completion within an hour of mixing. Approximately 1 mmole of CO was released for each 2 mmoles of $Tc_2(CO)_{10}$ used in the reaction.

Infrared spectra of tetrahydrofuran solutions showed two strong bands near 1850 cm.$^{-1}$ in the carbonyl stretching region. A comparison of these bands with those from solutions of $Mn(CO)_5^-$ indicates the presence of $Tc(CO)_5^-$ (see Table V). In addition, some weaker bands also were seen at 2000 cm.$^{-1}$. The anionic species obtained from the carbonyls of manganese and rhenium were prepared as described below. The action of Na-amalgam on purified $Mn_2(CO)_{10}$ occurred without any evolution of gas, to give essentially colorless solutions giving rise to only the strong broad bands (see Table V) expected for $Mn(CO)_5^-$.[14] The action of Na-amalgam on $Re_2(CO)_{10}$ also led principally to $Re(CO)_5^-$, but as with the compound of technetium, some CO was evolved and a reddish coloration was imparted to the solution. The latter side reaction did not account for an appreciable amount of $Re_2(CO)_{10}$ since acidification of the reddish solution gave the expected[15] good yields of $HRe(CO)_5$. The solution containing $Tc(CO)_5^-$ (along with other as yet unidentified species)

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(12) (a) W. Hieber and G. Wagner, *Z. Naturforsch.*, **13b**, 339 (1958); (b) W. Hieber and G. Braun, *ibid.*, **14b**, 132 (1959); (c) R. B. King and F. G. A. Stone, manuscript submitted to *Inorg. Syn.*, **8**, presently in preparation.

(13) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948; see Fig. 20. p. 71.

(14) W. Hieber, W. Beck, and G. Braun, *Angew. Chem.*, **72**, 795 (1960).

(15) W. Beck, W. Hieber, and G. Braun, *Z. anorg. allgem. Chem.*, **308**, 23 (1961).

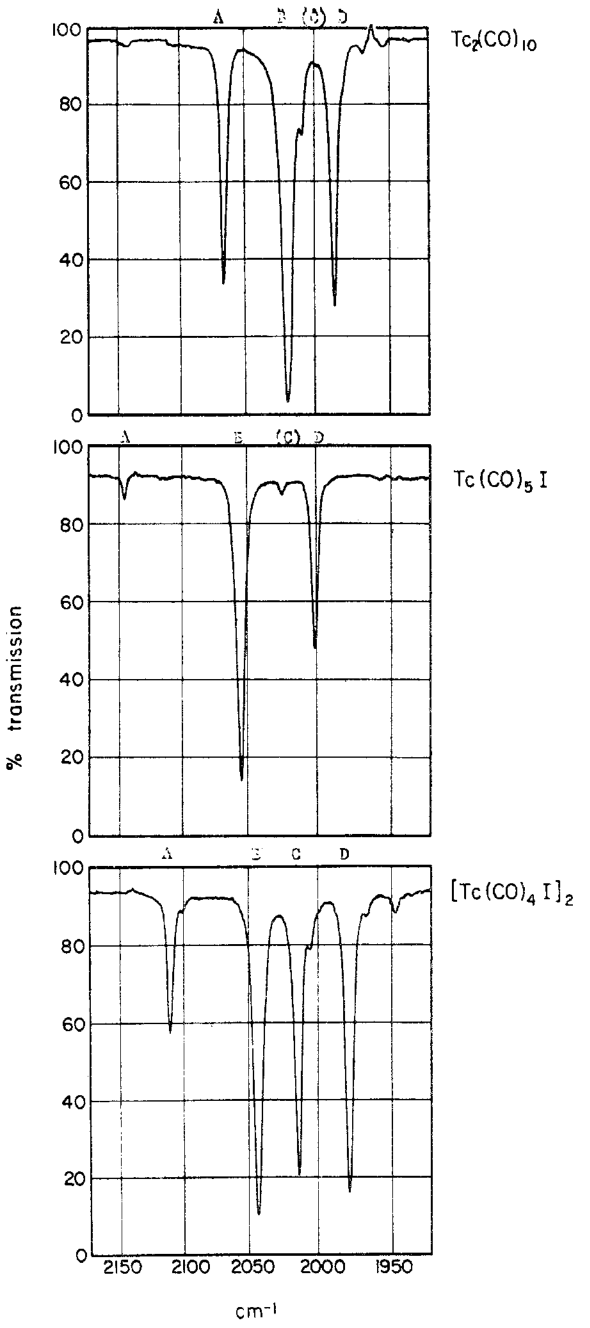

Fig. 1.—High-resolution infrared spectra in the carbonyl stretching region of the carbonyl and two representative carbonyl halides of technetium; cyclohexane solution. The capital letters above each spectrum identify the bands listed in Tables I and II.

was separated from the excess Na-amalgam and the tetrahydrofuran removed under high vacuum. Cyclohexane, which previously had been treated with $LiAlH_4$, subsequently was distilled into the reaction flask. An infrared spectrum at this point revealed no absorptions in the carbonyl stretching region, *i.e.*, no unreacted $Tc_2(CO)_{10}$ had remained. Still using vacuum manipulation, the heterogeneous mixture then was treated at 0° with an excess of thoroughly degassed H_3PO_4 (5 ml.). About 1.5 mmoles of H_2 was evolved immediately during this acidification for each mmole of $Tc_2(CO)_{10}$ originally used. The infrared spectrum of the cyclohexane solution showed ten well resolved strong or medium strong bands in the carbonyl region, in contrast to the simple pattern obtained from the cyclohexane solutions of $HMn(CO)_5$[16] and $HRe(CO)_5$[15] (see Table V; only the two most intense bands are listed, as obtained for dilute solutions). It is clear that the reaction with the carbonyl of technetium is more complex.

Three of the bands observed in the above cyclohexane solution of technetium compounds are those of $Tc_2(CO)_{10}$. From the relative band intensities, it is clear that appreciable quantities of $Tc_2(CO)_{10}$ had been produced, which would account for much of the H_2 that had been evolved. Removal of some of the more volatile components by distillation at 15 mm. gave a distillate with two principal carbonyl absorptions at 2021 (s) and 2015 (m) and one strong band at 685 cm.$^{-1}$ (most likely the metal–hydrogen deformation) similar to the analogous bands of $HRe(CO)_5$ and $HMn(CO)_5$, as summarized in Table V. These bands are appropriately assigned to $HTc(CO)_5$ by their position, pattern, and by the volatility of the product giving rise to them. Inspection of the reaction mixture now revealed the same pattern in the carbonyl stretching region as before, except for the loss of the strong band at 2021 cm.$^{-1}$ (the band of medium intensity of $HTc(CO)_5$ was hidden in this mixture by the intense absorption of $Tc_2(CO)_{10}$ at 2016 cm.$^{-1}$).

At the present, the pentacarbonyl hydride of technetium has been isolated only in small amounts, as a solution in cyclohexane at such concentrations that only its principal absorption bands could be observed. Attempts to isolate this product in greater quantities are in progress in our Laboratories.

Discussion

The chemical properties of the organometallic compounds of technetium considered here appear to be intermediate to those of the compounds of manganese and rhenium, except for the properties of the Tc–H bond. The latter displays a greater tendency in the reaction mixtures in which it is formed to evolve hydrogen along with the formation of a metal–metal bond than is displayed by the corresponding derivatives of manganese or rhenium. It is interesting to note, in this connection, that a cyclopentadienyl derivative of technetium[17] is isolated as the dimer, $[(C_5H_5)_2Tc]_2$, while the corresponding derivative of rhenium is known as the hydride, $(C_5H_5)_2ReH$.

Our experiments also have uncovered anomalous behavior for technetium carbonyl during cleavage of the metal–metal bond by Na-amalgam. The evolution of CO and the reddish coloration imparted to the resulting solutions in tetrahydro-

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(16) W. E. Wilson, *Z. Naturforsch.*, **13b**, 349 (1958).

(17) D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 4474 (1961).

TABLE V

PRINCIPAL ABSORPTIONS FOR THE PENTACARBONYL ANION AND HYDRIDE OF TECHNETIUM AND THOSE OF ITS CONGENERS

	M	Carbonyl bands (cm.$^{-1}$)			Others (cm.$^{-1}$)	
$M(CO)_5^{-a}$	Mn^b	1898	1863			
	Mn	1898 s	1864 s	(1829 w, ^{13}CO)		
	Tc	1911 s	1865 s	(1827 w, ^{13}CO)		
	Re	1910 s	1864 s	(1829 w, ^{13}CO)		
$HM(CO)_5^c$	Mn	2014 s	2007 m		724 m	656 m
	Tc	2021 s	2015 m			685 m
	Re	2015 s	2006 m			683 m

[a] Observed for the sodium salt, tetrahydrofuran solution. All absorptions very broad. [b] From ref. 14. [c] Only the two most intense bands are listed, observed for extremely dilute solutions in cyclohexane, used here to identify the presence of the pentacarbonyl hydrides.

furan are under further investigation. It is interesting to note in this connection that the species $Mn_2(CO)_9^{-2}$, obtained from the reaction of BH_4^- with $Mn_2(CO)_{10}$,[18] imparts a red coloration to its solutions. The red coloration and evolution of CO in our reactions could very well indicate that cleavage of a carbonyl group is competing with the cleavage of the metal–metal bond, in $Tc_2(CO)_{10}$, and to a lesser extent, in $Re_2(CO)_{10}$. Only one-third as much gas was evolved from $Re_2(CO)_{10}$ as from $Tc_2(CO)_{10}$, while almost none at all was obtained from $Mn_2(CO)_{10}$. These observations may be explained by assuming a relative ease of cleavage of carbonyl groups in $M_2(CO)_{10}$, in the order $M = Tc > Re > Mn$. It is interesting to point out in this connection that the carbonyl of molybdenum also occupies an anomalous position by its relatively greater ease toward substitution of carbonyl groups in $M(CO)_6$, in the order $M = Mo > W > Cr$.[19] The anomalous behavior of the compounds of technetium in the *ease of cleavage of carbonyl groups as well as in the apparent greater stability of the metal–metal bond* is under further investigation in these Laboratories.

The carbonyl stretching frequencies in the infrared of some of the derivatives discussed here already have been analyzed in terms of possible structures. The spectra of the pentacarbonyl halides are in agreement with a C_{4v} structure, as determined for the derivatives of manganese and rhenium[20] and also independently arrived at for the complete set including technetium.[21] For the tetracarbonyl halide dimers, the four observed bands in the carbonyl stretching region do not allow for a differentiation between two possible structures, C_{2h} (metal–metal bonds) or D_{2h} (halogen bridging). Further information, such as the absorptions of these dimers in the lower energy region of the infrared (700–250 cm.$^{-1}$) favors the latter structure,[22] in agreement with recent X-ray diffraction studies.[23]

A comparison of the shift in the position of carbonyl absorptions with change in metal atom in the series of derivatives presented here reveals a complex pattern which does not lend itself to ready correlation at this time. Most of the bands display an alternation in position upon substitution of the heavier metal atoms for manganese, which could reflect the superposition of a number of different trends. Often, the position of the absorption is seen to shift to higher frequency on going from manganese to technetium and then either to move only imperceptibly, or back to lower frequencies, upon substitution of rhenium. Such a trend produces near coincidences in some of the absorptions in the pairs of compounds of either technetium and rhenium, or manganese and rhenium.

The trends observed in the position of carbonyl absorptions with change in metal atom cannot be explained solely on the basis of varying π and σ contributions in the bonding of the ligands to the metal. The relative position of any given absorption may be affected equally by small structural variations which would affect the interaction of the local oscillating dipoles in the mode.[21,22] Such structural variations would arise from the relative size of metal and ligands. In view of the complex interaction of electronic and structural changes encountered in changing

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(18) W. Hieber, W. Beck, and G. Zeitler, *Angew. Chem.*, **73**, 364 (1961).

(19) R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 4557 (1960); *cf.*, also, R. B. King, Dissertation, Harvard University, 1960, p. 25.

(20) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

(21) M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectry.*, in press (1962).

(22) M. A. El-Sayed and H. D. Kaesz, *Inorg. Chem.*, in press.

(23) L. F. Dahl, University of Wisconsin, private communication, 1961.

the central metal atom, it is not possible at this time to draw any quantitative conclusions from the trends observed.

Acknowledgment.—The authors wish to thank Professor M. A. El-Sayed of this Department for valuable discussions concerning the interpretation of spectra presented here, the Ethyl Corporation for a gift of manganese carbonyl, and Miss Heather King, Microanalytical Laboratories (this Department) for her assistance in the analyses of noncondensable gases.

CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY,
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The Heat of Formation of Crystalline Sodium α-Oxyhyponitrite. The Structure of Aqueous α-Oxyhyponitrite Ion[1]

BY HAROLD R. HUNT, JR., JAMES R. COX, JR., AND JAMES D. RAY

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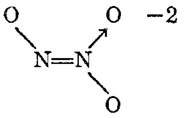
The heat of decomposition of sodium α-oxyhyponitrite (Angeli's salt, α-$Na_2N_2O_3$, sodium N-nitrohydroxylamate) in 0.996 *m* aqueous sulfuric acid to form sodium sulfate solution and nitric oxide gas was found to be -8.42 ± 0.40 kcal./mole. The calculated heat for the reaction: α-$Na_2N_2O_3(aq) = Na_2N_2O_2(aq) + {}^1/_2\, O_2$, $\Delta H = +20{,}000$ cal., is shown to be compatible with assignment of the structure $Na_2ONN^{O}_{O}$ and not Na_2ONNOO.

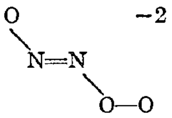
Introduction

The two forms of $Na_2N_2O_3$ which have been isolated to date are designated by Addison, Gamlen, and Thompson[2] as sodium α-oxyhyponitrite (Angeli's salt) and sodium β-oxyhyponitrite with the assigned structures



I

Angeli's salt, sodium
α-oxyhyponitrite



II

sodium
β-oxyhyponitrite

The original structural assignment was based on spectrophotometric evidence and analyses of hydrolysis products. The present study gives thermochemical evidence that the assignment of structure I as the α isomer is correct.

Experimental

Materials.—Sodium α-oxyhyponitrite was prepared by a modification of Angeli's[3] method, eq. 1. The data in Table I show that Angeli's maximum yield of 50% can be greatly surpassed by carrying out the reaction at low temperature with a large mole ratio of hydroxylamine to butyl nitrate. In the best synthetic experiment 0.16 mole of butyl nitrate was added to a solution of 2.0 moles of free hydroxylamine in 1 l. of anhydrous methanol. The solution was kept at 0° during the addition of 0.32 mole of methanolic sodium methoxide in small portions over a 48-hr. period. At the end of this time the solution was heated to boiling for a few minutes to effect conversion of the last approximately 10% of the reagents; yield, 17.88 g. of anhydrous sodium α-oxyhyponitrite, 99.8% of theory, based on butyl nitrate. The material was recrystallized by dissolving 23 g. in 58 ml. of water at 0° and precipitating with 1 l. of anhydrous methanol to recover 19.4 g. Analysis was effected by potentiometric titration at 0° under nitrogen using standard hydrochloric acid. To convert 5.00 mequiv. $Na_2N_2O_3$ to $NaHN_2O_3$ required 4.99 ± 0.02 mequiv. of the hydrochloric acid. Further verifica-

$$C_4HO_9NO_2 + H_2NOH + 2NaOCH_3 = Na_2(ONNO_2) + C_4H_9OH + 2CH_3OH \quad (1)$$

TABLE I

EFFECT OF TEMPERATURE AND MOLE RATIO OF REACTANTS ON YIELD OF SODIUM α-OXYHYPONITRITE FROM BUTYL NITRATE

Mole ratio $NH_2OH/C_4H_9ONO_2$	Temp., °C.	% Yield $Na_2N_2O_4$
3.6	65	63.0
0.74	25	48.5
1.00	25	55.0
1.35	25	61.5
3.15	25	71.3
5.2	25	83.0
10	25	82.0
12	25	83.0
2.75	0	85.0
12.5	0	99.8

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[1] Presented at the 140th National Meeting of the American Chemical Society, Chicago, Illinois, Sept. 3–8, 1961.

[2] C. C. Addison, G. A. Gamlen, and R. Thompson, *J. Chem. Soc.*, 338 (1952).

[3] A. Angeli, *Ahrens Samm. Chem. Tech, Vortrage*, **13**, 2 (1908).