with the fact that pentaborane(9) is thermally stable up to 200°. It may have included heterogeneous reactions, since they made no mention of seasoning the reaction chamber. To determine whether heterogeneous reactions took place in this study, additional pyrolyses were done using vessels packed with Pyrex glass tubing, which increased the surface to volume ratio by a factor of 10. Pyrolyses were done in these vessels as previously described and no increase in decomposition rate was observed.

Hydrogen Evolution.—In the previously mentioned pyrolyses at 202, 204, 213.5, and 228° and in another pyrolysis in which the temperature varied between 228 and 235°, the hydrogen evolution was measured. A 2.9-mol amount of hydrogen was evolved for each mole of pentaborane(9) decomposed in all pyrolyses, in spite of variations in reaction temperature, reaction time, and amount of decomposition. The overall pyrolysis reaction is

$$B_5H_9 \longrightarrow 5BH_{0.6}(s) + 3H_2 \tag{1}$$

No attempt was made to analyze this reddish orange $BH_{0.6}$ solid because of the extremely small amount produced. In the study by Cheney, *et al.*,[3] the reaction is described by the equation

$$B_5H_9 \longrightarrow 2H_2 + 5(BH)_x \tag{2}$$

However, this value was obtained by studying the volatile contents of the reaction vessel after pyrolysis by infrared absorption techniques. Hydrogen was not analyzed for but was computed by difference.

When Stock and Pohland[8] heated decaborane(14) to 250° for 24 hr, they found as products only hydrogen and a nonvolatile solid of composition $BH_{0.6}$. Beachell and Haugh[9] observed the same overall stoichiometry for the pyrolysis of decaborane(14). Unlike the pentaborane(9) pyrolysis, the pyrolysis of decaborane(14) initially yields less than 1 mol of hydrogen per mole of decaborane(14) decomposed. This produces a relatively hydrogen-rich solid, which then yields more hydrogen until the composition of the solid becomes $BH_{0.6}$.[9,10] In the early part of the pyrolysis of decaborane(14), Beachell and Haugh[9] found the molecular weight of the decomposition product to be 375 and observed some whitish materials that were slightly volatile and could be sublimed with gentle warming. Owen[10] isolated a small quantity of viscous liquid by vacuum distillation, which he said could be $B_{20}H_{24}$.

This low molecular weight, hydrogen-rich solid gives off hydrogen at 230° at a rate similar to the rate of decomposition of decaborane(14) at 230°.[10] The first-order rate constant for the pyrolysis of decaborane(14) is 1.62×10^{-2} min^{-1} at 230°[9] which is 30 times the first-order rate constant for the pyrolysis of pentaborane(9) at this temperature. If the initial step in the pyrolysis of pentaborane(9) produced less than 3 mol of hydrogen per mole of pentaborane(9) decomposed and similar low molecular weight, hydrogen-rich solids, these solids would give off hydrogen at a rate 30 times more rapid than they were being produced until the composition reached $(BH_{0.6})_x$ and the stoichiometry of the reaction would be unaffected by their existence.

In an attempt to isolate any volatile molecular decomposition product, another pyrolysis was done in reaction vessels which had a cold finger (similar in design to a sublimater). About 40 mm of pentaborane(9) was introduced into the vessels and the exterior walls of the vessels were heated to 210° in the glycerine bath as previously described while cold tap water was circulated through the cold finger. After 40 hr of heating, there was nonvolatile solid on the exterior walls but no solid on the cold finger. Analysis of the volatile products showed the relative amount of hydrogen evoltuion to be unchanged from the pyrolysis without the cold finger. This indicates that unlike the decaborane(14) pyrolysis there is no volatile, molecular, intermediate decomposition product in the pyrolysis of pentaborane(9). Whether or not there exists a nonvolatile solid richer in hydrogen than $(BH_{0.6})_x$ in the pyrolysis of pentaborane(9) is open to speculation. It should be noted that the $(BH_{0.6})_x$ solid from the pyrolysis of pentaborane(9) or decaborane(14) has different composition than another boron hydride polymeric solid, which is stable in this temperature range (200–230°). Shapiro and Williams[11] prepared $(BH)_x$ solid by copyrolysis of decaborane(14) and diborane at 100°. They observed that this solid gives up slightly more than half of its hydrogen on heating to 200–230° resulting in a solid with the formula $(BH_{0.45})_x$.

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A Carbonyl Fluoride of Molybdenum

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Molecular carbonyl halides of transition metals in which the halogen is chlorine, bromine, or iodine are well known. The formal oxidation states of the metals are usually I or II and only rarely III.[1] Some extremely reactive substances which may be carbonyl fluorides of transition metals have been reported[2,3] but they have not been characterized.

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(2) N. Bartlett in "Preparative Inorganic Reactions," Vol. 2, W. L. Jolly, Ed., Interscience, New York, N. Y., 1965, pp 334, 337.

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We have isolated a compound which we postulate to be a polymer of dicarbonyltetrafluoromolybdenum(IV), $Mo(CO)_2F_4$. We first isolated this compound from the reaction in Kel-F apparatus of molybdenum hexafluoride and hexacarbonylmolybdenum(0). This reaction had been previously studied in glass apparatus.[4] The products were reported to be fluorides of molybdenum with no evidence for formation of other compounds. We find that the carbonyl fluoride decomposes in contact with glass. However, in Kel-F the reaction proceeds in two stages: the first stage yields mainly the orange carbonyl fluoride; the second stage is very much slower and forms the yellow pentafluoride. This reaction cannot be used without modification as a preparative method because the orange product is always contaminated with unreacted hexacarbonyl, even if the reaction is allowed to proceed well into the second stage. The product is also contaminated with molybdenum pentafluoride, some of which forms even during the first stage. In addition, the product may also contain some molybdenum oxide tetrafluoride which is usually present as an impurity in the molybdenum hexafluoride. To eliminate these contaminants we have devised a procedure in which the first step is to condense anhydrous hydrogen fluoride onto about 0.25 g of hexacarbonylmolybdenum(0). No apparent reaction occurs, but when a small amount of molybdenum hexafluoride is condensed in, some orange product is formed, accompanied by evolution of a very small amount of carbon monoxide. Successive addition of the hexafluoride is repeated until the mixture separates into two liquid layers and addition is then stopped to prevent formation of major amounts of molybdenum pentafluoride. The lower layer is bright orange while the upper layer is pale yellow. No solid hexacarbonyl remains. Its removal was confirmed by the absence of its characteristic ir absorption at 2000 cm^{-1} in the final solid. The hydrogen fluoride is distilled off leaving a mixture containing the orange carbonyl fluoride and yellow molybdenum pentafluoride with possible oxide tetrafluoride.

The latter two compounds are then removed by dissolution. Molybdenum hexafluoride has been shown to be an excellent solvent for both of the compounds[5] but it cannot be used as a solvent in this situation because more pentafluoride would be formed as indicated above. However, tungsten hexafluoride has similar solvent properties but is much less reactive.[6]

In the second step in the overall procedure, the solids recovered after removal of the hydrogen fluoride are transferred to one of a pair of Kel-F tubes joined, at 90° to each other, through a Kel-F block fitted with a Kel-F vacuum valve at a third opening. A sintered Teflon disk is inserted at the top of the tube containing the sample. Tungsten hexafluoride is condensed onto the solids and allowed to melt. The carbonyl fluoride is insoluble and a pale yellow solution containing molybdenum pentafluoride forms. This solution is poured through the Teflon disk into the second tube. The tungsten hexafluoride is condensed back onto the solids and this washing process is continued until the solvent is colorless, indicating removal of the pentafluoride. Removal of any oxide tetrafluoride was confirmed by the absence of metal-oxygen bands in the ir spectrum of the final solid.

Results

Addition of a solution of triphenylphosphine in dichloromethane to the carbonyl fluoride causes precipitation of a yellow solid. *Anal.* Calcd for $Mo(PC_{18}H_{15})_2F_4$: Mo, 13.8; P, 8.9; C, 62.0; H, 4.34; F, 10.9. Found: Mo, 13.9; P, 8.5; C, 59.6; H, 4.34; F, 10.2. Precipitation of the derivative is accompanied by evolution of carbon monoxide. Pressure-volume measurements indicated 1.84 mol of carbon monoxide per mole of molybdenum.

The only significant difference between the ir spectrum of the derivative in a potassium bromide disk and that of triphenylphosphine is the occurrence of a single sharp absorption at 585 cm^{-1}.

Hydrolysis of the carbonyl fluoride in alkaline hydrogen peroxide solution is extremely vigorous and is accompanied by evolution of carbon monoxide. Molybdenum and fluoride were determined in the solution and carbon monoxide was calculated by difference. *Anal.* Calcd for $Mo(CO)_2F_4$: Mo, 42.1; CO, 24.6; F, 33.3. Found: Mo, 43.2; CO, 24.2; F, 32.6.

The ir spectrum of the carbonyl fluoride in a Nujol mull has absorptions in the carbonyl region and in the metal-fluoride region (see Figure 1).

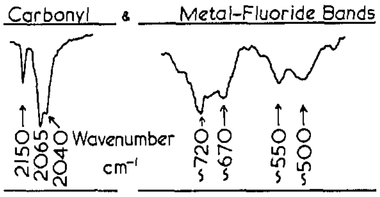

Figure 1.—Carbonyl and metal-fluoride absorptions in the ir spectrum of a Nujol mull of poly(dicarbonyltetrafluoromolybdenum(IV)).

Relatively polar solvents, such as acetonitrile, ethanol, and nitrobenzene, cause decomposition of the carbonyl fluoride. On the other hand, it is insoluble in tetrachloromethane and trichloromethane and only slightly soluble in dichloromethane. However, it is soluble in dioxane and tetrahydrofuran. In dioxane (dielectric constant 2.2) and tetrahydrofuran (dielectric constant 7.4), orange-red solutions are formed and these have only one carbonyl ir absorption at 1980 cm^{-1}. The solutions in these two solvents have molar conductances which are only 10^{-4} of the molar conductances of ionic solutes.[7,8] No further information could be obtained from these solutions because they slowly decompose.

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The carbonyl fluoride is paramagnetic over the temperature range studied. The reciprocal of the susceptibility is proportional to $T + 112°\text{K}$ (see Table I).

TABLE I

CORRECTED MOLAR SUSCEPTIBILITIES PER MOLE OF MOLYBDENUM (χ) AND CALCULATED MAGNETIC MOMENTS PER ATOM OF MOLYBDENUM (μ_{eff}) FOR POLY(DICARBONYLTETRAFLUOROMOLYBDENUM(IV))

T, °K	$10^3\chi$, cm^3 mol^{-1}	μ_{eff} per Mo, BM	
		$2.83(\chi T)^{1/2}$	$2.83(\chi(T + 112))^{1/2}$
93	1.990	1.22	1.81
111	1.830	1.28	1.81
129	1.708	1.33	1.82
139	1.639	1.36	1.82
158	1.507	1.39	1.81
168	1.459	1.41	1.82
189	1.369	1.44	1.82
214	1.258	1.47	1.82
220	1.242	1.48	1.82
251	1.124	1.51	1.81
282	1.031	1.53	1.81
297	0.997	1.55	1.81

Discussion

The single 585-cm^{-1} peak for the triphenylphosphine derivative can be compared with the metal–fluoride absorptions at 741 cm^{-1} for molybdenum hexafluoride, 623 cm^{-1} for the hexafluoromolybdate(V) anion, and 602–541 cm^{-1} for various hexafluorometalate(IV) anions,[9] and, hence, the peak is due to fluoride ligands bonded to molybdenum(IV) and suggests a trans configuration for the derivative. The amount of carbon monoxide evolved indicates complete displacement of the carbonyl ligands and this is confirmed by the absence of carbonyl peaks in the spectrum of the derivative. This is consistent with the proposed configuration because then the trans-labilizing effect of the entering phosphine ligands would lead to displacement of both carbonyl ligands. By contrast, for the carbonyl halides previously known, complete displacement is unusual. Since all of these compounds are in lower oxidation states, they have more than two carbonyl ligands, some of which are cis to the phosphine ligands and not labilized. The triphenylphosphine derivative is therefore postulated as a monomeric, octahedral species with the four fluoride ligands coplanar.[9a]

The 2150-, 2065-, and 2040-cm^{-1} absorptions in the ir spectrum of the parent compound are typical of terminal carbonyl ligands.[10] No other carbonyl halides in oxidation state IV exist, but the absorptions are at higher frequencies than for the known carbonyl halides of molybdenum(II),[11,12] as would be expected. The 720–670- and 550–500-cm^{-1} bands indicate terminal and bridging fluoride ligands, respectively.[13] The significance of the values of these frequencies will be discussed below.

A polymeric structure with terminal carbonyl ligands and both terminal and bridging fluoride ligands is proposed for the carbonyl fluoride. This type of structure is typical for the known carbonyl halides of transition metals.[1] Since the empirical formula is $\text{Mo(CO)}_2\text{F}_4$, a polymeric structure would require a coordination number greater than 6 but this is not uncommon in molybdenum compounds.[14]

During reaction with triphenylphosphine, a monomeric derivative is formed from the polymeric parent compound. This behavior is usual for the known polymeric carbonyl halides.[1] The colors of the solutions of the compound in dioxane and tetrahydrofuran suggest charge-transfer phenomena, and this, together with the appearance of only one carbonyl ir absorption shifted to 1980 cm^{-1}, suggests that monomers are formed in these solvents. The single peak is consistent with the proposed trans configuration of the carbonyl ligands. The very low conductances indicate that the solute is molecular and not ionic.

Thus, poly(dicarbonyltetrafluoromolybdenum(IV)) is unique in that it is a molecular carbonyl halide of a transition metal containing fluoride as the halide ligands and because the metal is in formal oxidation state IV.

The simplest possible polymeric structure is a dimer and such structures have been proposed to account for diamagnetism of the carbonyl halides of molybdenum(II).[11,12] A similar dimeric structure for the carbonyl fluoride (see Figure 2) has four electrons. However, the value of μ_{eff} calculated from the Curie–Weiss law, 1.82 BM, is close to the spin-only value for two unpaired electrons: $\mu^2 = 8$ per Mo_2; hence $\mu_{\text{eff}} = 2$ BM per Mo. This suggests a direct Mo–Mo single bond leaving one unpaired electron on each atom, an electronic structure similar to molybdenum(V). The metal–fluoride ir bands are consistent with this proposal. They are in the same regions as those observed for several polymeric pentafluorides.[13] They are very close to the observed values, 745–647 cm^{-1} for terminal fluoride ligands and 520–480 cm^{-1} for bridging fluoride ligands, in molybdenum pentafluoride.[15] The values of μ_{eff} calculated from the Curie law are consistent with the large value of the Weiss constant, $\Theta = 112°\text{K}$, which indicates antiferromagnetic interactions between the remaining two electrons. A Boltzmann distribution

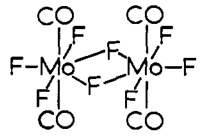

Figure 2.—A proposed dimeric structure for poly(dicarbonyltetrafluoromolybdenum(IV)).

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[9a] NOTE ADDED IN PROOF.—The triphenylphosphine derivative decomposes fairly rapidly in glass but we have now found that it is stable in silica and we have made magnetic measurements. The derivative is paramagnetic with $g = 1.96$ and closely obeys the Curie–Weiss law: $\Theta = 23°\text{K}$; μ (temperature independent) = 2.71 BM. This is consistent with the d^2 Mo(IV) monomeric structure which was proposed for tne derivative.

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between the manifold of spin levels $S' = 0$ and 1 with the singlet level lying lowest could account for the decrease in μ_{eff} with decreasing temperature.[16] Thus, the proposed dimeric structure is consistent with the spectral and magnetic properties of the carbonyl fluoride.

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Electrolytic Preparation of Nitrosodisulfonate Radical Anion

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Teuber, *et al.*,[1] have found that potassium nitrosodisulfonate is an extremely useful reagent for introducing an oxygen function into an aromatic nucleus, for example, the conversion of a variety of phenols and anilines to quinones.

The reagent itself, despite its potential utility in organic chemistry, has not become industrially important because its preparation has been tedious and expensive. The classical preparation[1–3] of Frémy's salt involves the oxidation of a solution of hydroxylaminedisulfonate with inorganic oxidizing agents such as lead dioxide or potassium permanganate. This procedure necessitates the removal of the reduced metal oxides very carefully prior to the isolation of the Frémy salt.

We now wish to report a different, facile process by which the nitrosodisulfonate radical is formed in high yield. The disadvantages, already mentioned, which are inherent in the classical approach are completely eliminated by this procedure.

Hydrolxyaminedisulfonate, conveniently prepared from sodium nitrite, sulfur dioxide, and sodium bicarbonate (eq 1), can be oxidized electrolytically to the Frémy radical in high yield (eq 2). It is necessary, however, to work in a solution buffered at approximately pH 9–11 since the nitrosodisulfonate radical is unstable under acidic conditions.

$$NaNO_2 + NaHCO_3 + 2SO_2 \longrightarrow HON(SO_3Na)_2 + CO_2 \qquad (1)$$

$$HON(SO_3Na)_2 \xrightarrow[\text{anode}]{\text{pH11}} ON(SO_3Na)_2 \qquad (2)$$

The electrolytic oxidation is carried out in a conventional electrolytic cell, utilizing stainless steel anodes and cathodes. The cathode is separated from the anolite by a semiporous porcelain thimble. With continuous cooling a current of approximately 6 mA/cm^2 is maintained throughout the reaction at a potential of *ca.* 7–12 V. The appearance of a deep purple color indicates the formation of the Frémy radical which shows a characteristic absorption in the visible region at 540 mμ (1 N KOH, ϵ for the radical anion is 14.5). This band serves as an excellent quantitative tool for concentration measurements.

Isolation of the potassium salt can easily be achieved by addition of a saturated solution of KCl (eq 3). We

$$ON(SO_3Na)_2 \xrightarrow{\text{KCl}} ON(SO_3K)_2 \qquad (3)$$

recommend, however, that the electrolytically prepared solution of the disodium salt be used as is, since two small samples of isolated Frémy's salt decomposed spontaneously at room temperature. At this point it is interesting to note the conflicting data in the literature concerning the stability of Frémy's salt. Raschig[2] stated that dried samples of potassium nitrosodisulfonate may *sometimes* be kept in a desiccator for 24 hr without decomposition. Harvey, *et al.*,[3] stated that dry crystalline Frémy's salt is very stable. Teuber, *et al.*,[1] claimed that pure samples are stable indefinitely if stored in evacuated clean glass containers. These published statements appear to support our recommendation that the nitrosodisulfonate radical should be handled only in solution. This can be done conveniently since the half-life of a buffered solution (Na_2CO_3, pH 10) is approximately 2 weeks.

The Raman spectrum of a solution of Frémy's salt (*ca.* 5% in 10% Na_2CO_3 solution) shows the following nine absorption lines: 290, 450, 665, 930, 990, 1025, 1075, 1350, and 1420 cm^{-1}. The band at 1075 cm^{-1} is due to the CO_3^{2-} ion. There are no differences in the Raman spectrum of authentic[4] and that of electrolytically prepared Frémy's salt.

Experimental Section

Apparatus.—An NJE power supply (NJE Corp., Kenilworth, N. J.), Model RVC-36-25, 0–36 V dc, 0–25 A, was used. The anode was stainless steel mesh (*ca.* 16 mesh/cm^2). The cathode was a stainless steel coil (1.5-mm wire diameter) which was set into a porous porcelain thimble filled to the level of the anolite with 10% sodium carbonate solution.

Procedure.—In a 1-l. resin jar, equipped with a mechanical stirrer, thermometer, gas-inlet tube, and ice cooling bath, were placed 15.0 g (0.217 mol) of sodium nitrite, 16.8 g (0.200 mol) of sodium bicarbonate, and 400 g of ice. With stirring, 25.6 g (0.40 mol) of SO_2 was bubbled into the initially heterogeneous mixture *via* the inlet tube which was placed approximately 2.5 cm from the bottom of the jar. The addition time was *ca.* 20 min. Near the end of the SO_2 absorption the light brown color faded almost completely. The SO_2 cylinder was mounted on a balance in order to have continuous control over the amount of sulfur dioxide added. The resulting solution of hydroxylaminedisulfonate had a pH of about 4. This clear and almost color-

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[4] Obtained from Alfa Inorganics, Inc., Beverly, Mass. 01915.