None of these 1:1 complexes has a sharp melting point; in fact, for the most part, they do not melt below 300° although most of them show signs of decomposition below this temperature. These complexes are relatively intractable; they have very little solubility in polar, nonprotonic solvents. Protonic solvents such as water and alcohols rapidly dissolve and decompose these complexes with deposition of colloidal TiO_2 and SnO_2 in a matter of seconds to minutes depending upon the particular complex. In contrast to this behavior $TiF_4 \cdot 2(CH_3)_2SO$ can be recrystallized from water without any evidence of decomposition, and $TiF_4 \cdot 2(CH_3)_2NCHO$ can be recrystallized from water with only slight decomposition.

The physical properties of the amine complexes, *i.e.*, absence of sharp melting points and the intractability, certainly indicate that they are not molecular, pentacovalent complexes but rather that they are polymeric complexes. Octahedral coördination could be preserved in a polymeric complex through "fluorine bonding."[25] This type of polymeric complex is wholly consistent with the reactivity toward protonic substances. An analogy may be drawn to illustrate this point. Antimony pentafluoride has octahedral coördination[17] in the liquid state through "fluorine bonding" and may be considered formally analogous to the 1:1 amine complexes. The hexafluoroantimonate anion also has octahedral coördination but, of course, no fluorine bridge bonds and may be considered formally analogous to a 2:1 MF_4 complex, *e.g.*, $TiF_4 \cdot 2(CH_3)_2SO$. Both SbF_6^- and $TiF_4 \cdot (CH_3)_2SO$ have the central atoms well shielded by negative substituents from nucleophilic attack and, accordingly, are not attacked readily by water. The central atoms in $(SbF_5)_x$ and the 1:1 amine complexes are similarly protected but the fluorine bridge bonds serve as reactive sites as witness the violent reaction of $(SbF_5)_x$ and water and the facile hydrolysis of the 1:1 amine complexes.

E. Complexes of Group VI Fluorides.—In the case of the Group VI tetrafluorides, the only complexes of any stability were those of MoF_4. Sulfur tetrafluoride is a very weak acceptor molecule, and although there is a heat of reaction or solution with many bases such as ethers and amides, only tertiary amines proved sufficiently basic to perturb the characteristic F^{19} resonance spectrum of SF_4. The F^{19} spectra of the amine SF_4 solutions consisted of single resonances and were essentially temperature ($\sim -100°$ to $+50°$) insensitive. Tellurium tetrafluoride reacted exothermally with a number of bases but secondary reactions occurred before the complexes could be isolated in pure form. With the exception of a very bulky amine $[C_6H_5N(CH_3)_2]$, the composition of the MoF_4 complexes is two molecules of base to one of MoF_4. The complexes are not paramagnetic, thus the non-bonding electrons are either in a pure *s* orbital or are involved in the hybridization of the molecule. Since there are no established instances of fluorine compounds in which non-bonding electrons are in pure *s* orbitals, the $MoF_4 \cdot 2$ base complexes are probably isostructural with IF_7 or TaF_7^-. The F^{19} resonance of solutions of these complexes consisted of a broad, single peak.

Acknowledgments.—The advice of Dr. W. D. Phillips is gratefully acknowledged.

WILMINGTON, DELAWARE

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[25] Amine bridging is another possibility but in view of the association present in the parent fluorides, fluorine bonding seems more likely.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Reaction of Dithiol with Molybdenum

BY T. W. GILBERT, JR.,[1] AND E. B. SANDELL

RECEIVED JUNE 16, 1959

The reaction of molybdate in mineral acid solution with dithiol (H_2Di) gives a green complex in which the dithiol/molybdenum ratio is 3 and molybdenum is sexivalent, as shown by reacting ratios and magnetic susceptibility measurement. Its composition is probably $MoDi_3$. When molybdenum(V) reacts with dithiol in acid medium, disproportionation occurs and a quadrivalent red complex, probably to be formulated as $Mo^{IV}\ Di_2(H_2Di)$ or $Mo^{IV}\ Di(HDi)_2$, is formed in addition to the sexivalent green complex. Because of side reactions, the two complexes are usually not formed in equivalent amounts. Observations on the rate of reaction and equilibrium in the system Mo(VI)–dithiol are recorded.

Toluene-3,4-dithiol (4-methyl-1,2-dimercaptobenzene), commonly called dithiol, reacts with molybdate in acid solutions to give a slightly soluble green product, whose composition has not been established, which dissolves in various organic solvents immiscible with water.[2] The present paper deals with this reaction and also that between dithiol and molybdenum(V).

Molybdenum(VI)–Dithiol Reaction

Experimental

Materials.—A 0.1 *M* solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in water was standardized gravimetrically by precipitation as silver molybdate and stored in a paraffin-coated bottle.

Dithiol (L. Light and Co., Colnbrook, England) was dissolved in a slight excess of sodium hydroxide solution which had been deaerated with nitrogen. The storage bottle was sealed with a rubber self-sealing serum bottle cap and solution was withdrawn by means of a hypodermic syringe. The strength of the solution ($\sim 0.5\%$) was determined by amperometric titration with silver nitrate; iodimetric titration gave the same results. Three lots contained 87.6, 94.9 and 95.7% of the active reagent. Purification was not

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[1] This paper is based on the Ph.D. Thesis of T. W. Gilbert, Jr., University of Minnesota, 1956.

[2] (a) J. H. Hamence, *Analyst*, **65**, 152 (1940); (b) C. C. Miller and A. J. Lowe, *J. Chem. Soc.*, 1258 (1940); (c) J. E. Wells and R. Pemberton, *Analyst*, **72**, 185 (1947); (d) H. G. Short, *ibid.*, **76**, 710 (1951).

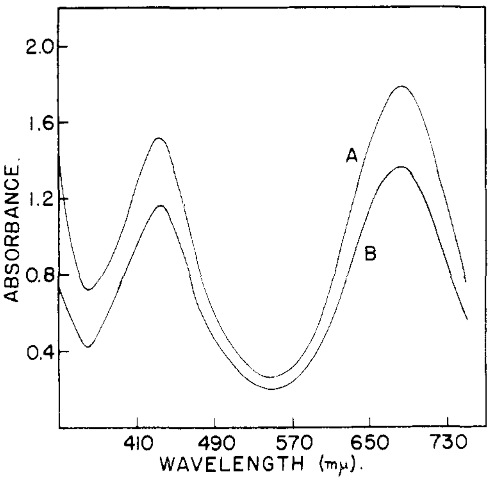

Fig. 1.—Absorbance (log I_0/I) curves of green complex ($MoDi_3$) in benzene. Approximate concentration = 8×10^{-5} *M.*: A, complex formed with excess dithiol; B, with excess molybdate. (Measurements made with Cary model 11 spectrophotometer, 1 cm. cells, temperature approximately 25°.)

attempted because the solutions are unstable (one decreased in strength by 35% in 95 days).

Preparation and Analysis of Solid Mo(VI) Complex.—Dithiol solution was added to a slight excess of ammonium molybdate in 8 *N* sulfuric acid and the mixture was heated at 75° for one-half hour to transform the precipitated dithiol to the green molybdenum complex. The solid was dissolved by shaking with benzene and the extract was washed with water, dilute sodium hydroxide and finally water. Evaporation of the benzene gave the solid complex which was dried at 60° in a vacuum oven. Recrystallization was not practicable. The absorption spectrum of the dried solid in benzene was identical with that of a fresh extract, showing that no decomposition occurred on drying.

Determination of C and H by the usual combustion method did not give reproducible results owing to the presence of molybdenum, and the averages recorded under Discussion are only approximate. Molybdenum was determined by ignition of the sample to MoO_3 at 450°; closely agreeing results were obtained by precipitating molybdenum with 8-hydroxyquinoline and weighing as the oxinate after destruction of the complex with nitric acid in a sealed tube. Sulfur was determined by decomposing the sample with sodium peroxide and potassium nitrate in a Parr bomb, removing molybdenum by precipitation with 8-hydroxyquinoline and precipitating as barium sulfate. The solid complex dissolved in benzene-ethanol was titrated with a solution of silver perchlorate in benzene. Prior to the end point, which was taken at the disappearance of the green color, the bulk of the precipitated silver dithiolate was removed by filtration. The dithiol/molybdenum ratio indicated for the complex was 2.9.

The molecular weight of the solid complex determined by the Rast camphor method was 556.

Reacting Ratios of Mo(VI) and Dithiol from Continuous Variations and Molar Ratio Methods.—These studies were carried out not only to establish the composition of the complex but also to learn whether reduction of molybdenum(VI) by dithiol occurs. The continuous variations method is valid for this system since only one molybdenum–dithiol complex is formed under the conditions used, as shown by identical absorption spectra obtained when molybdenum and dithiol are respectively present in large excess (Fig. 1).

The continuous variations method, carried out in deaerated 8 *N* sulfuric acid, led to the same results whether the absorbance was measured at 432 or 680 mμ, and showed that molybdenum and dithiol reacted in the molar ratio 1:3.

In the mole ratio variation method, a series of deaerated solutions, each containing 5.37×10^{-3} mmole of dithiol in 30 ml. of 8 *N* sulfuric acid, were treated with increasing amounts of ammonium molybdate and the complex was formed by heating at 75° for one-half hour. After cooling, the solutions were extracted with 50 ml. of benzene, the absorbance of which was measured at 680 mμ. The results are plotted as curve A in Fig. 2. The amount of molybdenum remaining in each aqueous phase after extraction was determined and is plotted in curve B. Curve OPQ is the absorbance curve that would be obtained if all the dithiol present had been converted into the complex and the molar extinction coefficient (ε) of the complex is taken to be 24,400. Curve C gives the amount of molybdenum in the aqueous phase less that which should have combined with dithiol if the reaction were quantitative. This curve has been obtained on the assumption that dithiol and molybdenum(VI) combine in the ratio 3:1 and has been calculated from the ordinate differences between curves OPQ and A and the known value of ε. The right-hand segment of C intersects the abscissa axis at dithiol/molybdenum = 3.0, thus confirming the assumption.

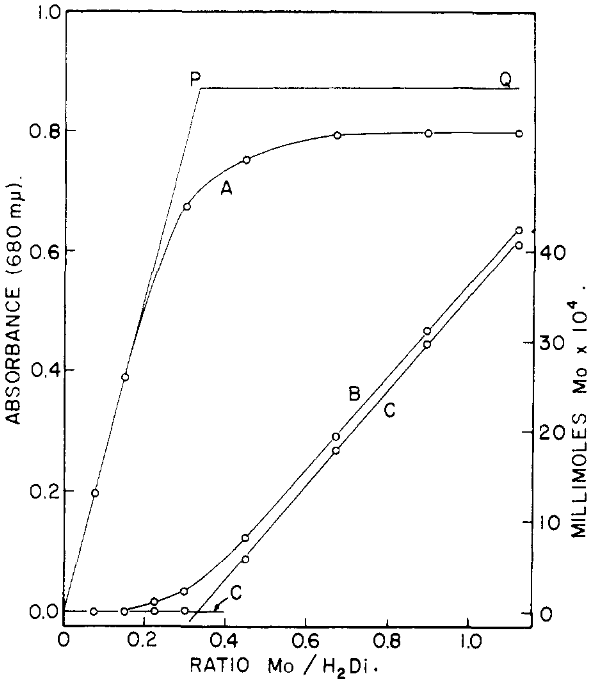

Fig. 2.—Mole ratio variation method: OPQ is curve that would be obtained with quantitative reaction, B gives the amount of Mo remaining in aqueous phase and C gives the amount of Mo which would have remained in the aqueous phase if the reaction with dithiol were quantitative.

The molar extinction coefficient of the complex in benzene was determined by treating molybdate with large excesses of dithiol (molar ratios from 150 to 600). The same value, 24,400 at 680 mμ, was obtained at different ratios. The molar extinction coefficient obtained by dissolving the solid green complex in benzene and assuming the composition $MoDi_3$ is 23,200. The difference is attributed to impurities in the solid complex. Since the solid was obtained by evaporating the benzene extract, it will be contaminated by benzene-soluble impurities in the dithiol and possibly by a little entrapped benzene.

Effect of Acidity.—The absorbance of benzene extracts (10 ml. of each phase, 2.0×10^{-4} mmole Mo(VI) and 1.86×10^{-2} mmole dithiol) remains constant at 0.48 (680 mμ) for sulfuric acid concentrations between 8 and 12 *N*; above and below these limits it falls off gradually. In hydrochloric and perchloric acid solutions between *p*H 2.0 and 1.0 the absorbance remains constant at about 0.28, then rises with decreasing *p*H.

Rate of Reaction.—At 25° the rate of formation of the complex is very slow and the reaction is only about 90% complete after 100 minutes in a mixture of 1 ml. of 0.0010 *M* Mo(VI), 1 ml. of 0.0155 *M* dithiol and 8 ml. of 8 *N* sulfuric acid. The reaction is much more rapid at 75° and the absorbance becomes constant in about 20 minutes, and remains the same after 1 or 2 hours. The color intensity is the same whether or not air is excluded during the heating.

Because iron has been stated to intensify the molybdenum–dithiol color,[3] its effect on the reaction was briefly examined. The absorbances of benzene extracts of the following mixtures, with and without iron, were determined: 0.10 ml. of 2×10^{-3} *M* Mo(VI) and 0.5 ml. of 0.029 *M* dithiol in a total volume of 10.1 ml., 8.3 *N* in sulfuric acid. Iron (2.0 mg.) was added as ferrous ammonium sulfate. Absorbances of extracts (10 ml.), obtained at various times at room temperature after addition of dithiol, had these values:

	A (680 mμ), iron absent	A (680 mμ), iron present
10 min.	0.373	0.442
40 min.	.455	.456
100 min.	.425	.437

With heating at 75°, these absorbances were obtained, with and without iron:

	A (680 mμ), iron absent	A (680 mμ), iron present
5 min.	0.467	0.460
15 min.	.464	.462
30 min.	.463	.463

The benzene extract of the molybdenum complex from an aqueous solution containing 10 mg. of ferrous iron contained not more than 1 γ Fe, or less than $^1/_{100}$ of the molybdenum present. The ultraviolet absorption spectrum of ammonium molybdate in 8 *N* sulfuric acid shows no change on addition of an equal amount of ferrous iron (4×10^{-4} *M*).

Miscellaneous.—pK_1 of dithiol in alcoholic solutions was determined by *p*H measurements (glass electrode) on titration with sodium hydroxide: 6.00 (32% ethanol), 5.65 (22%), 5.50 (12%). The extrapolated value for pK_1 in water is about 5.4 ($K_1 = 4 \times 10^{-6}$). The value of K_2 is very small but has not been determined.

The solubility of Mo(VI) dithiolate in benzene at 25°, as determined by weighing the dried residue obtained by evaporating 5-ml. portions of saturated solution, is 0.125 g. per 100 ml. or, if the molecular weight is 559 (see Discussion), 2.3×10^{-2} *M*. This value may be in error by 5–10%. The solubility in aqueous solution has not been determined because of its very low value, but it is estimated not to exceed 10^{-7} *M*.

Magnetic Susceptibility of Mo(VI)-Dithiol Complex.—The Gouy method was applied, with an Ainsworth micro balance and a magnet having a field strength of approximately 5000 gauss. A 2.64-gram sample of the complex was taken. The specific susceptibility, χ, of the Mo-dithiol complex was found to be -0.46×10^{-6} c.g.s.u./g.

Discussion

The atomic ratio S/Mo (6.24) found by analysis and the dithiol/Mo ratio (2.9) found by titration show that the green complex formed by reaction of dithiol with molybdenum(VI) in mineral acid solution contains 3 dithiol radicals per molybdenum atom. Since the continuous variations and molar ratio methods show that the reacting ratio is also very close to 3, the product must contain molybdenum in the + 6 state.

The results of the elemental analysis of the solid green complex are not sufficiently accurate to establish its formula. Moreover, the analyzed material is probably not sufficiently pure, even if the analyses were accurate, to furnish conclusive evidence. There are two principal possibilities, $MoDi_3$ and $MoOOH(HDi)_3$, where H_2Di = dithiol: (table).

	C, %	H, %	S, %	Mo, %
$MoDi_3$ ($C_{21}H_{18}S_6Mo$) mol. wt. 559	45.1	3.24	34.4	17.2
$MoOOH(HDi)_3$ ($C_{21}H_{22}S_6MoO_2$) mol. wt. 595	42.4	3.73	32.3	16.1
Analytical values, green complex mol. wt. 556	47.0	3.6	33.6	16.1

The value for molybdenum is considered the most accurate of the four elemental values. Assuming that the analyzed solid has 5% of impurities not containing molybdenum (from the difference in ε's already mentioned), a corrected Mo content of 16.9% is obtained, compared to 17.2% calculated for $MoDi_3$. This may be taken as evidence in favor of the composition $MoDi_3$. The molecular weight determination indicates the presence of only one molybdenum atom in the molecule.

Magnetic Susceptibility Evidence.—This confirms the conclusion that the green complex is a compound of sexivalent molybdenum and excludes the possibility of quinquevalency. Compounds of molybdenum(VI) should be diamagnetic since unpaired electrons are absent or at most should show slight paramagnetism after correction for diamagnetism of the rest of the molecule. We wish to exclude the possibility of molybdenum being present wholly or partly in the +5 state in a complex such as $MoO(HDi)_3$. The latter complex should be paramagnetic and, after diamagnetic corrections have been made, should show a magnetic moment corresponding to a single unpaired electron, provided no spin coupling between molybdenum atoms occurs. Spin coupling should not occur because the complex is not polynuclear and has a chelate structure. The complex cannot be planar because of spatial requirements and hence it seems unlikely that a molybdenum atom surrounded by six sulfur atoms and three bulky benzene rings could approach another molybdenum atom similarly surrounded within the range of atomic diameters necessary for spin coupling. Thus the measurement of magnetic susceptibility should conclusively distinguish between the two possibilities.

The theoretical molar magnetic susceptibilities χ_M were calculated from the expression

$$\chi_M = \Sigma n_a \chi_a + \lambda$$

where the constitutive correction λ was taken as that of benzene ($3\lambda = 3 \times 1.5 \times 10^{-6}$). Values of χ_a were taken from Selwood.[4] Values for the diamagnetic corrections for Mo(VI) and Mo(V) were taken from Klemm and Steinberg.[5] χ_M for $Mo^{VI}Di_3$ is found to be -284×10^{-6} c.g.s.u./mole. χ'_M for $Mo^{V}O(HDi)_3$ (diamagnetic contribution) is -307×10^{-6} c.g.s.u./mole. The paramagnetic contribution to the susceptibility of the latter compound was calculated from the "spin only" formula

$$\mu_{eff} = 2.839\sqrt{\chi_M T} = 2.839\sqrt{299.4\chi_M} = 1.732$$

$$\chi''_M = +1243 \times 10^{-6} \text{ c.g.s.u./mole}$$

The net molar magnetic susceptibility is then

$$\chi_M = \chi'_M + \chi''_M = (+1243 - 307)10^{-6} = +936 \times 10^{-6} \text{ c.g.s.u./mole}$$

$$\chi = +1.62 \times 10^{-6} \text{ c.g.s.u./g.}$$

Since the observed susceptibility of the complex is -0.46×10^{-6} c.g.s.u./g., the quinquevalent com-

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(3) (a) C. S. Piper and R. S. Beckwith, *J. Soc. Chem. Ind.*, **67**, 374 (1948); (b) S. H. Allen and M. B. Hamilton, *Anal. Chim. Acta*, **7**, 483 (1952).

(4) P. W. Selwood, in A. Weissberger, editor, "Techniques of Organic Chemistry," Vol. I, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1954, Part IV, p. 2455.

(5) W. Klemm and R. Steinberg, *Z. anorg. u. allgem. chem.*, **227**, 193 (1936).

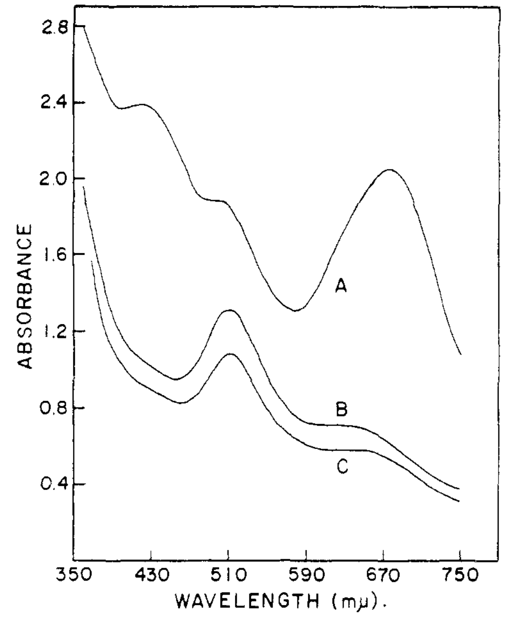


Fig. 3.—A, absorbance (log I_0/I) curve (benzene) of mixture of Mo(VI) and Mo(IV) dithiol complexes formed by reaction of Mo(V) with dithiol in 1.7 *N* HCl. B, approximate absorbance curve of Mo(IV) complex (Mo(VI) complex removed by shaking benzene extract for 2 days with 6 *N* sodium hydroxide). C, absorbance curve of solid Mo(IV) complex which had been separated chromatographically from the Mo(VI) complex and then redissolved in benzene. (Measurements made with Cary model 11 spectrophotometer at 25°, 1 cm. cells.)

pound $MoO(HDi)_3$ is ruled out as a possibility. The observed value agrees fairly well with the value -0.51×10^{-6} c.g.s.u./g. calculated for $Mo^{VI}Di_3$. If the small temperature-independent paramagnetism of Mo(VI) shown in compounds such as MoO_3 and Na_2MoO_4 is also included, the calculated specific susceptibility becomes -0.43×10^{-6} c.g.s.u./g.

For comparison, χ of $(NH_4)_2MoOCl_5$ was determined and found to be $+3.13 \times 10^{-6}$ c.g.s.u./g., compared to the calculated value $+3.34 \times 10^{-6}$.

Reaction Constant.—An approximate constant expressing the extent of the molybdenum(VI)-dithiol reaction in 8 *N* sulfuric acid can be calculated from the data in Fig. 2. Even though the solubility of dithiol in the aqueous phase is extremely small, so that solid or liquid dithiol is present before benzene extraction, the amount of molybdenum dithiolate formed and extracted is a function of the free dithiol concentration, *i.e.*, the system behaves in accordance with

$$Mo(VI) + 3H_2Di \longrightarrow MoDi_3 \text{ (solid)} + 6H^+$$

At constant acidity and ionic strength

$$K' = 1/\{[Mo(VI)]\ [H_2Di]^3\}$$

$$\log K' = \log 1/[Mo(VI)] + \log 1/[H_2Di]^3$$

The differences between the ordinates of OPQ and A at 6 points in Fig. 2 allow the calculation of the concentrations of unreacted H_2Di and Mo(VI) and give these values of log K': 18.0, 18.3, 18.4, 18.6, 18.4 and 18.3. The values are reasonably constant, considering that they are derived from the differences between two large numbers.

Because of our limited understanding of the constitution of acidic molybdate solutions, the rise in extractability of molybdenum dithiolate with increasing hydrogen ion concentration cannot be correlated quantitatively with the latter. The rise in extractability at about *p*H 1 in hydrochloric or perchloric acid corresponds to the isoelectric point. The extractability increases with increasing acidity as the concentration of cationic molybdenum species increases. The decrease in extraction at high sulfuric acid concentrations is likely due to formation of sulfate complexes such as $MoO_2(SO_4)_2^=$.

Effect of Ferrous Iron.—Both Piper and Beckwith[3a] and Allen and Hamilton[3b] noted that the presence of a small amount of iron was necessary for the complete extraction of molybdenum as dithiolate with petroleum ether at room temperature. The present results show that ferrous iron does not increase the extraction or color intensity of molybdenum in the benzene extract over that obtained by complete reaction at 75° in 8 *N* sulfuric acid. No significant amount of iron is found in the benzene extract and the suggestion that "iron is in some way incorporated into the molybdenum-dithiol complex" seems unlikely. Apparently there is no reaction between ferrous iron and molybdate in the aqueous phase (the ultraviolet absorption spectrum is unchanged). Ferrous iron serves solely to speed up the heterogeneous reaction at room temperature, but the reason for this is obscure.

Molybdenum(V)-Dithiol Reaction

The reaction of dithiol with molybdenum(V) in acid solution gives a mixture of green and red complexes. The green complex is $MoDi_3$, already described, and the red is a dithiolate of Mo(IV) in which the dithiol-molybdenum ratio is 3.

Experimental

To avoid the possibility of formation of Mo(VI) by air oxidation, an aqueous solution of molybdenum(V) chloride (obtained by passing acidified ammonium molybdate through a silver reductor) was deaerated with nitrogen, treated with dithiol and extracted with deaerated benzene in a closed system without exposure to the atmosphere at any time. The absorption curve of the extract is shown in Fig. 3. Similar curves are obtained even if air is not rigorously excluded.

The easiest way of preparing the red complex in reasonably large amounts is by chromatographic separation with alumina. The benzene extract containing the red and green complexes, from which excess dithiol had been removed by shaking with aqueous sodium hydroxide, was passed through a column of Merck activated alumina. The green complex was adsorbed at the top of the column and the red complex formed a diffuse band down the column. Elution with benzene containing 20% v./v. anhydrous ethyl ether removed the red complex, leaving the green at the top of the column. The solvent was removed by evaporation and the complex was obtained as a shiny jet-black scale. The product was analyzed as described for $MoDi_3$ after vacuum drying at 60°. Comparison of absorption curves showed no change produced by evaporation and drying. An average of 580 was found for the molecular weight of the complex by the Rast method.

The proportions of the red and green complexes formed by heating Mo(V) (obtained by electrolytic reduction of molybdate) in deaerated 8 *N* sulfuric acid with various ratios of dithiol are given in Fig. 4. The amounts of the two complexes were found by measuring the specific extinction coefficients of the solid Mo(VI) and Mo(IV) complexes at 680 and 510 mμ. The molar concentrations of the complexes were found approximately by making the assumption that both complexes have a molecular weight of 559.

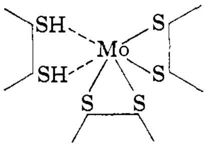
The specific extinction coefficients used for these calculations are

	Mo(VI) complex	Mo(IV) complex
680 mμ	41.6 cm.²/mg.	8.35 cm.²/mg.
510 mμ	8.16 cm.²/mg.	18.6 cm.²/mg.

Discussion

The green complex formed as one of the products when molybdenum(V) reacts with dithiol is identified as $Mo^{VI}Di_3$ by its spectral characteristics. Because formation of molybdenum(VI) by air-oxidation is believed to be ruled out, disproportionation must occur and the red complex is a compound of molybdenum(IV).

The red complex shows a S/Mo ratio of 5.95 and therefore contains 3 dithiol radicals per molybdenum atom. Three possible structures suggest themselves, disregarding coördinated water molecules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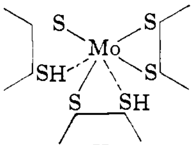
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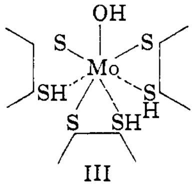
III

The calculated percentage compositions and the analytical values for the red complex are

	C, %	H, %	S, %	Mo, %
$MoDi_2(H_2Di)$ or $MoDi(HDi)_2$	45.0	3.60	34.32	17.11
$MoOH(HDi)_3$	43.6	3.83	33.2	16.59
Red complex	47.1	3.7	34.0	17.1

Because of the difficulties in the C and H determinations, values for these are of little significance. The Mo and S values give some support for formulas I and II.

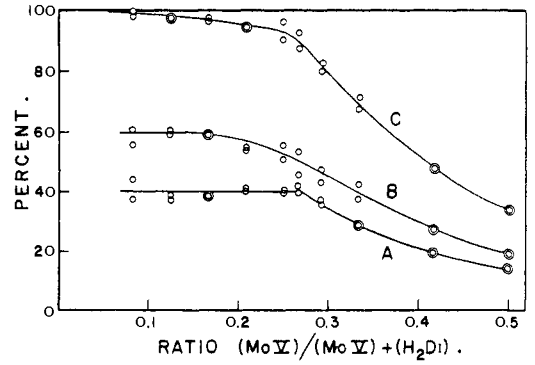

Fig. 4.—Proportions of green (Mo(VI)) and red (Mo(IV)) complexes formed by reaction of Mo(V) in 8 *N* sulfuric acid at different ratios of Mo/dithiol ([Mo(V)] + [H_2Di] = 2.4×10^{-4} *M*; phase ratio, benzene/aqueous = 1/1): A, per cent. of total Mo in form of extracted Mo(VI) complex; B, per cent. of total Mo in form of extracted Mo(IV) complex; C, sum of A and B.

The disproportionation is accompanied by side reactions so that equal amounts of Mo(IV) and Mo(VI) complexes are not formed, nor is all of the original molybdenum necessarily transformed into dithiolates. The greater proportion of the Mo(IV) complex formed in 8 *N* sulfuric acid (Fig. 4) can be ascribed to some reduction of Mo(V) by dithiol. As the excess of dithiol becomes smaller, complete formation of the dithiolates does not occur. Mo(IV) not combined with dithiol disproportionates in the aqueous phase to Mo(V) and Mo(III). Dithiol does not react with Mo(III). Especially at high acid concentrations the formation of Mo(IV) is impeded or prevented entirely, as postulated by the reaction

$$3Mo(V) + 6H_2Di \longrightarrow 2MoDi_3 + Mo(III) + 12H^+$$

In 12 *N* hydrochloric acid, the formation of the red Mo(IV) complex seems to be suppressed completely, but the green Mo(VI) complex still is formed.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE POLYMER STRUCTURE SECTION, NATIONAL BUREAU OF STANDARDS]

The Melting Temperature of Natural Rubber Networks

BY D. E. ROBERTS AND L. MANDELKERN

RECEIVED SEPTEMBER 24, 1959

The isotropic melting temperatures $T_m{}^1$ of natural rubber networks which were formed either by chemical reaction or by the action of ionizing irradiation were determined by dilatometric techniques. Substantial depression of the melting temperature with increasing amounts of crosslinking was observed for networks formed from randomly coiled chains irrespective of the method by which the crosslinks were introduced. It is also found that the melting temperatures of networks formed from highly ordered chains are substantially higher than those of corresponding networks formed from random chains. The difference in melting temperatures for these two types of networks can be quantitatively attributed to the decrease in configurational entropy of the former type networks which occur as a consequence of the chain disposition at the time of their formation.

Introduction

It has been shown recently that in accord with the theoretical predictions of Flory[1] many of the properties of polymer networks will depend on the relative arrangement of the chain units at the time of network formation.[2-4] In particular, if the network being studied is crystallizable its

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(1) P. J. Flory, THIS JOURNAL, **78**, 5222 (1956).

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