tein at *p*H 4, but some binding at *p*H 9. Both dialysis and rate experiments indicate no association with polyvinylpyrrolidone.

There is no ready explanation for the behavior with lauryl sulfate (Table IV). At concentrations of 0.0005 *M* lauryl sulfate and greater the usual straight line first-order plot of the data is not obtained. Instead the line begins to decrease noticeably in slope beyond about the first 30% of the reaction. Therefore, the rate constants reported (Table IV) for the 0.00050 and 0.00100 *M* lauryl sulfate reaction mixture were determined from the data collected during the initial 25% of the reaction. That association occurs is evident from the shift in the spectrum of the complex from 266 to 268 mμ found with solutions of 0.001 *M* sodium lauryl sulfate. It may be significant that in this case the visible spectrum is also affected, being broadened and shifted 10 mμ toward longer wave lengths. The visible spectrum is generally unaffected by ionic association, and substitution in the phenanthroline rings themselves causes only small shifts.[10]

In all the previous discussion we have ignored the possibility of micelle formation by the large ions. The association between $Fe(phen)_3^{2+}$ and lauryl sulfate ions cannot be due to micelle formation because of the low concentrations used. However micelles are formed by 0.1 *M* *d,l*-10-camphor sulfonate in 0.02 *M* NaCl. Ultracentrifuge measurements[12] indicate an average molecular weight of a few thousand. The micelles would resemble the polyanions, and behave similarly with respect to their effect on the rate of dissociation. The less rigid structure of the micelle as compared to that of the polyelectrolyte would not be expected to cause a decrease in the rate of racemization as is caused by the polyelectrolyte.

Acknowledgment.—The authors wish to acknowledge that a few preliminary measurements on the effects of large ions were made by Dr. J. E. Dickens. They also thank Professor I. M. Klotz for many helpful suggestions, in particular with reference to the dialysis experiments.

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[12] These measurements were made by Dr. L. Fuchs.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

Complexes of Organic Phosphorus Compounds with Peroxymolybdic Acids[1]

BY ELLIS K. FIELDS

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Organic compounds of phosphorus react with molybdenum trioxide and 90% hydrogen peroxide to form novel complexes that are derivatives of two peroxymolybdic acids, H_2MoO_5 and H_2MoO_6. Dialkyl and trialkyl phosphites, trialkyl phosphates, alkylphosphonic acids and triphenylphosphine have been converted in good yields. The complexes are shades of orange, from yellow to red. Heating to temperatures between 100 and 165° converts them to intense blue products that contain 1 or 2 oxygen atoms less. Orange and blue forms are soluble in most organic solvents; they are unaffected by light and air, but are decomposed by strong bases and acids.

Molybdenum compounds are of great industrial importance as catalysts in petroleum processes, as pigments and as enzymes. A series of molybdenum compounds that are relatively unknown are the molybdenum peracids. Peroxymolybdic acids H_2MoO_5, H_2MoO_6 and H_2MoO_8 have been mentioned, often without isolation of derivatives to prove the compositions.[2] Organic complexes of molybdenum with polybasic acids, polyhydric alcohols and phenols, β-diketones, aromatic amines, thiophenols and xanthates have been described.[3] However, no complexes of peroxymolybdic acids have appeared in the literature.

A variety of organic phosphorus compounds has been found to form complexes with molybdenum trioxide when reacting with hydrogen peroxide. These are the first complexes of organic phosphorus compounds with molybdenum to be reported. Twenty-four new complexes have been prepared in good yields from dialkyl and trialkyl phosphites, trialkyl phosphates, alkyl-phosphonic acids and triphenylphosphine. The properties of these complexes have been studied, and the probable structures have been deduced from elemental analyses, molecular weights, stoichiometry and infrared absorption data.

Preparation of Complexes.—The complexes formed upon adding 90% hydrogen peroxide to a stirred mixture of MoO_3 and the phosphorus compound. Less-concentrated peroxide also gave complexes, but 90% H_2O_2 was used to reduce hydrolysis effects. Such molybdenum compounds as MoS_2, MoS_3, MoO_2 and ammonium molybdate gave complexes, but MoO_3 gave the most consistent results; the other compounds functioned only insofar as they were first converted to MoO_3 by the hydrogen peroxide.

Phosphorus compounds were obtained commercially or synthesized. Six phosphate esters were obtained from Virginia–Carolina Chemical Corporation; tributyl phosphate and triphenylphosphine, from Eastman Kodak Co.; tri-2-ethylhexyl phosphate, from Carbide and Carbon Chemicals Company; and tri-butoxyethyl phosphate, from Ohio-Apex Company. The alkanephosphonic acids were prepared by peroxide-catalyzed addition of diethyl phosphite to 1-olefins to give alkanephosphonic esters in 74–80% yields[4] and hydrolysis of the resulting esters by stirring and refluxing with concentrated hydrochloric acid for 40 hours. 1-Olefins were obtained from Humphrey–Wilkinson Company. All esters were distilled *in vacuo*. The acids, ob-

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[1] Presented at the XVI International Congress of Pure and Applied Chemistry, Paris, France, July, 1957.

[2] E. Péchard, *Ann. chim. phys.*, [6] **28**, 537 (1893); G. Moeller, *Z. physik. Chem.*, **12**, 561 (1893); W. Muthmann and W. Nagel, *Ber.*, **31**, 1838 (1898); L. Pissarjewsky, *Z. anorg. Chem.*, **24**, 108 (1900); K. F. Jahr, *Chem. Zentr.*, **112**, **I**, 184 (1941); J. B. Martinez, *Anales fis. y. quim. (Madrid)*, **40**, 348 (1944); *C. A.*, **44**, 968g (1950).

[3] A thorough bibliography is available in Bulletin Cbd-9, Climax Molybdenum Company, New York, New York, June, 1956.

[4] Dutch Patent 69,357, January 15, 1952, to N. V. de Bataafsche Petroleum Maatschappij.

tained in quantitative yields, were crystallized from *n*-heptane. The physical properties of the purified compounds are shown in Table I. Molybdenum trioxide, 99.5+%, was obtained from Mallinckrodt Chemical Works, and 90% hydrogen peroxide, from Buffalo Chemical Company.

TABLE I

PHYSICAL PROPERTIES OF ORGANIC PHOSPHORUS COMPOUNDS

Compound	B.p.		$n^{20}D$
	°C.	Mm.	
Di-*n*-butyl phosphite	112	5.0	1.4237
Di-2-ethylhexyl phosphite	159	1.2	1.4426
Tri-isopropyl phosphite	58	7.0	1.4104
Tri-*n*-butyl phosphite	114–115	5.0	1.4324
Tri-*n*-hexyl phosphite	138–139	0.4	1.4421
Tri-isoöctyl phosphite	164–165	0.6	1.4479
Tri-*n*-butyl phosphate	136–137	5.5	1.4249
Tri-2-ethylhexyl phosphate	201–203	1.8	1.4432
Tri-butoxyethyl phosphate	198–199	0.7	1.4373
Diethyl-*n*-octyl phosphonate	125–127	2.2	1.4339
Diethyl-*n*-decyl phosphonate	137–138	0.8	1.4364
Diethyl-*n*-tetradecyl phosphonate	183–186	1.9	1.4427
n-Octane phosphonic acid	100[a]	..	....
n-Decane phosphonic acid	102[a]	..	....
n-Tetradecane phosphonic acid	96–97[a]	..	....

[a] Melting point.

The general procedure consisted of adding 0.4 mole 90% hydrogen peroxide a few drops at a time to a stirred mixture of 0.2 mole phosphorus compound and 0.1 mole MoO_3. The acids and triphenylphosphine first were dissolved in 100–150 ml. benzene, whereas no solvent was used for the esters. The temperature was held at 30–35° by cooling if necessary. Little heat was liberated in the reactions with dialkyl phosphites, trialkyl phosphates and alkanephosphonic acids. Trialkyl phosphites reacted vigorously with hydrogen peroxide; trimethyl phosphite caught fire with every addition of peroxide, even when the mixture was cooled to −20°.

After the addition of peroxide, the mixtures were stirred at 30° for 40 to 60 hours and filtered. The filtrates were evaporated at 70 to 80° at 0.1 to 0.7 mm. in a stream of dry nitrogen. Water and alcohols that were evolved were collected in a trap cooled with Dry Ice and acetone; in no case did any peroxidic material collect. The solid complexes were purified by filtration, solution in benzene or acetone, and precipitation with pentane at 0 to −10°. The preparation of a typical complex from each class is described.

Dibutyl Phosphite Complex.—To a stirred mixture of 58.5 ml. (58.26 g., 0.3 mole) of dibutyl phosphite and 21.6 g. (0.15 mole) of molybdenum trioxide was added 16.44 ml. (0.6 mole) of 90% hydrogen peroxide dropwise over a period of 1 hour. No heat evolved. The mixture was stirred 48 hours at 30° and filtered. The unreacted molybdenum trioxide collected on the filter was washed with ether and dried; it weighed 7.3 g.

The filtrate was evaporated at 0.5 mm. up to 50°. The residue, 56.3 g., was taken up in 150 ml. of anhydrous ether, filtered through Celite to remove a slight haziness, and again evaporated *in vacuo*. The residue, 53.6 g., 94%, was a deep, reddish-orange viscous oil, $n^{20}D$ 1.4297, freely soluble in acetone, ether and ethanol, slightly soluble in benzene and water, insoluble in heptane. It was strongly acidic and dissolved in aqueous sodium hydroxide.

Anal. Calcd. for $C_{12}H_{31}P_3MoO_{13}$: C, 25.2; H, 6.1; P, 16.3; Mo, 16.8; mol. wt., 570; peroxide O, 5.6. Found: C, 24.9; H, 6.0; P, 16.1; Mo, 16.9; mol. wt., 560; peroxide O, 5.3.

The red color deepened as the complex was heated; at 135° the complex turned deep blue.

The distillate obtained by evaporation of the complex was collected in a trap cooled in Dry Ice and acetone. It consisted of 10.6 g. water and 22 g. of butanol. There was no peroxide in the distillate.

Tributyl Phosphite Complex.—To a stirred mixture of 55.5 ml. (50 g., 0.2 mole) of tributyl phosphite and 14.4 g. (0.1 mole) of molybdenum trioxide was added 10.84 ml. (0.4 mole) of 90% hydrogen peroxide dropwise over a 3-hour period. Reaction temperature was maintained at 30–35° by cooling with an ice-bath. The mixture was stirred at 25° for 48 hours, filtered from 0.2 g. of unreacted molybdenum trioxide, and evaporated at 0.7 mm. up to 50° with dry nitrogen bubbling through the liquid. The distillate consisted of 10 g. of water and 3.8 g. of butanol, but no peroxide. The residue, 54 g., was a mixture of solid and liquid products. It was diluted with 100 ml. of *n*-pentane, chilled to −10°, and filtered. The yellow solid collected on the filter was dissolved in 60 ml. of benzene, the solution was diluted with 150 ml. of pentane, and chilled to −10°. The precipitated solid was collected on a filter and dried. It weighed 27 g. (54% yield).

Anal. Calcd. for $C_{12}H_{28}P_2MoO_{11}$: C, 28.5; H, 5.5; P, 12.2; Mo, 19.0; mol. wt., 500; peroxide O, 3.1. Found: C, 28.3; H, 5.5; P, 12.2; Mo, 18.6; mol. wt., 480; peroxide O, 2.8.

The yellow solid on heating started to turn green at 140°, melted to a deep blue liquid at 186–187° with slight decomposition and at 270° became a dark brittle solid. It was very soluble in methanol and acetone, soluble in benzene, insoluble in water, ether and pentane.

The original filtrate on evaporation *in vacuo* gave 62.4 g. (40%) of deep orange filtrate, $n^{20}D$ 1.4750.

Anal. Calcd. for $C_{16}H_{36}P_2MoO_{11}$: C, 34.2; H, 6.4; P, 11.0; Mo, 17.1; mol. wt., 560; peroxide O, 2.8. Found: C, 34.0; H, 6.3; P, 11.3; Mo, 17.1; mol. wt., 580; peroxide O, 2.5.

At 125° the orange liquid became deep blue in color and gave a product containing 1 less oxygen atom.

Reaction of Tributyl Phosphite, Molybdenum Trioxide and Water.—A mixture of 55.5 ml. (50 g., 0.2 mole) of tributyl phosphite, 14.4 g. (0.1 mole) of molybdenum trioxide and 7.2 g. (0.4 mole) of water was stirred at 25° for 48 hours. The unreacted solid was collected on a filter, washed with ether and dried. There was recovered 14.4 g. of molybdenum trioxide, showing that no complex had formed in the absence of hydrogen peroxide.

Reaction of Tributyl Phosphite, Molybdenum Trioxide and Oxygen.—A mixture of 27.75 ml. (25 g., 0.1 mole) of tributyl phosphite and 7.2 g. (0.05 mole) of molybdenum trioxide was shaken in a pressure bottle under 10 pounds per square inch oxygen pressure at 25°. After 40 hours there had been no oxygen uptake. Water (1.8 ml., 0.1 mole) was added to the mixture, and it was again shaken under 10 lb. pressure at 25° for 48 hours and at 50° for 4 hours. There was no oxygen absorption. The mixture was filtered, giving 7.2 g. of unreacted molybdenum trioxide. No complex formed.

Reaction of Tributyl Phosphite, Molybdenum Trioxide and *t*-Butyl Hydroperoxide.—To a stirred mixture of 55.5 ml. (50 g., 0.2 mole) of tributyl phosphite and 14.4 g. (0.1 mole) of molybdenum trioxide was added 36 g. (0.4 mole) of *t*-butyl hydroperoxide dropwise over 2 hours. The temperature was maintained at 45–50° by ice-bath cooling. The mixture was stirred for 36 hours, then filtered. The unreacted molybdenum trioxide weighed 14.4 g., showing that no complex had formed.

Tributyl Phosphate Complex.—To a stirred mixture of 53.3 g. (0.2 mole) of tri-*n*-butyl phosphate and 14.4 g. (0.1 mole) of molybdenum trioxide was added 10.84 ml. (0.4 mole) of 90% hydrogen peroxide dropwise over 30 minutes. Very little heat was evolved. The mixture was stirred at 30° for 60 hours and filtered, giving 7.3 g. of unreacted molybdenum trioxide and a filtrate that contained an immiscible aqueous phase. The organic layer was separated and evaporated at 0.1 mm. and 40°. Only water collected in the cold trap. The residue, 61.7 g., was a deep yellow liquid, $n^{20}D$ 1.4427.

Anal. Calcd. for $C_{48}H_{110}P_4MoO_{22}$: C, 45.8; H, 8.7; P, 9.8; Mo, 7.6; mol. wt., 1260; peroxide O, 2.5. Found: C, 45.6; H, 9.0; P, 9.7; Mo, 7.6; mol. wt., 320; peroxide O, 2.5.

The complex turned deep red at 80–85°, then deep blue at 125°, and gave off oxygen. The blue complex analyzed for the original complex minus 2 oxygen atoms.

Decane Phosphonic Acid Complex.—A mixture of 11.1 g. (0.05 mole) of decane phosphonic acid, 100 ml. of benzene, 3.6 g. (0.025 mole) of molybdenum trioxide and 2.71 ml. (0.1 mole) of 90% hydrogen peroxide was stirred at 25°. After 24 hours almost all the solid had disappeared. The benzene solution was filtered, leaving 0.1 g. of unreacted molybdenum trioxide, and evaporated *in vacuo*. The orange solid residue was purified by solution in benzene and precipitation with *n*-pentane. It weighed 14.7 g. (98% yield), melted at 104–105° with slight gas evolution, and turned deep blue at 130°. It was soluble in benzene and water, insoluble in pentane.

Anal. Calcd. for $C_{20}H_{44}P_2MoO_{10}$: C, 39.7; H, 7.3; P, 10.3; Mo, 15.9; mol. wt., 600; peroxide O, 5.2. Found: C, 39.4; H, 7.4; P, 10.2; Mo, 15.6; mol. wt., 2410; peroxide O, 4.4.

Triphenyl Phosphine Oxide Complex.—To a stirred mixture of 26.2 g. (0.1 mole) of triphenyl phosphine in 100 ml. of benzene and 7.2 g. (0.05 mole) of molybdenum trioxide was added 5.42 ml. (0.2 mole) of 90% hydrogen peroxide dropwise over 2 hours. Considerable heat was evolved; the temperature was kept at 40–45° by cooling with an ice-bath. The mixture was stirred 70 hours, then filtered. The yellow solid was washed thoroughly with benzene and dried. There resulted 29.6 g. (98%) bright yellow complex insoluble in water, acid, base, benzene and acetone.

Anal. Calcd. for $C_{54}H_{49}P_3Mo_2O_{14}$: C, 53.7; H, 4.1; P, 7.7; Mo, 15.9; peroxide O, 4.0. Found: C, 53.5; H, 4.1; P, 7.9; Mo, 15.9; peroxide O, 3.7.

The solid sintered at 180° and melted at 327° to a deep blue liquid. It dissolved in boiling *o*-dichlorobenzene. Molybdenum trioxide deposited in a few seconds. The filtered solution gave triphenyl phosphine oxide, melting at 154–155°, on being evaporated.

Molecular weights were determined by ebullioscopy in benzene using a modified Menzies–Wright molecular weight apparatus.[5]

The complexes are of orange shades varying from yellow to red. Solids are yellow; oils are deep orange to red. When heated to 120–160° they give up 1 to 2 oxygen atoms and become deep blue, a color resembling inorganic molybdenum blue. However, the organic blue complexes, in contrast to inorganic molybdenum blue, are stable to light and air in bulk, as films on glass, or on fabrics. Both orange and blue forms are stable to dilute inorganic acids, but are decomposed rapidly by concentrated acid and slowly by bases. Both forms are soluble in a variety of organic solvents. Physical properties of the complexes are listed in Table II.

Infrared Absorption Spectra.—Phosphorus compounds and their molybdenum complexes were examined in a Perkin–Elmer model 21 double-beam spectrophotometer, firstly to study absorption bands as clues to structure, and secondly to determine the effects of complexing on absorption bands. All liquids were run as capillary films between rock salt plates. Solids were run as Nujol mulls. Band numbers are in reciprocal centimeters (cm.$^{-1}$).

Bands and Structures.—The characteristic P → O band at 1270 is very strong in dibutyl phosphite. In the red molybdenum complex it has shifted to a weaker band at 1230; in the blue form, it is again strong but broadened from 1230–1000. Tributyl phosphite does not show this band; however, the orange and blue forms of the solid and liquid complexes show a very strong band at 1235. Tributyl phosphate shows a strong band at 1280–1270; in both orange and blue complexes, the band is even stronger. Triphenyl phosphine oxide shows a very strong band at 1192; this band is completely missing in the molybdenum complex. Instead, a double band of medium intensity appears at 1175 and 1165.

A clean P → O band is not obtained from the alkylphosphonic acids[6]; because of H bonding, a broad general absorption results in the 1350–1110 region. Tetradecane phosphonic acid and its orange and blue complexes gave this general broad absorption with no distinct features.

The P–H band is in the 2350–2480 region. It is shown only by dibutyl phosphite and its red molybdenum complex; the blue complex does not have it at all.

The P–C band in aliphatic compounds, generally weak, is shown only by tetradecane phosphonic acid at 760 and 740; these weak bands are gone in the orange and blue complexes. The P–C band in aromatic compounds at 1000 is present in both triphenyl phosphine oxide and its complex.

The P–OH band generally shows as broad, shallow absorption at 2700–2560. Monobasic acids often have another broad, shallow absorption region at 2500–1600. Dibutyl phosphite does not absorb in these regions, but the red complex absorbs at 2770–2560 and at 1640–1610. Tributyl phosphite also does not have these bands, but the orange and blue forms of the solid and liquid complexes have bands at 2630–2560 and 1600. Tetradecane phosphonic acid and its complexes absorb at 2700–2650.

The P–O–C band lies in the 1050–995 region. The phosphite and phosphate esters and their molybdenum complexes all absorb strongly here. Individual variation is great, but there is no basis for judging what these differences mean.

Unfortunately, the O–O band for peroxide oxygen at 880–870 is at best weak. Some complexes showed it; some did not. It was not even noticeable in the spectrum of tributyl phosphate to which had been added 2% of 90% hydrogen peroxide.

Effects of Complexing.—Comparison of spectra of original phosphorus compounds with corresponding orange and blue complexes can be made only in the cases of the phosphate esters, phosphonic acids and triphenyl phosphine oxide. In the other cases structural changes are too great to interpret.

The orange complex of tributyl phosphate has a medium band at 1730 not shown by the ester; the 2940 band is much stronger. All other bands are identical. The blue complex has a strong band at 1730 and a medium band at 870 not shown by the ester or orange complex. The 4200 band in the other two is missing.

A strong band at 788 in tetradecane phosphonic acid disappears in the orange complex and reappears in the blue. Both orange and blue complexes have strong bands at 1660, 1050–1020 and 918 not shown by the acid.

The very strong P → O band at 1195 in triphenyl phosphine oxide has disappeared in the complex. The complex has a very strong band at 951 and strong bands at 1175, 1165, 856 and 853 not in the phosphine oxide.

Structures of Complexes.—The structures of the complexes differ markedly and depend on the phosphorus compounds from which they are derived. They were deduced by correlating elemental analyses, molecular weights, stoichiometry of reactants and products, including alcohols liberated, and infrared absorption data with structures that have been put forth for organic molyb-

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(5) W. E. Barr and V. J. Anhorn, *Instruments*, **20**, 342 (1947).

(6) F. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951); *N.R.L.* Report 3657.

TABLE 11

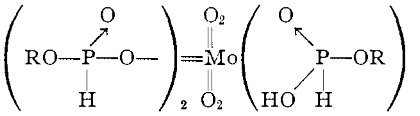
COMPLEXES OF ORGANIC PHOSPHORUS COMPOUNDS WITH PERMOLYBDIC ACIDS

Starting material	Yield, %	Color	Empirical formula	Mol. wt.		M.p., °C. or (n^{20}D)	Carbon, %		Hydrogen, %		Phosphorus, %		Molybdenum, %		Peroxide oxygen, %	
				Calcd.	Found		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Di-*n*-butyl phosphite	94	Red	$C_{12}H_{31}P_3MoO_{13}$	570	560	(1.4297)	25.2	24.9	6.1	6.0	16.3	16.1	16.8	16.9	5.6	5.3
Di-(2-ethylhexyl) phosphite	92	Red	$C_{24}H_{55}P_3MoO_{13}$	740	750	(1.4488)	38.9	38.7	9.6	9.3	12.6	12.8	13.0	13.0	4.3	3.9
Tri-isopropyl phosphite	64	Orange	$C_9H_{22}P_2MoO_{11}$	460	470	155 dec.	23.3	23.3	4.7	4.9	13.4	13.6	20.7	20.4	3.4	2.9
	32	Orange	$C_{12}H_{28}P_2MoO_{11}$	500	490	(1.4533)	28.5	28.7	5.5	5.7	12.2	12.4	19.0	18.7	3.1	2.7
	..	Blue	$C_{12}H_{28}P_2MoO_{10}$	490	520	[a]	29.4	29.3	5.7	5.8	12.6	12.8	19.6	19.3	..	..
Tri-*n*-butyl phosphite	54	Yellow	$C_{12}H_{28}P_2MoO_{11}$	500	480	186–187	28.5	28.3	5.5	5.5	12.2	12.2	19.0	18.6	3.1	2.8
	40	Orange	$C_{16}H_{36}P_2MoO_{11}$	560	580	(1.4750)	34.2	34.0	6.4	6.3	11.0	11.3	17.1	17.1	2.8	2.5
	..	Blue	$C_{16}H_{36}P_2MoO_{10}$	550	600	[a]	35.2	34.9	6.6	6.4	11.3	11.5	17.6	17.3	0	0
Tri-*n*-hexyl phosphite	61	Orange	$C_{18}H_{40}P_2MoO_{11}$	590	570	170	34.7	34.8	6.8	7.1	10.5	10.5	16.3	16.1	2.7	2.4
	..	Blue	$C_{18}H_{40}P_2MoO_{10}$	570	650	160--163	35.7	35.9	7.0	7.1	10.8	10.7	16.7	16.5	..	..
	34	Orange	$C_{24}H_{52}P_2MoO_{11}$	670	680	(1.4738)	42.7	43.0	7.7	8.0	9.2	8.9	14.2	14.0	2.3	2.1
	..	Blue	$C_{24}H_{52}P_2MoO_{10}$	660	730	[a]	43.8	43.6	7.9	8.1	9.4	9.2	14.6	14.4	..	..
Tri-isoöctyl phosphite	63	Orange	$C_{24}H_{52}P_2MoO_{11}$	670	680	160–162	42.7	42.5	7.7	7.9	9.2	8.9	14.2	14.5	2.3	1.9
Tri-*n*-butyl phosphate	98	Orange	$C_{48}H_{110}P_4MoO_{22}$	1260	320	(1.4427)	45.8	45.6	8.7	9.0	9.8	9.7	7.6	7.6	2.5	2.5
	..	Blue	$C_{48}H_{110}P_4MoO_{20}$	1230	350	....	47.0	46.7	9.0	9.2	10.1	10.3	7.8	7.7	0	0
Tri-2-ethylhexyl phosphate	98	Orange	$C_{96}H_{206}P_4MoO_{22}$	1930	480	(1.4535)	59.9	60.1	10.7	10.9	6.4	6.5	5.0	5.0	1.6	1.2
	..	Blue	$C_{96}H_{206}P_4MoO_{20}$	1900	500	....	60.7	61.0	10.9	11.1	6.5	6.5	5.1	5.0	0	0
Tri-butoxyethyl phosphate	98	Orange	$C_{72}H_{158}P_4MoO_{34}$	1790	440	(1.4488)	48.4	48.1	8.8	8.6	6.9	7.1	5.4	5.7	1.7	1.3
	..	Blue	$C_{72}H_{158}P_4MoO_{32}$	1750	470	....	49.3	49.0	9.0	8.9	7.1	7.2	5.5	5.7	0	0
Octane phosphonic acid	98	Orange	$C_{16}H_{36}P_2MoO_{10}$	550	2250	170 dec.	35.2	34.9	6.6	6.8	11.3	11.2	17.6	17.8	5.8	5.0
Decane phosphonic acid	98	Orange	$C_{20}H_{44}P_2MoO_{10}$	600	2410	104–105 dec.	39.7	39.4	7.3	7.4	10.3	10.2	15.9	15.6	5.2	4.4
Tetradecane phosphonic acid	98	Orange	$C_{28}H_{60}P_2MoO_{10}$	710	1480	....	47.2	47.1	8.4	8.5	8.7	8.6	13.5	13.7	4.4	3.7
	..	Blue	$C_{28}H_{60}P_2MoO_8$	680	1630	....	49.1	48.9	8.8	8.7	9.1	8.9	14.1	14.0	0	0
Triphenyl phosphine	98	Yellow	$C_{54}H_{49}P_3Mo_2O_{14}$	..	..	M. 327[b]	53.7	53.5	4.1	4.1	7.7	7.9	15.9	15.9	4.0	3.7

[a] Opaque viscous liquid. [b] Sinters 180°.

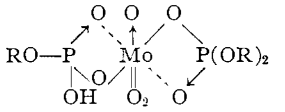
denum complexes.[3] It must be emphasized that the exact nature of the bonds holding these complexes together is not known.

Dialkyl phosphites give red complexes presumably of structure

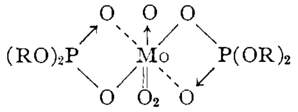


In both dibutyl and di-2-ethylhexyl phosphite the P–H bond is present in the same structure which has peroxide oxygen. Hydrolysis to the monoalkyl phosphite and 1 mole of alcohol takes place, yet no evidence arises for the hydroperoxide derived from the alcohol. The orange complexes go over to the blue form at 125° with loss of 2 oxygen atoms; the resulting blue complexes no longer show the P–H band and show extensive structural changes that are difficult to interpret.

Trialkyl phosphites evolve much heat when they react with hydrogen peroxide and molybdenum trioxide. The products are yellow solids, melting at about 150°, possibly of structure



and orange oils possibly of structure



The P → O band, missing in tributyl phosphite, shows strongly in the complexes; the P–OH band also shows in the yellow solid complexes, but weakly or not at all in the orange oils.

Heating converts these complexes to the blue forms with loss of 1 oxygen atom, but molecular weights are consistently about 10% too high. Complexes of the molybdyl–molybdate type, postulated for inorganic molybdenum blue,[7] may be formed in part. These would be of higher molecular weight than the original complexes.

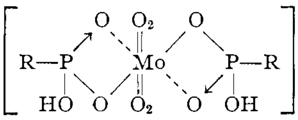
Hydrolysis, as well as oxidation, no doubt takes place when the trialkyl phosphites and MoO_3 react with hydrogen peroxide. These reactions must be simultaneous. If hydrolysis took place first, the resulting dialkyl phosphite would retain a P–H bond in the resulting complex; such is not the case. If oxidation to the trialkyl phosphate occurred first, no appreciable hydrolysis could occur thereafter.

Trialkyl phosphates give orange oils of structure

$$[(RO)_3P \rightarrow O]_4H_2MoO_6$$

The ebullioscopic molecular weights are about one fourth of that called for by the formula; this indicates that the complex dissociates into its constituents sufficiently to give a molecular weight average. The lack of any covalent P–O–Mo bond is reflected in the ease of dissociation. No hydrolysis takes place during the reaction, as no alcohol ever is isolated.

Alkanephosphonic acid complexes have the probable structure



They are the only complexes that are definitely not monomers. The data suggest that polymer formation is related to the presence of C–P bonds, as in benzene phosphinic acid.

Triphenyl phosphine and triphenyl phosphine oxide give the same complex of structure

$$[(C_6H_5)_3P \rightarrow O]_3[H_4Mo_2O_{11}]$$

The stability of this complex is unusual in that no covalent bonds are present. The strong hydrogen bonding that probably holds the structure together is reflected in the spectrum; the very strong P → O band of triphenyl phosphine oxide at 1192 has shifted to a double band at 1175 and 1165 in the complex. The extreme insolubility of the complex in ordinary solvents suggests it is a polymer. It dissolves only in high-boiling solvents, such as *o*-dichlorobenzene and acetonyl acetone, at 150–160°. The solutions at these temperatures release oxygen, precipitate MoO_3 and leave triphenyl phosphine oxide in solution.

Conclusion

Thus, Mo^{+6} in the presence of various phosphorus compounds has been converted to peracids that are stabilized by complex formation. Hydrogen peroxide is essential for formation of the complexes. Oxygen, alkyl peroxides, and hydroperoxides—with or without water—are ineffective. The peroxymolybdic acids H_2MoO_5 and H_2MoO_6 are formed in the reaction mixtures, and the complexes result by reaction of the organic phosphorus compounds with the peroxymolybdic acids.

This novel series of complexes represents the first organic derivatives of peroxymolybdic acids.

Acknowledgment.—The author is grateful for suggestions from Dr. M. C. Hoff of these laboratories, who discovered the existence of such molybdenum complexes.

WHITING, INDIANA

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[7] W. D. Treadwell and Y. Schaeppi, *Helv. Chim. Acta*, **29**, 771 (1946).