gravity is acceptable for most applications. Accuracy of specific gravity estimates from oil yield is acceptable for calculation of oil-shale reserves or resources. Consequently, the D-5 specific gravity–oil yield relationship may be applied to oil shales in the areas of the Piceance Creek and Uinta basins covered by this study. It may also apply generally to all Green River oil shales, but this should be confirmed by performing similar tests on oil-shale deposits in other areas of Utah and Wyoming.

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Preparation and Properties of Some Organophosphorus Compounds

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The excellent properties of tributyl phosphate (TBP) as a solvent for the extraction of metal salts from aqueous solutions prompted a survey of other organophosphorus compounds in these laboratories. Tributyl phosphate contains the electronegative phosphoryl oxygen and it was of interest to observe the effect of changing the basicity of this oxygen by comparing phosphine oxides, R_3PO; phosphinates, R_2 (RO) PO; and phosphonates $R(RO)_2PO$; with the phosphates $(RO)_3PO$. Differences in polarity as indicated by heats of solution have been demonstrated for several of these compounds by Kosolapoff and McCullough (*14*). Within any of these classes further modifications could be made by substitution in the alkyl groups. In addition to changing the solvent strength, this variation in structure should influence the solubilities, densities, viscosities, and vapor pressures. In the present discussion these properties are compared for a number of compounds of the above classes. A discussion of the extraction properties for uranium and plutonium has been published (*2*).

PREPARATION OF COMPOUNDS

The compounds studied are listed in Table I. As indicated, several of the phosphates and a few phosphonates were obtained from Victor Chemical Co., Virginia Carolina Chemical Corp., Monsanto Chemical Co., and Ohio-Apex Co. The remaining compounds were synthesized by the methods indicated. Many of these methods are discussed by Kosolapoff (*11*).

The final compounds were purified by distillation at reduced pressure. The compounds are hygroscopic in varying degrees and hence were kept in tightly stoppered bottles. Where not otherwise identified, the literature values listed in the table are those cited by Kosolapoff (*11*).

MEASUREMENTS

Boiling points reported are those obtained during purification. Density, refractive index, and viscosity were measured in the conventional manner. Water-free samples were used for all physical measurements, because hydrogen bonding, which results when water is added, markedly influences these properties. The viscosity of tributyl phosphate, for example, changes from 33.2 to 39.9 millipoises when the compound is saturated with water. Solubility was determined by the cloud point technique and must be considered an approximation. Solubility data for tributyl phosphate are an exception and were obtained with the phosphorus-32 labeled ester.

RESULTS AND DISCUSSION

Boiling Points. The boiling points observed during vacuum fractionation are listed in Table I, with literature values when available. The alkyl esters of phosphinic and phosphonic acid show a boiling point increase of about 9° per CH_2 group at 1 mm. of mercury pressure. The vapor pressure curve of tributyl phosphate given by Evans (*5*), $\log P_{\text{mm.}} = 8.5861 - 3206.5/^\circ \text{K.}$, was used as a reference for this comparison. The phosphates, phosphonates, and phosphinates containing the same number of carbon atoms appear to have about the same boiling points. The drop in molecular weight on changing from phosphate to phosphinate is perhaps compensated by increased polarity. More refined measurements would probably show more differences between them. Kosolapoff (*12*) has pointed out

References to Table I:

A. Victor Chemical Works.
B. $(RO)_2\ POCl + R'OH + \text{pyridine} \longrightarrow (RO)_2\ P(O)OR' + \text{pyr} \cdot HCl$ (*11*, p. 224).
C. Tributyl phosphate has been obtained from several vendors. Physical properties have been well established in this and other laboratories.
D. Ohio-Apex, Inc.
E. $3ROH + POCl_3 + \text{pyridine} \longrightarrow (RO)_3PO + \text{pyr} \cdot HCl$ (*17*).
F. Michaelis–Arbuzov Reaction (*6*)
$P(OR)_3 + R'X \longrightarrow (RO)_2P(O)R' + RX$ (*11*, p. 121).
G. Monsanto Chemical Co.
H. $(C_4H_9O)_2P(O)H + Na + RBr \longrightarrow RP(O)\ (OC_4H_9)_2 + NaBr$ (*9*).
I. $RMgBr + ClP(O)\ (OC_4H_9)_2 \longrightarrow RP(O)\ (OC_4H_9)_2$.
Standard Grignard technique. Cleavage occurred when attempted with diethyl-chlorophosphate.
J. $\phi POCl_2 + 2\ ROH \longrightarrow (RO)_2P(O)\phi + 2HCl$ (*18*).
K. $CCl_4 + P(OC_2H_5)_3 \longrightarrow CCl_3P(O)\ (OC_2H_5)_2 + C_2H_5Cl$ (*10*).
L. $\phi C(O)Cl + P(OC_2H_5)_3 \longrightarrow \phi C(O)P(O)\ (OC_2H_5)_2 + C_2H_5Cl$ (*7*).
M. $RBr + Mg + (R'O)_2P(O)H \longrightarrow R_2P(O)H$
$R_2P(O)H + H_2O_2 \longrightarrow R_2P(O)OH + H_2O$
$R_2P(O)OH + PCl_5 \longrightarrow R_2P(O)Cl$
$R_2P(O)Cl + R'ONa \longrightarrow R_2P(O)OR'$ (*15*).
N. $POCl_3 + RBr + Mg \longrightarrow R_3PO$ (*8*).
O. $(BuO)_2P(O)H + OctBr + Mg \longrightarrow (Oct)_2P(O)H$ (*19*).
P. Virginia–Carolina Chemical Corp.

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Table I. Physical Properties

Compound	Source or Ref.	Boiling Point, °C. per Mm.		Density, 25° C.		Refractive Index N_D^{25}		Viscosity, 25° C., Millipoises	Solubility, 25° C.	
Phosphates		Obsd.	Lit. ref.	Obsd.	Lit. ref.	Obsd.	Lit. ref.		Ester in water, g./liter	Water in ester, g./liter
Diethyl butyl	A	80/4	82-7/3-4 123/15	1.0238	1.0243	1.4110	1.4131^{20}	22.4	15	250
Diethyl isobutyl	B	82/3		1.0209		1.4074		19.0	14	250
Diethyl amyl	A	80/3,80/5		1.0095		1.4152		25.4	7.5	180
Diethyl decyl	B	136/3		0.9660		1.4266		59.2	< 0.1	130
Dibutyl methyl	B	97/2		1.0145		1.4172		27.7	7.1	145
Dibutyl ethyl	B	92/4	95-6/3-4	0.9984	0.9984	1.4168	1.4182^{20}	25.9	3.4	120
Tributyl	C	161/15	See text	0.9730	0.9726(*5*)	1.42256	1.4223(*5*)	33.2	0.39	64
Dibutyl hexyl	B	165/8, 167/10		0.9551		1.4263		39.6	< 0.1	49
Dibutyl octyl	B	165/4		0.9440		1.4296		54.1	< 0.1	44
Dibutyl decyl	B	180/2		0.9378		1.4329		75.3	< 0.1	42
Butyl octyl phenyl	A	161/3		1.1465		1.4691		102	< 0.2	16
Butyl diphenyl	A	170/4		1.1462		1.5183		128	< 0.2	16
Dibutyl ethoxybutyl	B	147/4		1.0127		1.4254		45.8	0.7	111
Tributoxyethyl	D	220/4		1.0142		1.4360		122^{20}	1.1	73
Tri-β-chloroethyl	E	161/0.6	180/2-3, 180/5	1.4242		1.4712		357	< 0.2	78
Phosphonates										
Diethyl methyl	F	194/760	90/10 64/4,80.5/11 56.5/3.5(*16*)	1.0410	1.0548^{20}_{0}(*1*)	1.4119	1.4140^{20}(*15*) 1.4110^{20}(*1*)	14.9	Miscible	...
Diethyl butyl	F	73/1	74/1	0.9879		1.4212		19.8	Miscible	...
Diethyl hexyl	F	98/1.5	140–5/17, 103/2 149.5–50.5/10(*1*)	0.9605	0.9659^{20}_{0}(*1*)	1.4284	1.4295^{20}(*1*)	29.9	0.6	275
Diethyl octyl	F	128/2.5	119/1.2 149.5–50.5/10(*1*)	0.9494	0.9490(*1*)	1.4314	1.4335^{20}(*1*)	40.4	< 0.2	172
Diethyl hexadecyl	F	192/3		0.9095		1.4456		134	Solid formed (hydrate?)	
Diethyl phenyl	G	122/2	117–8/1.5	1.1152		1.4930	1.4935(*13*)	58.9	< 0.2	...
Dibutyl methyl	H	105/6, 82/2	105.5–6/5(*1*)	0.9742	0.9776^{20}_{0}(*1*)	(1.4244) (1.4253)	1.4235^{20}(*1*)	28.5	8	(270)
Dibutyl ethyl	I	113/4	137–9/17	0.9670	0.9623	1.4257	1.4258	31.9	6	175
Dibutyl butyl	I, P	134/3	·160–2/20 97/0.3 (G) 127–8/2.5(P)	0.9500	0.9462 0.948 (P)	1.4305	1.4302 1.4310^{20}(P) 1.4321^{17}(*14*)	36.7	0.5	103
Dibutyl hexyl	I	125/2	182–4/20	0.9383	0.9366	1.4332	1.4332	46.3	< 0.2	75
Dibutyl isooctyl	A	148/2		0.9195		1.4367		58.2	< 0.2	54
Dibutyl decyl	H	177/4	161/1	0.9200	0.9232	1.4404	1.4402	74.9	< 0.2	55
Dibutyl hexadecyl	H	214/1 229/2	226–8/2	0.9078	0.9090	1.4485	1.4481	157	< 0.2	50
Dibutyl phenyl	J	160/3	166/4	1.0390		1.4875		76.6	< 0.2	64
Dioctyl phenyl	A	207/4		0.9728		1.4787 1.4782		180	< 0.2	22
Diisooctyl phenyl	A	206/4		0.9707		1.4784		194	< 0.1	25
Dibutyl hydrogen[a]	A	108/6	131/18(*14*) 124–5/12, 116–17/8, 115/10	0.9878		1.4227	1.4252(*14*)	22.0	7.3	102
Diallyl phenyl	A	128/1		1.1125		1.5145		59.8	0.3	90
Dioctyl styrene	A	196/2		0.9776		1.5000		...	...	...
Diethyl trichloromethyl	K	83/1.5	135–7/16	1.3622		1.4597	1.4582	62.5	4.5	69
Diethyl benzoyl	L	130/1	141/2.5	1.1558	1.1599^{20}	1.5053	1.5065^{20}	99.5	< 0.2	...
Phosphinates										
Methyl dibutyl	M	95/3		0.9545		1.4425		43.5	Miscible	...
Ethyl dibutyl	M	103/2	149–51/18(*15*)	0.9361	0.9349^{22}(*15*)	1.4404	1.4421^{22}(*15*)	40.8	13	416
Butyl dibutyl	M	126/1	125–6/1(*14*)	0.9192	0.9271^{24}(*14*)	1.4422	1.4445^{24}(*14*)	53.9	4.5	160
Ethyl dihexyl	M	143/1.5		0.9102		1.4460 (1.442)		75.7	< 0.1	150
Ethyl dichlorophenyl	G	185/2	202–6/3(*13*)	1.3045	1.2942(*13*)	1.5838	1.5848(*13*)	...	...	...
Phosphine oxides										
Tributyl	N	310/760	Hygroscopic solid			...		...	40	(330)
Dioctyl hydrogen	O	...	Solid m.p. 84.5°–84.9°C.			...		...	...	...
Triphenyl	N	360/760	Solid m.p. 152°C.			...		...	...	...

[a] Dibutyl hydrogen phosphonate is marketed as "dibutyl phosphite." Although there has been considerable discussion of its structure [see Daasch and Smith (*4*), pp. 28–9], the phosphonate structure is fairly well established. This sample showed a strong infrared absorption band at 4.15 μ which can be assigned to the pH bond. Infrared evidence for the phosphonate structure was first presented by Meyrick and Thompson (*16*). The index of refraction reported by Kosolapoff and McCullough (*14*) was a typographical error and should have read 1.4252.

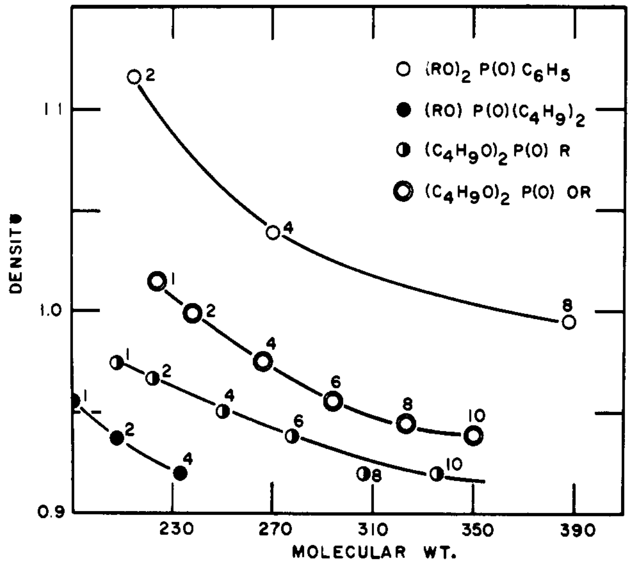

Figure 1. Densities of esters at 25° C. Numbers refer to the number of carbon atoms in R group

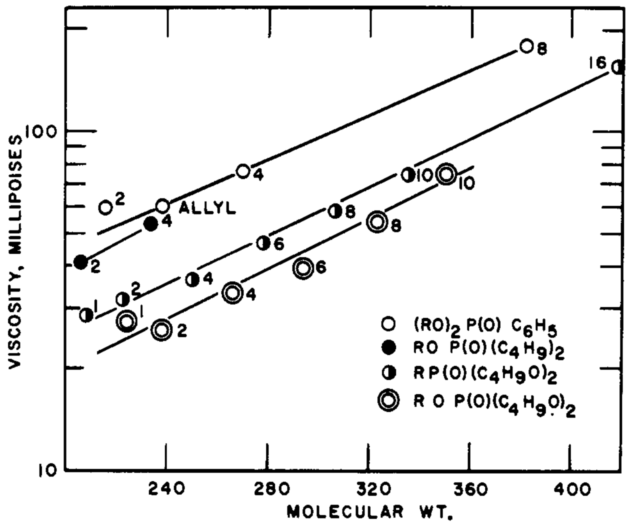

Figure 2. Viscosities of esters at 25° C. Numbers refer to number of carbon atoms in R group

that isopropyl derivatives exhibit a drop in boiling point relative to the *n*-isomers.

Density. Density data selected from Table I are shown in Figure 1. The phosphates have the highest density, and the effect of removing the oxygen bond to form a phosphonate or phosphinate can be seen in the lower three curves. The increase in density caused by the phenyl group is illustrated by the upper curve. The phosphine oxides are solids at room temperature and are not compared here.

Viscosity. The effect of structure and molecular weight on viscosity is shown in Figure 2. For the alkyl derivatives, the phosphinate series has the highest viscosity and the phosphate series the lowest. This behavior can be attributed to two factors: increase in polarity in going from a phosphate to a phosphinate, and the observation—supported by data on other organic molecules—that the presence of an oxygen bridge introduces flexibility into a molecule and thus lowers its viscosity.

Solubility. Solubility in water increases in the order: phosphates < phosphonates < phosphinates < phosphine oxides, which again suggests increasing polarity of the P—O bond. Compounds containing only methyl or ethyl groups are miscible with water. However, the presence of a hexyl or larger group will keep the solubility low, as illustrated by diethyl hexylphosphonate.

The solubility of tributyl phosphate in water is 1.5×10^{-3} mole per liter at 25°C. The vapor pressure is 6.8×10^{-3} mm. of mercury, which would give a calculated solubility at 1 mm. of mercury of 0.22 mole per liter. This is a reasonably large value, as can be seen by comparison of the solubilities of butyl alcohol and methyl isobutyl ketone reduced to 1 mm. of pressure, 0.19 and 0.009 mole per liter, respectively. The three other classes of organophosphorus compounds would be even more soluble if compared on this basis.

The solubility in aqueous solution falls off rapidly as the ionic strength increases. This is illustrated by tributyl phosphate which is soluble to the extent of only 0.01 gram per liter in 2*M* uranyl nitrate. Its solubility in nitric acid solutions is shown in Table II (*3*).

A minimum solubility for several of the trialkyl phosphates in water has been observed at about 70° C. Data for diethyl isobutyl phosphate showed a solubility at 75 °C. about 15% less than at 25°C. At higher temperatures the solubility again increased.

The solubility of water in the organic compounds varies over a wide range. The data in Table I give mole ratios of water to ester, which vary from 0.5 to 10.

Chemical Properties. Like tributyl phosphate the compounds are stable to hydrolysis with either acids or bases. Qualitative comparisons of phosphonates and phosphates indicated little difference in the stability of the P—O—C linkage toward either nitric acid or hydrochloric acid in the two types of compounds. The P—C bond is much more stable, and as a result the phosphine oxides are very stable compounds.

CONCLUSIONS

The above physical properties are consistent with an increasing phosphoryl-oxygen basicity on progressing from phosphates to phosphine oxides. On interchanging P—O—C (R) linkages for P—C (R) linkages, a marked change in physical properties results, largely as a result of changed basicity of the phosphoryl group. On the other hand, physical properties can be modified with or without a change in basicity by substituting on the (R) group, or changing the size of the alkyl groups.

The changed basicity is more strikingly seen in the solvent extraction studies (*2*), where it was also shown that substitution in the alkyl groups could also change the phosphoryl basicity. In the latter paper infrared data for the stretching frequencies of the phosphoryl bonds were correlated with solvent strength.

ACKNOWLEDGMENT

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Table II. Solubility of Tributyl Phosphate in Nitric Acid Solutions at 25°C.

Concn. HNO_3, *M*	Solubility, Gram/Liter
0.00	0.39
0.79	0.36
1.97	0.31
4.01	0.24
6.41	0.16
9.61	0.17
12.0	0.29
13.8	0.61
15.6	1.56

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Infrared Emission Spectra of Two-Stage Hydrocarbon Flames

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For solving modern combustion problems, the role of chemical reaction kinetics must be further examined and developed. In such processes as autoignition in Diesel engines and preignition and knock in spark-ignition engines, it is highly probable that low temperature reactions have an effect. These reactions in many instances give rise to visible flames termed cool and/or two-stage flames, the temperatures of which may be on the order of 200° to 500° C. in the case of the first-stage or cool flame and 800° to 1200° C. for the second-stage flame.

A number of investigators have proposed chemical reaction theories which attempt to outline the reactions that lead up to and follow cool flame formation. Insight into the reaction mechanisms comes largely from fundamental experimental data which will validate or void previous hypotheses. Up to the present time the great majority of data supporting various proposed mechanisms has been obtained by wet chemical methods. These methods have the disadvantage that the products of combustion must be removed from the experimental apparatus for chemical analysis. In most cases this requires a change in sample temperature and pressure, and considerable time may be required for sampling and analysis. As a result, the chemical constituents determined in the sample could be different qualitatively and quantitatively from those actually existent in the reaction.

One of the most useful means of studying cool flame reactions with no external disturbance is by spectroscopic techniques coupled with a flat-flame burner. Spectroscopic analysis may utilize either emission spectra of thermally

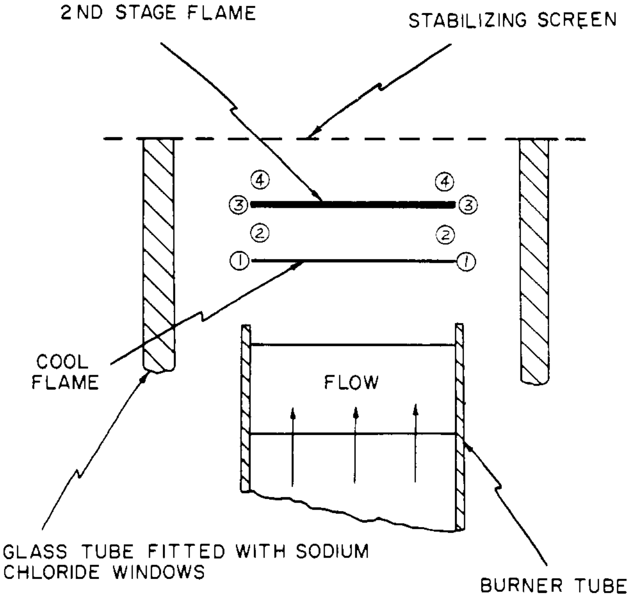

Figure 1. Diagrammatic sketch of two-stage flat flame

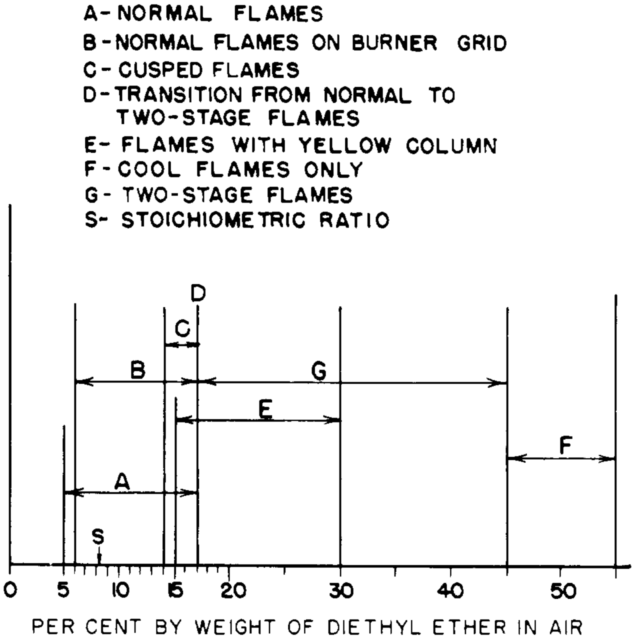

Figure 2. Flame structure at various fuel-air ratios