Chemical and Physical Properties of Alkyl Aryl Phosphates

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ORTHOPHOSPHATE esters consist of three classes, trialkyl phosphates, triaryl phosphates, and mixed alkyl aryl phosphates.

The chemical history of the orthophosphate ester is old and well established. Trialkyl phosphates were prepared at least 100 years ago (*7*), and triphenyl phosphate was synthesized as early as 1854 (*8*). However, phosphate esters did not assume significant large volume commercial importance until sometime in the early twenties when an attempt was made to find substitute plasticizers for cellulose nitrate in order to break the camphor monopoly held by the Japanese.

In the past several years the phosphate esters have become even more important. These products are now used not only as plasticizers but also as medicinals, antifoam agents, oil additives, combustion engine fuel additives, synthetic lubricant components, hydraulic fluids, pesticides, and so on.

Recently, the alkyl aryl phosphates have become commercially available (*3*). Because of the specialized properties possessed by this group of compounds, these esters may be particularly well suited for a wide variety of industrial applications.

For ready comparison of the properties of individual members, the alkyl aryl phosphates may be still further divided into monoalkyl diaryl phosphates and dialkyl monoaryl phosphates.

This paper is restricted to a description of many of the chemical and physical properties of the alkyl diaryl phosphates and a comparison with the trialkyl and triaryl esters.

Of the variety of techniques available for the preparation of alkyl diaryl phosphates, the more commonly used procedures will be described. These esters can be made in a two-step operation by reacting a primary alcohol with phosphorus oxychloride to form an alkyl phosphoryl dichloride, which in turn is reacted with an alkali metal arylate. The ester may be made by reacting a diaryl phosphoryl chloride with an alcohol.

PREPARATION OF ALKYL DIARYL PHOSPHATES

Although some of the esters have been previously made, detailed physical properties have not been reported (*4, 9*). In the synthetic work reported here a single method of preparation was used for all of the alkyl diaryl phosphates described. This method consisted of the reaction of the alkyl phosphoryl dichloride with sodium arylate. When primary alcohols of lower molecular weights are employed, for example, butyl alcohol or lower, the phosphoryl dichloride derivative can be best prepared by reacting phosphorus oxychloride and the alcohol and separating the pure alkyl phosphoryl dichloride from the reaction mixture by fractionating under reduced pressure. When higher molecular weight alcohols are used, a substantially pure alkyl phosphoryl dichloride can be obtained directly from the reaction mixture of stoichiometrical quantities of phosphorus oxychloride and alcohol.

In general, all of the alkyl diaryl phosphates wherein the alkyl group contains six or more carbon atoms were prepared in the same manner as exemplified by the detailed description for 2-ethylhexyl diphenyl phosphate.

The 2-ethylhexyl phosphoryl dichloride was made by charging a suitable reactor with 1 mole of phosphorus oxychloride and cooling this mass to about 5° to 10° C. While the reaction mixture was stirred, 1 mole of 2-ethyl-1-hexanol was added dropwise, keeping the reaction temperature below 15° C. After the alcohol had been added, and while stirring was continued, the temperature of the reaction mass was allowed to increase to about 25° C., during which time vigorous evolution of hydrogen chloride occurred. To complete the removal of hydrogen chloride, the reactor was placed under reduced pressure. When analysis showed that the hydrogen chloride had been removed, the reaction mass was essentially pure 2-ethylhexyl phosphoryl dichloride. This dichloride was then added to an aqueous solution of 2 moles of sodium phenate, while the reaction temperature was kept below 25° C. After all the phosphoryl derivative had been added, stirring was continued until the reaction was completed. When the agitation was stopped, the reaction mixture separated into an ester layer and an aqueous salt layer and the ester layer was then separated from the aqueous layer by decantation. Purification of the ester was effected by the application of dilute sodium hydroxide washes to remove acidic materials, followed by water washes to remove residual alkalinity. Volatile materials were removed from the ester by a steaming operation. Refining operations were completed by heating the ester under reduced pressure to dehydrate the product (*2*).

By utilizing this technique with minor variations to meet specific requirements, the compounds listed in Table I were prepared. These products were all essentially colorless mobile liquids possessing little or no odor.

In order to obtain the pure neutral phosphate esters by the procedure just described, it is essential that the intermediate alkyl

TABLE I. PHYSICAL PROPERTIES OF ALKYL DIARYL PHOSPHATES

	Yield on $POCl_3$, %	Specific Gravity, d_{25}^{25}	Refractive Index, n_D^{25}
Alkyl diphenyl phosphate			
Methyl	82	1.231	1.5373
Ethyl	88	1.202	1.5318
Propyl	85	1.175	1.5249
n-Butyl	88	1.151	1.5190
2-Methylpropyl	91	1.149	1.5188
n-Pentyl	82	1.139	1.5192
3-Methylbutyl	90	1.133	1.5164
2-Methylbutyl	88	1.136	1.5197
2,2-Dimethylpropyl	76	1.124	1.5132
n-Hexyl	87	1.117	1.5131
2-Methylpentyl	92	1.116	1.5130
2-Ethylbutyl	90	1.122	1.5152
2,2-Dimethylbutyl	70	1.115	1.5118
n-Heptyl	87	1.098	1.5086
n-Octyl	90	1.086	1.5070
6-Methylheptyl	90	1.090	1.5076
2-Ethylhexyl	93	1.090	1.5080
3,5,5-Trimethylhexyl	92	1.075	1.5057
n-Decyl	83	1.061	1.5022
2-Butylhexyl	82	1.076	1.5069
n-Dodecyl	86	1.040	1.4987
2-Butyloctyl	80	1.043	1.4996
Tridecyl (branched)	89	1.044	1.5014
Tetradecyl (branched)	87	1.038	1.5007
n-Hexadecyl	79	1.012	1.4934
Octadecyl (branched)	73	1.007	1.4940
Alkyl ditolyl phosphate			
Ethyl	80	1.147	1.5248
n-Hexyl	84	1.085	1.5125
2-Methylpentyl	90	1.061	1.5003
2-Ethylbutyl	87	1.088	1.5135
n-Octyl	86	1.060	1.5065
2-Ethylhexyl	92	1.063	1.5086
3,5,5-Trimethylhexyl	85	1.051	1.5044
n-Decyl	80	1.041	1.5033
2-Butylhexyl	76	1.054	1.5071
n-Dodecyl	78	1.025	1.5008
2-Butyloctyl	77	1.026	1.5004
Tridecyl (branched)	78	1.023	1.5018

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phosphoryl dichlorides be pure. Because of the greater reactivity of the lower molecular weight alcohols with phosphorus oxychloride, impure reaction mixtures are obtained and purification is effected best through fractionation. For primary alcohols of less than five carbon atoms the thermal stability of the alkyl phosphoryl dichloride is such that the product can be fractionated, since the boiling temperature under readily obtainable reduced pressures is lower than the decomposition temperature for the phosphoryl dichloride. Higher molecular weight phosphoryl dichlorides cannot be conveniently distilled. All alkyl phosphoryl dichlorides are thermally unstable, the instability being dependent upon time and temperature. For example, at 25° C., 2-ethylhexyl phosphoryl dichloride shows physical evidence of decomposition in approximately 2 weeks, whereas, at about 100° to 110° C., 2-ethylhexyl phosphoryl dichloride will show physical evidence of decomposition in less than 10 minutes. The decomposition reaction is exothermic and results in two liquid phases.

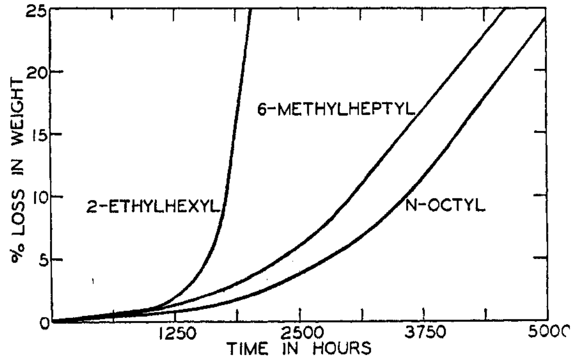

Figure 1. Thermal Stability of Alkyl Diphenyl Phosphates at 100° to 105° C.

Although the chemical nature of the individual layers was not investigated in detail, several observations were made which are worthy of description. The upper layer is essentially hydrocarbon in nature and water immiscible, and generates no heat when the two materials are mixed. When the lower layer is mixed with water, considerable heat is generated and the resulting solution is very acidic. The bulk of the chlorine is found in the lower layer. Table II illustrates the thermal instability of a number of alkyl phosphoryl dichlorides (*2*).

Table II. Thermal Stability of Alkyl Phosphoryl Dichlorides

	Specific Gravity, d_{25}^{25}	Time at 100–110° C., Min.[a]
Alkyl phosphoryl dichloride		
3-Methylbutyl	1.210	45
n-Hexyl	1.181	40–50
6-Methylheptyl	1.133	35–40
2-Ethylhexyl	1.132	7–9
Decyl	1.092	40–45
Tridecyl (branched)	1.061	80
Tetradecyl (branched)	1.056	60

[a] Interval of exposure to heat required to initiate decomposition and produce two phases.

THERMAL AND HYDROLYTIC STABILITY

The neutral alkyl diaryl phosphate esters are very stable at room temperature (approximately 25° C.). Samples have been stored for years without significant change in neutrality. However, these esters at higher temperatures are thermally unstable and, like the alkyl phosphoryl dichlorides, stability is dependent on time, temperature, and structure. This is illustrated in Figures 1 and 2.

The rate of decomposition can be catalyzed by acids. As would be expected, this decomposition is inhibited by the removal of acids. The most obvious way is through the addition of suitable neutralizing agents.

It is believed that all alkyl diaryl phosphates decompose in the same manner—that is, the decomposition reaction produces an unsaturated aliphatic hydrocarbon and a diaryl phosphoric acid. 2-Ethylhexyl diphenyl phosphate can be quantitatively decomposed on heating into 2-ethyl-1-hexene and diphenyl phosphoric acid. There is evidence that in the thermal decomposition the weakest point of the molecule is the oxygen-aliphatic carbon linkage, as will now be indicated in the discussion of the relative stabilities of the individual esters.

Table III. Heat Stability of Alkyl Diaryl Phosphates at 150° C.

(24-Hour exposure)

	Loss in Weight, %	1*N* NaOH/Mole, Ml.
Alkyl diphenyl phosphate		
n-Butyl	2.4	9
2-Methylpropyl	2.8	11
n-Pentyl	2.0	26
3-Methylbutyl	3.2	28
2-Methylbutyl	14.0	560
2,2-Dimethylpropyl	..	3.5
n-Hexyl	1.4	15
2-Methylpentyl	2.4	28
2-Ethylbutyl	3.0	76
n-Octyl	0.8	31
6-Methylheptyl	1.6	40
2-Ethylhexyl	2.9	92
Alkyl ditolyl phosphate		
2-Ethylbutyl	0.8	11
n-Octyl	0.4	10
2-Ethylhexyl	0.8	28
Comparative phosphate		
Tri(*n*-octyl)	3.2	12
Tri(2-ethylhexyl)	2.8	82
Tritolyl	0.4	3.5

The thermal stability of the alkyl diaryl phosphate esters as a class was measured by determining the loss in weight and the development of acidity. Specifically, a weighed sample of the ester was placed for a definite time period in a heated bath thermostatically controlled. The loss in weight was determined and then an aliquot portion was dissolved in ethyl alcohol and titrated with standard alkali using thymol blue as indicator. In Table III, the comparative data on heat stability for the alkyl diaryl phosphates are shown.

Several conclusions concerning the effects of structure may be drawn from these data. The alkyl ditolyl phosphates are more heat stable than the alkyl diphenyl phosphates. When the alkyl portions of the molecules are subjected to comparison, it appears that normal alkyl esters are more stable than the isomeric branched alkyl esters. It also appears that the greater the amount of branching in the alkyl group, the less heat stable is the alkyl diaryl phosphate. For example, heat stability decreases in the series of *n*-hexyl, 2-methylpentyl, and 2-ethylbutyl diphenyl phosphates. The nearer the branching approaches the number one carbon position, the greater the instability of the ester, as exemplified by the decrease in stability of the *n*-octyl, 6-methylheptyl, and 2-ethylhexyl esters.

In the thermal decomposition of these phosphates esters, it is postulated that a hydrogen is necessary on the number two carbon atom for the initial formation of 1-alkene hydrocarbon and diaryl phosphoric acid. If both hydrogens on the number two carbon atom are replaced by alkyl groups, such as methyl groups, the resulting phosphate ester is considerably more heat stable, as can be seen from the data in Table III for 2,2-dimethylpropyl diphenyl phosphate. This was also noted for 2,2-dimethylbutyl diphenyl phosphate.

The heat stability characteristics of the alkyl diaryl phosphates are generally intermediate when compared with the trialkyl and triaryl esters.

In addition to the thermal stability characteristics of these phosphate esters, hydrolytic stability was also investigated and in so far as the structure of alkyl is concerned the general significance is that hydrolytic stability is the reverse of thermal stability. Data were obtained by refluxing a weighed sample of the ester with freshly boiled distilled water for a definite time. The total acidity of both water and oil layers was determined. Detailed results are recorded in Table IV.

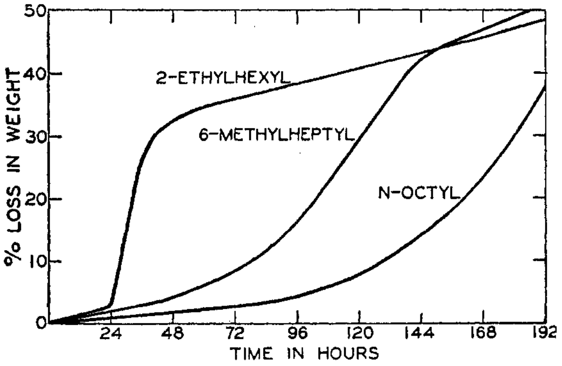

Figure 2. Thermal Stability of Alkyl Diphenyl Phosphates at 150° C.

Several conclusions may be drawn concerning the effect of structure on the hydrolytic stability of the alkyl diaryl phosphates. In general, an increase in the molecular weight of the alkyl group increases the resistance to hydrolysis. The alkyl ditolyl phosphates are more hydrolytically stable than the corresponding alkyl diphenyl phosphates. In a series of isomeric alkyl diaryl phosphates, the *n*-alkyl isomer is less hydrolytically stable than the branched chain isomer. In this experimental work, the maximum resistance to hydrolysis was found in the ester where the alkyl part of the molecule had both hydrogens on the number two carbon replaced by methyl groups. Apparently this blocking effect of groups larger than hydrogen atoms was also observed in the hydrolytic stability of alkyl esters of dibasic acids, as was shown by Bried *et al.* (*1*).

As a class, the alkyl diaryl phosphates are slightly less hydrolytically stable than the trialkyl and triaryl esters, although (as can be seen from Table IV) individual members have stabilities equivalent to both comparative classes.

TABLE IV. HYDROLYTIC STABILITY OF ALKYL DIARYL PHOSPHATES

(24-Hour reflux period)

	1*N* NaOH/Mole, Ml.
Alkyl diphenyl phosphate	
n-Butyl	27.8
2-Methylpropyl	7.3
n-Pentyl	19.7
3-Methylbutyl	8.5
2-Methylbutyl	15.4
2,2-Dimethylpropyl	1.6
n-Hexyl	16.5
2-Methylpentyl	2.7
2-Ethylbutyl	4.8
n-Octyl	14.6
6-Methylheptyl	7.6
2-Ethylhexyl	3.6
n-Decyl	8.2
2-Ethyloctyl	7.0
n-Dodecyl	6.5
2-Butyloctyl	4.0
Alkyl ditolyl phosphate	
n-Hexyl	4.5
2-Ethylbutyl	2.3
n-Octyl	4.4
2-Ethylhexyl	1.7
n-Decyl	3.3
2-Ethyloctyl	2.9
n-Dodecyl	3.5
2-Butyloctyl	2.2
Comparative phosphate	
Tri(*n*-butyl)	4.0
Tri(2-ethylhexyl)	0.2
Tritolyl	1.2

FLAMMABILITY

Another measure of stability, especially thermal stability, may be found in the burning characteristics if the postulation is accepted that the compounds under discussion decompose in essentially the same manner and the fragments are combustible. The flash and fire points of a number of alkyl diaryl phosphates were determined using the Cleveland open cup method in accordance with ASTM Method D92-46 and the data are recorded in Table V. From these data it can be seen that the ranges of flash and fire points are rather narrow. It would be expected that in a homologous series the flash and fire points would increase regularly with increase in molecular weight. This was not found to be the case with the alkyl diaryl phosphates studied and it is believed that the data are seriously influenced by combustion of the products of decomposition. The latter is also indicated by comparing the individual members of the two isomeric series listed in the table. The *n*-alkyl esters have the highest flash and fire properties, these same *n*-alkyl esters being the more heat stable when measured by acidity development, as previously described.

The flammability characteristics of the alkyl diaryl phosphates are between those of the trialkyl and triaryl esters.

TABLE V. FLASH AND FIRE POINTS OF ALKYL DIARYL PHOSPHATES

	Flash Point, ° F.	Fire Point, ° F.
Alkyl diaryl phosphate		
Diphenyl methyl	405	525
n-Butyl diphenyl	405	475
Diphenyl 2-methylpropyl	385	455
Diphenyl *n*-octyl	425	510
Diphenyl 6-methylheptyl	405	485
Diphenyl 2-ethylhexyl	420	460
Ditolyl 2-ethylhexyl	425	485
Diphenyl *n*-dodecyl	420	505
Ditolyl *n*-dodecyl	440	510
Comparative phosphate		
Tri(*n*-butyl)	320	355
Tri(2-ethylhexyl)	375	460
Triphenyl	435	590
Tritolyl	465	655

TABLE VI. VISCOSITY CHARACTERISTICS OF ALKYL DIARYL PHOSPHATES

	Viscosity, Cs.			Viscosity Index
	210° F.	100° F.	−40° F.	
Alkyl diphenyl phosphate				
n-Butyl	2.02	7.30	1700	67
2-Methylpropyl	2.16	8.53	6000	47
n-Pentyl	2.19	8.26	..	69
3-Methylbutyl	2.21	8.49	..	64
2-Methylbutyl	2.24	8.72	..	62
n-Hexyl	2.23	8.36	2400	76
2-Methylpentyl	2.26	8.87	..	61
2-Ethylbutyl	2.25	8.71	4200	65
2,2-Dimethylbutyl	2.56	11.29	20400	45
n-Heptyl	2.32	8.72	..	84
n-Octyl	2.51	9.73	2400	90
6-Methylheptyl	2.61	10.87	8800	73
2-Ethylhexyl	2.45	10.01	5800	65
3,5,5-Trimethylhexyl	2.91	12.30	13800	93
n-Decyl	2.87	11.54	3100	107
2-Butylhexyl	2.79	12.37	..	65
n-Dodecyl	3.25	13.76	..	117
2-Butyloctyl	3.00	13.52	..	77
Tridecyl (branched)	3.79	19.97	..	79
Tetradecyl (branched)	3.97	22.19	..	69
n-Hexadecyl	4.70	20.70	..	162
Octadecyl (branched)	6.27	57.70	..	38
Alkyl ditolyl phosphate				
n-Hexyl	2.83	13.39	19800	43
2-Ethylbutyl	2.85	14.02	42000	29
n-Octyl	3.15	15.30	..	61
2-Ethylhexyl	3.17	16.94	..	25
n-Decyl	3.49	17.42	..	77
2-Butylhexyl	3.53	20.05	..	31
n-Dodecyl	3.95	20.25	..	98
2-Butyloctyl	3.76	21.78	..	41
Tridecyl (branched)	4.87	37.50	..	23
Comparative phosphate				
Tri(*n*-butyl)	1.06	2.67	40	..
Tri(*n*-octyl)	2.56	8.48	..	148
Tri(2-ethylhexyl)	2.23	7.98	840	94
Tritolyl	4.37	35.11	..	−15

Table VII. Pour Points of Alkyl Diaryl Phosphates

	Pour Point, ° F.
Alkyl diaryl phosphate	
Diphenyl methyl	< −70
n-Butyl diphenyl	< −70
Diphenyl 2-ethylhexyl	< −70
Diphenyl *n*-octyl	< −70
Ditolyl *n*-octyl	−60
Ditolyl 2-ethylhexyl	−55
Diphenyl tridecyl (branched)	−45
Ditolyl *n*-dodecyl	−45
Diphenyl tetradecyl (branched)	−40
Ditolyl tridecyl (branched)	−40
Diphenyl *n*-dodecyl	−10
Diphenyl octadecyl (branched)	−10
Diphenyl *n*-hexadecyl	+45
Comparative phosphate	
Tri(2-ethylhexyl)	< −70
Tri(*n*-octyl)	−30
Tritolyl	−15

Table VIII. Miscellaneous Alkyl Diaryl Phosphates

Phosphate	Specific Gravity, d_{25}^{25}	Refractive Index, n_D^{25}	Viscosity, Cs. 210° F.	Viscosity, Cs. 100° F.	Viscosity Index	Pour Point, ° F.
Butoxyethyl diphenyl	1.145	1.5109	2.56	10.66	68	−70
Butoxyethyl di(*o*-chlorophenyl)	1.237	1.5247	..	..	..	..
Benzoxyethyl diphenyl	1.209	1.5528	..	..	..	..
2-Chloroethyl diphenyl	1.278	1.5386	2.71	12.94	27	..
2-Ethylbexyl phenyl tolyl	1.077	1.5084	2.78	12.80	49	−60
Di(isopropylphenyl) 2-ethylhexyl	1.033	1.5038	3.85	22.4	46	−60
Di(α-naphthyl) 6-methylheptyl	1.155	..	18.4	557.2	−33	+10
Di(β-naphthyl) 2-ethylhexyl	1.142	1.5821	9.26	167.3	−41	+5
Di(*o*-methoxyphenyl) 2-ethylhexyl	1.134	1.5166	6.26	84.9	−71	−25
Di(*o*-chlorophenyl) 2-ethylhexyl	1.205	1.523	..	..	..	..
Di(*o*-nitrophenyl) 2-ethylhexyl	1.236	1.5285	7.32	82.2	27	−20

VISCOSITY

Viscosity is a fundamental property of liquids and this property has been used with practical significance to elucidate structure in homologous series. A study was made of the effects of structure variation of alkyl diaryl phosphates on viscosity. The data are recorded in Table VI and were determined using modified Ostwald-Fenske viscometers in accordance with ASTM Method D445-46T. The variation of viscosity with temperature as well as the actual viscosity can be considered. A convenient measure of this characteristic is the viscosity index which was calculated from data at 210° F. and 100° F. using ASTM Method D567-41. The alkyl ditolyl phosphate esters are more viscous than the corresponding alkyl diphenyl esters. In addition, the ditolyl derivatives have lower viscosity indexes. When the molecular weight increase is due to a change of the alkyl group of the alkyl diaryl phosphate, the viscosity increases with increasing molecular weight. If an increment of a molecular weight change occurs in the aryl portion of the phosphate ester molecule, the viscosity increase is greater than if this same molecular weight change occurs in the alkyl portion of an alkyl diaryl phosphate.

Not only does the viscosity vary with the molecular weight in the alkyl diaryl phosphate series, but it also changes with differences in the structure of the alkyl group. In an isomeric series the normal alkyl diaryl phosphate ester has the lowest viscosity at low temperatures. This relationship does not hold at higher temperatures because of differences of viscosity indexes. The normal alkyl diaryl phosphates have higher viscosity indexes than the branched alkyl isomers.

When comparing the alkyl diaryl phosphates with the trialkyl and triaryl esters of similar molecular weight, it will be observed that viscosities of the mixed esters are intermediate.

POUR POINTS

Another low temperature property of fluids is the pour point. The data collected are recorded in Table VII. These data show that the alkyl diphenyl phosphates where the alkyl portion contains eight or less carbon atoms possess very low pour points. As the molecular weight increases above this level the pour point temperatures increase also. In general, the normal alkyl diphenyl phosphates have higher pour points than the isomeric branched chain esters.

OTHER PHYSICAL PROPERTIES

The alkyl diaryl phosphates are miscible with common organic solvents such as hydrocarbons, both aromatic and aliphatic, chlorohydrocarbons, ketones, esters, monohydric alcohols, and to a degree, polyhydric alcohols. These esters are essentially insoluble in water, the solubility of 2-ethylhexyl diphenyl phosphate being of the order of 0.003% at 25° to 30° C.

As would be expected, the esters of median molecular weights or higher have reasonably low vapor pressures. The vapor pressures of 2-ethylhexyl and 6-methylheptyl diphenyl phosphates have been determined and the data are presented in Figure 3. The method of Natelson and Zuckerman was used (*6*).

SUBSTITUTED ALKYL DIARYL PHOSPHATES

Although the discussion of the chemical and physical properties of these esters was limited to the simple hydrocarbon orthophosphates, many additional esters were prepared and studied which contained substituents in both the alkyl and aryl groups. Such changes, however, did not cause unexpected variations in the general characteristics already discussed and, therefore, a detailed examination of the observations will not be repeated. Data for representative types in which such indicated changes have been made are given in Table VIII.

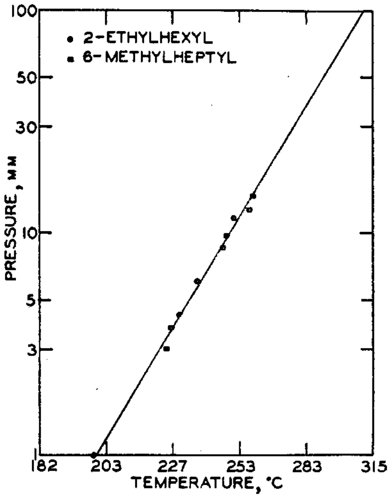

Figure 3. Vapor Pressure of Alkyl Diphenyl Phosphates

Furthermore, many dialkyl monoaryl phosphates were also prepared. Here too, as would be expected, properties and characteristics were intermediate between the triaryl and the trialkyl phosphates and were generally more similar to the trialkyl phosphates.

COMMERCIAL UTILITY

The alkyl diaryl phosphates are useful plasticizers, 2-ethylhexyl diphenyl phosphate having achieved some commercial significance (*5*). The latter phosphate ester is compatible with most common base resins and is especially effective in polyvinyl chloride, polyvinyl copolymers, and Buna N type synthetic rubbers. It imparts low temperature flexibility, toughness, and resistance to flame, moisture, oil, and abrasion.

As would be expected, the lower molecular weight alkyl diaryl phosphate esters are more readily volatilized from plasticized compositions than the higher molecular weight members.

The alkyl ditolyl esters are less volatile than the corresponding alkyl diphenyl compounds. As was noted in the thermal stability of these phosphate esters per se, the alkyl ditolyl esters impart greater heat stability to plasticized compositions than the alkyl diphenyl esters. With respect to the low temperature properties of plasticized compositions, the alkyl diphenyl phosphate esters are more efficient than the alkyl ditolyl phosphates, the normal alkyl derivatives of a homologous series imparting generally the greatest efficiency. The apparent similarities between the low temperature properties of the plasticized compositions and the viscosity characteristics of the phosphate esters should be noted.

The commercial usefulness of the triaryl and the trialkyl orthophosphate esters is well known. A comparison of the properties of these two classes with the properties of the alkyl diaryl phosphates suggests many similar utilizations.

CONCLUSIONS

Many of the chemical and physical properties of the alkyl diaryl phosphates have been described in this paper. Considering that they are esters of an inorganic acid, they exhibit good stability and other excellent characteristics in comparison with esters in general. The alkyl diaryl phosphates are chemically intermediate between trialkyl and triaryl phosphates and their properties are also intermediate. Alkyl diaryl phosphates are useful as plasticizers, especially for polyvinyl chloride and polyvinyl copolymers. The economic value of these compounds is the substitution of lower cost aryl groups for essentially functional equivalent alkyl groups.

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Reaction Processes Leading to the Spontaneous Ignition of Hydrocarbons

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A CONSIDERABLE amount of data is available showing the formation of peroxides, aldehydes, ketones, and other products by the partial oxidation of hydrocarbons (*10*). However, because of the extreme complexity of the reaction, there is a lack of quantitative information concerning variation in the nature and amounts of these intermediates with hydrocarbon structure and with reaction conditions. Earlier studies in this laboratory have shown the effect of hydrocarbon structure on ease of spontaneous ignition (*4*). The present work was initiated to uncover fundamental information regarding the intermediates leading to spontaneous ignition, and the variation in these intermediates with different representative hydrocarbons and at different stages of reaction. Results along similar lines have been reported recently by Malmberg (*11*).

APPARATUS

The apparatus used comprises essentially three stages: the hydrocarbon-oxygen mixing tube, the oxidation chamber, and a series of traps.

Oxygen from a cylinder was dried by bubbling through sulfuric acid, passed through a flowmeter, and bubbled into the hydrocarbon, which was held at a constant temperature to secure a constant fuel-oxygen ratio. The fuel-oxygen mixture entered the oxidation chamber through a glass tube heated slightly higher than the vapor bath to prevent any condensation. This tube contained a plug of glass wool to inhibit the propagation of the reaction from the oxidation chamber back to the fuel reservoir. Despite this precaution, an explosion occurred in the fuel reservoir on two occasions; accordingly, the apparatus should be shielded to minimize this hazard. In the case of isobutane, a second flowmeter was used instead of the hydrocarbon-oxygen bubbler. All oxidations employed a stoichiometric mixture of oxygen and hydrocarbon.

Reaction has been carried out either in a single glass tube $^1/_{16}$ inch in inside diameter, or in a bundle of six such tubes employed to obtain larger amounts of product. With the single tube, thermal equilibrium and contact were obtained by inserting the glass tube in a drilled steel rod which fitted into a 12-inch combustion furnace mounted vertically; the multiple reaction tubes were inserted in a single glass tube filled with iron fillings.

The various contact times and temperatures are listed in the tabulations of experimental results. The temperature distribution throughout the reaction tube was measured at various temperature settings at zero gas flow rate. The characteristic curves obtained are shown in Figure 1. Another series of readings was made at 550° C. and at several gas flow rates. As the only appreciable difference in readings occurred within the first inch of the furnace length, the temperature distribution throughout the furnace was considered essentially unchanged within the range of gas flow rates employed.

The use of the $^1/_{16}$-inch tube throughout this work is a major factor in obtaining reaction control. This is in accord with previous observations regarding the effect of reaction chamber dimensions on the course of a vapor phase, free-radical reaction.

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