

# Syntheses of Dialkyl Trichloromethylphosphonates and Their Properties for Additives<sup>1</sup>

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## Abstract

Nine dialkyl trichloromethylphosphonates (TCMPs) were synthesized by the Arbusov reaction from the corresponding trialkyl phosphite and carbon tetrachloride. Some characteristics of these compounds were studied. The alkyl groups contained from 2 to 18 even carbon atoms. The reaction of triethyl phosphite and carbon tetrachloride was completed in about 4 hr under an indoor natural light. However, in the preparation of the lower dialkyl TCMPs the mixture of trialkyl phosphite and carbon tetrachloride was refluxed for 8 hr. With alkyl groups higher than decyl, a reaction time of 8 hr was insufficient. Utilization of these dialkyl TCMPs was discussed. These compounds were shown to be effective chelating, antistatic and flame resistant additives in a formulation of polyvinyl chloride. Moreover, they were found to be very excellent extreme pressure additives for lubricating oil; especially the dibutyl TCMP which was extremely effective at concentrations as low as 0.25%.

## Introduction

Trialkyl phosphites react with carbon tetrachloride in the Arbusov type reaction to give dialkyl trichloromethylphosphonates (TCMPs). This reaction was reported by Kamai and Egorova (1), and by Kosolapoff (2). The syntheses and properties of dimethyl, diethyl and dibutyl TCMP obtained by the above reaction have been previously reported. However, no investigation involving other higher alkyls has previously been reported.

In the present experiment, nine dialkyl TCMPs were synthesized and some properties were studied. The alkyl groups contained from 2 to 18 even carbon atoms. Their characteristics as additives for polyvinyl chloride and lubricating oil are discussed.

## Experimental Procedures

### Preparation of Trialkyl Phosphites

Nine trialkyl phosphites were prepared from the corresponding alcohols according to the direction of Ford-Moore and Perry (3). The trialkyl phosphites from ethyl to dodecyl were purified by distillation under reduced pressure. Trihexadecyl and trioctadecyl phosphites were recrystallized from ethyl alcohol. Boiling points, refractive indexes, and phosphorus contents of the resulting phosphites are shown in Table I.

### Reaction of Triethyl Phosphite With Carbon Tetrachloride

A mixture of 50 g of triethyl phosphite and 150 ml of carbon tetrachloride was refluxed under an indoor natural light. At constant intervals, the diethyl TCMP formed in the reaction mixture was determined by gas liquid chromatography (GLC). GLC analyses were carried out in Shimadzu GC-1C equipped with a thermal conductivity detector. The column (2.75m × 3mm, stainless steel) was packed with 20% Silicon

TABLE I  
Characteristics of Trialkyl Phosphite, (RO)<sub>3</sub>P

R	bp C (mm Hg)	n <sub>D</sub> <sup>20</sup>	P, %	
			Found	Calcd.
C <sub>2</sub> H <sub>5</sub>	44-45 (11)	1.3974	19.24	18.63
C <sub>4</sub> H <sub>9</sub>	102-106 (6)	1.4235	12.64	12.37
C <sub>6</sub> H <sub>13</sub>	153-158 (2)	1.4377	9.28	9.26
C <sub>8</sub> H <sub>17</sub>	215-217 (3)	1.4445	7.32	7.40
C <sub>10</sub> H <sub>21</sub>	220-230 (2)	1.4459	6.04	6.17
C <sub>12</sub> H <sub>25</sub>	256-270 (2)	1.4485	4.69	5.28
C <sub>14</sub> H <sub>29</sub>		1.4559	4.21	4.61
C <sub>16</sub> H <sub>33</sub>	mp 42.1-48.4		3.06	4.10
C <sub>18</sub> H <sub>37</sub>	mp 56.2-59.8		2.43	3.69

E301 on Chromosorb W AW. The temperature was 150 C and the helium flow was 60 ml/min. The amount of diethyl TCMP was calculated from the calibration curve of known amounts of triethyl phosphite and diethyl TCMP.

### Preparation of Dialkyl TCMP

A mixture of 50 g of each trialkyl phosphite and 150 ml of carbon tetrachloride was refluxed for 8 hr under an indoor natural light. The excess of carbon tetrachloride and the alkyl chloride produced were evaporated under atmospheric or slightly reduced pressure. Then, in the case of alkyl groups from ethyl to hexyl, dialkyl TCMP was obtained from the residue by a vacuum distillation, and in the case of alkyls from octyl to dodecyl by a molecular distillation.

### Analysis

The phosphorus contents were determined by the same method as reported in a previous paper (4);

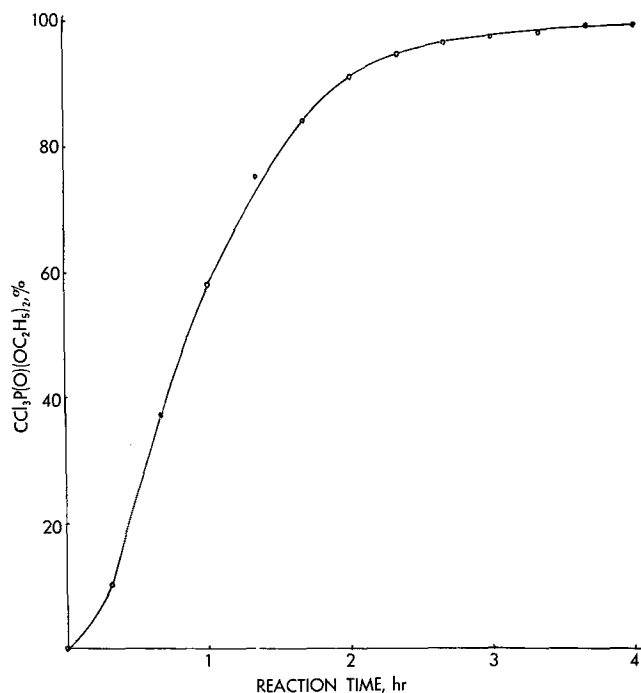


FIG. 1. Relation between the produced amount of diethyl TCMP and the reaction time of the triethyl phosphite with carbon tetrachloride.

<sup>1</sup> Presented at the Japan Oil Chemists' Society Meeting in Tokyo, October 1968.

TABLE II  
Characteristics of Dialkyl Trichloromethylphosphonate  $\text{CCl}_3\text{P}(\text{O})(\text{OR})_2$

R	bp C (mm Hg)	$n_D^{25}$	P, %		Cl, %	
			Found	Calcd.	Found	Calcd.
$\text{C}_2\text{H}_5$	120-123 (10)	1.4433	12.74	12.12	46.80	41.63
$\text{C}_4\text{H}_9$	114-132 (2)	1.4535	10.49	9.94	33.50	34.14
$\text{C}_6\text{H}_{13}$	164-167 (2)	1.4570	8.46	8.42	25.77	28.93
$\text{C}_8\text{H}_{17}$	91-116 (10 <sup>-4</sup> )	1.4577	7.37	7.31	23.18	25.10
$\text{C}_{10}\text{H}_{21}$	130-150 (10 <sup>-4</sup> )	1.4586	6.57	6.45	17.89	22.16
$\text{C}_{12}\text{H}_{25}$	170-200 (10 <sup>-4</sup> )	1.4593	5.82	5.78	15.19	19.84

namely, after the degradation of the sample by heating with sulfuric acid, nitric acid and hydrogen peroxide, the phosphorus was determined as magnesium pyrophosphate.

IR spectra were obtained with aid of a Hitachi EPI-S spectrophotometer with a thin film of liquid using a sodium chloride cell.

#### Evaluation of Dialkyl TCMP as Polyvinyl Chloride Additive

The dialkyl TCMPs were screened as chelating, antistatic and flame resistant additives for polyvinyl chloride.

The compounding formulation used was: 65.5% Geon 103EP, 31% DOP, 1% Ba-stearate, 1% Cd-stearate, with 1.5% dialkyl TCMP or a commercial chelator or a commercial antistatic agent. The composition was milled for 5 min on a 15 × 6 in. roll mill at 170 C, and the sheet obtained of about 0.5 mm thickness was subjected to the flame resistance test. Several layers of sheeting were then pressed together under gradually increasing pressure until a maximum of 250 kg/cm<sup>2</sup> was reached over a 10 min period, after which the pressure was held for an additional 10 min at 180 C. The resulting pressed sheet was about 2 mm thick and was used to test the effectiveness of the additive as a chelating and an antistatic agent.

The flame resistance test was carried out as follows. The test specimen (25 × 200 mm) was hung vertically and a bunsen flame about 30 mm in height was applied to the end of the specimen for 5 sec. Then the burner was taken away. The time for the test specimen to be extinguished was determined.

The chelating effect was determined by the transparency of the pressed sheet using a color meter (Toyo Rika Instruments Inc.).

The evaluation of the additive as an antistatic agent was carried out as follows: The test specimen (40 × 10 mm) was rubbed by woolen cloth rotating at about 80 rpm for 5 min. The residual electrostatic potential was then determined on the surface of the specimen after 2 min by a collecting potentiometer.

#### Evaluation as Extreme Pressure Additives for Lubricating Oil

The extreme pressure properties of a spindle oil (RC Spindle Oil, Daikyo Oil Co., Ltd.) containing

TABLE III

Evaluation of Dialkyl Trichloromethylphosphonates as Additives for Polyvinyl Chloride Formulations

Additives R	Trans- parency, %	Flame resistivity, sec	Antistatic property, KV
None	86.4	5.0	0.90
DPDP <sup>a</sup>	89.2	1.8	0.75
$\text{C}_2\text{H}_5$	88.4	1.3	0.65
$\text{C}_4\text{H}_9$	90.8	1.8	0.65
$\text{C}_6\text{H}_{13}$	88.5	2.8	0.65
$\text{C}_8\text{H}_{17}$	87.9	2.9	0.55
$\text{C}_{10}\text{H}_{21}$	87.9	4.2	0.58
$\text{C}_{12}\text{H}_{25}$	84.2	1.8	0.78
Electrostripper EA <sup>b</sup>			0.70

<sup>a</sup> Commercial chelator (diphenyl decyl phosphite).  
<sup>b</sup> Trade name of a kind of popular antistatic agent (amine derivative) in Japan.

dialkyl TCMP were determined. The seizure loads and the coefficients of friction were determined by means of the four-ball machine according to JIS (Japanese Industrial Standards) K 2519. The rate of rotation of the main shaft was 200 rpm instead of 750 rpm as described in the Standard.

#### Results and Discussion

In the reaction between triethyl phosphite and carbon tetrachloride, the correlation between the produced amount of diethyl TCMP and the reaction time is shown in Figure 1. A reaction time of overnight was required by Kosolapoff (2), and of 3 hr by Kamai and Egorova (1). Cadogan and Sharp (5) reported that the amount of TCMP produced after 1 hr was about 50%. In the present experiment it was shown that a reaction time of about 4 hr was sufficient under an indoor natural light.

Kamai and Kharrasova (6) concluded that this reaction was a radical chain process, showing an induction period in the reaction curve. In the work reported here, however, it is ambiguous from Figure 1 whether or not the reaction is a radical chain process.

There were some reports that diethyl TCMP was obtained readily by distillation. On the other hand, Kasolapoff (2) reported that thermal cracking occurred when 25% of dibutyl TCMP was distilled at 150-155 C/5 mm Hg from the reaction mixture. In the present experiment it was shown that dibutyl TCMP can be distilled under a vacuum of 3 mm Hg without thermal cracking. Attempts to purify three dialkyl TCMPs higher than tetradecyl by molecular distillation or recrystallization were unsuccessful. Boiling points, refractive indexes, phosphorus contents and chlorine contents of the dialkyl TCMPs obtained are shown in Table II.

The IR spectrum of diethyl TCMP is shown in comparison with that of triethyl phosphite in Figure 2. The spectrum shows the P=O stretching absorption peak at 1275 cm<sup>-1</sup> and the C-Cl stretching absorption peak at 760 cm<sup>-1</sup>.

The evaluation of dialkyl TCMPs as additives for a polyvinyl chloride formulation are shown in Table III. Every dialkyl TCMP shows some chelating effect, but dibutyl TCMP is more effective than a commercial chelator (DPDP). Except for dodecyl, all the dialkyl TCMPs show more antistatic effect than a commercial antistatic agent containing an amine derivative (Elec-

TABLE IV

Evaluation of Dialkyl Trichloromethylphosphonates on Extreme Pressure Additives for Lubricating Oil

Additives 1%, R	$\text{CCl}_3\text{P}(\text{O})(\text{OR})_2$		$(\text{RO})_2\text{P}$	
	Seizure load, kg/cm <sup>2</sup>	Coef- ficient of friction	Seizure load, kg/ cm <sup>2</sup>	Co- efficient of friction
None	4.5	0.1187		
$\text{C}_2\text{H}_5$	15.0	0.0732		
$\text{C}_4\text{H}_9$	14.5	0.0966	5.5	0.1067
$\text{C}_6\text{H}_{13}$	15.0	0.0867	4.0	0.0856
$\text{C}_8\text{H}_{17}$	11.0	0.0977	3.0	0.0952
$\text{C}_{10}\text{H}_{21}$	10.0	0.0854	3.0	0.0965
$\text{C}_{12}\text{H}_{25}$	12.0	0.0878	3.0	0.0955

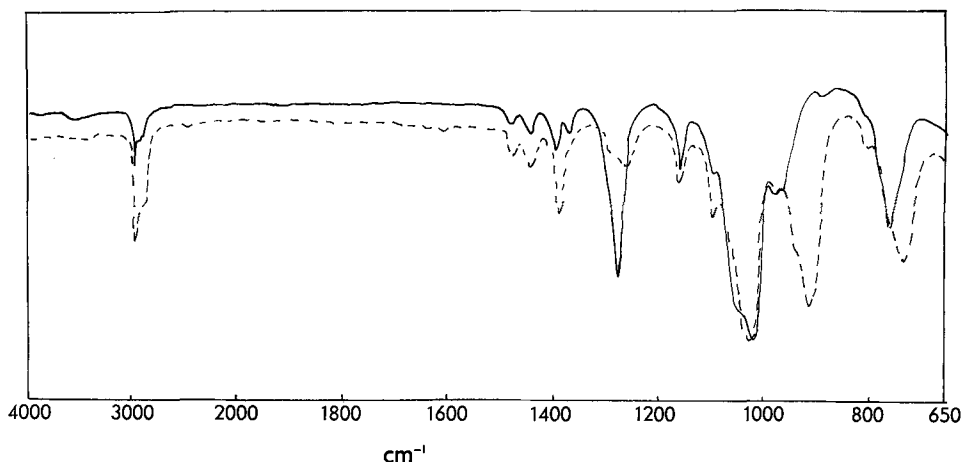


Fig. 2. IR spectra (thin film) of the diethyl TCMP (—) and the triethyl phosphite (---).

trostripper EA). Also, the dialkyl TCMPs are useful as flame resistant additives for polyvinyl chloride.

It is well known that phosphites are superior extreme pressure additives for lubricating oils. The extreme pressure properties of compounds containing a  $\text{Cl}_3\text{-C}$  group in the alkyl group of the phosphite, such as tris(trichloroethyl) phosphite, were reported by Davey (7), but results of compounds containing a  $\text{Cl}_3\text{-C-P}$  group have not previously been reported.

The seizure loads and the coefficients of friction of the spindle oil containing 1% dialkyl TCMP are shown in comparison with the corresponding trialkyl phosphite in Table IV. The dialkyl TCMPs showed better extreme pressure properties than the corresponding trialkyl phosphites, and diethyl, dibutyl and dihexyl TCMP were found to possess particularly excellent extreme pressure properties. Contrary to expectation, the trialkyl phosphites tested showed only

slight extreme pressure effect. Regarding this result it seems reasonable to assume the following: The temperature of the contact surface of the test balls was relatively low at a rate of rotation as low as 200 rpm. The chlorine in the molecule of the dialkyl TCMP reacts with the iron under contact at this low temperature providing the extreme boundary lubrication that occurred. Under the same conditions, however, the trialkyl phosphite containing no chlorine in the molecule does not react sufficiently. The dialkyl TCMPs therefore were effective as extreme pressure additives under a condition of high load and low speed.

The results at concentrations lower than 1% of dibutyl, dioctyl and didodecyl TCMP in lubricating oil are shown in Table V. In general they are less effective at lower concentration but the dibutyl TCMP is very excellent at a concentration as low as 0.25%.

#### ACKNOWLEDGMENT

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TABLE V

Extreme Pressure Properties of Dialkyl Trichloromethylphosphonates at Concentration Less Than 1%

Additives, R	Concentration, %	Seizure load, kg/cm <sup>2</sup>	Coefficient of friction
C <sub>4</sub> H <sub>9</sub>	0.75	12.5	0.0773
	0.5	14.0	0.0852
	0.25	14.0	0.0890
	0.1	7.0	0.0978
	0.05	4.5	0.0951
C <sub>8</sub> H <sub>17</sub>	0.75	5.0	0.0984
	0.5	6.0	0.0956
	0.25	4.5	0.0996
C <sub>12</sub> H <sub>25</sub>	0.75	7.5	0.1017
	0.5	6.5	0.0963
	0.25	4.5	0.1062