

mer-filler interaction can be obtained directly from the experiments. On the assumption that a small amount of TMTD is rendered ineffective by direct reaction with the carbon black, the yields of dithiocarbamate, of combined sulfur, and of crosslinks are substantially those expected on theoretical grounds.⁴

References

1. E. M. Bevilacqua, *J. Polymer Sci.*, **28**, 651 (1958).
2. C. G. Moore and W. F. Watson, *J. Polymer Sci.*, **19**, 237 (1956).
3. C. G. Moore, *J. Polymer Sci.*, **32**, 503 (1958).
4. E. M. Bevilacqua, *Science*, **128**, 840 (1958).
5. G. Bielstein and W. Scheele, *Kolloid-Z.*, **147**, 152 (1956).
6. R. S. Stearns and B. L. Johnson, *Ind. Eng. Chem.*, **43**, 146 (1951); V. A. Garten and G. K. Sutherland, *Proc. Third Rubber Tech. Conf. (London)*, **1954**, 536; D. Parkinson, *Reinforcement of Rubber*, Lakeman, London, 1957; M. L. Studebaker, *Rubber Chem. Tech.*, **30**, 1400 (1957).
7. C. L. Hilton and J. E. Newell, *Rubber Age (N.Y.)*, **83**, 981 (1958).
8. W. Scheele, *Kolloid-Z.*, **146**, 14 (1956).

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The Preparation and Polymerization of Triallyl Phosphite

Permanent flame retardant compounds for application to cellulose are of considerable interest to the Government and to industry. From the application of inorganic compounds to cloth it was found that a combination of phosphorus and bromine conferred flame and glow resistance. To attain permanency it was necessary to use polymeric phosphates.¹ For example, triallyl phosphate was prepared, polymerized, partially brominated, and applied to cloth with good results.² Because of the high cost of triallyl phosphate, related compounds which might be easier and cheaper to prepare were investigated.³ In the course of this investigation, triallyl phosphite was prepared and was polymerized with di-*tert*-butyl peroxide. However, with benzoyl peroxide, triallyl phosphite readily underwent an oxidation-reduction reaction rather than polymerization.

Experimental

Triallyl Phosphite. Three hundred and seventy grams (6.4 moles) of allyl alcohol, 475 g. (6.1 moles) of pyridine, and 300 g. of toluene were placed in a 2-liter three-necked flask fitted with a thermometer, dropping funnel, and a Hershberg stirrer. The reaction mixture was cooled in an ice bath to 15°C. and then 275 g. (2.0 moles) of phosphorus trichloride in 100 g. of toluene was added through the dropping funnel over a period of 2 hours. The reaction mixture was stirred during the addition and for an additional half hour. The pyridine hydrochloride was filtered and

washed with two 150 ml. portions of toluene which were added to the filtrate. The total filtrate was washed with 1 liter of water, 500 ml. of 8% aqueous sodium carbonate, and finally 1 liter of water. The toluene solution was dried over sodium sulfate, filtered, and placed in a vacuum distillation apparatus. The toluene was removed by vacuum distillation up to 70°C. at 10 mm. reduced pressure. The residue was distilled at a reduced pressure of 0.5 mm. and a temperature of 58–60°C. Three hundred sixty-one grams of water white liquid corresponding to a 90% yield of triallyl phosphite was obtained. $N_D^{25} = 1.4572$. Anal.: Calc. for $C_9H_{15}O_3P$: P, 15.4. Found: P, 15.1.

Polymerization of Triallyl Phosphite. Two hundred grams of triallyl phosphite and 200 g. of β,β' -dichloroethyl ether were placed in a 2-liter, three-necked flask fitted with a Hershberg stirrer, thermometer, 5 ml. pipet, and an air condenser. The reaction mixture was heated to 150°C. by means of a Glasco mantle. The efflux time from the pipet was recorded and 5 ml. of di-*tert*-butyl peroxide was added. The temperature increased. The heat liberated by the reaction required intermittent replacement of the heating mantle with a wet cloth in order to maintain a temperature between 150–155°C. Viscosity measurements were made at frequent intervals until the efflux time from the pipet was four times the original value. The reaction mixture was then cooled in an ice bath to stop the polymerization and then poured, with stirring, into an equal volume of Solvasol No. 3. The polymer was washed four times with Solvasol. It had a taffy-like appearance. After drying *in vacuo* a yield of 130 g. (65% per cycle) was obtained.

Brominated Triallyl Phosphite Polymer. Triallyl phosphite polymer was brominated using a method analogous to that used for triallyl phosphate.^{2,4} One hundred thirty grams of triallyl phosphite polymer was dissolved in 800 ml. of 30–70 methyl alcohol–dichloroethylene solution in a 2-liter beaker fitted with a stirrer, a thermometer, and a dropping funnel. The solution was cooled in an ice bath to 10–15°C. and 68 g. of bromine was added over a period of 1 hour. When the addition of the bromine was completed, the solution was stirred for an additional half hour. The solution had an orange color. It was neutralized with 34 ml. of triethylamine. The color of the solution changed to light green-gray. The brominated polymer imparted good flame retardant properties to cloth but is of dubious value as a practical flame retardant due to its removal under laundering condition.

Reaction of Triallyl phosphite with Benzoyl Peroxide. Two hundred grams of triallyl phosphite and 200 g. of β,β' -dichloroethyl ether were placed in a 2-liter, three-necked flask, fitted with a Hershberg stirrer, thermometer, 5 ml. pipet, and an air condenser. The reaction mixture was heated to 100°C. by means of a Glasco mantle. The efflux time from the pipet was recorded and 3 g. of benzoyl peroxide added. The temperature rose to 110°C. but no increase in efflux time occurred in 1 hour. An additional 3 g. of benzoyl peroxide was added with similar results, i.e., a temperature rise but no polymerization. The infrared spectrum showed the presence of phosphate and benzoic anhydride as described below. (Spectra were taken in carbon tetrachloride solutions using a Perkin-Elmer Model 112 Spectrometer with sodium chloride optics.)

In another experiment 102 g. of doubly-distilled triallyl phosphite was placed in a two-necked flask equipped with an

efficient stirrer. The flask was kept in a water bath at $25 \pm 1^\circ\text{C}$. and 22 g. of benzoyl peroxide added in small increments over several days to minimize temperature variations. Each time the benzoyl peroxide was added the temperature rose several degrees and then settled back to the original 25°C . The reaction was followed by withdrawing samples for phosphite analysis and for infrared analysis. (Phosphite was determined by titration with iodine.⁵) As increasing quantities of benzoyl peroxide were added the amount of phosphite decreased and a 1290 cm^{-1} absorption band, characteristic of $\text{P}=\text{O}$, appeared in the spectrum of the reaction mixture.⁶ It was not present in the original phosphite spectrum. The 1652 cm^{-1} band due to the allyl group did not change. The strong peroxide band at 1773 cm^{-1} did not appear in the reaction mixture. (Benzoyl peroxide also has a weaker band at 1792 cm^{-1} .) Instead, two strong bands at 1795 and 1735 cm^{-1} appeared and gained in strength with increasing addition of benzoyl peroxide. These bands are characteristic of benzoic anhydride. The ratio of intensities of the 1735 cm^{-1} band compared to the 1795 cm^{-1} band was somewhat higher than for pure benzoic anhydride, and the 1735 cm^{-1} band had a shoulder at approximately 1721 cm^{-1} . This probably indicated the presence of some benzoic acid hidden by a much larger amount of benzoic anhydride.

Discussion

Triallyl phosphate is easily polymerized in the presence of benzoyl peroxide under conditions similar to those in which triallyl phosphite is oxidized without polymerization.^{3,4} Empirically, triallyl phosphite differs from triallyl phosphate only by the absence of an oxygen atom and the presence of two unshared electrons on the phosphorus. The fact that these unshared electrons would change the polymerization characteristics could be suspected from analogy with the amines. Amines have been found to react violently with peroxides, in some cases accelerating and other cases inhibiting a particular polymerization.^{7,8}

As seen from Table I, there were differences even in the case of preparation. In the preparation of triallyl phosphate, the temperature must be kept very low (-20°C .) to prevent side reactions and ensure good yields,⁴ while the preparation of triallyl phosphite could be carried out at room temperature without deleterious effects. Whereas the distillation of triallyl phosphate is quite dangerous and must be accompanied by the presence of an inhibitor, the distillation of triallyl phosphite proceeds without incident in the absence of an inhibitor.⁹ Polymerization of triallyl phosphate gives about 40% yield with both benzoyl peroxide and di-*tert*-butyl peroxide. Triallyl phosphite gives a good yield of 65% when polymerized with the latter catalyst, but undergoes oxidation instead of polymerization with benzoyl peroxide.

Kosolapoff has pointed out that tertiary phosphites are very reactive, undergoing addition reactions such as the formation of cuprous halide salts, addition of sulfur to yield tertiary thionophosphates, and oxidation (under mild and anhydrous conditions) to the corresponding phosphates.¹⁰ The inhibition of the benzoyl peroxide polymerization of triallyl phosphite can be represented by the following equation which shows the overall oxidation-reduction reaction.

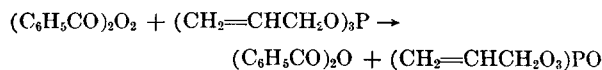
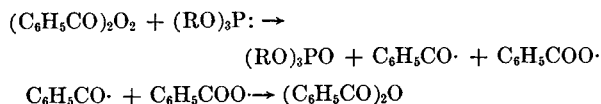


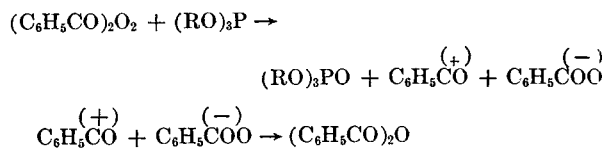
TABLE I
Comparison of Triallyl Phosphite with Triallyl Phosphate

Property	Triallyl phosphite	Triallyl phosphate
Maximum temperature for preparation, $^\circ\text{C}$.	20	-20
Yield of monomer, %	90	85
Boiling point	55-60 $^\circ\text{C}$. at 0.5 mm. reduced pressure	80 $^\circ\text{C}$. at 0.5 mm. reduced pressure
Refractive index (at 22 $^\circ\text{C}$.)	1.4572	1.4474
I Polymerization catalyst	Benzoyl peroxide	Benzoyl peroxide
I Polymerization temperature, $^\circ\text{C}$.	100	100
I Polymerization results	Sudden temperature rise but no polymerization	Polymerization; 40% yield of polymer
II Polymerization catalyst	Di- <i>tert</i> -butyl peroxide (2.5%)	Di- <i>tert</i> -butyl peroxide (1.3%)
II Polymerization temperature, $^\circ\text{C}$.	155	125
II Polymerization time, min.	130	80
Yield, % per cycle	65	40
Appearance of polymer after washing	Taffy-like	White powder

Evidence for this reaction is given by infrared analysis in which bands characteristic of benzoic anhydride and phosphate appear and gain in strength as increasing quantities of benzoyl peroxide are added to triallyl phosphite. Consideration of the mechanism of this reaction must be based on the fact that at both 100°C . and 25°C . the rate at which phosphite takes oxygen from benzoyl peroxide and the rate at which the resultant fragments combine to form benzoic anhydride is considerably faster than the competing free radical polymerization reaction. On the other hand, polymerization is the faster reaction with di-*tert*-butyl peroxide at 150°C . and no reaction was found to occur between di-*tert*-butyl peroxide and triallyl phosphite at room temperature. The mechanism of the phosphite oxidation reaction could be represented as a free radical process.



However, because the reaction occurs readily at room temperature, the possibility of an ionic mechanism should also be considered.



The peroxide group in benzoyl peroxide has a lower bond strength, has less steric hindrance to the approach of the phosphite, and has a more positive character than that in di-*tert*-butyl peroxide.¹¹ The partial plus character would favor the ionic mechanism which might actually involve the

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formation of a complex such as $(RO)_3P-OCOC_6H_5$. Similar complexes have been postulated for reactions of amines with benzoyl peroxide and are discussed by Walling.⁸

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References

1. A. J. McQuade, *Am. Dyestuff Repr.*, **44**, 749 (1955).
2. G. E. Walter and I. Hornstein, U.S. Pat. 2,574,515, Nov. 13, 1951.
3. R. C. Laible, *Chem. Rev.*, **58**, 808 (1958).
4. R. Esteve and R. C. Laible, QM R&E Contract DA44-109-QM-421, Progress Report No. 2 (August 1951).
5. I. Hechenbleikner, private communication.

6. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen, London, 1954, p. 257.

7. P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc.*, **69**, 2299 (1947).

8. C. Walling, *Free Radicals in Solution*, Wiley, New York, 1957, p. 590.

9. W. T. Dye and G. E. Ham, *Chem. and Eng. News*, **28**, 3452 (1950).

10. G. M. Kosolapoff, *Organophosphorous Compounds*, Wiley, New York, 1950.

11. M. Imoto and K. Takemoto, *J. Polymer Sci.*, **19**, 579 (1956).

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