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The Reaction Between Tri-p-Tolyl Phosphate
and Nonanoic Acid at 260 Degrees C

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13. ABSTRACT The reaction between tri- <u>p</u> -tolyl phosphate and nonanoic acid has been studied at 260°C in the absence of air. For an undiluted equimolar mixture the reactants are consumed within 24 hours giving a reaction mixture containing phenol and cresols, phosphoric acid species, small amounts of unidentified products, and an intractable tarry material. Two intermediate products were also identified: <u>p</u> -tolyl nonanoate and 2'-hydroxy-5'-methyl-nonaphenone. Their concentrations increase during the first 4 hours of reaction and then start to fall off. Free radical species of unidentified structure were detected during all stages of the reaction.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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THE REACTION BETWEEN TRI-*p*-TOLYL PHOSPHATE AND NONANOIC ACID AT 260°C

INTRODUCTION

Neopentyl polyol ester oils exhibit greater oxidative and thermal stability than oils derived from esters of dicarboxylic acids and are widely used in lubricant formulations for gas turbine aircraft engines. However, because in isolated instances some engines have shown evidence of chemical attack, questions have been raised concerning the cause of this attack and the possibility of controlling it. Though normally stable at elevated temperature, neopentyl polyol ester oils undergo thermal breakdown in the presence of metals, resulting in increased acidity, changes in viscosity, and corrosive attack on the metals (1).

In none of the cases of corrosion in aircraft engines did the lubricant formulation contain tritoyl phosphate, an antiwear additive. Cottington and Ravner found that 1 to 5 percent tritoyl phosphate* in the neopentyl polyol ester formulations increased the stability of the metal-sensitive esters by promoting the formation of a protective film of iron spinel (1, 2). Their work also showed that tritoyl phosphate can react with mono-carboxylic acids that could be present in the lubricant formulations as a result of hydrolysis or degradation of the esters. Preliminary studies of the reaction between tritoyl phosphate and valeric acid in white mineral oil showed that significant changes occurred in the infrared spectrum of the reaction mixture and indicated the formation of a strongly acidic component (1). This report presents the detailed studies undertaken to further characterize the reaction between tritoyl phosphate and carboxylic acids.

It is important to keep in mind the differences between the conditions of the laboratory study and those of the actual lubrication system. In the present work, equimolar mixtures of reactants were heated in evacuated, sealed Pyrex tubes. Thus, the reactants were present in much higher concentrations than they would normally be in practice, air was excluded, and volatile products could not escape. Each of these factors could alter the reaction sequence that might occur in an operational aircraft lubrication system.

EXPERIMENTAL PROCEDURES

Tritoyl phosphate (technical grade consisting of 80% *para*- and 20% *meta*-tolyl isomers) was percolated through alumina and Florisil before use. Tri-*p*-tolyl phosphate and nonanoic acid, both reagent grade, were used as received. Pyrex tubes containing equimolar mixtures of tritoyl phosphate or tri-*p*-tolyl phosphate and nonanoic acid were evacuated, sealed, then heated at 260°C following the procedure described by Cottington and Ravner (1). Some runs were carried out at 177°C and the results showed the same general course of reaction but at a slower rate; 3 hours heating at 260°C produced the same extent of reaction as 168 hours heating at 177°C.

Infrared spectra were recorded on either a Beckman IR-12 or a Perkin-Elmer Model 457 grating spectrophotometer. Samples of unseparated reaction mixtures were run as capillary films between KBr plates. Although this procedure did not give uniform path length from

*This material is commonly known as tricresyl phosphate or TCP. The tricresyl phosphate used in their work was a mixture of 80% tri-*p*-tolyl phosphate and 20% tri-*m*-tolyl phosphate. Throughout this report, this isomeric mixture will be called tritoyl phosphate.

run to run, it did simplify repolishing the windows, which were etched by many of the samples. Samples recovered from thin-layer chromatographic separations were run on a Wilks Model 9 attenuated total reflectance (ATR) attachment by evaporating an acetone extract of a separated component on the ATR plate. Nuclear magnetic resonance (nmr) spectra were recorded on a Varian HA-100 spectrometer system; electron spin resonance (esr) spectra were obtained with a Varian V-4500 spectrometer.

Thin-layer chromatograms were developed with an 80/20 (v/v) mixture of heptane/ethyl ether. Glass plates and plastic sheets coated with silica gel containing fluorescent indicator gave similar results, but the plastic sheets were more convenient to use in obtaining samples for infrared analysis. A temperature-programmed Beckman GC-5 gas chromatograph equipped with an XE-60 silicone column was used for the gas chromatographic analyses. For the determination of acidic materials, weighed aliquots of the reaction sample were dissolved in 100 ml of toluene-isopropanol (95/5) and titrated with alcoholic potassium hydroxide; the pH was recorded electrometrically throughout the titration.

RESULTS

Initially, experiments were run on solutions containing 5% tritoyl phosphate and 5% nonanoic acid in white mineral oil. The oil was an unnecessary complication in studying the reaction, because tests using equimolar mixtures of tritoyl phosphate and nonanoic acid without the mineral oil showed that the same reaction took place, but at a much greater rate than in the oil-diluted mixture. In fact, products seen in oil-diluted systems after 96 hr of heating were found to be only intermediate products which themselves react on further heating.

Figure 1 shows infrared spectra obtained from a mixture of 3% nonanoic acid and 3% tritoyl phosphate in white mineral oil before and after heating (96 hr at 260°C). Significant changes are seen in the carbonyl stretching region. The band at 1710 cm^{-1} (C=O stretching vibration of nonanoic acid) decreases upon heating and new bands appear in the spectrum at 1760 and 1640 cm^{-1} . Other changes are also seen: (a) appearance of a new band at 3400 cm^{-1} , probably from cresol formation, and (b) decrease in the 1300 cm^{-1} (P=O stretch) and 970 cm^{-1} (P-O stretch) bands of tritoyl phosphate, indicating loss of some of this component. During the heating period, an immiscible layer formed which was found to be strongly acidic and to have an infrared spectrum resembling that of polyphosphoric acid.

The infrared spectra of an undiluted equimolar mixture of tritoyl phosphate and nonanoic acid before and after heating (96 hr at 260°C) are shown in Fig. 2. Table 1 summarizes the information obtained from infrared spectra of a series of such mixtures. The changes in the various bands indicate that some compounds are being formed while others are consumed in the course of the reaction. Although it was possible to speculate on the nature of the reaction products by examining the spectra of the unseparated reaction mixtures, positive identifications were impossible without isolating individual components.

Table 2 summarizes the data obtained from gas chromatographic and thin-layer chromatographic studies of reaction mixtures of nonanoic acid and tri-*p*-tolyl phosphate, which was substituted for tritoyl phosphate to simplify analysis of the reaction mixture. It should be noted that compounds other than those listed in the table were present; the table presents data only for identified compounds. One of the earliest products was *p*-cresol; its relative concentration increased up to 8 hr and then began a gradual decrease. Phenol first appeared in the 8-hr samples and *m*- and *o*-cresol were found in the 24 hr and subsequent samples. The intermediate product responsible for the 1760 cm^{-1} band

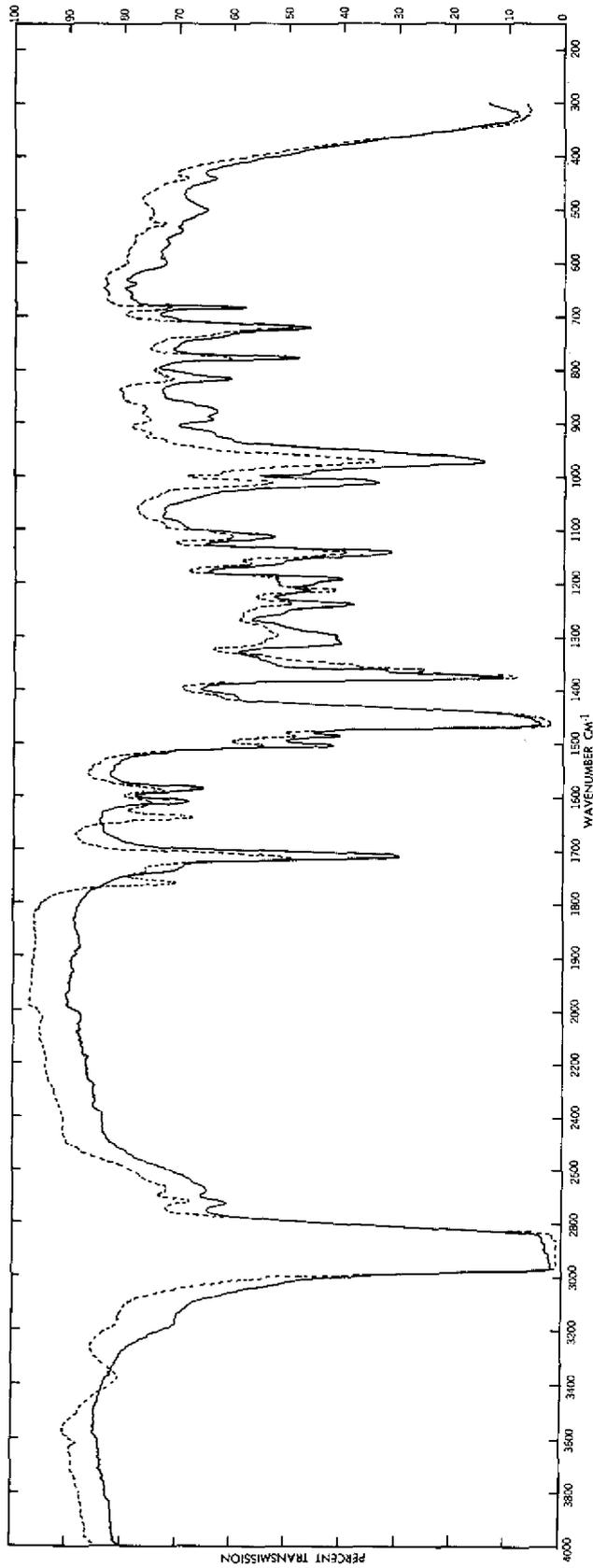


Fig. 1 - Infrared spectra of a reaction mixture consisting of 3% tritolylyl phosphate and 3% nonanoic acid in white mineral oil (— before heating; --- after 96 hours at 260°C)

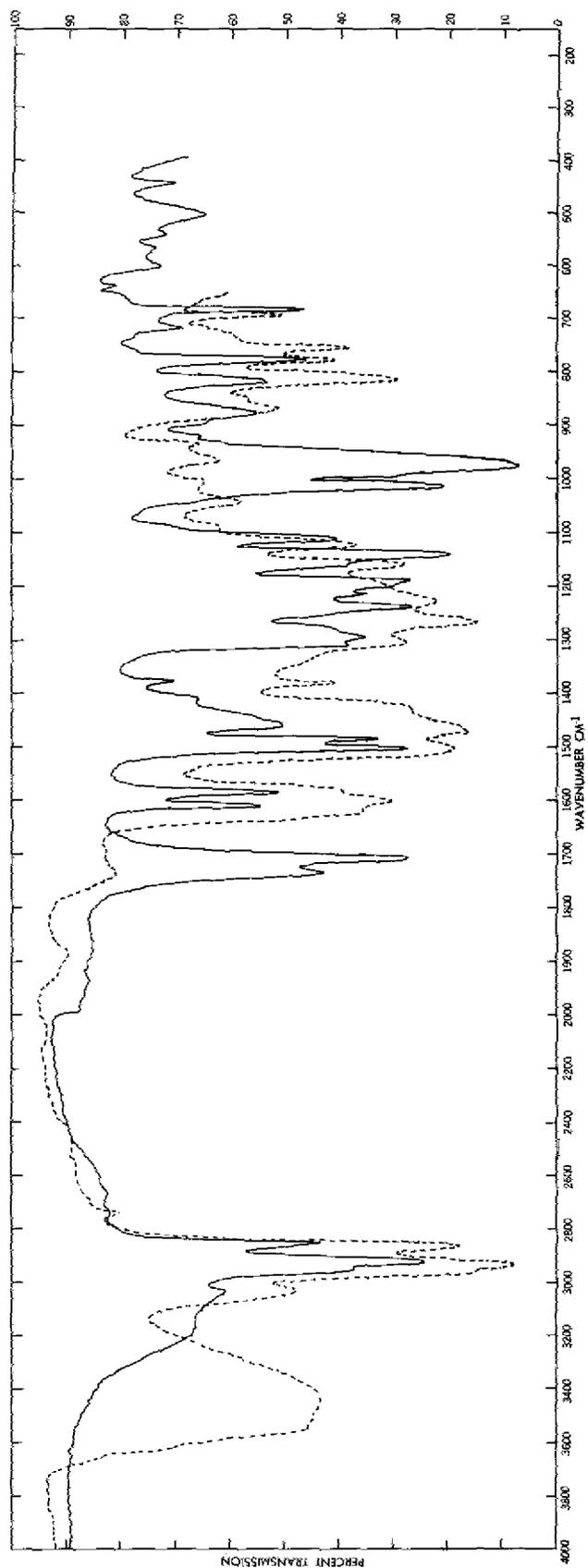


Fig. 2 - Infrared spectra of an equimolar mixture of tritolylyl phosphate and nonanoic acid
(— before heating; --- after 96 hours at 260°C)

Table 1
Infrared Spectral Changes During Reaction of Tri-p-tolyl
Phosphate and Nonanoic Acid at 260°C*

Time (hr)	% Absorption at Several Wavelengths (cm ⁻¹)														
	3360	2300	1760	1710	1640	1350	1300	1260	1020	970	820	750	740	720	690
1	0	0	21	30	1	0	57	21	38	90	63	0	1	21	12
2	1	3	53	49	17	3	63	45	68	98	81	0	3	30	12
4	25	13	56	28	69	30	51	87	94	98	89	0	15	29	17
8	58	15	9	0	23	19	34	97	91	91	91	38	32	13	26
24	48	8	5	0	13	11	29	94	60	62	87	56	26	8	19
168	87	38	0	0	0	9	43	†	†	†	41	27	0	39	0

*Data from spectra of unseparated reaction mixtures.

†Broad, overlapping, unresolvable band.

Table 2
Products of the Reaction of Tri-p-tolyl Phosphate
and Nonanoic Acid (260°C)

Product	Length of Reaction Time (hr)						
	0	1	2	4	8	24	168
Nonanoic acid	x	x	x	x			
Tri- <u>p</u> -tolyl phosphate	x	x	x	x	x		
<u>p</u> -Cresol		x	x	x	x	x	x
<u>p</u> -Tolyl nonanoate		x	x	?			
2'-Hydroxy-5'-methyl-nonaphenone			x	x	x		
Phenol					x	x	x
<u>o</u> - and <u>m</u> -Cresols						x	x
Phosphoric acid species		x	x	x	x	x	x

in the heated sample in Fig. 1 was identified by infrared and nmr spectra as p-tolyl nonanoate; it appeared as early as 1 hr and was nearly consumed by 8 hr. The infrared and nmr spectra of the compound, given in Fig. 3, match those of an authentic sample synthesized for comparison. The band at 1640 cm⁻¹ (Fig. 1) is the carbonyl stretching vibration of 2'-hydroxy-5'-methyl-nonaphenone. The abnormally low frequency of this C=O stretching vibration and the large shift to low field of the nmr peak of the hydroxyl proton (12 ppm) are caused by intramolecular hydrogen bonding between the hydroxyl proton and the carbonyl oxygen and by conjugation of the carbonyl group with the aromatic ring (3, 4). When the reaction mixtures were prepared with tritolyl phosphate, the nonaphenone isolated was shown by nmr to be a mixture of the two possible isomers.

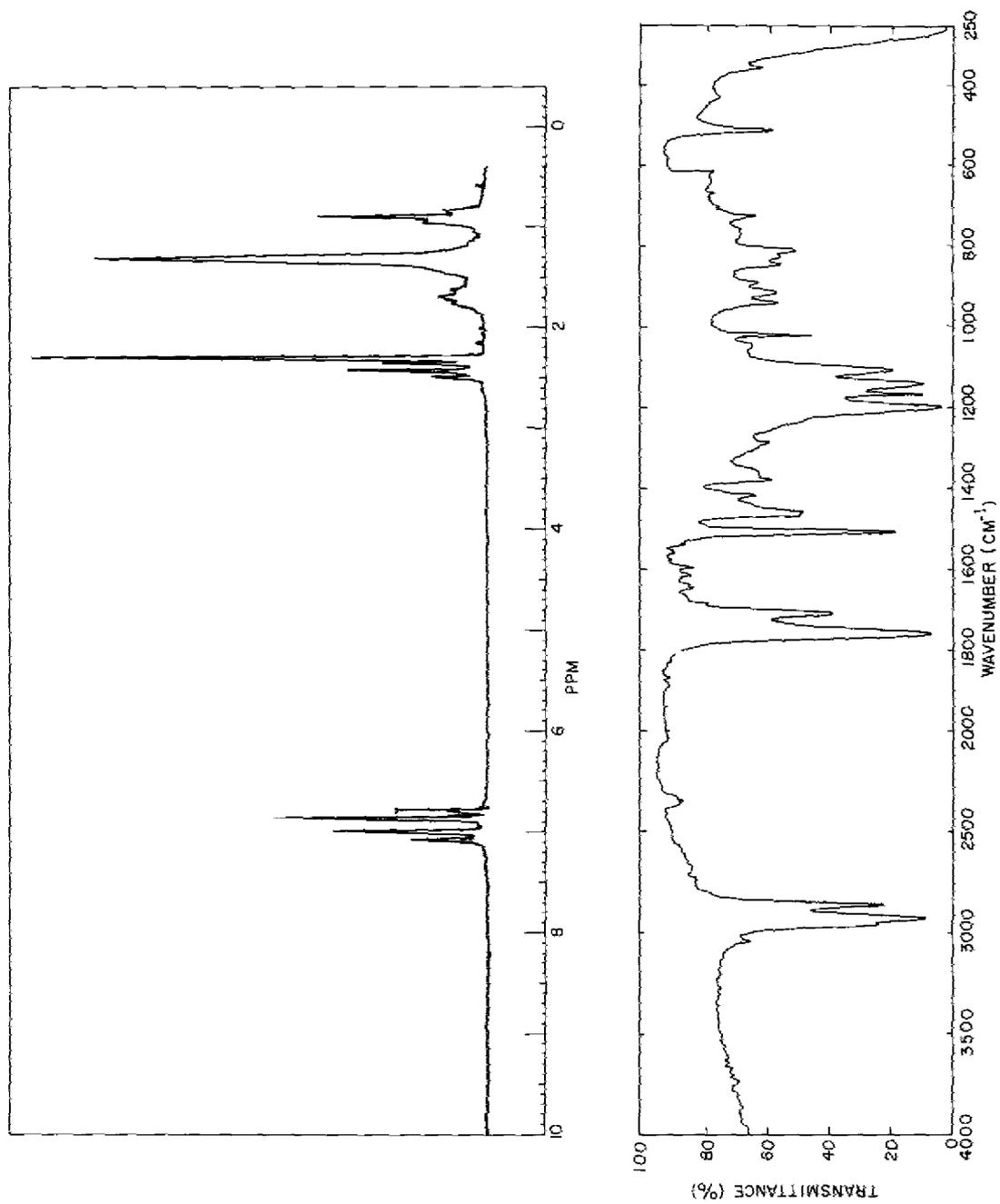
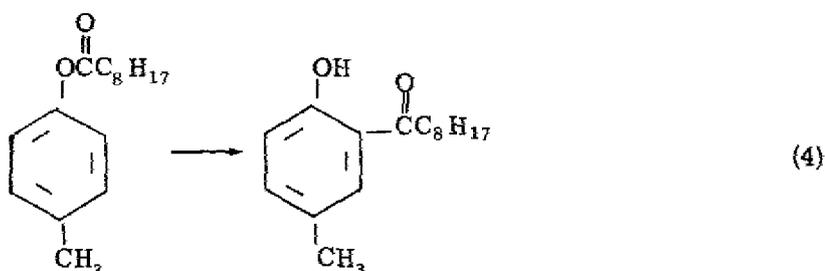
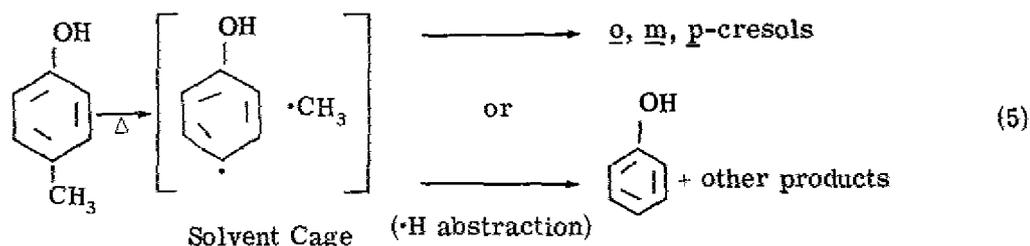


Fig. 3 - Nuclear magnetic resonance (upper) and infrared (lower) spectra of p-tolyl nonanoate

An early product, 2'-hydroxy-5'-methyl-nonaphenone, is formed by a Fries rearrangement of *p*-tolyl nonanoate, shown in Eq. (4) (Ref. 5). The ultimate fate of this material is not known, but it may be the precursor of the compounds which have not yet been identified.



The formation of toluene, butane, carbon monoxide, phenol, and *o*- and *m*-cresol can be explained by a number of free radical reaction paths. For example, phenol and the cresols may be formed via the reaction shown in Eq. (5), the *p*-cresol being supplied as shown in Eq. (3).



The presence of free radicals in the reaction mixtures was established by electron spin resonance (esr) spectroscopy of unseparated mixtures after heating at 260°C for 2, 8, 24, and 96 hours. All four samples gave esr spectra consisting of one line with a 6 to 7 gauss line width whose intensity increased with heating time. No attempt was made to identify the free radical species responsible for the esr signals. Lewis and Singer (6) point out that the identification of free radical intermediates in pyrolysis reactions requires the fulfillment of several conditions, the chief one being the formation of a single species at a detectable concentration in a suitable solvent. Further esr investigations of the acid-tritoyl phosphate system as well as the actual lubricant formulations would be useful to determine the relative importance of free radical degradation pathways in these systems.

It is interesting to compare the results of some photochemical free radical reactions of aromatic esters with the present work. The results of Finnegan and Knutson (7) on the irradiation of aryl esters with ultraviolet light are summarized in Fig. 4. Several of the products shown in Fig. 4 have been identified in the thermal reaction mixtures of this work: hydroxyketones, CO, HAr (toluene), and ArOH (phenol and cresols). In the photochemical work also, the amount of hydroxyketone is found to increase at first, but then the concentration decreases due to its reaction to form other products, which may be polymers formed by self-condensation reactions. The photochemical reactions appear to be solvent dependent, and complete correspondence between the solvent-moderated, energetically defined photoprocesses and the thermal reactions of the present study cannot be expected.

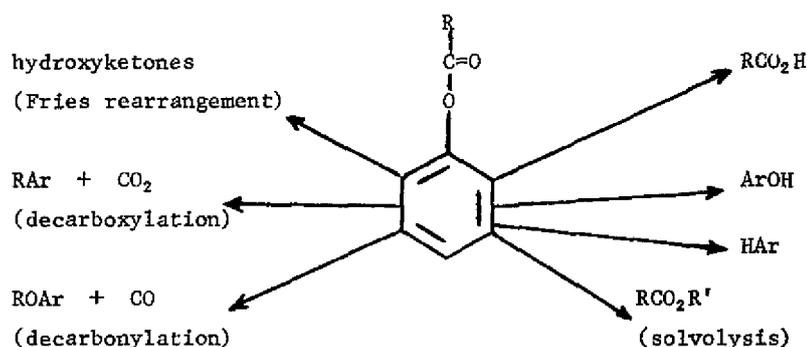


Fig. 4 - Products identified in photochemical reactions of aryl esters (R is alkyl group, Ar is aryl group, and R' comes from the solvent)

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

Tri-*p*-tolyl phosphate reacts with carboxylic acids at 260°C in the absence of air to produce mainly phenol, cresols, phosphoric acid species, and a tarry material. During early stages of the reaction the tolyl carboxylate is formed and rearranges to the corresponding 2'-hydroxy-5'-methyl-alkylphenone. The nature of several minor products, presumably formed from the alkylphenone, was not completely defined. The presence of free radicals was demonstrated.

Interpretation of these results with respect to the actual lubrication systems is difficult. However, the work suggests that similar reactions can occur in the lubricant formulations during storage and use. Laboratory tests can establish the effects of the identified products on turbine engine components.

Future work on the tritolyl phosphate-carboxylic acid reaction should be aimed at determining the initiating reaction, subsequent reaction paths, the effects of molecular oxygen, and the identification of free radicals and their role in the reaction.

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REFERENCES

1. R.L. Cottingham and H. Ravner, "Neopentyl Polyol Esters for Jet Engine Lubricants—Effect of Tricresyl Phosphate on Thermal Stability and Corrosivity," NRL Report 6667 (1968); ASLE Trans. 12, 280 (1969)
 2. R.L. Jones, H. Ravner, and R.L. Cottingham, ASLE Trans. 13, 1 (1970)
 3. F. Krausz, R. Martin, and J.P. Gavard, Bull. Soc. Chim. Fr., 640 (1966); F. Krausz and R. Martin, Bull. Soc. Chim. Fr., 2192 (1965)
 4. G. Pala, Nature 204, 1190 (1964)
 5. A.H. Blatt, Org. Reactions 1, 342 (1942)
 6. I.C. Lewis and L.S. Singer, Carbon 5, 373 (1967)
 7. R.A. Finnegan and D. Knutson, Tetrahedron Letters, No. 30, 3429 (1968)
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