NRC Publications Archive Archives des publications du CNRC

Reactions of polyphosphoric acid and bitumen model compounds with oxygenated functional groups : Where is the phosphorylation?

Masson, J-F.; Gagné, M.; Robertson, G.; Collins, P.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1021/ef800511v>

Energy & Fuels, 22, 6, pp. 4151-4157, 2008-10-15

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=cd063c78-e97d-40d3-af26-f6c0adc07acb>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=cd063c78-e97d-40d3-af26-f6c0adc07acb>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

<http://irc.nrc-cnrc.gc.ca>

Reactions of polyphosphoric acid and bitumen model compounds with oxygenated functional groups : where is the phosphorylation

NRCC-50561

Masson, J-F.; Gagné, M.; Robertson, G.;
Collins, P.

2008-10-15

A version of this document is published in / Une version de ce document se trouve dans:
Energy Fuels, v. 22, no. 6, 2008, pp. 4151-4157

The material in this document is covered by the provisions of the Copyright Act, by Canadian laws, policies, regulations and international agreements. Such provisions serve to identify the information source and, in specific instances, to prohibit reproduction of materials without written permission. For more information visit <http://laws.justice.gc.ca/en/showtdm/cs/C-42>

Les renseignements dans ce document sont protégés par la Loi sur le droit d'auteur, par les lois, les politiques et les règlements du Canada et des accords internationaux. Ces dispositions permettent d'identifier la source de l'information et, dans certains cas, d'interdire la copie de documents sans permission écrite. Pour obtenir de plus amples renseignements : <http://lois.justice.gc.ca/fr/showtdm/cs/C-42>

National Research
Council Canada

Conseil national
de recherches Canada

Canada

Reactions of Polyphosphoric Acid and Bitumen Model Compounds with Oxygenated Functional Groups: Where is the Phosphorylation?

J-F. Masson,* M. Gagné, G. Robertson, P. Collins

National Research Council of Canada

Ottawa, Ontario, Canada, K1A 0R6

Abstract

Polyphosphoric acid (PPA) is used to modify bitumen, but the chemical reactions responsible for the change in bitumen properties remain, for the most part, undetermined. In an effort to better understand these reactions, and phosphorylation in particular, four bitumen model compounds with various oxygenated functional groups were heated with PPA in conditions typical of those used to prepare PPA-modified bitumens, namely, bisphenol A (phenol), butyl phenyl ether (ether), acetophenone (ketone) and benzoic acid (carboxylic acid). The reactions were followed by thin-layer chromatography and infrared spectroscopy. It was found that the extent of the reactions decreased as bisphenol A > acetophenone > benzoic acid > butyl phenyl ether. The detailed analysis of the infrared spectra revealed that the hydroxyl group of bisphenol A was not phosphorylated by PPA. Instead, it facilitated the scission of the bisphenol into fragments of lower molecular weight. The reaction of acetophenone had the reverse effect, as it led to condensation. Benzoic acid and butyl phenyl ether were immune to the effect of PPA when heated alone with PPA, but heated together they condensed into higher molecular weight aryl-aryl ketones and esters. These findings are consistent with changes known to occur in PPA-modified bitumen. For instance, the breaking down of bisphenol may relate to the decrease in the molecular weight of asphaltenes, whereas the intermolecular reactions translates into an extension of the bitumen molecular backbone that helps explain bitumen stiffening. The key finding, however, is the lack of hydroxyl phosphorylation in phenol, bisphenol and benzoic acid, which indicate that phosphate esters cannot be held responsible for the modification of bitumen with PPA.

Introduction

In the development and synthesis of fine chemicals, polyphosphoric acid (PPA) has been used as an acid and a catalyst for several decades.^{1,2} In engineering applications, bitumen has been heated with PPA to increase its viscosity or stiffness in high summer temperatures.³ In contrast to organic synthesis, where the reaction products are isolated and their structure resolved, the products of the reaction between PPA and bitumen are not isolated. They are lost in the bitumen matrix, so the chemical reactions that explain stiffening remain uncertain and hypothetical.^{4,5} Bitumen is a complex mixture of hydrocarbons conveniently separated into fractions of increasing polarity, namely, the saturates, aromatics, resins and asphaltenes,^{6,7} which most often increase in molecular weight and heteroatomic content, in that same order. Given the high dielectric constant (ϵ) of PPA and the increase in ϵ with heteroatomic content,⁸ we postulated that PPA would principally react with heteroatomic functional groups.⁹ In efforts to verify this postulate and better establish the nature of the reaction between PPA and bitumen, we resorted to the use of bitumen model compounds.^{10,11} In working with nitrogenated compounds, it was found that PPA could act as a simple acid to produce ionic-pairs¹⁰ or facilitate intermolecular coupling,¹¹ and that it could also be a reactive catalyst that produces phosphorylated amines.¹¹

Here, we report on the reaction of PPA with four oxygenated bitumen model compounds, heated alone or together with PPA (Figure 1). They are representatives of compounds with phenol, ether, ketone, and carboxylic acid functionalities. The goal of the exercise was to determine the extent of their reactions in conditions typical of those used to prepare PPA-modified bitumen, and to provide some insights into the course of

the reactions. In this respect, it was of particular interest to verify the postulate⁵ that PPA reacts with bitumen alcohols or carboxylic acids to produce aromatic phosphate esters.

Experimental Section

Reactants. Bisphenol A, butyl phenyl ether, benzoic acid and acetophenone were obtained from Sigma-Aldrich. They were 99% pure or better. The oligomeric PPA, $H_{n+2}(P_nO_{3n+1})$, whose composition was reviewed earlier,⁹ was provided by ICL Performance Product LP. Its grade was 83.3 % P_2O_5 , or stated otherwise, 115% H_3PO_4 equivalent. To probe the reactivity of the model compounds, they were individually heated with PPA at 150 °C for 1 h under an argon gas blanket. The PPA/reactant weight ratio was 1:5. Details are provided elsewhere.¹⁰ As an exception to these conditions, the mixture with bisphenol A was heated to 170 °C because it only melted at 159 °C. With a 1:5 PPA/reactant ratio, the PPA concentration was much lower than in synthetic applications where PPA is the solvent, but it was higher than with PPA-modified bitumen (1:100) so that enough potential new products would be obtained for analysis.

Reactions and work-ups. The reactivity of the model compounds with PPA and the production of new compounds were followed by thin-layer chromatography (TLC) by eluting the starting compound(s) and the reaction products with various eluents, including for instance, heptane, toluene, ethyl acetate, methanol, and their mixtures.

After the reactions, unreacted acids (PPA, benzoic acid) were converted to their salt by washing in aqueous alkali solutions and the reaction products were extracted from water with diethyl ether or ethyl acetate,¹² along with the diluent, butyl phenyl ether or indan, if any. The solvent was evaporated to retrieve the extract. Diluents were separated from the reactants by flash chromatography¹³ with solvents selected based on TLC trials. Flushing the column with ethyl acetate or methanol, or their blend, allowed for the

retrieval of the compounds from the column. After the evaporation of the solvent, the mixture of starting material and products was analyzed by spectroscopy. Reaction yields were calculated from the ratios of infrared peaks or from the integration of proton signals in nuclear magnetic resonance.

Spectroscopy. Fourier-transform infrared spectroscopy (FTIR) was performed with a Bomem MB100 spectrometer. Fifty scans were acquired in transmission at a resolution of 4 cm^{-1} between 400 cm^{-1} and 4000 cm^{-1} . With a software (Grams 386 v. 3, Galactic Industries Corporation), spectra were baseline corrected and normalized to an absorbance not affected by the reaction, e.g., C–O in the case of bisphenol.

Nuclear magnetic resonance (NMR) was used to analyze the products of the reaction between benzoic acid and butyl phenyl ether. The results were obtained from a Varian Unity Inova spectrometer at a resonance frequency of 399.961 MHz for ^1H and 100.579 MHz for ^{13}C . ^1H NMR spectra were obtained from samples dissolved in CDCl_3 using a 5 mm probe. The solvent signals (CHCl_3 ^1H 7.25 ppm, ^{13}C 77.00 ppm) were used as the chemical shift reference. Quantitative ^{13}C NMR spectra were recorded with the following pulse sequence: 55° pulse angle, 5 s acquisition time with ^1H decoupling, 40 s relaxation delay without ^1H decoupling. ^1H – ^{13}C heteronuclear 2D experiments were also obtained based on coupling constants $^1J_{\text{C-H}} = 140\text{ Hz}$ and $^3J_{\text{C-C-C-H}} = 8\text{ Hz}$.¹⁴

Results and Discussion

Phenols. Upon the reaction of PPA with alkanol, the hydroxyl group is often readily phosphorylated, the product being a phosphate ester,^{1,2,15} but complicated reactions are common.² Aromatic alkanols, for instance, often rearrange and dehydrate,^{1,2} and for this reason, PPA is often considered a dehydrating agent. Accordingly, in working with PPA-modified bitumen, Orange et al.⁵ proposed that hydroxyls are phosphorylated and

Baumgardner et al.⁴ suggested that aromatic alkanols dehydrate. However, petroleum alcohols are not alkanols, but phenols,⁶ so dehydration is most unlikely in this case. We therefore expected the reaction between bisphenol A and PPA to produce an oligomeric ester of PPA and bisphenol A (Figure 2). In contrast, and as detailed below, the FTIR findings demonstrated that no phenol phosphorylation occurred.

At room temperature, PPA is a thick liquid and bisphenol A is a solid. Upon heating to 170 °C, bisphenol A and PPA formed a single homogeneous phase of dark copper color. After an hour of heating and the subsequent cooling to room temperature, the mixture appeared as a single solid phase. The formation of a homogeneous phase suggested that a reaction had occurred, and accordingly, TLC showed that three new compounds were produced and that bisphenol A had been consumed entirely. Water and ether extracts were analyzed by FTIR and TLC.

The FTIR spectrum of the ether extract is shown in Figure 3, along with those for PPA and bisphenol A. It showed a slight loss of hydrogen-bonded hydroxyls at 3311 cm⁻¹, compensated by a gain in unbonded hydroxyls at 3500 cm⁻¹. Overall there was no loss of phenolic hydroxyl groups. Consequently, a PPA-bisphenol ester was not produced, as it would have led to the loss of hydroxyl absorbances at 3200-3600 cm⁻¹. This was consistent with the lack of a discrete PO-H absorbance near 2680 cm⁻¹.^{10,16} As will be seen later, the raised background of the reaction product (Rx) between 2500 and 3000 cm⁻¹ was only assigned to a diffuse PO-H signal after further analysis. The absence of a PPA-bisphenol ester was also consistent with a report that phenol is only converted to its phosphorylated ester at 280-300°C.¹⁷ A repeat of the reaction with phenol established clearly that phosphorylation proceeded to no practical extent at 150°C, and that, as will

be seen later, only a trace of a methylated-phosphorus compound was obtained from bisphenol A.

The FTIR spectrum of the ether extract in Figure 3 also indicated that the aromatic ring of bisphenol A was subject to nucleophilic attack by PPA. It showed a loss in the absorbances typical of para-substituted aromatics at 1512, 1180, and 831 cm^{-1} ,¹⁸⁻²⁰ compensated with new absorbances at 1499, 1473, 812, 754, and 691 cm^{-1} , the latter two being typical of mono-substituted aromatics.¹⁸⁻²⁰ Such a change in aromatic substitution could only be obtained upon de-alkylation. Figure 4 shows a possible route to a mono-substituted aromatic, whereupon a quinine intermediate protonated in the para position is subject to double nucleophilic displacement²¹ by an anion of PPA to produce two phenol molecules and a non-aromatic phosphorylated by-product.

To validate the scheme in Figure 4, the FTIR spectrum of the reaction product was overlaid with that of phenol (Figure 5). The excellent overlap of absorbances supported a reaction course such as that proposed in Figure 4. The peaks that did not correspond to phenol could readily be assigned to a methylated compound (as indicated by CH_3 in Figure 5), including the broad absorbance centered at 1000 cm^{-1} assigned to C–O–P vibrations.¹⁶ Given that PO–H stretching only seemed to raise the background near 2700 cm^{-1} , the methylated product likely contained a single phosphorus and hydroxyl (Figure 4), as opposed to four hydroxyls in two separate C–OP(O)(OH)₂ groups. This indicated that bisphenol A was likely subject to nucleophilic displacement by H_2PO_4^- , or by a PPA–OP(O)(OH)O[−] oligomer that came to lose its end repeat unit. This would be ascertained by a kinetic study of the reaction, including ³¹P NMR, but such an investigation was outside the scope of this work.

The third product of the reaction between PPA and bisphenol A, the water extract, was obtained in very low yield (ca. 1%). Just enough material was obtained to acquire an FTIR spectrum (Figure 6). It showed peaks from aromatic rings at 690, 755, 774, 1490, and 1590 cm^{-1} . The first two and the last of these peaks were also found in phenol (Figure 6). The strong and sharp bands, between 950 and 1200 cm^{-1} , arise from O–P=O. Between 2000 and 4000 cm^{-1} , there were only weak aromatic CH bands, and no OH absorptions (not shown). Consequently, this fraction was likely a trace of phosphorylated phenol, either $(\text{ArO})_3\text{P}=\text{O}$ from the reaction of phenol and H_3PO_4 , or $\text{Ar}[\text{OP}(\text{O})(\text{OAr})]_n\text{OAr}$ from phenol and PPA, where Ar is the aromatic group. Given that H_3PO_4 and PPA respectively show one and two bands in this area, the two peaks at 961 and 1026 cm^{-1} in Figure 6 were consistent with a reaction of phenol with PPA oligomers, not with H_3PO_4 .

The essence of the bisphenol A reaction, and for the purpose of assessing the reactivity of phenols with PPA, it was noteworthy that bisphenol A was totally consumed in the course of the reaction, and that contrary to the original premise,⁵ aromatic (poly)phosphoric esters were not produced above trace level from phenols.

Alkyl aromatic ether. Ethers can be cleaved upon the action of PPA.¹ Given that alkyl aromatic ethers are common in petroleum,⁶ and the postulated phosphorylation in PPA-modified bitumen,⁵ Baumgardner et al.⁴ proposed ether cleavage through phosphorylation to explain the lowering of molecular weight in these modified bitumens.^{4,5} As such, the nucleophilic displacement that cleaved bisphenol A might also reduce the molecular weight of ethers as illustrated in Figure 7.

To investigate the possibility of ether cleavage in PPA-modified bitumen, butyl phenyl ether was heated with PPA. After 1 h at 150 °C, both FTIR and TLC showed that butyl

phenyl ether was immune to the effect of PPA. In the infrared spectrum (not shown), the strong and characteristic ArOCH_2 ether absorbance near 1240 cm^{-1} was unaffected by the reaction and no new product was visible by TLC. It was therefore concluded that in conditions typical of those for mixing bitumen and PPA, no ether cleavage occurs. As an interesting corollary, we thus had in butyl phenyl ether an effective diluent in probing the reactivity of other bitumen model compounds.

Aromatic alkyl ketones. In synthetic applications with PPA, a number of reactions with ketones can be carried out.^{1,2} Bitumen normally contains very low concentrations of ketones, and possibly for this reason, neither Baumgardner et al.⁴ nor Orange et al.⁵ associated the reaction of ketones with the change in bitumen viscosity upon the preparation of PPA-modified bitumen. Notwithstanding, the concentration of ketones may be important in oxidized bitumens. It was therefore of interest to see how a simple ketone, acetophenone, would react with PPA in conditions typical of those used to prepare PPA-modified bitumen.

Acetophenone and PPA were colorless immiscible liquids at 22°C , but upon heating to 150°C , a monophasic orange liquid was obtained. Upon cooling to room temperature, they became immiscible again as a PPA gel precipitated out of solution. FTIR of the supernatant liquid showed a decrease in the ketone band at 1680 cm^{-1} and several new absorbances as indicated in Figure 8. TLC showed that acetophenone was not totally consumed by the reaction and that at least three new compounds were produced.

In acidic conditions, ketones usually condense to an α,β -unsaturated ketone, with a ketol intermediate normally too reactive to be isolated.²¹ Upon refluxing acetophenone and PPA in benzene for 7 h, Roeske et al.²² isolated dypnone (the corresponding diaryl α,β -unsaturated ketone) and several heavier condensed aromatics, all thought to have

arisen from cascading condensations (Figure 9). The reaction also led to the formation of benzoic acid through an unspecified competing reaction.

The spectrum of the products in Figure 8 suggests that the cascading condensation illustrated in Figure 9 did not occur when PPA was not in excess to the ketone. The absence of new absorbances between 600 and 800 cm^{-1} (not shown) for di- or tri-substituted aromatics¹⁸ indicated that no aromatic ring condensation had occurred. It was also noteworthy that in addition to a new strong C=C peak at 1654 cm^{-1} , attributed to the α,β -unsaturated ketone, an equally intense C–O band was visible at 1213 cm^{-1} . This might have been from the benzoic acid isolated by Roeske et al.,²² but the absence of a corresponding O–H band at 3300 cm^{-1} (not shown) indicated that no carboxylic acid was produced, and that no hydroxyl from a ketol intermediate remained in the mixture, if it ever formed. Consequently, acetophenone and PPA must have produced an ether from a competing reaction, or a molecular rearrangement, so common under the influence of PPA.^{1,2} Given the scope of this work and the numerous studies on ketone condensations,^{2,21} there was little benefit in the elucidation of their possible structure. It was sufficient for our purpose to measure from the loss of the carbonyl absorbance that about 53% of the starting ketone was converted to new products.

Of greater interest to us than the reaction of a ketone by itself was the reaction of a diluted ketone, which would be more representative of the situation in bitumen, where heteroatomic functional groups are dispersed in a sea of alkyl aromatics. So, in a second series of experiments, acetophenone was diluted with butyl phenyl ether. Based on the work of Berney,²³ the reaction of acetophenone and butyl phenyl ether to produce a ketal²¹ was entertained, but FTIR analysis showed that no such reaction took place, and that acetophenone condensation still occurred as before, albeit the conversion was lower.

The extent of the acetophenone reaction was estimated at about 5%. Consequently, in the reaction of PPA with bitumen, the condensation of ketones likely plays a minor role.

Aromatic carboxylic acid. In PPA as solvent, the intermolecular reaction of aromatic carboxylic acids with activated aromatic rings can lead to aryl-aryl ketones,²⁴ whereas the intramolecular dehydration of aromatic alkyl carboxylic acids can produce an aromatic cycloalkyl ketone² as illustrated in Figure 10. It was suggested that the latter might contribute to the stiffening of bitumen reacted with PPA,⁴ but in bitumen, ketones are found next to an aromatic nucleus not at the end of alkyl chains.²⁵ As it was also proposed that phosphate esters might be obtained from aromatic carboxylic acids,⁵ we used benzoic acid as a model compound for carboxylic acids in bitumen.

Benzoic acid was first heated alone with PPA. Past the melting point of benzoic acid, both reactants were liquid, but they remained immiscible throughout the heating time despite vigorous magnetic stirring. TLC and FTIR analysis of the heated material showed that benzoic acid was immune to the effect of PPA. This lack of reactivity was hardly surprising, however. In contrast to acetophenone, it has no extractable hydrogen next to the carbonyl group that would allow for ketone condensation, and aromatic substitution is rendered inefficient by the deactivating effect of the carboxylic acid group.²¹ As illustrated in Figure 10, an activating group on the ring, such as an ether, is required for a ring substitution reaction to occur. Consequently, benzoic acid was heated with butyl phenyl ether (an activated aromatic ring) and PPA in a second series of experiments. The weight ratio was 5:5:1. Contrary to our expectations based on the intermolecular reaction illustrated in Figure 10, the infrared spectrum of the reaction mixture, from which unreacted benzoic acid had been removed, showed two new carbonyl absorbances (Figure 11). From their frequencies, their structure could readily

be assigned.¹⁸⁻²⁰ The typical absorbance at 1656 cm^{-1} confirmed that aryl-aryl ketones could form in PPA-modified bitumen, and interestingly an absorbance at 1739 cm^{-1} also showed that an ester was produced. With FTIR, it was unclear whether it was an aryl-aryl or an aryl-alkyl ester, however. By means of NMR, it was found that it was an aryl-aryl ester (the detailed NMR results are shown in the Appendix). From the integration of the NMR signals, about 30% of the benzoic acid was found to have reacted to produce the ketone and the ester in a 2:1 ratio.

Given the above reaction, PPA and benzoic acid were heated with indan in a third series of experiments. Indan is a 1,2-substituted cyclopentyl aromatic typical of fused rings in bitumen. Indan, like benzoic acid and butyl phenyl ether, remained unreactive when heated alone with PPA. The indan/benzoic acid/PA ratio was 5:5:1. TLC analysis of the product indicated that not two, but three new compounds were produced. This was consistent with FTIR analysis. After the removal of benzoic acid, the spectrum revealed absorbances at 1660 and 1740 cm^{-1} assigned to an aryl-aryl ketone and an aryl-aryl ester (Figure 12). Other bands not assigned to indan were attributed to a third product thought to be an indan-derived phosphorus compound. From the compilation work of Thomas on organophosphorus compounds,¹⁶ new absorbances at 1790 and 1270 cm^{-1} were attributed to $\text{P}=\text{O}$, and absorbances at 1210 , 1170 , 995 and 970 cm^{-1} were attributed to POC stretching. As such, the 1210 cm^{-1} absorbance were tentatively attributed to $\text{P}^{\text{I-III}}\text{OC}$ stretching¹⁶ (i.e., phosphenic or phosphonic compounds {one and two hydroxyls, respectively} as opposed to phosphate {three hydroxyls}), and the 1170 and 970 cm^{-1} absorbances were attributed to aliphatic POC stretches.¹⁶ Combined with the new absorbance at 700 cm^{-1} , typical of mono-substituted aromatics,¹⁸⁻¹⁹ we speculated that PPA and benzoic acid both catalyzed the opening of the cycloalkyl ring of indan to

produce a monosubstituted aromatic-phosphorus compound of the type $\text{Ar}(\text{CH}_2)_3\text{OP}(\text{O})(\text{OH})_n\text{R}_m$, where the integers $n + m = 3$. Based on the integration of ^1H NMR signals, the combined yield of the products of the reaction between benzoic acid and indan was estimated at less than 10%, so no attempts were made to separate the three products for a more detailed analysis of their structure.

Conclusion

In synthetic organic chemistry, polyphosphoric acid (PPA) is often used as a solvent with or without a co-reactant to carry out a large number of reactions. These conditions are remote from those used to prepare PPA-modified bitumen, so the goal of this work was to establish the relative reactivity of bitumen model compounds that contained an oxygenated functional group when they were heated 1 h at 150 °C with PPA, and to determine the extent of phosphorylation, if any. In this respect, the order of reactivity of the various functional groups was found to be phenols > ketones > carboxylic acids > ethers. Phenols or aromatic carboxylic acids were not found to be phosphorylated to any practical extent, contrary to a prior suggestion based on work with bitumen. Notwithstanding, there was some evidence for the minor production of aliphatic organo-phosphorus by-products.

FTIR analysis showed that alkylated phenol (bisphenol A) was dealkylated by PPA and produced fragments of lower molecular weights, whereas ketones condensed into units of higher molecular weights. These reactions would help explain the decrease of asphaltene molecular weight and bitumen stiffening when bitumen is treated with PPA. In contrast, aromatic carboxylic acids and ethers did not react directly with PPA, but when they were heated together, they produced aryl-aryl ketones and esters. The extent of

this reaction was low, however, so their contribution to bitumen stiffening is likely modest.

Acknowledgements. J-F. M. thanks René Maldonado, Darrell Fee, and Michael Falkiewicz for their review of the draft paper and for their comments. J-F. M. also thanks ICL Performance Products LP and Paragon Technical Services, Inc. for their support.

References

- (1) Rowlands, D. A. Polyphosphoric acid (PPA). In *Synthetic Reagents*; Pizey, J. S., Ed.; Ellis Horwood Limited: Chichester, U.K., 1985; Vol. 6, Chapter 3.
- (2) Popp, F. D.; McEwen, W. E. Polyphosphoric acid as a reagent in organic chemistry. *Chem. Rev.* **1958**, 58, 321–401.
- (3) Baumgardner, G. L.; Burrow, M. R. Asphalt compositions and methods of preparation thereof. US Patent 6228909, 2001.
- (4) Baumgardner, G. L.; Masson, J-F.; Hardee, J. R.; Menapace, A. M.; Williams, A. G. Polyphosphoric acid modified asphalt: Proposed mechanisms. *Proc. Assoc. Asphalt Paving Technol.* **2005**, 74, 283–305.
- (5) Orange, G.; Dupuis, D.; Martin, J.-V.; Farcas, F.; Such, C.; Marcant, B. Chemical modification of bitumen through PPA: Properties–microstructure relationship. Third Euraphalt and Eurobitume Congress, Vienna, Austria, 2004; paper 334, book 1, pp. 733–745.
- (6) Speight, J. G. *The Chemistry and Technology of Petroleum*. 3rd ed; Marcel Dekker: New York, 1999.
- (7) Jones IV, D., SHRP materials reference library for asphalt cements: A concise data compilation. Report SHRP-A-645; Strategic Highway Research Program, National Research Council, Washington, D.C., 1993; <http://onlinepubs.trb.org/Onlinepubs/shrp/SHRP-A-645.pdf> (accessed Sept. 3rd, 2008)
- (8) *Handbook of Chemistry and Physics*, 63rd ed; Weast, R. C., Astle, M. J. Eds.; CRC Press: Boca Raton, FL, 1982; pp E50–E54.

- (9) Masson, J-F, A brief review of the chemistry of polyphosphoric acid (PPA) and bitumen. *Energy Fuels*, **2008**, 22, 2637–2640; Erratum, in press, doi 10.1021/ef8005433.
- (10) Masson, J-F.; Gagné, M. Ionic pairs in polyphosphoric acid (PPA)-modified bitumen: Insights from model compounds. *Energy Fuels*, in press, doi 10.1021/ef8002526.
- (11) Masson, J-F.; Gagné, M. PPA-modified bitumen: Disruption of the asphaltenes network based on the reaction of non-basic nitrogen with polyphosphoric acid. *Energy Fuels*, **2008**, in press, doi 10.1021/ef8002944, accepted for publication.
- (12) Vogel, A. I.; Smith, B.V.; Waldron, N. M. *Vogel's Elementary Practical Organic Chemistry I: Preparations*; 3rd ed; Longman: New York, NY, 1980.
- (13) Raki, L.; Masson, J-F. Rapid bulk fractionation of maltenes into saturates, aromatics and resins by flash chromatography. *Energy Fuels* **2000**, 14, 160–163.
- (14) Günther, H. NMR spectroscopy: Basic principles, concepts, and applications in chemistry. 2nd ed; Wiley: New York, 1994.
- (15) Cherbuliez E. Organic derivatives of phosphoric acid. In *Organic Phosphorus Compounds*; Kosolapoff G. M., Maier, L., Eds.; Wiley-Interscience: New York, NY, 1973; Chapter 15.
- (16) Thomas, L. C. Interpretation of the infrared spectra of organophosphorus compounds. Heyden: London, 1974.
- (17) Kharlampovich, G. D.; Aksenova, T. F. Preparation of trisilenyl phosphate and other triaryl phosphates by esterification of phenols of phosphoric acid. *Chem. Abst.* **1967**, 66, 9790, entry 104766h.

- (18) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: San Diego, CA, 1991.
- (19) Lambert, J. B.; Shurvell, H. F.; Verbit, L.; Cooks, R. G.; Stout, G. H. *Organic Structural Analysis*; Macmillan Publishing Co., Inc: New York, NY, 1976.
- (20) Pavia, D. L.; Lampman, G. M.; Kriz, G. S. *Introduction to Spectroscopy*; Saunders College Publishing: Philadelphia, PA, 1979; Chapter 2.
- (21) Ternay, A. L. *Contemporary Organic Chemistry*. 2nd ed.; W. B. Saunders Company: Philadelphia, PA, 1979.
- (22) Roeske, R. W.; Bright, D. B.; Johnson, R. L.; DeJarlais, W. J.; Bush, R. W.; Snyder, H. R. Polyphosphoric acid as a reagent in organic chemistry. X. Two yellow hydrocarbons from acetophenone. *J. Am. Chem. Soc.* **1960**, 82, 3128–3133.
- (23) Berney, D. The condensation of cyclic aminoketones, cyclohexanone and cyclohexane-1,4-dione with some phenolic ethers in polyphosphoric acid. *Helv. Chim. Acta* **1978**, 61, 1110–1114.
- (24) Kasbekar, A. B.; Hosangadi, B. D. Novel reactions with polyphosphoric acid: Part I–benzophenones from alkoxy aromatic carboxylic acids and a new type of trans-carbonylation reaction. *Indian J. Chem.* **1970**, 8, 1059–1061.
- (25) Peterson, J. C. A dual sequential mechanism for the oxidation of petroleum asphalts. *Petrol. Sci. Technol.* **1998**, 16, 1023–1059.

Appendix

The products of the reaction between benzoic acid and butyl phenyl ether were analyzed by NMR spectroscopy. FTIR allowed for the identification of the aryl-aryl ketone (Figure 11), but it could not differentiate between the two possible esters. From ^1H and ^{13}C NMR spectra, the products were found to be an aryl-aryl ketone and an aryl-aryl ester.

With ^1H and ^{13}C NMR, signals for the aryl-aryl ketone were unambiguously assigned (Figure 13). The carbon signal at 195 ppm was assigned to C-5 because peaks at such high frequencies are typical for ketone groups. By means of 2D ^1H - ^{13}C correlation (Figure 14), C-5 was found to be three bond coupled ($^3J_{\text{C-C-H}}$) to two hydrogen doublets at 8.03 and 7.96 ppm for H-7 and H-3, respectively. The aromatic hydrogen signals H-7 and H-3 also appeared at high frequencies because they are exposed to the de-shielding effect of the ketone. The 2D correlation spectrum showed a hydrogen signal H-3 (7.96 ppm) three bond coupled to C-1 and C-3' in the 130 ppm region. On the other hand, H-7 (8.03 ppm) was coupled with C-7' in the 130 ppm region, but C-9 appeared at 163 ppm, a typical chemical shift for a C-O carbon atom. Furthermore, the 2D spectrum showed hydrogen coupling between H-7 and another proton at low frequency, H-8 at 7.1 ppm. Such low proton frequency for an aromatic signal was a clear indication of the presence of an electron donor group such as an ether moiety. H-8 located at the ortho-ether position was strongly shielded by delocalized electrons in the benzene ring. The presence of new aliphatic CH₂ signals (inset of Figure 13) confirmed the presence of a butyl group linked to the ether functionality. The rest of the aromatic and aliphatic signals for the

ketone derivative 1 were formally assigned with quantitative 1D, and homo and heteronuclear 2D correlation spectra. The reaction product was quantified by direct correlation of the signal intensities of H-3 (7.96 ppm, 2H) of the ketone derivative 1 with the two meta protons of *n*-butyl phenyl ether at 7.45 ppm, which had to be corrected due to the presence of overlapping H-g and H-i from the ester derivative 2.

The signals of the aryl-aryl ester were also assigned based on the 2D spectrum. The high frequency aromatic hydrogen signal at 8.4 ppm was three bond coupled with a C-O at 165 ppm. The combined ^1H and ^{13}C information was typical of a benzoate group, PhC(O)O- , where the electron rich carbonyl group had an enhanced anisotropic deshielding effect over the hydrogen at the ortho ester position (H-c, 8.4 ppm) and increased electron shielding over the ester carbon (C-e, 165 ppm). All of the benzoate signals were formally assigned. The functional group linked to the benzoate was assigned to phenyl group based on the following. A carbon atom attached to an electronegative oxygen from the benzoate ester group (Ph(CO)O-C) was expected and found at 151 ppm on the carbon spectrum. It had the same intensity as the ester C-e signal and therefore it could be confidently assigned to C-f. The 2D spectrum showed the C-f carbon being long range coupled with H-h ($^3J_{\text{C-H}}$, 7.6 ppm) and H-g ($^2J_{\text{C-H}}$, 7.42 ppm). The typical aromatic chemical shift displacements for those two protons indicated that no other functional group was on the ester phenyl ring. The total number of carbon and hydrogen signals along with their intensities also supported the presence of a simple phenyl moiety attached to the benzoate.

Figures

Figure 1. Oxygenated compounds studied. Clockwise from top left, bisphenol A, butyl phenyl ether, benzoic acid, and acetophenone.

Figure 2. Ester expected from the reaction between PPA and bisphenol A.

Figure 3. FTIR spectra of bisphenol A, PPA and their reaction products (Rx). Intensities are normalized to the C–O absorbance at 1228 cm^{-1} , excluding PPA.

Figure 4. Proposed mechanism for the conversion of bisphenol-A to phenol.

Figure 5. FTIR spectrum of phenol and the products of the reaction between PPA and bisphenol A. The overlapping phenol bands are identified with their wavenumbers between 400 and 1600 cm^{-1} . Spectra are normalized to the C–O absorbance at 1228 cm^{-1} .

Figure 6. Fingerprint region of the FTIR spectrum of phosphorylated phenol. The spectra of PPA and phenol are used as a reference.

Figure 7. Hypothetical phosphorylation by displacement of an alkoxy group to produce an alcohol or displacement of a phenoxy group to produce phenol.

Figure 8. Upper fingerprint region of the infrared spectrum of acetophenone before and after (R) its heating with PPA. Labels highlight new absorbances, except for that at 1680 cm^{-1} . The spectra were normalized to the aromatic C–H peak at 3063 cm^{-1} .

Figure 9. Condensation of acetophenone into dyprnone and postulated structures of further condensed compounds. Adapted from Roeske et al.²²

Figure 10. Possible intra and inter molecular reactions of aromatic carboxylic acids onto an activated aromatic ring (ROAr). Adapted from references 2 and 23.

Figure 11. Carbonyl region of the infrared spectra for butyl phenyl ether (BuPhO) and its reaction products with benzoic acid (Rx). The spectra were normalized to the common aromatic C–H peak at 3063 cm⁻¹.

Figure 12. Fingerprint region of the infrared spectrum of the reaction mixture from benzoic acid and PPA diluted with indan (BA-PPA-Indan). The spectrum of indan is provided as a reference. The legend is the same for both frequency regions and the spectra were normalized to the methylene absorbance at 1438 cm^{-1} .

Figure 13. ^1H (top) and ^{13}C (bottom) partial NMR spectra showing assigned signals for ketone 1 and ester 2.

Figure 14. Two dimensional heteronuclear ^1H – ^{13}C correlation spectrum with long range couplings (J) between carbon and hydrogen atoms for derivatives 1 and 2.