

THE ROLE OF HYDROAROMATICS IN OXIDATIVE AGING IN ASPHALT

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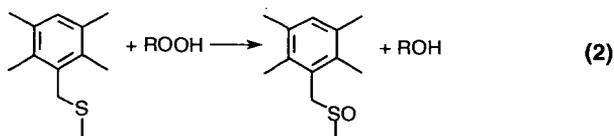
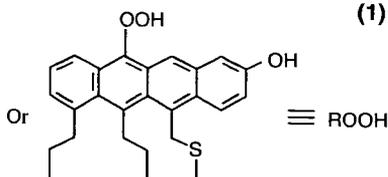
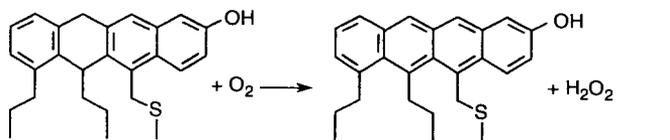
INTRODUCTION

The pavement engineering community recognized fifty years ago that age hardening and embrittlement of asphalt during service is a primary cause of road failure [Welborn, 1984] and that oxidation of asphalt is the major cause of age hardening [Nicholson, 1937; Traxler, 1961]. Oxidative aging is characterized by oxygen uptake, the formation of sulfoxide and carbonyl groups (as shown by IR spectra), and marked increases in dynamic viscosity and other rheological properties. [Petersen, 1975, 1981 and 1986]. Different asphalts show markedly different rheological changes for similar amounts of oxidation, although elemental analyses indicate a similarity in CHO ratios as well as in molecular weights, with variability only in the heteroatoms, functional groups, and trace metal compositions [Branthaver et al., 1993].

In a SHRP-supported research program, we developed a new hypothesis to account for the oxidation of asphalt, in which hydroaromatic groups in asphalt react with oxygen to form peroxides which are the proximate cause of chemical and physical changes induced by oxidative aging. The purpose of this paper is to examine how oxidation of hydroaromatic groups might proceed and whether hydroaromatics in asphalt fulfill the requirements in asphalt oxidation.

OXIDATION PATHWAYS AND AN OXIDATION MODEL

Triplet oxygen reacts with most organic compounds through free radical pathways, initiated with peroxides and metals [Mill and Hendry, 1980; Mill et al., 1995]. The unusual reactivity oxygen exhibits toward asphalt at temperatures below 100°C must be associated with some highly reactive structural features, such as polycyclic hydroaromatics. Reactions (1) and (2) illustrate the proposed reaction sequence during oxidation of asphalt.



A model for dihydroaromatic reaction with oxygen is found in the smooth reaction of dihydroanthracene ((DHA) with air or oxygen at 100°C in benzene to form hydrogen peroxide and anthracene [Mill et al., 1992]. Figure 1 shows the loss of DHA and the formation of anthracene at 100°C. Added dibutyl sulfide ((DBS), unoxidized by itself at 100°C with air, oxidizes rapidly in the presence of DHA and air at 100°C at rates that correspond to oxidation of DHA to form the peroxide. This induced oxidation is very similar to the induced oxidation of DBS by asphalt heated in air. Although asphalt contains no DHA, we believe that DHA-like hydroaromatics may be present in amounts sufficient to account for the greater part of the direct reaction with oxygen.

KINETICS OF HYDROAROMATIC-OXYGEN REACTIONS

Thermochemical kinetic estimates of the rates of reaction of oxygen and hydroaromatics start with the simple H-atom transfer from the hydroaromatic to oxygen to form the radical pair shown in Reaction (3).

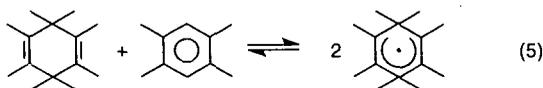


Using heats of formation of these four species, Reaction (1) has a heat of reaction ranging from 130 kJ/mole for DHA and dihydronaphthalene-like hydroaromatics to 159 kJ/mole for tetralin and tetraphenylethane-like hydroaromatics [Benson, 1968; McMillen et al., 1987]. These values correspond to the activation energies of the forward reactions, which, when combined with reasonable estimates for entropy changes, have kinetic parameters corresponding to

$$k_3 = 10^{8.5} \exp(-130,000/RT) \text{ to } 10^{8.5} \exp(-159,000/RT) \quad (4)$$

For DHA and tetralin, $k_3 = 2 \times 10^{-10} \text{ M}^{-1} \text{ s}^{-1}$ and $1.7 \times 10^{-14} \text{ M}^{-1} \text{ s}^{-1}$, respectively at 100°C. The rate constant for DHA corresponds to a half life for DHA in the presence of 25 atm of oxygen (~1 M) of about 100 years, and for tetralin, a million years! Clearly, this simple scheme fails by a wide margin to predict the experimental half life of 30-40 hours found for DHA in benzene at 100°C with 1 atm of air (see Figure 1).

An alternative model for oxidation of DHA and hydroaromatic analogs involves prior formation of the hydroaromatic (DHA) radical from the molecule assisted homolysis of the hydroaromatic (DHA) by the corresponding aromatic (anthracene) [Bilmers et al., 1986]. The resultant radicals then react with oxygen.



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For DHA, Bilmers et al [1986] estimate this process to have an activation energy and log A-factor close to 151 kJ/mol and 8.5, respectively, giving a rate constant at 100°C similar to the value for the tetralin-oxygen reaction and much too slow to be important, even if equimolar amounts of anthracene and DHA were initially present.

Concerted transfer of two hydroaromatic H-atoms to oxygen (Reaction (1)) is exothermic by 63 and 84 kJ/mol with DHA and dihydrophenanthrene,

respectively, and might account for the observed oxidation of DHA, although we do not know what the intrinsic activation energy is for the process. The fast radical-chain oxidation of DHA examined by Bickel and Kooyman [1956] and by Mahoney [1966] to give the corresponding hydroperoxide is difficult to reconcile with the non-initiated oxidation we observed for DHA in benzene. Moreover, radical chain oxidation of hydroaromatics in asphalt is unlikely owing to the presence of effective radical scavenging phenols [Branthaver et al., 1993]; the oxidation would proceed, but much more slowly with a chain length of one. We should point out that a related oxidation of anthrahydroquinone to anthraquinone is the basis for commercial production of hydrogen peroxide from oxygen [Kirchner, 1981]. Asphalts, however, have low concentrations of isolated phenols and probably much lower concentrations of hydroquinones [Branthaver et al., 1993], but we cannot rule out some contribution from this reaction.

HYDROAROMATIC CONTENT OF ASPHALTS

An additional test of the validity of the hydroaromatic model for oxidation of asphalts is the extent to which oxygen uptake is related to the known hydroaromatic content of asphalts. Oxygen uptake data for several SHRP standard asphalts including AAD-1 show that up to one mole of oxygen/kg is taken up over about 100 hrs at 100°C [Branthaver et al., 1993], a significant amount of oxygen, but a small fraction of the aromatic or aliphatic units in typical asphalts with molecular weights ranging from 700 to 1300 Daltons.

Although large numbers of studies of the hydroaromatic content of coals have been published in connection with liquefaction of coal and the role of H-atom donors in the process (Bilmers et al., 1986), few estimates of the hydroaromatic content of asphalts appear to be available. In one recent study, Farcasiu and Rubin [1987] determined the formation of polycyclic aromatic compounds on dehydrogenation of vacuum residues, using uv spectra and mass spectrometry. They found that some fractions of the resid were easily dehydrogenated to give polycyclic aromatic compounds; in one case an average of 13 saturated ring carbons were readily converted to aromatic carbons, indicating that a fairly abundant supply of reactive hydroaromatics are available in some asphalts for the proposed oxidation scheme.

REFERENCES

- Bateman, L. and K. R. Hargrave, 1954a, Oxidation of Organic Sulfides I, J. Chem. Soc. 389-398.
- Bateman, L., and K. R. Hargrave, 1954b, Oxidation of Organic Sulfides II., J. Chem. Soc., 399-411.
- Benson, S. W., 1968, Thermochemical Kinetics, John Wiley and Sons, New York.
- Bickel, A. F. and E. C. Kooyman, 1956, Inhibition of the Oxidation of Dihydroanthracene by Alkyl Phenols, J. Chem. Soc. 2215-2226.
- Bilmers, R., Griffith, L. L. and Stein, S. E., 1986, Hydrogen Transfer between Anthracene Structures, J. Phys. Chem., 90: 517-523.
- Branthaver, J. F., J. C. Petersen, R. E. Robertson, J. J. Duvall, S. S. Kim, P. M. Harnsberger, T. Mill, E. K. Ensley, F. A. Barbour, and J. F. Schabron, 1993, Binder Characterization and Evaluation, SHRP Report SHRP-A-368, Vol. 2, Chemistry.

- Farcasiu, M. and Rubin, B. R., 1987, Aliphatic Structures in Petroleum Resids, Energy Fuels 5: 381-386.
- Kirchner, J. R., 1981, Hydrogen Peroxide in Kirk-Othmer Encyclopedia of Chemical Technology, M. Grayson, Ed., John Wiley and Sons, New York, Vol. 13, pp. 12-38.
- Mahoney, L. R., 1965, Reactions of Peroxy Radicals with Polynuclear Aromatic Compounds II, Anthracene in Chlorobenzene, J. Amer. Chem. Soc. 87: 1089-1095.
- Mahoney, L. R., 1966, Inhibition of Free Radical Reactions. II. Kinetic Study of the Reaction of Peroxy Radicals with Hydroquinones and Hindered Phenols, J. Amer. Chem. Soc. 88: 3035-3041.
- McMillen, D. F., Malhotra, R., Chang, S.-J., Nigenda, S. E., Fleming, R. H., 1987, Mechanisms of hydrogen transfer and bond scission of strongly bonded coal structures in donor-solvent systems, Fuel, 66: 166611-1620.
- Mill, T. and Hendry, D. G., 1980, Kinetics and Mechanism of Free Radical Oxidation of Alkanes and Olefins in the Liquid Phase, in Comprehensive Chemical Kinetics, Vol. 16., C. H. Bamford and C.F.H. Tipper, Ed., Elsevier, Amsterdam, pp. 1-83.
- Mill, T., D. S. Tse, B. Loo, C. C. D. Yao, and E. Canavesi, 1992, Oxidation Pathways in Asphalt, 204th Meeting of the ACS, Washington DC, ACS Div. Fuel Chem. Preprints 37: 1367-1375
- Mill, T., Jayaweera, I., and Ross, D. S., 1995, Hydrothermal Oxidation of Phenol, in Physical Chemistry of Aqueous Solutions, H. J. White, J. V. Sengers, and J. C. Bellows, Eds., Begell House, New York, pp. 589-592.
- Nicholson, V., 1937, A Laboratory Oxidation Test for Bitumens, Proc. A.A.P.T. 9: 208-213.
- Petersen, J. C., 1975, Quantitative Methods Using Differential IR for Determining Compound Types Absorbing in the Carbonyl Region in Asphalts, Anal. Chem. 47:112.
- Petersen, J. C., 1986, Quantitative Differential Group Analysis of Asphalts Using Differential Infrared Spectrometry and Selective Chemical Reactions-Theor. and Applications, Preprint, 65th Ann. Tran. Res. Board Meeting, Washington, D.C., Jan. 13-17.
- Petersen, J. C., S. M. Dorrence, M. Nazir, H. Plancher, and F. A. Barbour, 1981, Oxidation of Sulfur Compounds in Petroleum Residues: Reactivity-Structural Relationships, Div. Petrol. Chem., 181st Meeting of the ACS, New York, NY.
- Traxler, R. N., 1961, Relation Between Asphalt Composition and Hardening by Volatilization and Oxidation. Proc. Assoc. Asphalt Paving Technologists 30: 359-373.
- Walling, C., 1963, Free Radicals in Solution. John Wiley and Sons, New York.
- Welborn, J. Y., 1984, Physical Properties as Related to Asphalt Durability: State of the Art. Trans. Res. Record 999: 31-37.

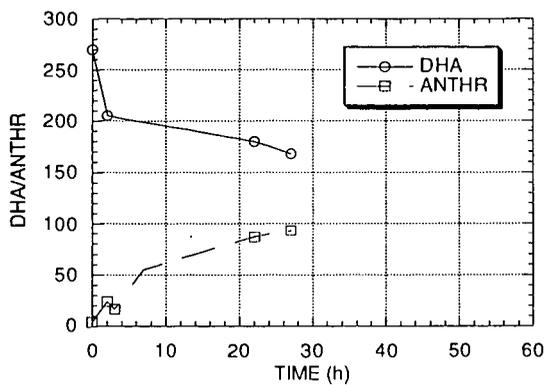


Figure 1. Conversion of 250 μ M DHA to A in benzene in air at 100°C