The Atmospheric Aerosol-Forming Potential of Whole Gasoline Vapor

J. R. Odum, T. P. W. Jungkamp, R. J. Griffin, R. C. Flagan, J. H. Seinfeld*

A series of sunlit-irradiated, smog-chamber experiments confirmed that the atmospheric organic aerosol formation potential of whole gasoline vapor can be accounted for solely in terms of the aromatic fraction of the fuel. The total amount of secondary organic aerosol produced from the atmospheric oxidation of whole gasoline vapor can be represented as the sum of the contributions of the individual aromatic molecular constituents of the fuel. The urban atmospheric, anthropogenic hydrocarbon profile is approximated well by evaporated whole gasoline, and thus these results suggest that it is possible to model atmospheric secondary organic aerosol formation.

Several recent epidemiologic studies have consistently reported increased daily mortality associated with exposure to fine particulate air pollution (1, 2). An important contribution to the atmospheric fine particulate burden, especially during severe urban smog episodes, is secondary organic aerosol (SOA) (3). Like ozone (O3), SOA is formed from the atmospheric oxidation of organic compounds. Whereas the oxidation of most hydrocarbons contributes to O3 formation, SOA is generally formed only from the oxidation of hydrocarbon molecules containing seven or more carbon atoms (4). To form SOA, oxidation products must have vapor pressures that are sufficiently low to enable them to partition into the particulate phase.

In an effort to achieve urban and regional O3 abatement through the reduction of mass emissions of nonmethane hydrocarbons, the 1990 amendments to the U.S. Clean Air Act mandate the use of reformulated gasoline in motor vehicles. Several recent studies have suggested that a more effective approach to controlling urban O3 associated with emissions from gasoline usage is to target the emissions of specific fuel components, rather than total nonmethane hydrocarbons, because of the extreme differences in the O3-formation potential of the hundreds of individual compounds that constitute gasoline (5). Considering the common link between urban O3 formation and SOA formation, this approach may also be an effective way to control SOA formation associated with emissions from gasoline usage.

Organic aerosol formation potentials depend on two factors: reactivity of the parent compound and volatility of the product species. The reactivity of the parent species can be directly measured by reaction rate constants. However, because atmospheric chemical reaction pathways for large hydrocarbon molecules are complex and the reaction heat budget of Hogg et al. at somewhat warmer bounding temperature for which we have more micrometeorological observations could address this. Third, there may be regional variation in the intensity of the mixing above rough bathymetry due to changes in the small-scale bottom roughness, near-bottom currents, and stratification, all of which affect the generation of internal waves.

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Characteristic of these studies, a heat flux divergence is found, associated with bottom water flowing horizontally into a basin at a colder average temperature. The cold water is apparently driven by near-bottom water flowing upslope, associated by downwelling turbulent diffusion, with the requisite heat flux commonly expressed as a vertical diffusivity (k) multiplied by the mean vertical temperature gradient averaged horizontally over the basin.

27. The diapycnal velocity w* was estimated as 8.25 N°/Δz over a 100-m interval about the 0.8°C isotherm. The neglected terms in this equation are small, and the density field associated with nonlinearities in the seawater equation of state that cause densification of water on mixing [T. McDougall, in Proceedings of Hawaiian Winter Workshop, SOEST Special Publication, 13 to 19 January 1991 (Univ. of Hawaii at Manoa, 1991), pp. 355–386] only exacerbate the problem with the mass budget closure.

28. Equivalently, in the vertical, our estimates of (k a) peak about the crests of the MAR spurs and decrease with still greater depth within the canyons.

29. With a flat bottom and uniform stratification, the flow would be zonal. However, basin-scale bottom-depth variations (Spence and Zenk [26]) and eddy-driven horizontal recirculations extending from the western boundary (M. A. Spall, J. Mar. Res. 52, 1051 (1994)) may strongly distort this interior circulation from simple zonal flow.

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resulting oxidation products are both numerous and difficult to quantify analytically, a more indirect measure of product volatility, the SOA yield, has been used. Traditionally, Y has been defined as the fraction of a reactive organic gas (ROG) that is converted to aerosol by means of atmospheric oxidation processes: \( Y = \frac{\Delta M_2}{\Delta ROG} \), that is, the total mass concentration of organic aerosol, \( \Delta M_2 \), produced for a given amount of ROG, \( \Delta ROG \). Yield data have been obtained for dozens of ROGs in controlled smog chamber studies (6–8).

The mixture of hydrocarbons that compose gasoline is representative of the atmospheric distribution of anthropogenic hydrocarbons in an urban airshed in terms of both complexity and composition (9), and therefore, determining the atmospheric aerosol formation potential of whole gasoline vapor is of significant interest. In general, gasoline contains four classes of reactive organics—oxygenates, alkanes, alkenes, and aromatics—which vary widely in their atmospheric reactivity and in the volatility of their atmospheric oxidation products. Our hypothesis is that the atmospheric aerosol-forming potential of whole gasoline vapor can be quantitatively accounted for in terms of the aromatic content of the fuel.

The outdoor smog chamber system used in this study has been described in detail previously (10). It consists of a 60-m³ sealed, collapsible polytetrafluoroethylene (Teflon) bag. Experiments are performed by (i) injecting into the bag (filled with humidified clean air) appropriate concentrations of seed aerosol [(NH₄)₂SO₄, about 5,000 to 10,000 particles per cubic centimeter, an initial aerosol volume of about 5 to 10 µm³ per cubic centimeter of air], a photochemical initiator [propene, about 150 to 300 parts per billion (ppb)], NO and NO₂, and the single hydrocarbon or hydrocarbon mixture of choice and then (ii) allowing the mixture to react under sunlight for 6 to 8 hours (11). During the course of the experiment, the concentration of each ROG species is either measured with the use of gas chromatography or is calculated on the basis of relative rates of reaction, in order to determine \( \Delta ROG \). Particle number and size are measured continuously throughout the experiment by scanning electrical mobility spectrometers to determine \( \Delta M_2 \) (7, 12).

Because the oxidation products responsible for forming SOA are semivolatile and partition themselves between the gas and absorbing organic aerosol phases (10, 13), SOA yields for individual ROGs (Y) are a function of \( M_o \). This dependence is represented by (10)

\[
Y = M_o \sum_i \left( \frac{\alpha_i K_{omi}}{1 + K_{omi} M_o} \right) \tag{1}
\]

where \( \alpha_i \) and \( K_{omi} \) are the mass-based stoichiometric coefficient and absorption equilibrium partitioning coefficient of product \( i \), respectively (14). Yield data for individual hydrocarbons can be fit well using Eq. 1 assuming a two-product model (that is, by choosing appropriate values for \( \alpha_i \), \( K_{omi} \), \( K_{om1} \), and \( K_{om2} \)) (10). Organic aerosol yields were measured as a function of \( \Delta M_2 \) for 17 aromatic species that represent the predominant mass fraction of aromatics present in gasoline (Fig. 1). Most of the data can be fit with only two curves. Curve 1 corresponds to propylbenzene and to those species having one or fewer methyl substituents plus one or fewer ethyl substituents, and curve 2 fits species that contain two or more methyl substituents. Curves 3 and 4 fit the only diethylbenzene and methyl-n-propylbenzene species that were studied. There is little variation of the yield for different isomers. For example, \( \alpha \)-, \( m \)-, and \( p \)-xylene all exhibit yields that are described by the same curve. It is likely that parent species that are sufficiently similar in nature generate, upon photooxidation, semivolatile products that have similar gas-aerosol partitioning behavior.

From yield curves for individual parent hydrocarbons, like those shown in Fig. 1, one can account for the aerosol that is formed from the oxidation of a mixture of two species as the sum of the yields of the individual parent species present in the mixture (10). To ensure that the aerosol formed in a more complex mixture could be accounted for in such a manner, we performed an experiment in which a mixture of five different aromatic species (toluene, \( m \)-xylene, \( m \)-ethyltoluene, propylbenzene, and 1,2,4-trimethylbenzene) was photooxidized. The total organic aerosol concentration produced in the chamber was 28 µg m⁻³. Using the curves from Fig. 1, an appropriate yield value (Y) for each of the five aromatics, corresponding to a total organic aerosol mass concentration \( \Delta M_2 = 28 \) µg m⁻³, is obtained, and each value is multiplied by the respective reacted ROG concentration to determine \( \Delta M_2 \) (7, 12).

![Fig. 1. Secondary organic aerosol yield as a function of total organic aerosol mass concentration (\( \Delta M_2 \)) for 17 individual aromatic species. Each point represents an individual experiment. Curves were fit to the data using a two-product model in conjunction with Eq. 1 by minimizing the weighted squared residuals. Curve 1 is fit with values 0.071, 0.053, 0.138, and 0.0019 for \( \alpha_i \), \( K_{om1} \), \( \alpha_2 \), and \( K_{om2} \), respectively. The corresponding values are 0.038, 0.042, 0.167, and 0.0014 for curve 2; 0.083, 0.093, 0.22, and 0.0010 for curve 3; and 0.05, 0.054, 0.136, and 0.0023 for curve 4.](http://www.sciencemag.org/)

<table>
<thead>
<tr>
<th>Species</th>
<th>Initial ROG (µg m⁻³)</th>
<th>( \Delta ROG ) (µg m⁻³)</th>
<th>Y</th>
<th>( \Delta ROG \times Y ) (µg m⁻³)</th>
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<tbody>
<tr>
<td>Toluene</td>
<td>663</td>
<td>265</td>
<td>0.049</td>
<td>13</td>
</tr>
<tr>
<td>( m )-Xylene</td>
<td>330</td>
<td>284</td>
<td>0.027</td>
<td>7.6</td>
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<tr>
<td>( m )-Ethyltoluene</td>
<td>105</td>
<td>89</td>
<td>0.049</td>
<td>4.4</td>
</tr>
<tr>
<td>( n )-Propylbenzene</td>
<td>40</td>
<td>16</td>
<td>0.049</td>
<td>0.8</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>162</td>
<td>147</td>
<td>0.027</td>
<td>3.9</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>29.7</td>
</tr>
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</table>
Table 2. Properties of AQIRP reformulated gasolines. MTBE = the fuel additive methyl tertiary butyl ether; the fuel identification code is derived from A (a) = high (low) aromatics, M (m) = high (low) MTBE, O (o) = high (low) olefins, R (t) = high (low) VCR, RMH = medium and heavy reformate cut (predominantly C₂ and C₁₀ aromatics), and AH = heavy alkylate cut (heavy paraffins).

<table>
<thead>
<tr>
<th>Fuel code</th>
<th>AQIRP phase</th>
<th>Fuel ID</th>
<th>Aromatics (vol %)</th>
<th>MTBE (vol %)</th>
<th>Olefins (vol %)</th>
<th>T∞ (°C)</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>I</td>
<td>Industry average</td>
<td>32.0</td>
<td>0.0</td>
<td>9.2</td>
<td>166</td>
</tr>
<tr>
<td>F</td>
<td>I</td>
<td>amot</td>
<td>20.0</td>
<td>0.0</td>
<td>3.2</td>
<td>137</td>
</tr>
<tr>
<td>G</td>
<td>I</td>
<td>AmOT</td>
<td>44.3</td>
<td>0.0</td>
<td>17.4</td>
<td>141</td>
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<tr>
<td>K</td>
<td>I</td>
<td>Amot</td>
<td>45.7</td>
<td>0.0</td>
<td>4.9</td>
<td>146</td>
</tr>
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<td>L</td>
<td>I</td>
<td>AmOT</td>
<td>47.8</td>
<td>0.0</td>
<td>17.7</td>
<td>181</td>
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<td>O</td>
<td>I</td>
<td>AMOT</td>
<td>46.7</td>
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<td>C2</td>
<td>II</td>
<td>California phase II</td>
<td>25.4</td>
<td>11.2</td>
<td>4.1</td>
<td>145</td>
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<tr>
<td>1B</td>
<td>II</td>
<td>Matrix B base</td>
<td>25.3</td>
<td>11.2</td>
<td>15.0</td>
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<tr>
<td>2B</td>
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<td>Base + RMH</td>
<td>35.1</td>
<td>10.4</td>
<td>11.2</td>
<td>157</td>
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<td>3B</td>
<td>II</td>
<td>Base + AH</td>
<td>22.1</td>
<td>10.4</td>
<td>13.3</td>
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<tr>
<td>4B</td>
<td>II</td>
<td>Base + AH + RMH</td>
<td>32.2</td>
<td>10.2</td>
<td>10.7</td>
<td>168</td>
</tr>
</tbody>
</table>

Fig. 2. Plot of ΔM/Δaromatic as a function of ΔM for 12 different AQIRP gasolines (Table 2). Curves 1 and 2 are taken from Fig. 1. ΔM/Δaromatic is equivalent to ΔROG. Each point represents an individual experiment. Changes in ΔM for an individual fuel were obtained by varying fuel initial concentrations.

Fig. 3. Comparison between observed total SOA concentrations produced from the oxidation of whole gasoline vapor and total SOA concentrations predicted to be formed solely from the fuel’s aromatic components.

We performed 20 smog chamber experiments with 12 different reformulated gasolines obtained from the Auto/Oil Air Quality Improvement Research Program (AQIRP) (Table 2) (15). Molecular speciation of the AQIRP fuels was used to calculate the reacted amount of each ROG (ΔROG) in the fuel mixture (16). We accomplished this procedure by quantifying the initial concentration of six to eight calibrated species present in each fuel using gas chromatography. Knowing the initial concentrations of these species, on the basis of the relative mass fractions of all the components in the fuel, we could calculate the initial concentration of every other species present. During the course of each experiment, the concentration time profiles of each of the calibrated species were measured and used along with their hydroxyl radical (OH) rate constants to determine the concentration time profile of OH in the chamber (17). Typical OH concentrations were 10⁷ molecules per cubic centimeter. This information, together with measured O₃ concentrations and the OH and O₃ rate constants for all other species, allowed us to determine the reacted amount of each species present in the fuel mixture during the course of an experiment.

The results of these experiments strongly support the hypothesis that aromatics play the predominant role in SOA formation as shown in Fig. 1, and assuming that all isomers of a given compound behave similarly, we see that points for all fuels other than RF-L fall within the range specified by the yield curves that describe the majority of SOA yields from the individual aromatic studies (curves 1 and 2 from Fig. 1) (19). If significant amounts of the SOA that was produced originated from species other than the aromatics, then most points would lie above the envelope specified by these two curves.

Using the curves for the 17 species shown in Fig. 1, and assuming that all isomers of a given compound behave similarly, we obtained yield curves for 19 of the 26 aromatics specified in Phase I of the AQIRP study. These 19 species represent, on average, 96% of Δaromatic for all fuels other than RF-A and RF-L. Of the 57 specified aromatic compounds for the AQIRP Phase II fuels, yield curves were available for 28, representing, on average, 95% of Δaromatic. Obtaining a yield value, corresponding to the amount of SOA formed in an individual experiment, for an individual aromatic (Y) and multiplying that value by the reacted amount of the respective aromatic (ΔROG) produces an estimate of the amount of SOA attributable to that given aromatic species. Summing these values for all aromatics gives a quantitative estimate of the amount of SOA (ΔM = ΣΔROG, Y) that was produced by the aromatic fraction of each fuel (Fig. 3). These results quantitatively support the hypothesis that aromatic content controls a fuel’s SOA formation potential. The average ratio of the SOA concentration predicted to be formed from a fuel’s aromatic constituents to the observed SOA concentration for all fuels, excluding RF-L, is 1.00 ± 0.16 (1σ). Thus, it is evident that aromatics dominate the process of SOA formation associated with the atmospheric oxidation of whole gasoline vapor. Given the chemical complexity of whole gasoline, the results of this study suggest that SOA formation in an urban airshed can be modeled using yield data such as those presented here.

REFERENCES AND NOTES

2. Fine particulate matter, also known as PM₂.₅ is, particles of diameter less than 2.5 μm, is the respirable fraction of atmospheric particulate matter.
SOA formed from the oxidation of this fuel. Because this 17% was not specified, 
aramatic for this fuel is most likely underestimated, explaining why this fuel 
do not fall within the envelope as all other fuels 
specified by curves 1 and 2 (Fig. 2).

(1994).

21. NIST Chemical Kinetics Database ver. 6.01; W. G. 
Mallard, F. Westley, J. T. Herron, R. F. Hampson, 
NIST Standard Reference Data, Gaithersburg, MD 
(1994).

22. E. S. C. Kwok and R. Atkinson, Atmos. Environ. A 

23. Temperature T_{soa} is the distillation temperature at 
which 90% of the fuel evaporates. It relates to a 
fuel’s heavy-end volatility. Fuels with high T_{soa} 
contain a significant fraction of heavy components. In 
Phase I of the AQIRP, only 143 compounds were 
speciated, and many of the heavy components (in 
cluding aromatics) were not accounted for.

In Phase II, 320 compounds were speciated, and 
many of the heavier aromatics were accounted for. 
Thus, more than 94% of the carbon, on average, 
as accounted for in all Phase II fuels (both high 
and low T_{soa}).

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Metathesis of Alkanes Catalyzed by 
Silica-Supported Transition Metal Hydrides

Véronique Vidal, Albert Théolier, Jean Thivolle-Cazat, 
Jean-Marie Basset*

The silica-supported transition metal hydrides ([Si-O-Si]=[Si-O-H]_xTa-H and ([Si-O-H])_yM-H 
(M, chromium or tungsten) catalyze the metathesis reaction of linear or branched alkanes 
into the next higher and lower alkanes at moderate temperature (25° to 200°C). With 
([Si-O-Si]=[Si-O-H]_xTa-H, ethane was transformed at room temperature into an equimolar 
mixture of propane and methane. Higher and lower homologs were obtained from propane, 
butane, and pentane as well as from branched alkanes such as isobutane and isopentane.

The mechanism of the step leading to carbon-carbon bond cleavage and formation likely 
involves a four-centered transition state between a tantalum-alkyl intermediate and a 
carbon-carbon σ-bond of a second molecule of alkane.

Paraffins, particularly methane and light alkanes, constitute an abundant yet low-
value fossil feedstock. Light alkanes would be very valuable if they could be transformed 
into higher molecular weight hydrocarbons (1); this represents a continuing 
scientific challenge (2). Here, we report observations of a catalytic reaction that we 

designate “metathesis of alkanes” and which, to our knowledge, has not previously 
been reported (3). The metathesis reaction proceeds by both the cleavage and the 
formation of the C-C bonds of aliphatic alkanes, which are transformed into a mixture of 
higher and lower homologs. It was observed in the presence of various silica-supported 
metal-hydride catalysts, particularly tanta-

The metathesis of alkanes (7) or alkynes (8), for which the cleavage of the 
molecule occurs selectively at the C=C or C≡C bond, the metathesis of acyclic alkanes 
seems to involve, at least to some extent, the reaction of all C=C bonds.

Thus, the reaction, even if it is selective in terms of the formation and cleavage of C-C 
bonds, is not restricted to the formation of the first higher and lower homologs but also 
can yield the next several higher and lower ones. The metathesis of acyclic olefins is 
hindered by thermodynamic limitations; such a reaction is close to thermoneutrality 
for most alkanes (9).

We recently reported that the reaction of 
Ta(CH_3),_x(C=CMe_3),_y(=CHCMe_3),_z(=Me, methyl) 
(10) with the surface hydroxyl groups of a 
dehydroxylated silica (11) leads to the formation of a mixture of two species: ([Si-O-H] 
Ta(CH_3),_x(C=CMe_3),_y(=CHCMe_3),_z(=Me) (56%) and 
([Si-O-H]_,_Ta(=C=CMe_3),_z(=CHCMe_3),_z(=CMe_3) (35%) (12). Treatment of these 
two surface complexes under hydrogen at 150°C 
night yields mainly a surface tantalum (III) 
monohydride, ([Si-O-Si]_x=[Si-O-H]_xTa-H ([Ta]), which has been fully char-
acterized by infrared spectroscopy, extended 
x-ray absorption fine structure (EXAFS) 
analysis, microanalysis, and quantitative 
chemical reactions (4).

When [Ta]=H was contacted at room 
temperature with a cyclic alkane (4, 13), no 
catalytic reaction occurred. Only a C-H
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