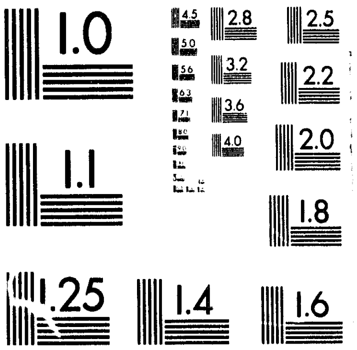
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1 of 1

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THE EFFECT OF CHEMICAL REACTIVITY ON SOURCE RECONCILIATION MODELING OF NONMETHANE HYDROCARBONS*

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ABSTRACT

Source fingerprints for 18 nonmethane hydrocarbons (NMHCs) containing 2-8 carbon atoms are currently used to apportion NMHC sources by chemical mass balance (CMB) modeling approaches. The source profiles must be stable in the troposphere to obtain accurate CMB model predictions. The NMHC source apportionment compounds are susceptible to gas phase oxidation in the atmosphere by hydroxyl radical (OH). Expected tropospheric lifetimes for peak concentrations of OH in typical urban air range from an hour to over 100 hours. When OH oxidation of a source profile for vehicle tailpipe emissions is simulated, significant changes occur in the distribution of the source apportionment compounds after a reaction time of 2-4 hr. These calculations indicate that sampling strategies to define source-receptor relationships of NMHCs by CMB modeling techniques must be carefully designed to minimize the possibility of NMHC oxidation by OH.

INTRODUCTION

The chemical mass balance (CMB) source reconciliation model has been used by a number of researchers to apportion nonmethane hydrocarbons (NMHCs) in urban air into their sources (Wadden et al., 1986; Scheff and Klevs, 1987; O'Shea and Scheff, 1988; Aronian et al., 1989). Source fingerprints for several NMHC sources that are composed of 18 NMHCs and 5 chlorinated hydrocarbons have been developed for CMB modeling applications (Scheff et al., 1989). These source apportionment compounds have been chosen on the basis of their ubiquity in ambient air and source emissions and also because most of the 23 species have hydroxyl radical (OH) reaction coefficients within an order of magnitude of each other. The major removal processes for these source apportionment hydrocarbon species will be gas phase oxidation by OH, nitrate radical (NO_3), and ozone (Finlayson-Pitts and Pitts, 1986). The emission profiles must be stable in the troposphere to obtain accurate NMHC source apportionments via CMB modeling techniques.

We have evaluated the gas phase oxidative removal processes for 18 CMB compounds and have estimated their lifetimes in a typical urban atmosphere. We then used the OH reaction loss identified as dominant to determine the possible effect of chemical oxidation on a typical vehicle tailpipe emission profile. These results are discussed here in light of the need to estimate OH reaction changes in CMB profiles in urban air and their subsequent effects on source-receptor modeling.

CALCULATIONS

The gas phase oxidation of hydrocarbons in the troposphere takes place primarily via the second-order reactions

$$\text{hydrocarbon} + \text{Ox} \xrightarrow{k} \text{products,} \tag{1}$$

where k is the second-order rate constant, Ox represents major oxidants in the troposphere, and the natural lifetime (τ) with respect to each oxidant is defined as

$$\tau_{\text{Ox}} = (k[\text{Ox}])^{-1}. \tag{2}$$

The principal gas phase oxidizing agents in the troposphere are OH during the daytime, NO_3 during the nighttime, and O_3 (ozone), which is present during both day and night. Table 1 contains reaction rate coefficients for OH, NO_3, and O_3 oxidation and the expected tropospheric lifetime of the 18 source apportionment compounds in typical urban air for peak levels of the oxidants (Finlayson-Pitts and Pitts, 1986; Atkinson, 1990).

As Table 1 shows, OH is the principal oxidant of concern for CMB model compounds. OH is formed in the atmosphere, primarily via the following reactions (Finlayson-Pitts and Pitts, 1986):

$$O_3 + h\upsilon\,(\lambda < 320\text{ nm}) \rightarrow O_2(^1\Delta_g) + O(^1D) \tag{3}$$

$$O(^1D) + H_2O \rightarrow 2OH \tag{4}$$

$$\text{HONO} + h\upsilon\ (\lambda < 400\text{ nm}) \rightarrow \text{OH} + \text{NO} \tag{5}$$

$$\text{H}_2\text{O}_2 + h\upsilon\ (\lambda < 360\text{ nm}) \rightarrow 2\text{OH} \tag{6}$$

Because light intensity is important in the formation of OH, concentrations are essentially zero at daybreak, increase throughout the daylight hours, and return to zero at night. Concentrations of HONO increase throughout the night and rapidly decrease after sunrise as a result of photolysis (Harris et al., 1982). Levels in heavily polluted air are 2-8 ppbv (Pitts et al., 1983). HONO can be formed in the atmosphere and is also emitted as a primary pollutant in vehicle exhaust. HONO photolysis can be a major source of OH in polluted urban atmospheres at dawn. After daybreak, as NMHCs are oxidized by OH, ozone is produced, and a steady-state concentration of OH is maintained via ozone photolysis.

We used the data in Table 1 in the following solution to the differential equation for the second-order reaction of hydrocarbons with OH,

$$\ln(A/A^{\circ}) = -k[\text{OH}]t, \tag{7}$$

where A° = initial concentration of the hydrocarbon,
A = concentration of the hydrocarbon at time, t, and
$[\text{OH}]$ = hydroxyl radical concentration,

to estimate the effect of chemical oxidation by OH on the integrity of a source fingerprint for vehicle tailpipe emissions. Because a steady-state concentration of OH is attained in the troposphere and the reactions of the hydrocarbons are not limited by [OH], the oxidations are treated as pseudo-first-order reactions. The final hydrocarbon concentrations after reaction periods of 2 and 4 hr were calculated and used to derive source fingerprints. Reactions of hydrocarbons with NO_3 and O_3 were neglected because they react with hydrocarbons much more slowly than OH (Table 1). This approach will be used to examine tendencies for the composition of the emission profile to change as the emissions are transported from the source to the receptor site.

RESULTS AND DISCUSSION

The natural lifetimes of the source apportionment compounds with respect to oxidation by OH range from about 1 hr for propene to over 100 hr for ethane. Oxidation by NO_3 and O_3 appear to be insignificant for CMB compounds. The effect of OH oxidation on a vehicle tailpipe fingerprint was apparent within a relatively short time span of 2 hr (Fig. 1). The most marked change in the fingerprint occurs for n-butane and the unsaturated and aromatic compounds. These species distinguish tailpipe emissions from refueling and petroleum refinery emissions (Scheff et al., 1989). For example, some similarities are apparent between the aged vehicle tailpipe emission fingerprint (4 hr reaction time) and a fingerprint for petroleum refinery emissions (Fig. 2). Within 2-4 hr during peak concentrations of OH, hydrocarbon oxidation is significant enough to alter emission profiles as they are transported from sources to receptor sites.

Doskey et al. (1991) presented data for 43 hydrocarbons that they identified in various NMHC source emissions. The 25 species that were found in addition to the 18 CMB model compounds could also be considered for CMB modeling applications. However, the expected tropospheric lifetimes with respect to OH oxidation for many of the additional compounds (Table 2) are shorter than those for the 18 CMB compounds (Table 1).

Ambient air samples for CMB model analysis are typically taken in the morning during seasons when ambient temperatures are low to minimize the potential for NMHC oxidation by OH (Aronian et al., 1989). However, this strategy may not be adequate because of the importance of HONO photolysis as a source of OH in polluted atmospheres during the early morning hours. Furthermore, as NMHC oxidation proceeds throughout the day, ozone photolysis will produce a steady-state level of OH. Meteorology must also be taken into account. For example, if samples are taken in the early morning hours and stagnant conditions prevailed overnight, oxidized emissions from the previous day may be sampled the following morning.

CONCLUSIONS

Gas phase oxidation of nonmethane hydrocarbons by OH during daylight hours in a typical urban atmosphere is a significant removal mechanism. OH sources at daybreak include HONO photolysis, while OH concentrations during the day are supported by ozone photolysis. Using peak concentrations of OH, we showed from theoretical calculations that the hydrocarbon distribution of vehicle tailpipe emissions can be significantly altered within a period of 2-4 hr. These calculations indicate that sampling strategies designed to evaluate source-receptor impacts by CMB modeling techniques should be designed so that gas phase oxidation of source apportionment compounds is minimized. The sensitivity of source apportionments by CMB modeling techniques to oxidation of CMB compounds should be determined.

ACKNOWLEDGEMENTS

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Table 1. Reactivity data for CMB model compounds*

	OH		NO_3		O_3	
	k x 10^{12a} (cm^3 molecule^{-1} s^{-1})	τ (hr)	k x 10^{17b} (cm^3 molecule^{-1} s^{-1})	τ (days)	k x 10^{18a} (cm^3 molecule^{-1} s^{-1})	τ (hr)
Ethene	8.52	3.26	21	5.0	1.7	65
Acetylene	0.90	31	-	-	<0.01	>500 d
Propene	26.3	1.06	940	0.11	11.3	9.83
				-	-	-
Ethane	0.268	104	-	-	-	-
Propane	1.15	24.1	-	-	-	-
Isobutane	2.34	11.9	9.7	11	-	-
n-Butane	2.54	10.94	6.5	16	<9.8 x 10^{-6}	>1300 a
Isopentane	3.9	7.12	-	-		-
n-Pentane	3.94	7.05	8.0	13	-	-
2,3-Dimethylbutane	6.3	4.4	40.6	2.59	-	-
2-Methylpentane	5.6	5.0	-	-	-	-
3-Methylpentane	5.7	4.9	-	-	-	-
n-Hexane	5.61	4.95	10.5	10.0	-	-
2,4-Dimethylpentane	5.1	5.5	-	-	-	-
Cyclohexane	7.49	3.71	13.4	7.85	-	-
						-
Benzene	1.23	22.6	≤2.0	≥53	-	-
Toluene	5.96	4.66	3.2	33	<1.01	>500 d
Ethylbenzene	7.1	3.9	-	-	-	-
p-Xylene	14.3	1.94	25	4.2	-	-
m-Xylene	23.6	1.18	14	7.5	-	-
o-Xylene	13.7	2.03	20	5.3	-	-

*[OH] = 1 x 10^7 radicals cm^{-3}; [NO_3] = 1.1 x 10^{10} radicals cm^{-3}; [O_3] = 2.5 x 10^{12} molecules cm^{-3}.

[a] 298°K

[b] 296° ± 2°K

Table 2. Reactivity data for OH oxidation of additional NMHCs*

	k x 10^{12} (cm^3 $molecule^{-1}$ s^{-1})	τ (hr)
Cyclopentane	5.16	5.38
Methylcyclopentane	-	-
2,3-Dimethylpentane	-	-
2-Methylhexane	-	-
3-Methylhexane	-	-
n-Heptane	7.15	3.89
2,2,4-Trimethylpentane	3.68	7.55
Methylcyclohexane	10.4	2.67
2,5-Dimethylhexane	-	-
2,3,4-Trimethylpentane	7.0	3.97
2-Methylheptane	-	-
4-Methylheptane	-	-
n-Octane	8.68	3.20
n-Decane	11.6	2.39
n-Undecane	13.2	2.10
n-Propylbenzene	6.0	4.63
m-Ethyltoluene	19.2	2.26
o-Ethyltoluene	12.3	1.45
p-Ethyltoluene	12.1	2.30
1,3,5-Trimethylbenzene	57.5	29 min
1,2,4-Trimethylbenzene	32.5	51 min
1,2,3-Trimethylbenzene	32.7	51 min
1,2,3,5-Tetramethylbenzene	-	-

*[OH] = 1 x 10^7 radicals cm^{-3}

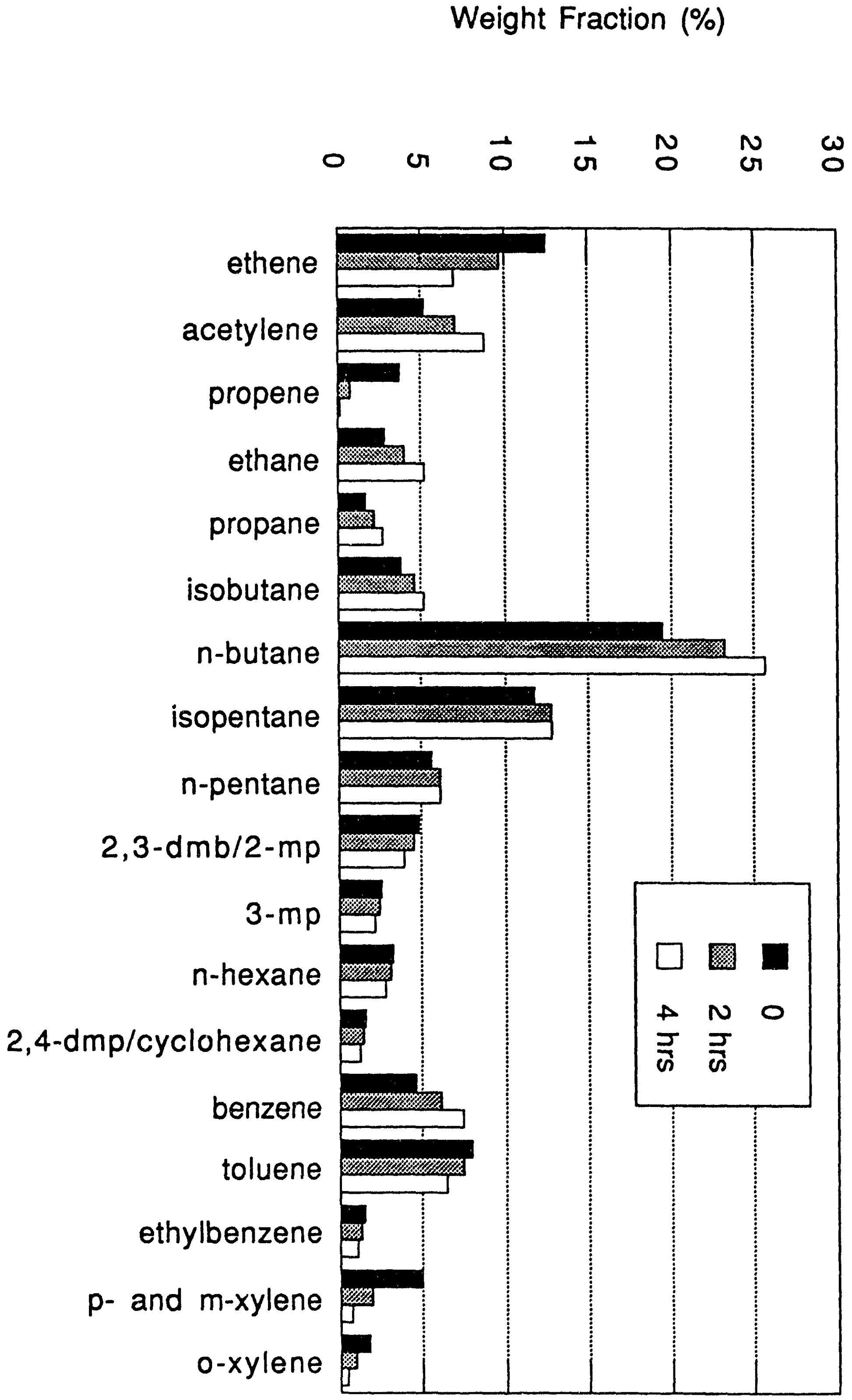
[a] 298° K

Figure Captions

Figure 1. Oxidation of vehicle tailpipe emission profile by OH (dmb, dimethylbutane, mp, methylpentane, dmp, dimethylpentane).

Figure 2. Comparison of aged (4 hr oxidation by OH) vehicle tailpipe emission profile with petroleum refinery emission profile (dmb, dimethylbutane, mp, methylpentane, dmp, dimethylpentane).

Figure 1.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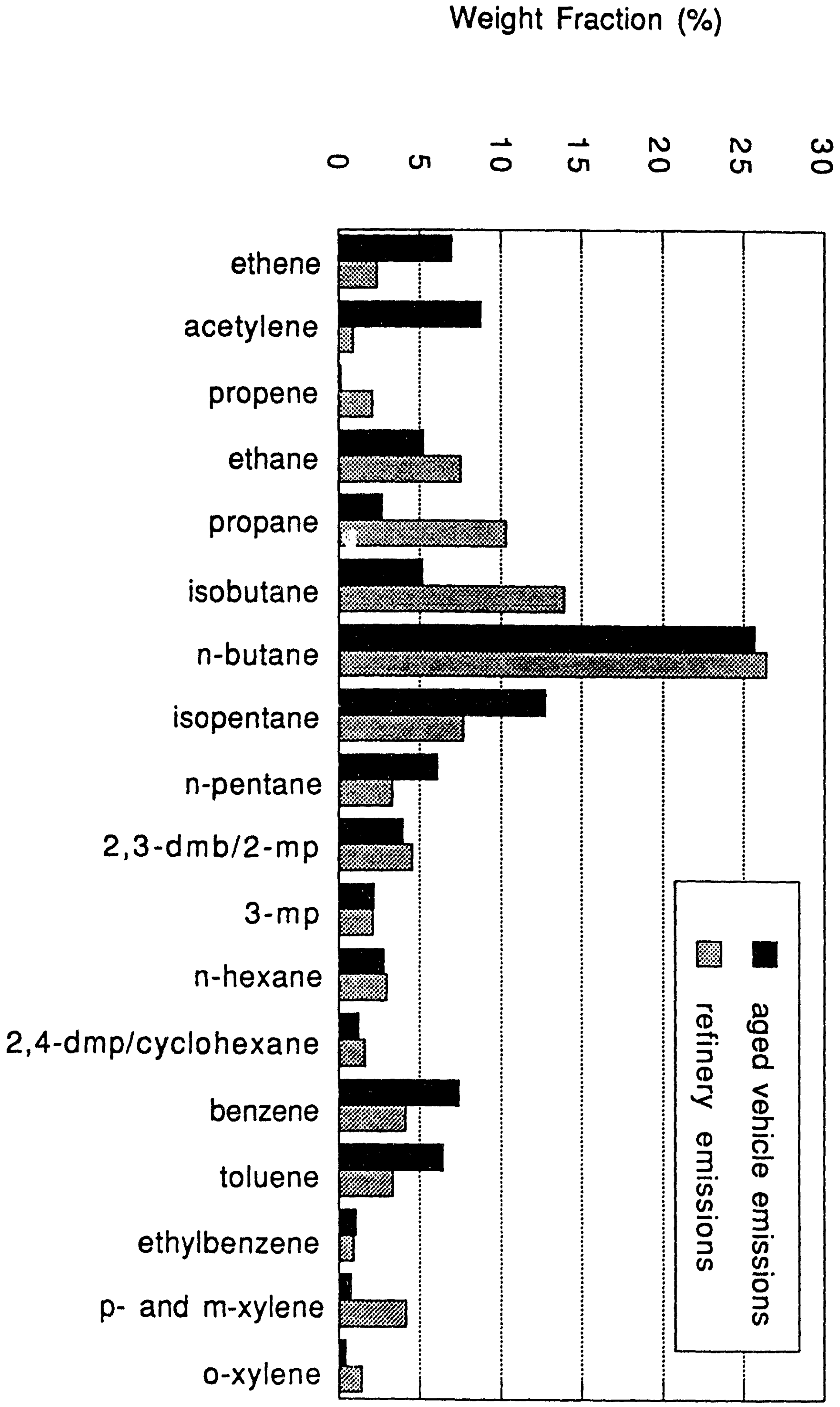
10
15
20
25
30
ethene
acetylene
propene
ethane
propane
isobutane
n-butane
isopentane
n-pentane
2,3-dmb/2-mp
3-mp
n-hexane
2,4-dmp/cyclohexane
benzene
toluene
ethylbenzene
p- and m-xylene
o-xylene
0
2 hrs
4 hrs

Figure 2.


Weight Fraction (%)
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5
10
15
20
25
30
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acetylene
propene
ethane
propane
isobutane
n-butane
isopentane
n-pentane
2,3-dmb/2-mp
3-mp
n-hexane
2,4-dmp/cyclohexane
benzene
toluene
ethylbenzene
p- and m-xylene
o-xylene
■ aged vehicle emissions
▨ refinery emissions

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