Studies of the Atmospheric Chemistry of Energy-Related Volatile Organic Compounds and of their Atmospheric Reaction Products

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Presented at:
DOE Atmospheric Sciences Program Meeting
March 19-21, 2002
Albuquerque, NM

At the End of Year 1 of this Program

Studies Completed

- Kinetics of OH + methyl- and dimethylnaphthalenes.
- Kinetics of NO_3 + methyl- and dimethylnaphthalenes.
- Photolysis rates of nitronaphthalenes and methylnitronaphthalenes.

Work in Progress

- Products of OH + biogenic VOCs, using API-MS and SPME/derivatization techniques.
- Products of NO_3 + monoterpenes, using API-MS and GC techniques.

Atmospheric Chemistry of Selected Polycyclic Aromatic Compounds

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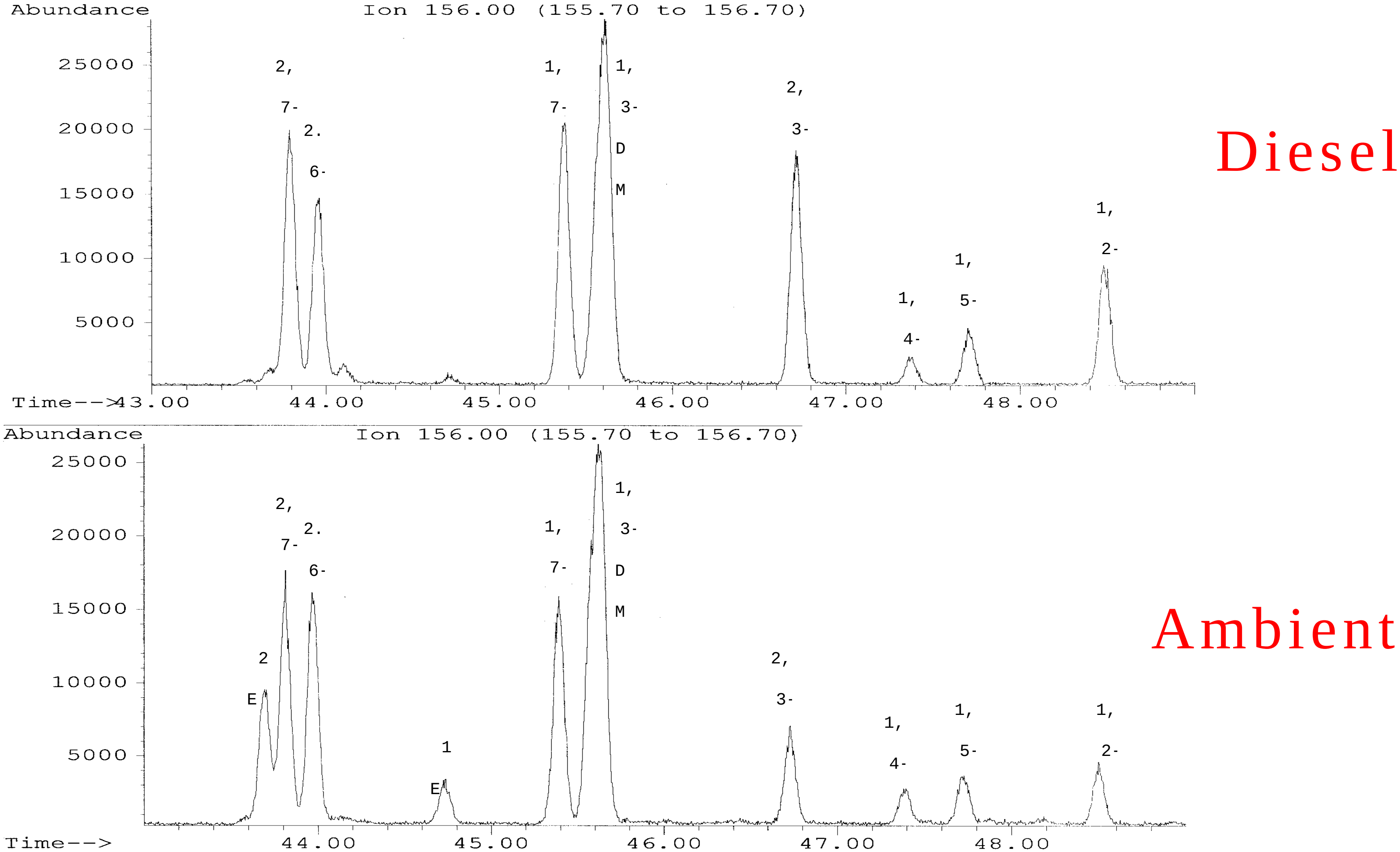
Aromatic VOCs and PAHs in Ambient Air

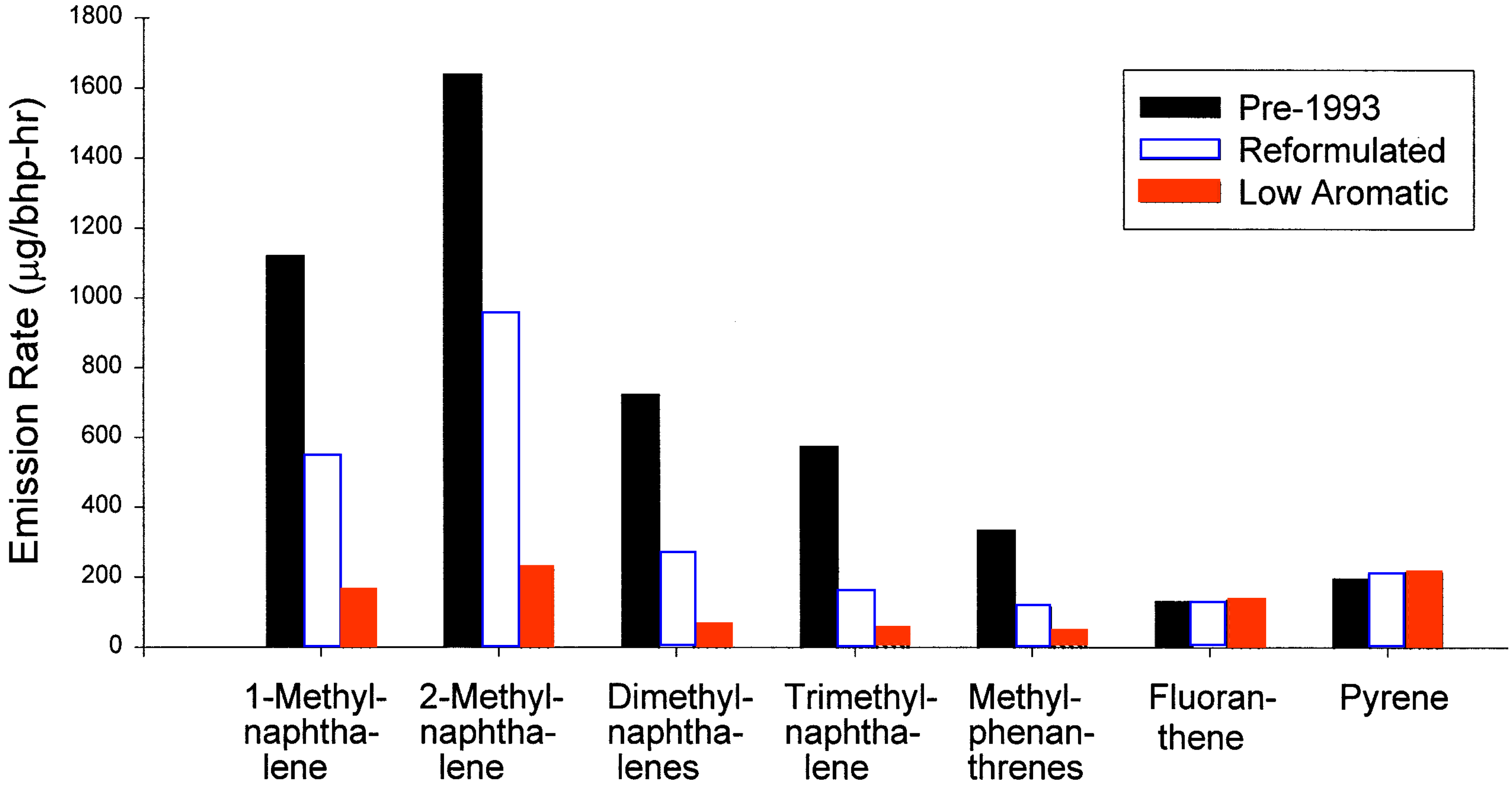
- from volatilized fuel
- formed during combustion

<u>Gasoline</u>	<u>Diesel</u>
BTEX	Naphthalene
Naphthalene	Methylnaphthalenes
PAHs	C_2-naphthalenes
	Methylphenanthrenes
	PAHs

Dimethylnaphthalenes



Total PAH in Diesel Exhaus



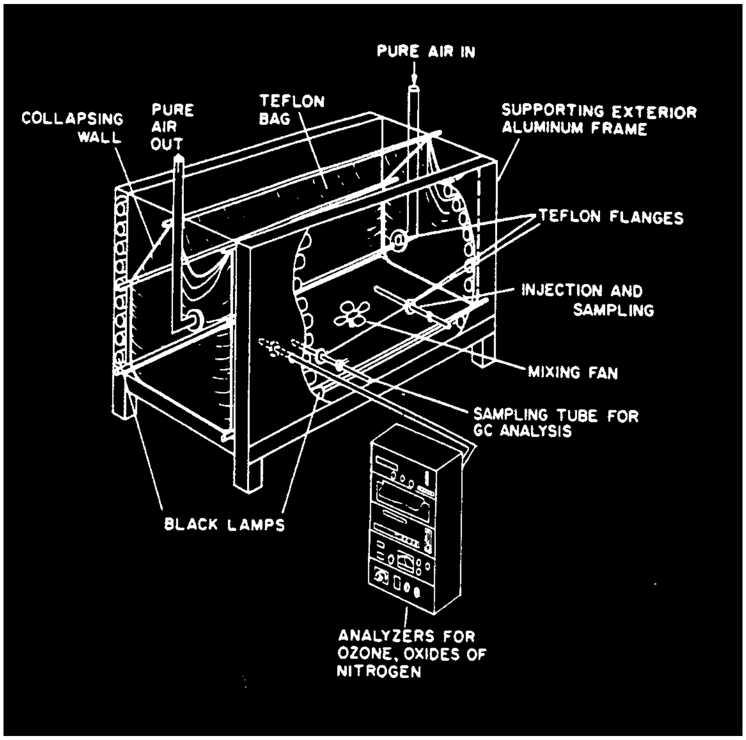
% PAH-wt in fuel	Pre-1993	Reformulated
	8%	

GAS-PHASE CHEMICALS

Major Atmospheric Loss Processes Are:

- Photolysis
- Reaction with Hydroxyl (OH) Radical (during daylight hours)
- Reaction with Nitrate (NO_3) Radical (during nighttime hours)
- Reaction with Ozone (O_3)

Indoor Teflon Chamber



Experimental Conditions

<u>OH Radical Generation</u>:

$CH_3ONO + h\nu \rightarrow CH_3O + NO$

$CH_3O + O_2 \rightarrow HCHO + HO_2$

$HO_2 + NO \rightarrow OH + NO_2$

<u>NO_3 Radical Generation</u>:

$N_2O_5 \rightarrow NO_3 + NO_2$

Relative rate methods used; for

$$\text{OH or } NO_3 + \text{ aromatic} \rightarrow \text{products} \qquad (1)$$

$$\text{OH or } NO_3 + \text{ reference compound} \rightarrow \text{products} \qquad (2)$$

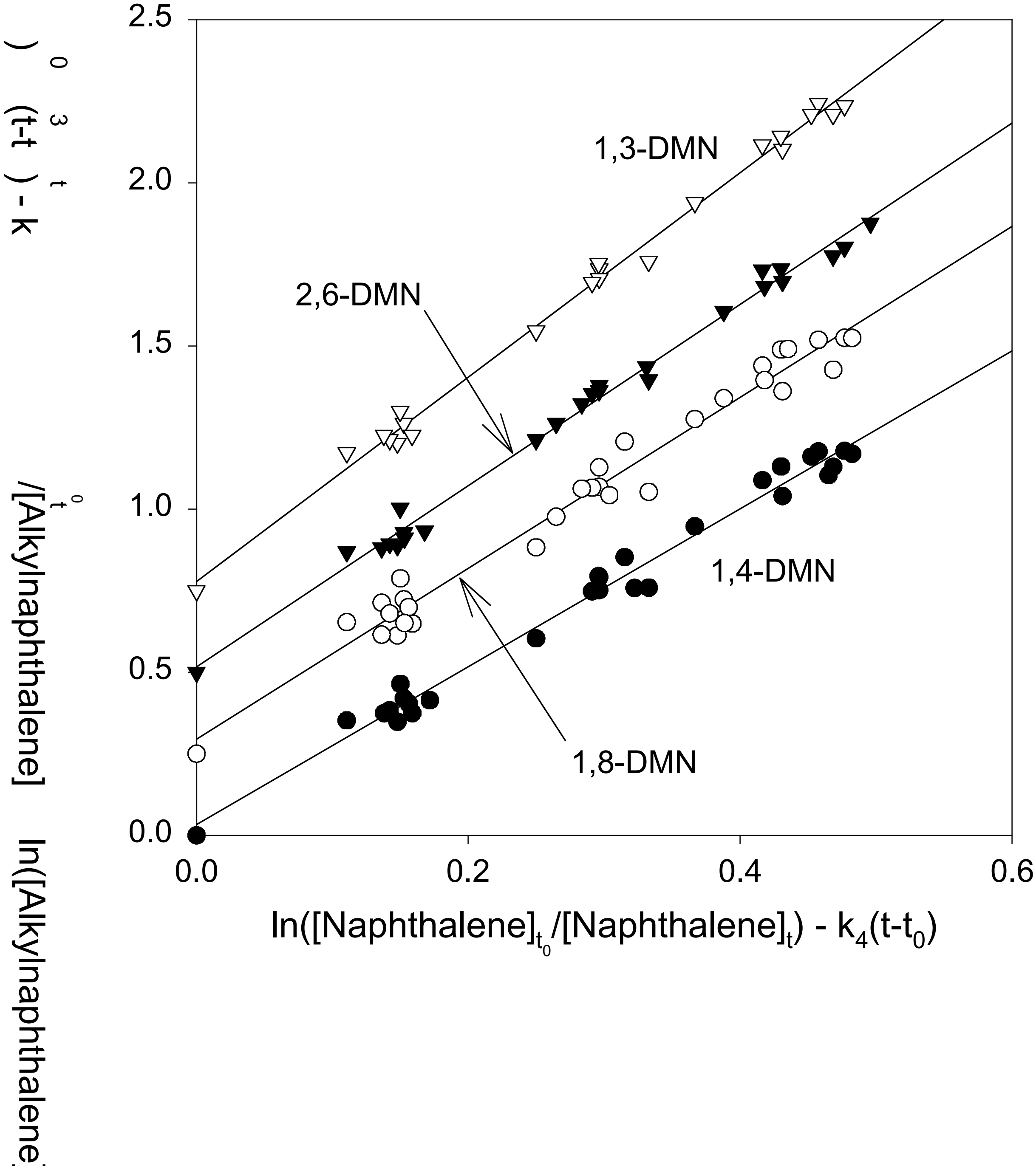
then

$$\ln\left(\frac{[\text{aromatic}]_{to}}{[\text{aromatic}]_t}\right) = \frac{k_1}{k_2} \ln\left(\frac{[\text{reference compound}]_{to}}{[\text{reference compound}]_t}\right) \qquad (I)$$

Minor corrections for measured wall losses and for additions to the chamber were taken into account.

Initial concentrations of aromatics were in the range 0.1-1 ppm. 0.1-1.0 liter samples were collected on Tenax solid adsorbent with thermal desorption and GC-FID analyses.

Plots of Rate Equation for the gas-phase reactions of the OH radical with 1,3-DMN, 1,4-DMN, 1,8-DMN and 2,6-DMN with naphthalene as the reference compound.



OH Rate Constants

Compound	10^{11} x k_{OH} (cm^3 $molecule^{-1}$ s^{-1}) This work	Literature	Reference
Naphthalene	2.44 ± 0.28	2.24 ± 0.15	Atkinson et al., 1984
	2.39 ± 0.10	2.35 ± 0.06	Biermann et al., 1985
		2.59 ± 0.24	Atkinson/Aschmann, 1986
		2.3	Brubaker/Hites, 1998
1-MN	4.09 ± 0.20	4.95 ± 0.66	Atkinson/Aschmann, 1987
		3.6	Banceu et al., 2001
2-MN	4.86 ± 0.25	4.83 ± 0.61	Atkinson/Aschmann, 1986
		5.1	Banceu et al., 2001
1-EN	3.64 ± 0.41		
2-EN	4.02 ± 0.55		
1,2-DMN	5.96 ± 0.55		
1,3-DMN	7.49 ± 0.39	2.2	Banceu et al., 2001
1,4-DMN	5.79 ± 0.36		
1,5-DMN	6.01 ± 0.35		
1,6-DMN	6.34 ± 0.36		
1,7-DMN	6.79 ± 0.45		
1,8-DMN	6.27 ± 0.43		
2,3-DMN	6.15 ± 0.47	7.09 ± 0.83	Atkinson/Aschmann, 1986
		2.2	Banceu et al., 2001
2,6-DMN	6.65 ± 0.35		
2,7-DMN	6.87 ± 0.43		

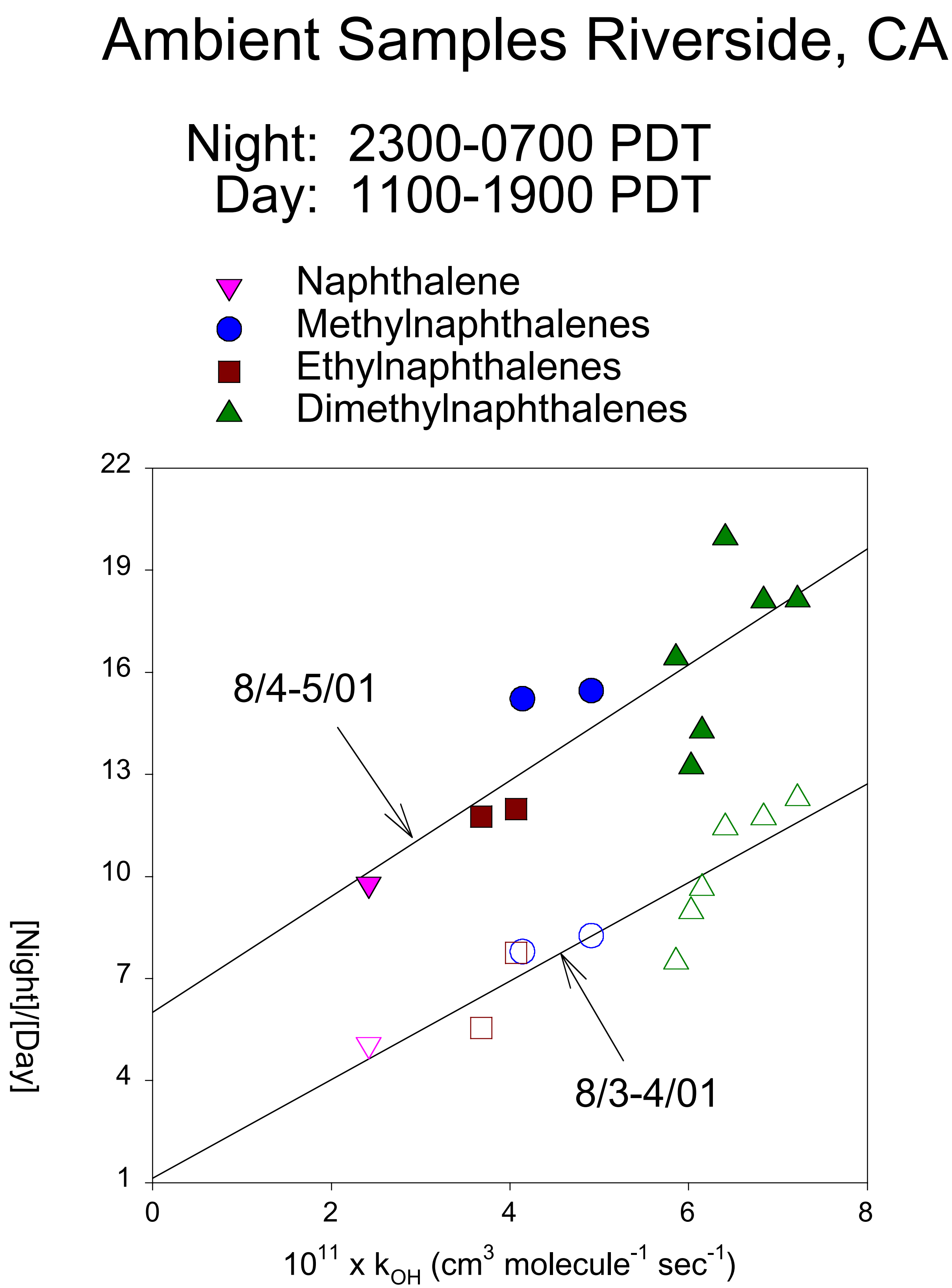
Atmospheric Lifetimes

Compound	τ (hours) Daytime[a] OH	Urban[b] NO_3	High[c] NO_3
Naphthalene	5.8	6100	92
1-MN	3.4	3100	47
2-MN	2.9	2200	33
1-EN	3.8	2300	34
2-EN	3.5	2800	42
1,2-DMN	2.3	350	5.2
1,3-DMN	1.9	1000	16
1,4-DMN	2.4	1700	26
1,5-DMN	2.3	1600	24
1,6-DMN	2.2	1300	20
1,7-DMN	2.0	1600	25
1,8-DMN	2.2	105	1.6
2,3-DMN	2.3	1500	22
2,6-DMN	2.1	1000	16
2,7-DMN	2.0	1100	16

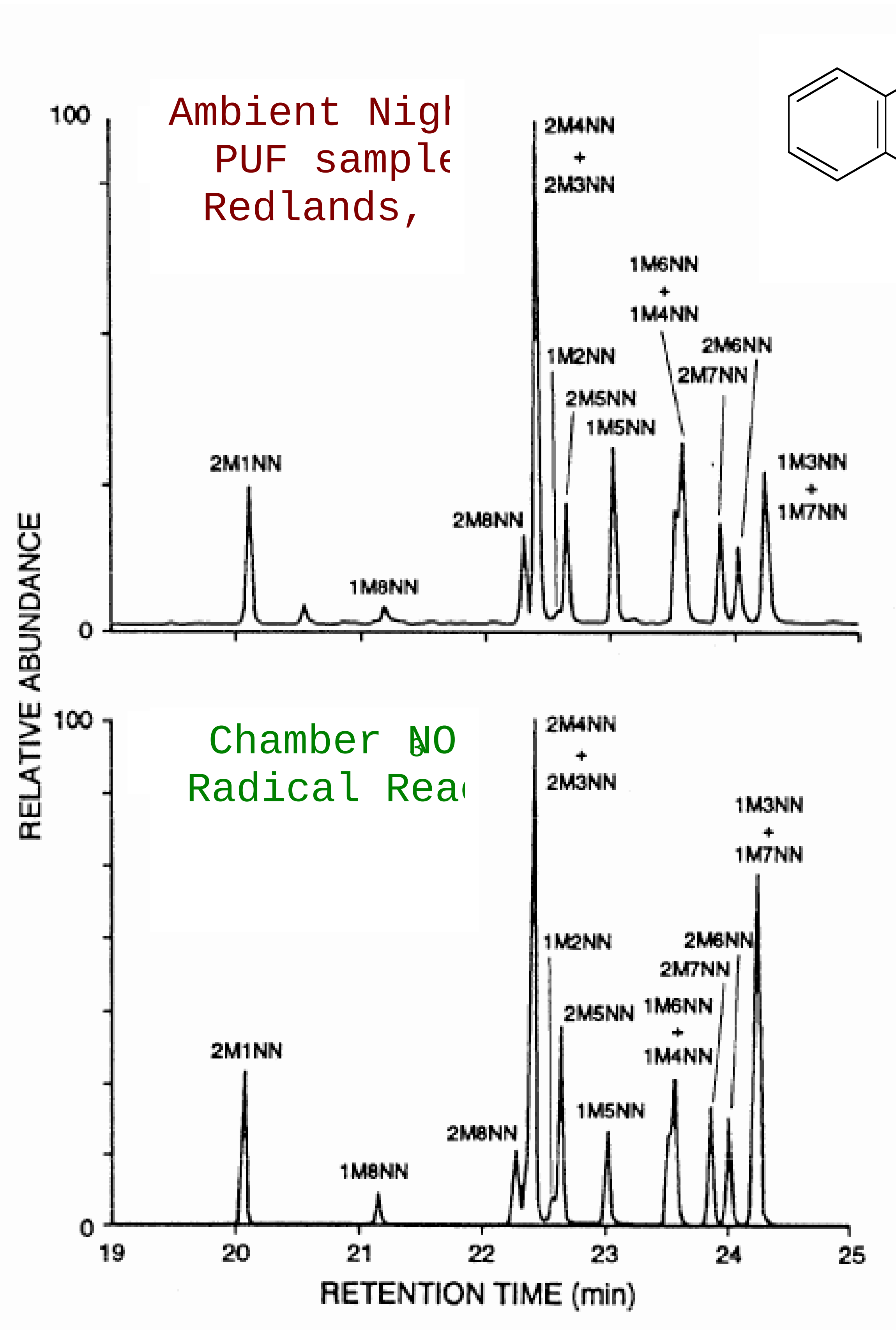
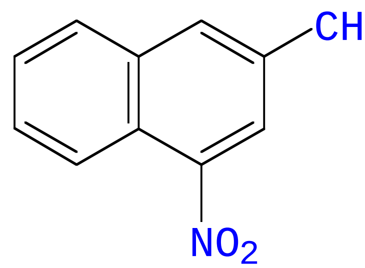
[a]Assumed [OH] = 2×10^6 molecule cm^{-3}.

[b]Assumed [NO_3] = 5×10^8 and [NO_2] = 2.5×10^{11} molecule cm^{-3}.

[c]Maximum reported [NO_3] = 1.0×10^{10} and [NO_2] = 8.3×10^{11} molecule cm^{-3}.



Ambient Samples Riverside, CA
Night: 2300-0700 PDT
Day: 1100-1900 PDT
Naphthalene
Methylnaphthalenes
Ethylnaphthalenes
Dimethylnaphthalenes
8/4-5/01
8/3-4/01
[Night]/[Day]
10^11 x k_OH (cm^3 molecule^-1 sec^-1)
22
19
16
13
10
7
4
1
0
2
4
6
8


Ambient Nigh
PUF sample
Redlands,
Chamber NO3
Radical Rea
RELATIVE ABUNDANCE
100
0
2M4NN + 2M3NN
1M2NN
2M5NN
1M5NN
1M6NN + 1M4NN
2M6NN
2M7NN
1M3NN + 1M7NN
2M1NN
1M8NN
2M8NN
19
20
21
22
23
24
25
RETENTION TIME (min)

CH
NO2

KINETICS OF THE GAS-PHASE REACTIONS OF OH RADICALS WITH VOLATILE ORGANIC COMPOUNDS

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REVIEW AND EVALUATION

RATE CONSTANTS FOR OH + VOCs

- Web-based only, at: http://cnas.ucr.edu/~aprc/atkinson.html

  in pdf files.

- To date, sections completed are:

  1. OH + VOCs. Introduction

  1.1. OH + Alkanes and Cycloalkanes. Introduction

  1.1.1. OH + Methane and Ethane

  1.1.2. OH + C_3- through C_5-Alkanes

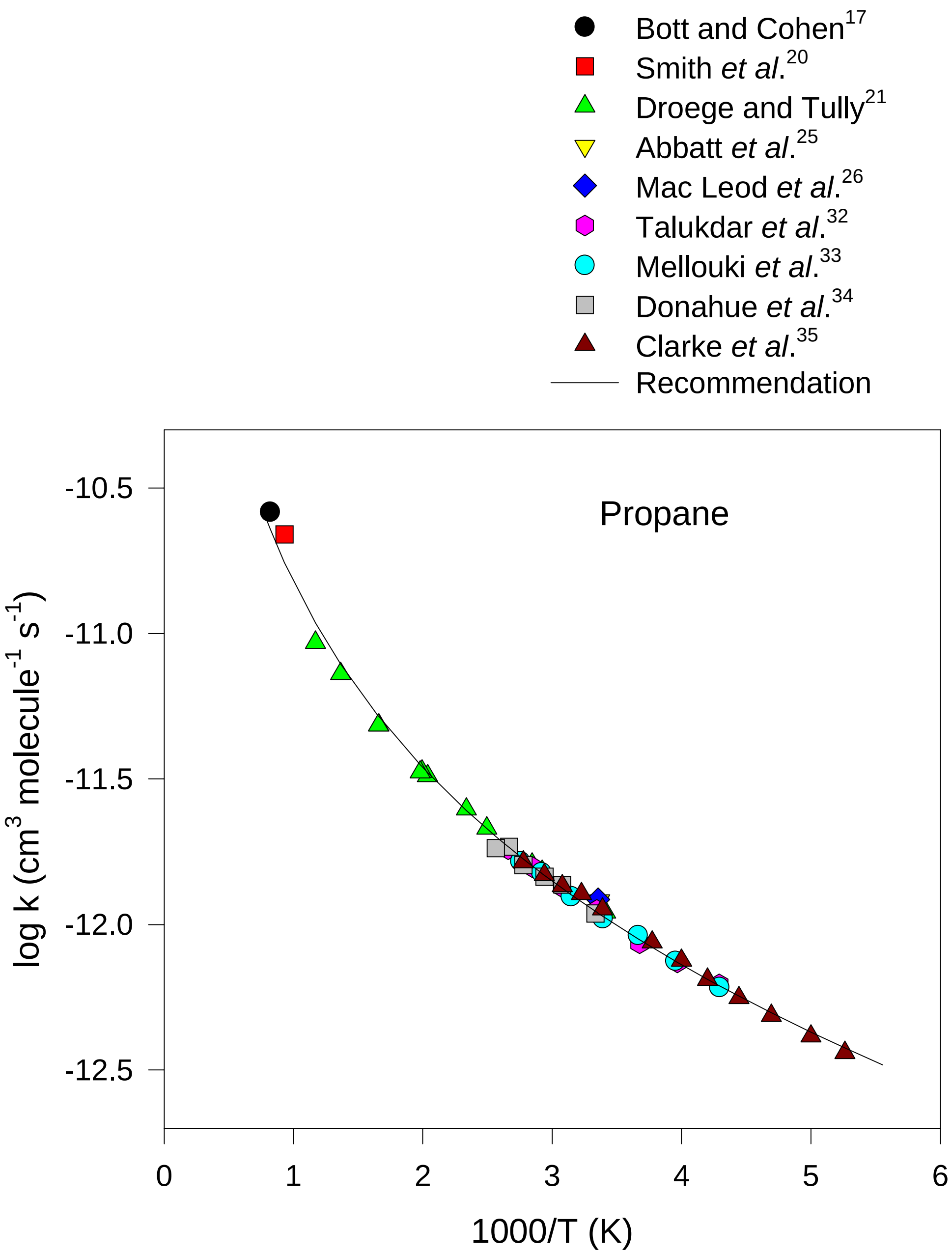
  1.1.3. OH + C_6- through C_{16}-Alkanes

  1.6. OH + Phosphorus-Containing Compounds

n-OCTANE March 2002

Rate constants and temperature-dependent parameters.

$10^{12} \times k$ (cm^3 $molecule^{-1}$ s^{-1})	n	B (K)	$10^{12} \times k$ (cm^3 $molecule^{-1}$ s^{-1})	at T (K)	Technique	Reference	Temperature Range (K)
29.5		364 ± 61	8.42 ± 1.25 12.0 ± 0.7 10.8 ± 0.5 14.3 ± 0.4	296 371 371 497	FP-KS	Greiner, 1970[1]	296-497
			8.25 ± 0.11	299 ± 2	RR [relative to k(n-hexane) = 5.22×10^{-12}]	Atkinson *et al*., 1982[2]	
			8.03	300 ± 3	RR [relative to k(n-butane) = 2.38×10^{-12}]	Behnke *et al*., 1987[3]	
			8.16 ± 0.28	312	RR [relative to k(n-heptane) = 6.97×10^{-12}]	Nolting *et al*., 1988[4]	
			44.2	1078 ± 16	SH-RA	Koffend and Cohen, 1996[5]	


Bott and Cohen[17]
Smith et al.[20]
Droege and Tully[21]
Abbatt et al.[25]
Mac Leod et al.[26]
Talukdar et al.[32]
Mellouki et al.[33]
Donahue et al.[34]
Clarke et al.[35]
Recommendation
Propane
-10.5
-11.0
-11.5
-12.0
-12.5
log k (cm3 molecule-1 s-1)
0
1
2
3
4
5
6
1000/T (K)