SUPPLEMENTAL MATERIAL

to

**FORMATION OF NITRO-PRODUCTS FROM THE GAS-PHASE OH RADICAL-
INITIATED REACTIONS OF TOLUENE, NAPHTHALENE AND BIPHENYL: EFFECT
OF NO₂ CONCENTRATION**

Noriko Nishino, Roger Atkinson and Janet Arey

Air Pollution Research Center

University of California

Riverside, CA 92521

Pages: 6

Tables: 1

Figures: 2

In addition to the data analysis presented in the manuscript, Equation (2),

$$\text{nitroaromatic yield (\%)} = \alpha k_2 [\text{NO}_2] / (k_2 [\text{NO}_2] + k_3 [\text{O}_2]) \quad (2)$$

where α is the yield of the nitroaromatic from the reaction of the OH-aromatic adduct with NO_2 and k_2 and k_3 are the rate constants for the reactions of the OH-aromatic adduct with NO_2 and O_2 , respectively (see Scheme 1), can be rearranged to

$$(\text{nitroaromatic yield})^{-1} = \alpha^{-1} (1 + (k_3 [\text{O}_2] / k_2 [\text{NO}_2])) = \alpha^{-1} + (k_3 [\text{O}_2] / \alpha k_2 [\text{NO}_2]) \quad (2a)$$

A plot of $1/(\text{nitroaromatic yield})$ against $1/[\text{NO}_2]$ should then have an intercept of $1/\alpha$ and a slope of $k_3 [\text{O}_2] / \alpha k_2$. Plots of Equation (2a) are shown in Figures S1 and S2 for formation of 3-nitrotoluene from toluene and 3-nitrobiphenyl from biphenyl (Figure S1) and formation of 1- and 2-nitronaphthalene from naphthalene (Figure S2), omitting in each case the data obtained at NO_2 concentrations between 0.075 and 0.15 ppmV. The intercepts and slopes obtained from least-squares analyses of these data are given in Table S1. While the intercepts are subject to large uncertainties, especially for the toluene and biphenyl reactions, in all cases the values of α derived from the plots in Figures S1 and S2 are consistent with those obtained from visual fits (or in the case of the toluene reaction, from a least-squares fit using literature values of k_2 and k_3) of the data to Equation (2) [see Figures 1-3]. Using the values of α derived from Figures 1-3, the slopes of the plots in Figures S1 and S2, and assuming that $k_2 = 3.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (1) for all OH-aromatic adducts, then the values of k_3 and the concentration of NO_2 at which $k_2 [\text{NO}_2] = k_3 [\text{O}_2]$ can be obtained and these are listed in Table S1. The values of k_3 obtained

using plots of Equation (2a) and from visual fits of the data to Equation (2) [or, for toluene, the measured rate constant of Koch et al. (1)] are in good agreement, and well within the likely overall uncertainties which are probably close to a factor of 2.

References

1. Koch, R.; Knispel, R.; Elend, M.; Siese, M.; Zetzsch, C., Consecutive reactions of aromatic-OH adducts with NO, NO₂ and O₂: benzene, naphthalene, toluene, m- and p-xylene, hexamethylbenzene, phenol, m-cresol and aniline. *Atmos. Chem. Phys.*, **2007**, 7, 2057-2071.

Figure S1. Plots of Equation (IIa) for formation of 3-nitrotoluene and 3-nitrobiphenyl from the OH radical-initiated reactions of toluene and biphenyl, respectively. Data obtained in the NO₂ concentrations range 0.075-0.15 ppmV have been omitted (see text).

Figure S2. Plots of Equation (IIa) for formation of 1- and 2-nitronaphthalene from the OH radical-initiated reaction of naphthalene. Data obtained in the NO₂ concentrations range 0.075-0.15 ppmV have been omitted (see text).

Table S1. Parameters obtained from least-squares analyses of data plotted in Figures S1 and S2 (see text)

aromatic	intercept ^a and α (%)	slope ^a	α (%) from Figs. 1-3	$10^{17} \times k_3$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) ^b	$k_2[\text{NO}_2] = k_3[\text{O}_2]$ at NO ₂ (ppmV) of
3-nitrotoluene	-0.08 ± 0.81 ($>1.4\%$)	0.63 ± 0.06	6.9	74 (57) ^c	4.3
1-nitronaphthalene	2.7 ± 2.1 (0.36%)	0.18 ± 0.07	0.35	1.1 (1.0) ^d	0.06
2-nitronaphthalene	1.5 ± 0.9 (0.67%)	0.10 ± 0.03	0.60	1.0 (1.0) ^d	0.06
3-nitrobiphenyl	0.10 ± 0.52 (10%)	0.08 ± 0.02	12	16 (10) ^d	0.9

^aIndicated errors are two least-squares standard deviations.

^bObtained using the values of α from Figures 1-3.

^cRate constant measured by Koch et al. (1).

^dRate constants derived from visual fits of data in Figures 2 and 3, assuming a rate constant k_2 of $3.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for all OH-aromatic adducts, as suggested by the rate data of Koch et al. (1).