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On the Uncertainties in the Rate Coefficients for OH Reactions with Hydrocarbons, and the Rate Coefficients of the 1,3,5-Trimethylbenzene and *m*-Xylene Reactions with OH Radicals in the Gas Phase

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Rate coefficients for the gas-phase reactions of 1,3,5-trimethylbenzene (TMB) and *m*-xylene with the OH radical relative to 10 reference compounds were measured yielding $(57.3 \pm 5.3) \times 10^{-12}$ and $(22.0 \pm 2.7) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, respectively (uncertainties are 2σ). These uncertainties arise from a combination of the uncertainty of the reference rate coefficients and experimental errors; thus, the average uncertainty for the rate coefficients of the 10 reference compounds must be less than or equal to the scatter observed in this study. For 16 and 21 measurements with TMB and *m*-xylene, the observed scatter was ±10% and ±12%, respectively. The average of the uncertainties is significantly smaller than the uncertainties that are frequently assumed or recommended, which range from ±15 to 35%. Absolute rate coefficients for the reaction of TMB and *m*-xylene with ozone are also reported. Relative rate coefficients for reaction with OH for di-*n*-butyl ether, methylcyclohexane, cyclopentane, toluene, and cyclohexane of 28.9 ± 2.3, 9.4 ± 0.6, 4.8 ± 0.6, 5.5 ± 0.5, and 7.2 ± 0.6 ($\times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) were also measured (uncertainties indicate the whole range of scatter).

Introduction

1,3,5-Trimethylbenzene (TMB) and *m*-xylene (1,3-dimethylbenzene) are a significant component of the suite of hydrocarbons that lead to oxidant and aerosol formation in urban areas.[1−4] Their dominant loss pathway is reaction with the OH radical. Since these compounds react very slowly with O_3 and rapidly with OH they are also ideal tracers for OH in ambient air[5] and have been used to trace OH radical formation from ozone reactions with alkenes.[6] Recent reviews report an uncertainty for the reaction rate coefficient of OH at 298 K with TMB of ±35% on the basis of five studies (Table 1). For the *m*-xylene the reported uncertainty is ±25% on the basis of 11 studies (Table 1). Finally, recent sensitivity studies for photochemical models have concluded that the uncertainties in rate coefficients for OH reacting with organics cause a significant portion of the uncertainty in model predictions and that there is need for higher accuracy.[7−10]

We have used the relative rate technique to measure the OH rate coefficients of TMB and *m*-xylene using 10 reference compounds. The reference compounds (Table 2) cover more than 1 order of magnitude in reactivity and include several classes of organic compounds. Further we report the rate coefficients for OH reaction with cyclopentane, cyclohexane, toluene, di-*n*-butyl ether, and methylcyclohexane, measurements of the ozone reaction with TMB and *m*-xylene, and wall loss rates for NO_x, O_3, TMB, *m*-xylene, and other hydrocarbons in Teflon chambers.

TABLE 1: Summary of Rate Coefficients for Reaction of the Target Compounds with OH Radicals

k(OH) × 10^{12} cm^3 molecule^{-1} s^{-1}	method[a]	temp (K)	ref
	TMB (1,3,5-trimethylbenzene)		
47.2 ± 4.8	FP-RF	297.1	13
44.4 ± 5.3	RR *n*-butane (2.61)	304 ± 1	14
62.4 ± 7.5	FP-RF	298.3	15
51.9 ± 6.3	FP-RF	318.4	15
38.9 ± 5.3	RR *n*-hexane (5.61)	RT	16
57.5 ± 3.0	RR propene (26.6 ± 4.0)	296 ± 2	11
57.5 ± 20.1	**recommended rate coeff.**	**295−325**	**11**
57.3 ± 5.3	RR 10 reference compounds	296 ± 2	this work
	m-Xylene (1,3-Dimethylbenzene)		
23.6 ± 2.4	FP-RF	297.3	13
19.6 ± 1.4	RR *n*-butane (2.61)	304 ± 1	14
18.8 ± 3.8	RR *n*-butane (2.62)	304 ± 1	17
24.0 ± 2.5	FP-RF	298.3	15
24.4 ± 3.6	FP-RF	314.5	15
20.6 ± 1.3	FP-RF	298	18
19.6	RR ethene (8.44)	300	19
26.5 ± 2.5	FP-RF	250	20
25.6 ± 4.3	FP-RF	269	20
25.4 ± 3.5	FP-RF	298	20
21.4 ± 1.4	RR cyclohexane (7.51)	299 ± 2	21
22.3 ± 0.7	RR *n*-hexane (5.61)	RT	16
23.1	RR cyclohexane (7.47)	297	22
23 ± 0.6	RR propene (26.6 ± 4.0)	296 ± 2	11
23.6 ± 5.9	**recommended rate coeff.**	**250−315**	**11**
22.0 ± 2.7	RR 10 reference compounds	296 ± 2	this work

[a] RR: Measured relative to a reference compound; values in parentheses indicate the rate coefficient for the reference compound assumed in that study ($\times 10^{12}$ cm^3 molecule^{-1} s^{-1}). FP-RF: Flash photolysis-resonance fluorescence.

Estimated overall uncertainties recommended in the literature[11,12] for all hydrocarbons, including some for which tens of rate coefficient measurements have been made, are equal to or higher than ±15%; most are ±25% or more. Throughout dozens of studies, results from absolute and relative methods are in good agreement with one another. While it is not likely that a significant systematic error pervades the whole data set,

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TABLE 2: Rate Coefficients of TMB and *m*-Xylene Relative to Different Reference Compounds from Least-Squares Analysis of the Data Plotted According to Eq 1

(a) TMB

experiment	ref compd	k_{OH}(ref) ($\times 10^{12}$ cm^3 molecule^{-1} s^{-1}) from lit.[a]	k_{OH}(TMB)[b] ($\times 10^{12}$ cm^3 molecule^{-1} s^{-1})
III	butadiene	66.6 ± 13	54.1 ± 0.4
IV	butadiene		54.0 ± 0.7
VIII	*trans*-2-butene	64.0 ± 13	57.1 ± 0.5
II	di-*n*-butyl ether	28.8 ± 10	54.4 ± 1
VI	propene	26.3 ± 4.0	56.0 ± 1
I	methylcyclohexane	10.4 ± 0.3	58.2 ± 0.5
II	methylcyclohexane		58.2 ± 1.6
III	*m*-xylene	23.6 ± 5.9	62.0 ± 0.3
I	*n*-nonane	10.2 ± 2.6	52.2 ± 0.5
V	*n*-nonane		55.2 ± 0.2
IV	cyclohexane	7.49 ± 1.9	60.4 ± 0.5
VII	cyclohexane		58.2 ± 0.7
VII	toluene	5.96 ± 1.5	60.0 ± 0.9
VI	toluene		58.9 ± 0.8
V	cyclopentane	5.16 ± 1.0	55.3 ± 0.4
VIII	cyclopentane		61.6 ± 0.8
X	di-*n*-butyl ether	28.8 ± 10	69.6 ± 3.3
X	propene	26.3 ± 4.0	49.3 ± 0.4
IX	cyclohexane	7.49 ± 1.9	61.4 ± 0.9
IX	cyclopentane	5.16 ± 1.0	59.1 ± 1.3

(b) *m*-Xylene

experiment	ref compd	k_{OH}(ref) ($\times 10^{12}$ cm^3 molecule^{-1} s^{-1}) from lit.[a]	k_{OH}(*m*-xylene)[b] ($\times 10^{12}$ cm^3 molecule^{-1} s^{-1})
XIV	butadiene	66.6 ± 13	20.4 ± 0.3
XIII	butadiene		19.5 ± 0.4
III	butadiene		20.6 ± 0.06
XII	butadiene		21.0 ± 0.2
VII	*trans*-2-butene	64 ± 13	21.7 ± 0.2
XI	*trans*-2-butene		21.2 ± 0.2
VII	TMB	57.5 ± 20.1	21.8 ± 0.04
XIV	di-*n*-butyl ether	28.8 ± 10	21.4 ± 0.1
XVII	di-*n*-butyl ether		21.5 ± 0.1
XV	propene	26.3 ± 4.0	21.5 ± 0.4
XVI	propene		21.9 ± 0.3
XI	methylcyclohexane	10.4 ± 0.3	24.5 ± 0.2
XVII	*n*-nonane	10.2 ± 2.6	21.3 ± 0.2
XV	*n*-nonane		21.5 ± 0.2
XI	cyclohexane	7.49 ± 1.9	23.3 ± 0.4
XII	cyclohexane		22.1 ± 0.1
XIII	toluene	5.96 ± 1.5	22.9 ± 0.3
XII	toluene		22.7 ± 0.3
XVI	cyclopentane	5.16 ± 1.0	23.4 ± 0.4
XIII	cyclopentane		23.3 ± 0.3
VII	cyclopentane		23.4 ± 0.3

[a] Di-*n*-butyl ether;[12] methylcyclohexane,[33] 1984; all others.[11] [b] The uncertainties include the 2σ-standard error of the calculated slopes (see text).

this possibility cannot be completely excluded. The uncertainty of relative rate measurements results from a combination of random and systematic experimental errors and the uncertainty of the reference rate coefficient. Consequently the average of the reference rate coefficient uncertainties must be less than the scatter observed in measurements of the target rate coefficient. The average of the uncertainties is a measure of the overall consistency of the whole set of rate coefficients, as well as a sense of the magnitude of the typical uncertainty for this set of OH-hydrocarbon rate coefficients. In the absence of a systematic bias in the many absolute rate coefficient measurements, it indicates that the OH reaction rate coefficients are much better understood than previously thought.

Experimental Description

Experiments were carried out in four different 250-L heat-sealed Teflon chambers at room temperature (296 ± 2 K) and atmospheric pressure (760 ± 10 Torr). Gas mixtures were prepared in ambient air purified by a zero-air generator (Thermo Environmental, model 111). The quality of the zero air was checked periodically. The concentrations of hydrocarbons, nitrogen oxides, and ozone were always below the detection limits (about 3 and 5 ppb, respectively). Target hydrocarbons (TMB or *m*-xylene) and two or three reference compounds (100 ppb−2 ppm), methyl nitrite (5−10 ppm), and NO (5−14 ppm) were added by injection of the liquid or gas using graduated microsyringes. Liquid hydrocarbons were evaporated into a stream of purified air as the chamber was filled. Once the gas mixture was prepared, the chamber was mixed by moving the walls and left to stand for at least 1 h to allow the reactants to stabilize. Several measurements of organic compounds, NO_x and O_3, in the dark chamber were made to establish the initial concentrations. The initial concentrations were varied to investigate this possible source of systematic bias (Table 1).

The chamber was surrounded by variable intensity UV lights, which were regulated with a potentiometer (Silvania Blacklights, 40 W, F40/350BL). Hydroxyl radicals were generated by photolysis of methyl nitrite (CH_3ONO; R1−R3). Nitric oxide was added to the reactant mixtures to convert peroxy radicals to OH (R3) and to avoid formation of elevated O_3 (R6).

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \tag{R1}$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \tag{R2}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{R3}$$

$$NO_2 + h\nu \rightarrow NO + O(^3P) \tag{R4}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \tag{R5}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{R6}$$

Analyses of the composition of the mixture were made regularly during the 4−5 h irradiations. Hydrocarbons were measured every 30 min through a heated Teflon line with a gas chromatograph/flame ionization detector (HP 5890), equipped with a DB-1 column (J&W, 30 m × 0.32 mm, 1 μm) and computer-controlled sampling and injection. Nitrogen oxides were measured with a chemiluminescence analyzer (Thermo Environmental, model 42) and ozone with UV absorption (Dasibi, model 1003RS). O_3 and NO_x measurements are affected by methyl nitrite: 10−15% of the methyl nitrite concentration was measured as NO_x due to partial conversion to NO over the molybdenum catalyst, and roughly 0.5% of the methyl nitrite (which absorbs in the UV) was detected as ozone. Additionally, aromatic compounds and their oxidation products may have affected the ozone measurements.

Experiments to determine the rate coefficients for the reaction of TMB and *m*-xylene with O_3 were conducted as above except that the chamber was dark and the reactive mixture consisted of 200−600 ppb of aromatic compound and 5−15 ppm of di-*n*-butyl ether (DBE) in zero air. DBE was added to scavenge OH radicals that may result from ozonolysis of the aromatic compounds or products. Once the initial hydrocarbon concentrations had stabilized, 4−10 ppm of ozone was added to the mixture. The ozone was generated by flowing pure oxygen (150 mL/min) through a mercury lamp generator (JeLight, model

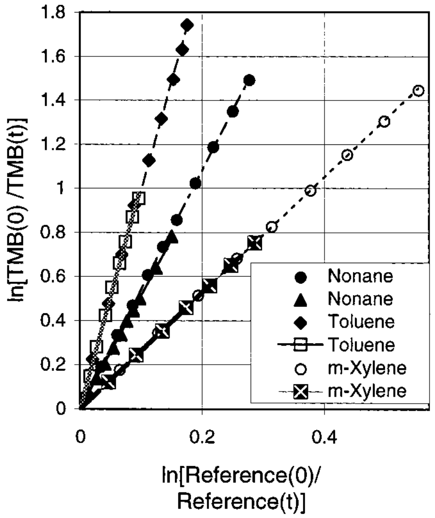

Figure 1. Linear least-squares analyses (lines) of the data sets (symbols) for the reaction of OH with TMB using *n*-nonane (experiments I and V), toluene (experiments VI and VII), and *m*-xylene (experiments III and VIII) as reference compounds.

600). In 8−15 min up to 2 L of O_3/O_2 mixture was added while the Teflon chamber was mixed. After ozone addition the hydrocarbon concentrations were measured every 2 h for a period of 30−40 h; O_3 measurements were made every 2 h over about half of this period.

Results and Discussion

The principle of the relative rate method for determination of rate coefficients is the simultaneous monitoring of the disappearance of the studied compound (*target*) and a reference compound:

$$\mathrm{OH} + \text{target} \xrightarrow{k_7} \text{products} \qquad (R7)$$

$$\mathrm{OH} + \text{reference} \xrightarrow{k_8} \text{products} \qquad (R8)$$

As long as other loss processes for the hydrocarbons are minimal, the hydrocarbon decay can be described by

$$\ln \frac{[\text{target}]_0}{[\text{target}]_t} = \frac{k_7}{k_8} \ln \frac{[\text{reference}]_0}{[\text{reference}]_t} \qquad (1)$$

where $[X_i]_0$ and $[X_i]_t$ refer to the concentrations at time = 0 and t, respectively. Plots of $\ln([\text{target}]_0/[\text{target}]_t)$ vs $\ln([\text{reference}]_0/[\text{reference}]_t)$ should yield straight lines of slope k_7/k_8 and zero intercept.

Sixteen experiments to determine the OH rate coefficients of TMB and *m*-xylene were conducted each using two or three reference compounds. The resulting data were plotted according to eq 1, and the rate coefficient ratios k_7/k_8 were derived from least-squares regression analyses. Rate coefficients together with uncertainties calculated from the standard error of the slopes are given in Table 2. For consistency all rate coefficients were calculated relative to the values recommended by Atkinson[11,12] including *m*-xylene and TMB. Experiments IX and X (Table 2a) were performed with very high NO_x concentrations and are discussed separately. Figure 1, which shows pairs of experiments using TMB/*n*-nonane, TMB/toluene, and TMB/*m*-xylene, illustrates the good reproducibility between experiments using the same target/reference pairs (see also Table 2).

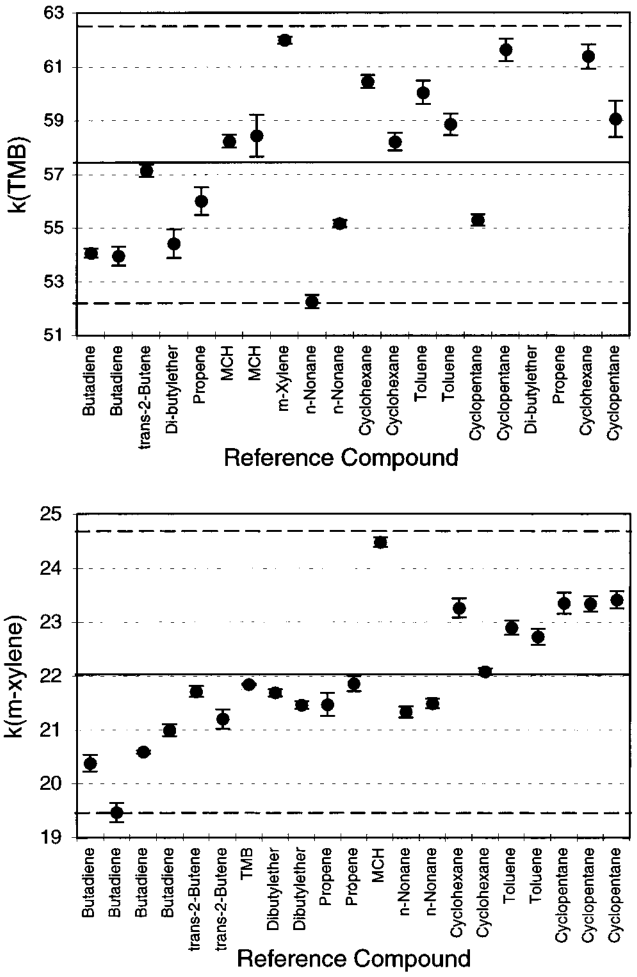

Figure 2. (a, top) Rate coefficients obtained for reaction of OH with TMB relative to 10 reference compounds in experiments I−VIII (Table 2a); (b, bottom) rate coefficients obtained for OH reaction with *m*-xylene relative to 10 reference compounds (Table 2b). The error bars indicate the 1σ-standard deviation of the slopes (eq 1) calculated by least-squares analysis. The solid lines represent the average rate coefficients and the dashed lines the overall uncertainties (2σ). MCH is methylcyclohexane.

Rate Coefficients for Hydrocarbon Reactions with OH Radicals. Sixteen measurements of k_{OH}(TMB) (experiments I−VIII) resulted in an average value of 57.3 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (solid line in Figure 2a), with a 2σ-standard deviation of ±10% (dashed lines in Figure 2a). This value is in excellent agreement with the rate coefficient recommended by Atkinson[11] of 57.5 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. In experiments III, VII, and XI−XVI we made 21 measurements of k_{OH}(*m*-xylene) relative to the same selection of reference compounds and found an average of 22.0 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Table 2b; solid line in Figure 2b) with a 2σ-standard deviation of ±12% (dashed lines in Figure 2b). This value is somewhat lower than the value recommended by Atkinson[11] of 23.6 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, but well within the stated uncertainty of ±25%.

Since experiments were conducted with two or three reference compounds, the rate coefficient of any reference compound could be calculated relative to another by plotting according to eq 1. However, once a compound has been designated a target, it cannot be used as a reference since the calculation of the rate coefficient of the remaining compounds would not provide independent information. This "elimination" process can be carried out in a number of possible combinations. To check for consistency, the relative rate coefficients for all compounds

TABLE 3: Rate Coefficients Calculated for the Reference Compounds by Comparing Them to Each Other

experiment[a]	target compd	ref compd	$k_{\mathrm{lit.}}$(ref) ($\times 10^{12}$ cm^3 molecule^{-1} s^{-1})	$k_{\mathrm{lit.}}$(target compd) ($\times 10^{12}$ cm^3 molecule^{-1} s^{-1})	k_{exptl}(target compd)[b] ($\times 10^{12}$ cm^3 molecule^{-1} s^{-1})	avg. k(target compd) ($\times 10^{12}$ cm^3 molecule^{-1} s^{-1}) (this work)[c]
XVII	di-*n*-butyl ether	*n*-nonane	10.2 ± 2.6	28.8	28.6 ± 0.2	28.9 ± 2.3
II	di-*n*-butyl ether	methylcyclohexane	10.4 ± 0.3		30.9 ± 0.3	
XIV	di-*n*-butyl ether	butadiene	66.6 ± 13		27.1 ± 0.3	
XI	methylcyclohexane	*trans*-2-butene	64.0 ± 13	10.4	9.0 ± 0.2	9.4 ± 0.6
I	methylcyclohexane	*n*-nonane	10.2 ± 2.6		9.3 ± 0.04	
XI	methylcyclohexane	cyclohexane	7.49 ± 1.9		9.9 ± 0.08	
V	cyclopentane	*n*-nonane	10.2 ± 2.6	5.16	5.1 ± 0.1	4.8 ± 0.6
XVI	cyclopentane	propene	26.3 ± 4.0		4.8 ± 0.08	
VIII	cyclopentane	*trans*-2-butene	64.0 ± 13		4.8 ± 0.2	
XIII	cyclopentane	butadiene	66.6 ± 13		4.3 ± 0.04	
XII	toluene	butadiene	66.6 ± 13	5.96	5.5 ± 0.06	5.5 ± 0.5
VI	toluene	propene	26.3 ± 4.0		5.7 ± 0.06	
XII	toluene	cyclohexane	7.49 ± 1.9		5.8 ± 0.08	
XIII	toluene	butadiene	66.6 ± 13		5.1 ± 0.1	
VII	cyclohexane	toluene	5.96 ± 1.5	7.49	7.7 ± 0.1	7.2 ± 0.6
IV	cyclohexane	butadiene	66.6 ± 13		6.7 ± 0.06	
XII	cyclohexane	butadiene	66.6 ± 13		7.1 ± 0.06	
XI	cyclohexane	*trans*-2-butene	64.0 ± 13		6.8 ± 0.2	
XV	*n*-nonane	propene	26.3 ± 4.0	10.2	10.2 ± 0.3	

[a] The very high concentration experiments X and IX were not included. [b] The uncertainties include the 2σ-standard error of the calculated slopes and do not consider the uncertainties of the reference rate coefficients. [c] The uncertainties reflect the whole range of scatter (see text). The averages were calculated before rounding to the reported k_{exptl}(target) (column 6).

TABLE 4: Summary of Ozone Experiments

experiment	initial ozone concentration (ppm)	end ozone concentration (ppm)	rate constant with ozone[a] $\times 10^{21}$ cm^3 molecule^{-1} s^{-1}
XVIII	2.6	2.3	k_{O3}(TMB) < 6.2 k_{O3}(*m*-xylene) < 3.3
XIX	10.3	9.2	k_{O3}(TMB) = (4.8 ± 1.4) k_{O3}(*m*-xylene) < 2.4
XX	12.2	9.7	k_{O3}(TMB) = (2.2 ± 1.2)
XXI	12.5	9.6	k_{O3}(TMB) = (1.8 ± 1.1)

[a] Uncertainties were calculated by combining the experimental error and uncertainties in the wall loss rates for the aromatic compounds (see text).

were calculated (not shown); all were in good agreement with the literature data (Table 2). Table 3 shows the calculations for five additional targets chosen from the reference compounds; their rate coefficients for OH reaction are ($\times 10^{-12}$ cm^3 molecule^{-1} s^{-1}): di-*n*-butyl ether, 28.9 ± 2.3; methylcyclohexane, 9.4 ± 0.6; cyclopentane, 4.8 ± 0.6; toluene, 5.5 ± 0.5; cyclohexane, 7.2 ± 0.6. The targets were chosen on the basis of two criteria: interest (e.g., only one measurement has been reported for methylcyclohexane in the literature) and to provide the best statistics (each value is based on three or four observations). The stated uncertainties reflect the whole range of scatter in the measurements. In all cases, the results are in good agreement with the literature data and the range of scatter is less than ±12% (Table 3).

O_3 Reactions. The rate coefficient of the TMB reaction with ozone was measured in four experiments (Table 4). In two of these experiments *m*-xylene was added to determine the *m*-xylene + ozone rate coefficient as well. Di-*n*-butyl ether was added as an OH scavenger in 30-fold excess. In contrast to the reaction with OH, the ozonolysis of aromatic compounds is very slow and wall losses for TMB and *m*-xylene result in decay rates that are comparable to reaction with about 10 ppm of ozone. Wall loss was also the predominant loss process for ozone. The rate coefficients for ozone reaction with the aromatics were derived by fitting a model to the experimental data. For the *m*-xylene−O_3 reaction, an upper limit of 2.9×10^{-21} cm^3 molecule^{-1} s^{-1} was calculated. The average rate coefficient for the TMB−O_3 reaction calculated from experiments XIX−XXI was $2.9 \pm 1.9 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} (1σ). Both results are in agreement with rate coefficients found in the literature; the value calculated for 298 K from the Arrhenius expression of Toby et al.[24] for *m*-xylene is 8.5×10^{-22} cm^3 molecule^{-1} s^{-1}, with an uncertainty of a factor of 5. Pate et al. reported $(2.2 \pm 0.6) \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} for TMB reaction with O_3.[23] Finally, one additional experiment was conducted without DBE to scavenge OH. Considerably higher rate coefficients were observed; 14×10^{-21} and 9×10^{-21} cm^3 molecule^{-1} s^{-1} for TMB and *m*-xylene, respectively. This suggests that OH radicals might be formed due to ozone reaction with the aromatic compounds or products.

Random and Systematic Errors in Relative Rate Measurements. Uncertainties in relative rate coefficients arise from a combination of measurement error and uncertainties in the reference rate coefficients. Measurement errors arise from variability in the GC signal and systematic errors from side reactions of the hydrocarbons with oxidants other than OH. Since relative measurements do not depend on the absolute concentrations of the reactants, calibration errors can be ignored. Random errors can be estimated from the residuals from the regression lines for the log−log plots (Figure 1); the 2σ-standard error of these slopes throughout was less than ±3% (Table 2). Brauers and Finlayson-Pitts[25] recently showed that a systematic error can result from using a least-squares analysis that does not account for random error in the concentration of the reference compound. Since this bias is proportional to the measurement error associated with the independent variable, in our case this systematic error from this source should be small. Nevertheless, the 2σ-standard deviation is a lower limit. Plotting k_{OH}(TMB) and k_{OH}(*m*-xylene) according to decreasing reactivity of the reference compounds (with respect to OH reactivity) reveals a slight but clear trend—the rate coefficients are slightly higher when calculated with respect to less reactive reference compounds. This trend indicates a systematic error due to reactions with other photooxidants.

The average OH concentration in the experiments was in the range $(0.7-1.6) \times 10^6$ cm^{-3}. Under these conditions 10 ppb of O_3 would cause 5−10% higher losses for propene and *trans*-

2-butene than OH chemistry alone. Formation of elevated ozone concentrations was completely suppressed with several parts per million of surplus NO, but this lead to high NO_2 concentrations resulting in potential side reactions with both NO_2 and $O(^3P)$ (R4−6). Since the concentrations of these photooxidants depend on the NO_x concentration (R4, R5) as well as the intensity of the irradiation, two experiments (IX, X) with exceptionally high NO_x concentrations (21 and 26 ppm) and maximal light intensity were conducted to investigate the effect of additional loss processes on the results. For experiment X, with propene as the reference compound, we found a significantly lower OH rate coefficient for TMB ($(49.8 \pm 0.4) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}) indicating that side reactions with NO_2, $O(^3P)$, and O_3 might have increased the alkene decay rate. In the same experiment, the rate coefficient calculated with respect to DBE was significantly higher; $k_{OH}(TMB) = (69.6 \pm 1.65) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. It seems that side reactions also increased the TMB losses relative to DBE.

Model Calculations. To estimate the contribution of side reactions, we constructed a model containing the reactions of hydrocarbons with OH, O_3, $O(^3P)$, and NO_2, as well as wall losses and inorganic reactions. $O(^3P)$ reacts 2−15 times more slowly with alkenes than OH and 20−50 times more slowly with aromatic compounds.[26] Reaction of $O(^3P)$ with alkanes is negligible. Rate coefficients for reaction of $O(^3P)$ with *m*-xylene, TMB, propene, and 1,3-butadiene are 0.4, 2.7, 4.0, and 20×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively.[27−29] The reactions of NO_2 are negligibly slow with hydrocarbons except conjugated dienes.[30,31] The rate coefficient for 1,3-butadiene is 3.0×10^{-20} cm^3 $molecule^{-1}$ s^{-1};[32] for propene the estimated upper limit is 1.4×10^{-21} cm^3 $molecule^{-1}$ s^{-1}.[31] Wall loss rates measured in our chambers were (10^{-6} s^{-1}): NO_x, 5 ± 2.5; O_3, 2 ± 1; TMB, 1.0 ± 0.3; *m*-xylene, 0.8 ± 0.3. Wall losses of other organics were negligible, with an estimated upper limit of 2×10^{-7} s^{-1}. Over the course of a typical experiment that lasted 4−5 h, 1−2% of the TMB and 3−4% of the *m*-xylene consumption was due to wall losses.

The model predictions are in good agreement with the experimental results; even for experiments with very high NO_x concentrations (IX and X), the model results agree except that the TMB rate coefficient relative to DBE is overestimated for experiment X. Figure 3 presents a comparison between experimental data and predicted concentrations for experiment X; calculations were made for the cases where losses due to reactions with NO_2, $O(^3P)$, and O_3 chemistry were included, and another where reaction with OH is the only hydrocarbon loss pathway. In this high-NO_x experiment, the hydrocarbon concentrations were affected considerably by loss processes other than reaction with OH radicals; about 20% of the alkene reacted with $O(^3P)$ and NO_2, leading to a significant underestimation of the target rate coefficient calculated with eq 1. In more typical experiments with lower NO_x concentrations, 8−15% of 1,3-butadiene losses were due to reaction with $O(^3P)$ and NO_2, 5−10% of propene reacted with $O(^3P)$, and about 3−5% of the aromatic compounds reacted with $O(^3P)$ or were lost to the walls. Losses due to ozone reaction were insignificant in all cases. These additional losses led to underestimation of the TMB and *m*-xylene rate coefficients relative to 1,3-butadiene and propene of (8 ± 4)% and (5 ± 3)%, respectively; the overestimation relative to aliphatic compounds was (3 ± 2)%. The model results show that the NO_x concentration was higher than necessary in some of the experiments; half of the NO_x would have been sufficient to avoid elevated ozone levels. Lower NO_x concentrations certainly would have decreased the impact of $O(^3P)$ and NO_2, and the overall scatter of the results might have been even smaller.

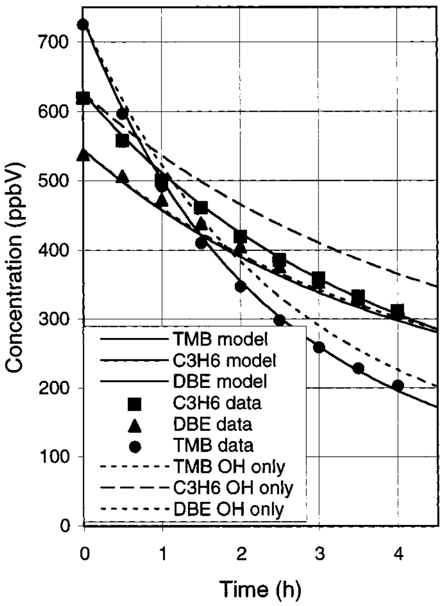

Figure 3. Comparison of the model with experimental results. Data (symbols) and model predictions (lines) for the hydrocarbon concentrations are plotted as a function of time for experiment X; this experiment had very high NO_x levels and high photolysis rates (see text). The solid lines were calculated including OH, $O(^3P)$, NO_2, and O_3 chemistry and wall losses, and dashed lines show the model predictions if the hydrocarbons react with OH only. C3H6 is propene and DBE is di-*n*-butyl ether.

The effects on the predicted rate coefficients derived from the model are too uncertain to provide useful corrections to the experimental data. On the other hand, the model does give an indication that the systematic error due to side reactions accounted for a large portion of the scatter in the experimental results.

Average Uncertainty of the Reference Rate Coefficients. The uncertainty of a rate coefficient measured with the relative-rate method is made up of the experimental error Δ(exptl), consisting of random and systematic error, and the uncertainty of the reference rate coefficient (Δk_{OH}(ref)), according to the equation (all uncertainties are in percentages):

$$\Delta k_{OH}(\text{target}) = (\Delta k_{OH}(\text{ref})^2 + \Delta(\text{exptl})^2)^{0.5} \qquad (2)$$

A conservative estimate of the average of the reference rate coefficient uncertainties can be derived by assuming that the scatter observed in the measurements of k_{OH}(target) arises exclusively from the uncertainty of the reference rate coefficients. In this case the average uncertainty of the reference compounds is just equal to the uncertainty derived for k_{OH}(target); the larger of the observed uncertainties was ±12% for k_{OH}(*m*-xylene). The experimental error, however, is not zero. In this study the random error is approximately ±3−4%. The model described above indicates that systematic errors might have caused a ±(3−8)% additional uncertainty. The best estimate for the experimental portion of the observed scatter is therefore (±5−9)%; thus, the average uncertainty of the reference compounds is ±(8−11)%. The *maximum* uncertainty in any one of the reference rate coefficients is the sum of the observed scatter plus the maximum error inherent in our measurements. This total ranges between ±15 and 21%.

It should be noted that this conclusion is only valid if the literature data does not contain an overall systematic bias. Most individual studies probably do contain a small systematic error. For both relative and absolute measurements these errors can be positive or negative; thus the whole data set should contain at most a small bias resulting from systematic errors. Except for methylcyclohexane (one relative rate study)[33] and *n*-nonane (five relative rate measurements),[11] the studies for all of the investigated compounds are divided about equally between absolute (e.g., flash photolysis-resonance fluorescence) and relative rate measurements. For the whole data set, the absolute measurements are consistent with one another, as evidenced by the absence of a trend between absolute vs relative rate studies. Thus it is not likely that the rate coefficients recommended by Atkinson[11,12] conceal a systematic error. The rate coefficients appear to be quite accurate, and within the set of compounds in this study there is no evidence that any one of the compounds carried a higher uncertainty than about ±15%; in many cases they are likely much smaller. Recently, a number of sensitivity studies conducted on photochemical models have drawn the conclusion that the rate coefficient uncertainties causes a significant portion of the uncertainty in the model predictions.[7−10] Our results indicate that many of the uncertainties may be much smaller than assumed in these studies and may be only a small contributor to the overall model uncertainties.

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