in the presence of NO is clearly understood.

Nevertheless, despite the uncertainties concerning some of the secondary reactions introduced by the presence of NO, the major observations made in our study of the gas-phase reaction of NO_2 with UDMH are consistent with a relatively simple and straightforward reaction mechanism, which is the same whether the reaction takes place in air or in N_2 . It should be noted that we have also studied the reactions of NO2 with hydrazine and methylhydrazine,¹¹ but found that these systems are apparently much more complex, and the reaction mechanisms involved are considerably more uncertain; although it is probable that the initial attack of NO_2 on these hydrazines is analogous to that in the UDMH system, i.e.

$$N_2H_4 + NO_2 \rightarrow HONO + H_2N-NH$$
 (14)

The hydrazyl (or methylhydrazyl) radical so formed, unlike

the dimethylhydrazyl radical (I) initially formed in the UDMH + NO_2 reactions, appears to react significantly with O_2 to form HO_2 and a diazene

$$H_2N-NH + O_2 \rightarrow HN=NH + HO_2$$
(15)

both of which react further, though the mechanism¹¹ is presently quite uncertain.

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Registry No. 1,1-Dimethylhydrazine, 57-14-7; tetramethyl-2-tetrazene, 6130-87-6; nitrogen dioxide, 10102-44-0; nitrous acid, 7782-77-6; N-nitrosodimethylamine, 62-75-9; nitric oxide, 10102-43-9.

Effects of Pressure on Product Yields in the NO_x Photooxidations of Selected Aromatic Hydrocarbons

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The yields of benzaldehyde and o-cresol from the photooxidation of toluene, and the yields of biacetyl from the photooxidation of o-xylene, have been determined over the pressure range $\sim 60-740$ torr at ~ 303 K by using the photolysis of $CH_3ONO-NO$ -air (or O_2) mixtures to generate OH radicals. In addition, the benzaldehyde and o-cresol yields from toluene were determined at 323 K and 740-torr total pressure. The benzaldehyde and o-cresol yields at ~ 303 K were observed to be independent of pressure (62–740 torr) within the experimental errors, with mean values of 0.073 ± 0.022 and 0.131 ± 0.072 , respectively. The data also do not indicate any significant effect of temperature on these yields between 303 and 323 K at 740-torr total pressure. The biacetyl yield from the o-xylene system at 301 ± 2 K, however, was observed to decrease from 0.137 ± 0.016 at 740 torr to 0.102 ± 0.004 at 67-torr total pressure. These results are compared with previous literature data and their implications for chemical kinetic computer modeling of the NO_x photooxidations of toluene and o-xylene are discussed.

Introduction

Since aromatic hydrocarbons are increasingly important constituents of polluted urban atmospheres,^{1,2} being major components of commercial and military fuels,³ an understanding of their atmospheric chemistry is needed to assess their impact on the environment. However, despite numerous experimental studies⁴⁻¹⁷ of their atmospheric

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chemistry, the reaction pathways and product yields occurring after the initial hydroxyl radical attack on the aromatic hydrocarbons are still poorly understood.^{14,18-20}

It is known that the major atmospheric fate of aromatics is via reaction with the OH radical, with the reaction proceeding via two routes: 19,20 H-atom abstraction, mainly from the substituent methyl groups (reaction 1), and OH

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radical addition to the aromatic ring (reaction 2), which becomes reversible at elevated temperatures.^{19,21,22} For example, for toluene the reactions are



By analogy with the reactions of alkyl radicals,²⁰ it is anticipated that under atmospheric conditions the benzyl-type radicals formed in reaction 1 will yield predominantly the aromatic aldehydes,^{7,13,14,18–20} while product and modeling studies^{7,12–15,18–20} have postulated that the hydroxycyclohexadienyl radicals formed in reaction 2 will react with O₂ to yield phenolic compounds or add O₂^{12,14} to ultimately lead, at least in part, to ring cleavage. Again taking the toluene system as an example, we expect the following reactions:



Three temperature-dependent kinetic studies²¹⁻²³ have derived rate constant ratios $k_1/(k_1 + k_2)$ at 298 K for a series of aromatic hydrocarbons, with values of $0.16^{+0.07}_{-0.05}$ (ref 21) and $0.04^{+0.06}_{-0.02}$ (ref 22) for toluene, while Kenley et al.¹³ have determined this rate constant ratio for several aromatic hydrocarbons from a product analysis study carried out at low (6–12 torr) total pressure. From that¹³ and other product studies,^{6,7,11} reported benzaldehyde yields from toluene have ranged from 2.5%¹¹ to ~50%.⁶ Clearly, there are significant discrepancies in the previous data for toluene concerning the importance of the H-atom abstraction pathway (reaction 1), and indeed concerning the yield of benzaldehyde under atmospheric conditions.

Furthermore, the importance of reaction 4 relative to reaction 3 has not been determined with certainty. Kenley et al.¹³ observed an $\sim 85\%$ yield of the cresol isomers (mainly *o*-cresol) at 6–12-torr total pressure and concluded

that under their low-pressure conditions the addition of O_2 to the OH-aromatic adduct results in the exclusive formation of phenolic products, with reaction 4 being negligible under these conditions. However, product studies at atmospheric pressure^{11,14} have shown much lower yields of o-cresol (5%¹¹ to ~21%¹⁴) indicating alternate reaction pathways.

The observation of significant yields of α -dicarbonyls from o-xylene^{12,15,24} and other aromatic hydrocarbons,²⁴ and of unsaturated 1,4-dicarbonyls from toluene¹⁷ and 1,2,4trimethylbenzene,¹⁶ also shows that ring cleavage, possibly via reaction 4^{12,14,20} or its analogues, does indeed occur under atmospheric conditions. Thus, either there are discrepancies between the results of Kenley et al.¹³ and the other previous studies,^{6,7,11} or the aromatic product yields exhibit significant pressure dependencies.

In order to resolve these uncertainties and, in particular, to determine whether pressure effects could account, at least partially, for these divergent data, we have determined the yields of benzaldehyde and o-cresol from toluene, and of biacetyl from o-xylene, over the pressure range $\sim 60-740$ -torr total pressure.

Experimental Section

Hydroxyl radicals were generated by the photolysis of methyl nitrite at $\gtrsim 290$ nm in the presence of O_2 :

$$CH_{3}ONO + h\nu \rightarrow CH_{3}O + NO$$
$$CH_{3}O + O_{2} \rightarrow HCHO + HO_{2}$$
$$HO_{2} + NO \rightarrow OH + NO_{2}$$

In order to minimize O_3 and hence NO_3 formation, we also added NO to the reaction mixtures, which had the following initial concentrations: toluene or o-xylene, $\sim (2-3)$ × 10¹³ molecules cm⁻³; CH₃ONO, \sim (2–5) × 10¹² molecules cm⁻³; and NO, \sim (2–3) × 10¹³ molecules cm⁻³. Air or O₂ was used as diluent gases. Irradiations of toluene (or oxylene)– CH_3ONO –NO-air (or O_2) mixtures were carried out in a 5800-L Teflon-coated, evacuable, thermostated, environmental chamber with a 25-kW solar simulator.²⁵ Prior to each irradiation the chamber was evacuated to $\lesssim 10^{-5}$ torr. Methyl nitrite, prepared as described previously,²⁶ and NO were introduced into the chamber from a vacuum gas handling system. The chamber was then filled to the desired pressure with dry purified matrix air^{25,27} or ultrahigh-purity O_2 . The known quantities of toluene or o-xylene were flushed into the chamber from an \sim 1-L Pyrex bulb by a stream of ultrahigh-purity N₂. The chamber was maintained at the desired temperature by means of the chamber's heating/cooling system.²⁵

Toluene and o-xylene were quantitatively analyzed by gas chromatography with flame ionization detection (GC FID) using a 10 ft \times 0.125 in. stainless-steel column of 10% Carbowax 600 on C-22 Firebrick (100/120 mesh), operated at 348 K. Biacetyl was monitored by gas chromatography with electron capture detection using a 12 in. \times 0.125 in. Teflon column of 5% Carbowax 400 on Chromasorb G (80/110 mesh) operated at 300 K. For these species, 100-cm³ gas samples were withdrawn into all-glass, gastight syringes from the chamber directly (for atmospheric pressure runs) or, for runs at reduced pressure, from \sim 5-L Pyrex bulbs which had been evacuated to \leq 10⁻³ torr and

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TABLE I: Experimental Data for the Toluene-CH₃ONO-NO-Air (or O_3) Irradiations

EC run no.	temp, K	total press., torr	10 ⁻¹³ (initial concn), molecules cm ⁻³		$10^{-12}(-\Delta - [toluene]),$	10 ⁻¹¹ [benzaldehyde], molecules cm ⁻³		$10^{-11}[o\text{-cresol}],$ molecules cm ⁻³		
			CH,ONO	NO	toluene	cm ⁻³	obsd	cor ^a	obsd	cor ^a
728	306 ± 2	740	0.49	2.40	2.39	3.07	2.29	2.62	2.38	3.74
						3.95	2.55	3.05	2.83	5.07
						4.74	2.91	3.62	3.29	6.65
729	302 ± 2	360	0.49	2.37	2.26	1.43	1.33	1.42	1.73	2.16
						2.57	2.22	2.50	2.84	4.24
						3.33	2.70	3.16	3.56	5.99
						4.22	3.06	3.76	3.97	7.67
730	303 ± 2	168	0.24	2.36	2.33	1.55	0.83	0.89	0.78	0.99
						2.64	1.19	1.34	0.81	1.20
						3.07	1.82	2.10	1.82	2.91
						3.24	2.03	2.36	1.82	2.98
731 ^b	302 ± 1	62	0.24	2.35	2.42	2.12	1.08	1.18	1.12	1.52
						3.57	1.88	2.20	1.98	3.34
						4.19	2.34	2.83	2.57	4.76
						5.62	2.71	3.53	2.94	6.73
732	302 ± 2	740	0.50	2.43	2.53	1.76	1.21	1.31	1.05	1.33
						2.91	1.88	2.12	1.76	2.64
						4.19	2.33	2.81	2.33	4.19
						4.65	2.64	3.24	2.48	4.76
733	302 ± 1	161	0.24	2.37	2.41	0.83	0.98	1.01	0.79	0.89
						2.26	1.38	1.52	1.38	1.92
						2.83	2.17	2.46	2.33	3.54
						3.38	2.17	2.53	2.29	3.75
734	323 ± 2	740	0.47	2.24	2.55	1.93	1.81	1.95	1.93	2.52
						3.38	2.83	3.26	3.12	4.98
						4.36	3.43	4.14	3.60	6.60
						5.19	3.95	4.95	4.14	8.53

^a Corrected for reaction with OH radicals (see text). ^b Diluent gas was O_2 in this irradiation.

EC	total	10^{-13} (initial concn), molecules cm ⁻³		$10^{-12}(-\Delta[o-xy])$	10 ⁻¹¹ [biacetyl], molecules cm ⁻³			
run no.	torr	CH ₃ ONO	NO	o-xylene	molecules cm ⁻³	obsd	cor ^a	
 721	740	0.48	2.35	2.53	4.36	5.96	6.55	
					7.17	7.41	9.05	
					8.67	9.15	12.10	
					9.79	9.36	13.77	
722	347	0.24	2.37	2.34	2.95	4.29	4.62	
					6.12	6.88	8.08	
					7.69	7.96	10.29	
					8.89	8.89	12.51	
723	160	0.25	2.35	2.40	3.48	4.05	4.38	
					6.29	6.19	7.31	
					8.17	7.10	9.24	
					10.41	7.88	11.17	
724^{b}	67	0.25	2.34	2.43	5.55	5.53	6.03	
· - -					9.15	8.08	9.62	
					12.03	9.36	12.24	
					14.41	10.43	14.84	

TABLE II: Experimental Data for o-Xylene-CH₃ONO-NO-Air (or O₂) Irradiations at 301 ± 2 K

^a Corrected for photolysis (see text). ^b Diluent gas was O₂ for this irradiation.

which were then opened to the chamber and then filled to atmospheric pressure by ultrahigh-purity N_2 .

Benzaldehyde and o-cresol were monitored by GC FID using a 6 ft \times 0.25 in. glass column packed with 80/100 Results Carbopack C/0.1% SP-1000, temperature programmed from 423 to 523 K at 20 K min⁻¹. Gas samples from the chamber of $\sim 0.1-1$ -L volume were drawn through 0.25 in. \times 3.25 in. glass traps packed with Tenax GC 50/80 mesh. These samples were then transferred by the carrier gas at 523 K from this trap to the column head which was at 423 K, followed by the temperature programming of the col-

umn as noted above. For the o-xylene-CH₃ONO-NO-air system the irradiations were of 80-min duration with analyses being carried out every 20 min. For the toluene-CH₃ONO-NO-air system however, because of the time involved in sampling via the Tenax-packed traps ($\sim 10-15$ min), four 10- or

15-min irradiations of the same mixture were carried out during each experiment, with GC analyses being conducted at the end of each irradiation period.

Irradiations of toluene-CH₃ONO-NO-air (or O₂) and o-xylene-CH₂ONO-NO-air (or O₂) mixtures were carried out at ~ 303 K over the pressure range $\sim 60-740$ -torr total pressure, and a toluene-CH₃ONO-NO-air irradiation was also carried out at 323 ± 2 K and 740-torr total pressure. The initial reactant concentrations and the observed amounts of aromatic hydrocarbon consumed and product species formed, as measured at various times during the irradiations, are given in Tables I and II for the toluene and o-xylene systems, respectively.

In addition, irradiations of biacetyl-NO-air and biacetyl-CH₃ONO-NO-air mixtures were carried out at 303 K and 740-torr total pressure to determine the photolytic lifetime of biacetyl under the experimental conditions employed in the o-xylene-CH₃ONO-NO-air irradiations. During these irradiations the biacetyl decays were strictly exponential, with first-order decay rates of (1.30 ± 0.07) $\times 10^{-4}$ s⁻¹ for the biacetyl-CH₃ONO-NO-air experiment and $(1.26 \pm 0.04) \times 10^{-4} \text{ s}^{-1}$ for the biacetyl-NO-air experiment (where the error limits are two least-squares standard deviations of the slopes of the plots of ln [biacetyl] against irradiation time). Since the presence of CH₃ONO in one of the reactant mixtures is expected to significantly increase the OH radical concentrations, the excellent agreement of the biacetyl decays for these two irradiations shows that reaction with OH radicals is a minor loss process for biacetyl in the CH₃ONO-NO-air system. Thus, the only significant loss process for biacetyl in these systems is via photolysis. This is consistent with the fact that the reaction of OH radicals with biacetyl is very slow, with a rate constant of $(2.4^{+0.8}_{-0.6}) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ at 298 K,^{12,19} corresponding to a biacetyl lifetime due to reaction with OH radicals of ~ 100 h at the OH radical concentrations ($\sim 1 \times 10^7$ cm⁻³) encountered in the o-xylene-CH₃ONO-NO-air irradiations.

Since biacetyl photolyzes rapidly¹² and benzaldehyde and o-cresol react with OH radicals more rapidly then does toluene,^{19,20} corrections must be made for these secondary reactions in order to derive the fraction of the OH radical reaction with the aromatics yielding biacetyl, benzaldehyde, and o-cresol. These corrections were made as described below.

Under the experimental conditions employed in the present study, the predominant loss process for benzaldehyde is via reaction with the OH radical, with photolysis²⁸ contributing $\lesssim 5\%$ of the OH radical reaction in consuming benzaldehyde. Similarly, the major loss process for o-cresol is also via reaction with the OH radical, with reaction with O_3^{29} and the NO_3 radical³⁰ being of very minor importance under the experimental conditions employed. Since these two products from the NO_x photooxidation of toluene, benzaldehyde and o-cresol, are formed and lost via OH radical reactions, then

$$-d[toluene]/dt = (k_1 + k_2)[OH][toluene]$$
(I)

d[product]/dt =

$$\alpha(k_1 + k_2)[OH][toluene] - k_5[OH][product]$$
(II)

where α is the fraction of the OH radical reaction with toluene yielding the product under consideration (either benzaldehyde or o-cresol), $k_1 + k_2$ is the overall rate constant for the reaction of OH radicals with toluene, and k_5 is the rate constant for the reaction of OH radicals with benzaldehyde or o-cresol.

$$OH + \{benzaldehyde \text{ or } o\text{-cresol}\} \rightarrow products$$
 (5)

Under conditions where the OH radical concentration is constant, these equations can be integrated to obtain

$$[\text{toluene}]_t = [\text{toluene}]_0 e^{-(k_1 + k_2)[\text{OH}]t}$$
(III)

 $[product]_t =$

$$[\text{toluene}]_0 \frac{\alpha(k_1 + k_2)}{[(k_1 + k_2) - k_5]} [e^{-k_5[\text{OH}]t} - e^{-(k_1 + k_2)[\text{OH}]t}]$$
(IV)

where $[toluene]_0$ is the initial toluene concentration, [OH]is the constant hydroxyl radical concentration, and [tolu-

TABLE III: Benzaldehyde and o-Cresol Yields from the NO, Photooxidation of Toluene

	total press di	diluent	yield ^a			
temp, K	torr	gas	benzaldehyde	o-cresol		
306 ± 2	740	air	0.077 ± 0.009	0.136 ± 0.020		
302 ± 2	740	air	0.068 ± 0.005	0.104 ± 0.013		
303 ± 2	360	air	0.090 ± 0.007	0.184 ± 0.016		
302 ± 1	168	air	0.068 ± 0.020	0.087 ± 0.047		
302 ± 2	161	air	0.073 ± 0.020	0.112 ± 0.029		
302 ± 1	62	0,	0.065 ± 0.007	0.121 ± 0.027		
323 ± 2	740	air	0.095 ± 0.003	0.162 ± 0.018		

^a Corrected for secondary reactions with OH radicals (see text). The indicated errors are two standard deviations of the slopes of plots of the corrected yields against the amount of toluene consumed.

ene]_t and $[product]_t$ are the toluene and product concentrations, respectively, at time t. Equations III and IV can be combined to obtain

$$\alpha = F\{[\text{product}]_t / \Delta[\text{toluene}]_t\}$$
(V)

where Δ [toluene]_t is the amount of toluene consumed at time t, and F is the correction factor which takes into account the reaction of the product with the OH radical:

$$F = \left(\frac{(k_1 + k_2) - k_5}{(k_1 + k_2)}\right) \left\{ \left[1 - \left(\frac{[\text{toluene}]_t}{[\text{toluene}]_0}\right)\right] \right/ \\ \left[\left(\frac{[\text{toluene}]_t}{[\text{toluene}]_0}\right)^{k_5/(k_1 + k_2)} - \left(\frac{[\text{toluene}]_t}{[\text{toluene}]_0}\right)\right] \right\} (VI)$$

Equation VI, which has been shown to be applicable even when the OH radical concentrations vary with time,³¹ was used to correct each of the data points for benzaldehyde and o-cresol in Table I. F was calculated by using the experimentally observed amounts of toluene consumed and the rate constant ratios $k_5/(k_1 + k_2) = 7.0$ for o-cresol and 2.0 for benzaldehyde, both independent of temperature over the small temperature range employed in this study (302-323 K).^{19,20} These correction factors were relatively minor for benzaldehyde ($F \leq 1.30$) but were much larger for o-cresol, with F being as high as 2.29 for the highest toluene conversion employed. For o-cresol, an uncertainty in the $k_5/(k_1 + k_2)$ ratio of ± 1 (i.e., 7 ± 1) led to a $\pm 10\%$ effect on the magnitude of F at the highest toluene conversions. Plots of the corrected benzaldehyde or o-cresol yield against the amount of toluene consumed yielded good straight lines, and Table III lists the leastsquares slopes obtained from these plots at the various temperatures and pressures employed. In all cases the least-squares intercepts of such plots were within two standard deviations of zero.

For the case of biacetyl formation from o-xylene, eq VI does not apply since, as noted above, the major biacetyl loss process is photolysis rather than reaction with the OH radical.

biacetyl +
$$h\nu \rightarrow$$
 products (6)

In this case

$$\frac{d[\text{biacetyl}]}{dt} = \alpha(k_1 + k_2)[\text{OH}][o\text{-xylene}] - k_6[\text{biacetyl}]$$
(VII)

where α is the fraction of the OH radical reaction with o-xylene forming biacetyl and k_6 is the experimentally determined photolysis rate constant for biacetyl of 1.28

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TABLE IV: Biacetyl Yields from the NO_x Photooxidation of o-Xylene at 301 ± 2 K

total press., torr	diluent gas	biacetyl yield ^a	
740	air	0.137 ± 0.016	
347	air	0.135 ± 0.012	
160	air	0.108 ± 0.009	
67	0 ₂	0.102 ± 0.004	

^a Corrected for photolysis of biacetyl (see text). The indicated error limits are two least-squares standard deviations of the slopes of plots of the corrected biacetyl concentrations against the amount of o-xylene consumed.

TABLE V: Comparison of the Present Benzaldehyde and o-Cresol Yields from the NO_x Photooxidation of Toluene at ~303 K with Previous Literature Values

yiel			
benzaldehyde	o-cresol	ref	
~25-35		7	
15 ± 2^{a}	$68^{a,b}$	13	
~50		6	
12^{c}	~ 21	14	
2.5	5	11	
7.3 ± 2.2^{d}	13.1 ± 7.2^{d}	this work	

^a At 6-12-torr total pressure. ^b At high O_2/NO_2 ratios $(>2 \times 10^5)$; ~17% *m*-, *p*-cresol also formed. ^c Value obtained by using $k_1/(k_1 + k_2)$ ratio of 0.156 from the literature^{13,21} and assuming 25% benzyl nitrate formation from the C₆H₅CH₂O₂ + NO reaction. ^d Independent of pressure over the range 62-740 torr.

 \times 10⁻⁴ s⁻¹. Integration of both sides of eq VII leads to the expression

$$[\text{biacetyl}]_t + k_6 \int_{t_0}^t [\text{biacetyl}] \, dt = \alpha \Delta [o\text{-xylene}]_t \quad (\text{VIII})$$

where $[\text{biacetyl}]_t$ and $\Delta[o\text{-xylene}]_t$ are the observed biacetyl yields and the amount of o-xylene consumed, respectively, at time t. The quantity $\int_{t_0} t[\text{biacetyl}] dt$ was obtained by measuring the area under the biacetyl concentration-time profiles. Each of the data points in Table II was corrected in this way for the biacetyl photolysis. Table IV lists the fractions, α , of the reaction of OH radicals with o-xylene yielding biacetyl, these being the least-squares analyses of plots of the corrected biacetyl yields against the amounts of o-xylene consumed. Again, in all cases the least-squares intercepts of such plots were within two standard deviations of zero.

Discussion

Benzaldehyde and o-Cresol From Toluene. The benzaldehyde and o-cresol yields determined in this work are plotted as a function of total pressure in Figure 1. Within the experimental uncertainties, they are seen to be independent of pressure, with weighted least-squares mean values of 0.073 ± 0.019 for benzaldehyde and 0.131 ± 0.066 for o-cresol (where the error limits are two weighted least-squares standard deviations). Inclusion of the uncertainties in the gas-chromatographic calibration factors leads to benzaldehyde and o-cresol yields of 0.073 ± 0.022 and 0.131 ± 0.072 , respectively, where the indicated errors are again two standard deviations.

These results are compared with literature data in Table V. For benzaldehyde the present datum is in between the reported values of O'Brien et al.¹¹ and Kenley et al.,¹³ with the benzaldehyde yield reported by Spicer and Jones⁶ obviously being much too high. For o-cresol the present yield is in reasonable agreement with that derived from the environmental chamber-computer modeling study of



Figure 1. Plot of the benzaldehyde and *o*-cresol yields from irradiated toluene-CH₃ONO-NO-air (or O₂) mixtures as a function of total pressure at \sim 303 K. The error bars are the two least-squares standard deviations given in Table III.

Atkinson et al.¹⁴ However, the data of Kenley et al.,¹³ which indicate that at low pressures and at high O_2/NO_x ratios the reaction of OH radicals with toluene yields ~ 15% benzaldehyde and ~68% o-cresol (together with ~ 17% of the other two cresol isomers), are in apparent conflict with our determination that the o-cresol yield is ~13%, independent of pressure over the range 62–740 torr. This discrepancy is possibly caused by the problems of sampling under the conditions employed by Kenley et al.,¹³ since they report only an ~10% sampling efficiency. However, further work at <50-torr total pressure is obviously necessary to definitely resolve this discrepancy.

While the reported benzaldehyde (and *o*-cresol) yields of Hoshino et al.⁷ and O'Brien et al.¹¹ are in disagreement with the present data, the ratios of the *o*-cresol/benzaldehyde yields of 2.1^7 and 2.0^{11} obtained in those studies are in good agreement with the ratio of 1.8 obtained in the present study.

Under atmospheric conditions the benzyl radical is expected to react via the following reaction sequence:

$$C_6H_5CH_2 + O_2 \rightarrow C_6H_5CH_2O_2 \tag{7}$$

$$C_6H_5CH_2O_2 + NO \rightarrow C_6H_5CH_2O + NO_2 \qquad (8a)$$

$$\xrightarrow{M} C_6 H_5 C H_2 O NO_2$$
 (8b)

$$C_6H_5CH_2O + O_2 \rightarrow C_6H_5CHO + HO_2$$
(9)

$$C_6H_5CH_2O + NO_2 \rightarrow C_6H_5CH_2ONO_2$$
(10)

(reaction of benzoyl radicals with NO to form benzyl nitrite is of negligible importance due to the expected rapid



Figure 2. Plot of the biacetyl yields from irradiated o-xylene-CH₃ONO-NO-air (or O₂) mixtures as a function of total pressure at 301 \pm 2 K. The error bars are the two least-squares standard deviations given in Table IV.

photolysis of benzyl nitrite). At high O_2/NO_x ratios (>2 × 10⁵) benzyl nitrate formation via reaction 10 is negligible.¹³ Hence, under these conditions benzyl radicals will ultimately form benzaldehyde and benzyl nitrate via reactions 7–9.

The fraction of reaction 8 forming benzyl nitrate is not totally known, but, since the ratio $k_{8b}/(k_{8a} + k_{8b})$ is expected to decrease with decreasing pressure,³² the lack of a pressure dependence for the benzaldehyde yield indicates that benzyl nitrate formation is not a major process. This is in agreement with the data of Hoshiono et al.⁷ which show that at atmospheric pressure the benzyl nitrate yields are ~12% of the benzaldehyde yields. Thus, the observed benzaldehyde yields should be close to, but somewhat lower (by ~10–15% due to benzyl nitrate formation) than, the primary rate constant ratio $k_1/(k_1 + k_2)$ for the initial OH radical reaction with toluene (see Introduction). Indeed, the present benzaldehyde yield of 0.073 ± 0.022 is in between the $k_1/(k_1 + k_2)$ ratios at 298 K of $0.16^{+0.07}_{-0.02}$ (ref 22) reported from kinetic studies. At 323 ± 2 K, the benzaldehyde yield was observed to

At 323 ± 2 K, the benzaldehyde yield was observed to be somewhat higher than at ~303 K, though any increase is probably within the experimental errors. Such an increase in the benzaldehyde yield with increasing temperature is expected from the results of kinetic studies, ^{19,21,22} which show that the rate constant ratio $k_1/(k_1 + k_2)$ increases with temperature. The *o*-cresol yields do not, within the wide experimental uncertainties, appear to show any significant temperature dependence in the range 303-323 K.

Biacetyl from o-Xylene. The fraction of the OH radical reaction with o-xylene yielding biacetyl of 0.137 ± 0.016 determined in the present work is in good agreement with the value of 0.18 ± 0.04 obtained previously in these laboratories by Darnall et al.¹² and is in agreement, within the large experimental error limits, with the value of $0.260 \pm$ 0.102 reported by Takagi et al.¹⁵ Both of these previous studies employed the irradiation of o-xylene-NO-air mixtures. Thus, it is evident that, at atmospheric pressure and ~ 300 K, $\sim 15\%$ of the overall reaction of OH radicals with o-xylene yields biacetyl, and previous work¹² has shown no effect of temperature on this biacetyl yield over the range 283-323 K.

However, the present data do suggest a small pressure effect, with the biacetyl yield decreasing by $\sim 25\%$ in going from 740- to 67-torr total pressure (Figure 2). If indeed there is a pressure effect on the biacetyl yield as these data suggest, then the specific reaction or reactions responsible for this pressure dependence are difficult to determine at this time, since several reactions in the sequence leading to ring cleavage could potentially be pressure dependent. For instance, the reaction of the OH-o-xylene adduct with O₂ to form the bicyclic intermediate I via reaction 4 may



|0₂ + CH3COCOCH3

HQ²

be pressure dependent (but this was not the case for ocresol formation from toluene), with reaction 4 becoming more important at higher pressures. The possible formation of bicyclic nitrates via reaction path a is also likely to be pressure dependent with the nitrate yield increasing with pressure,³² but this would be contrary to the observed trend of increasing biacetyl yields with increasing pressure.

Obviously much further work concerning the temperature and pressure dependencies of the individual elementary reactions is needed before any conclusions can be drawn as to the reactions responsible for any effects of pressure or temperature on observed final product yields. However, the present yields for biacetyl from o-xylene, and for benzaldehyde and o-cresol from toluene, can now serve as much needed inputs to chemical computer modeling studies of the NO_x -air photooxidations of these two aromatic hydrocarbons.

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⁽³²⁾ R. Atkinson, W. P. L. Carter, and A. M. Winer, J. Phys. Chem., in press.

Registry No. Toluene, 108-88-3; *o*-xylene, 95-47-6; *o*-cresol, 95-48-7; biacetyl, 431-03-8; benzaldehyde, 100-52-7; methyl nitrite, 624-91-9; nitrogen oxide, 10102-43-9; oxygen, 7782-44-7; hydroxyl, 3352-57-6.