September, 1985] © 1985 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 58, 2541—2548 (1985) 2541

Ring-cleavage Reactions of Aromatic Hydrocarbons Studied by FT-IR Spectroscopy. II. Photooxidation of *o*-, *m*-, and *p*-Xylenes in the NO_x-Air System

Hiroshi Bandow and Nobuaki Washida
Division of Atmospheric Environment, The National Institute for Environmental Studies,
P. O. Tsukuba-gakuen, Tsukuba, Ibaraki 305

(Received February 12, 1985)

α-Dicarbonyl compounds produced in the photooxidation of *o*-, *m*-, and *p*-xylenes were analyzed quantitatively using long-path FT-IR spectroscopy. Glyoxal, methylglyoxal, and biacetyl were observed in the case of *o*-xylene, and glyoxal and methylglyoxal were observed in cases of *m*- and *p*-xylenes. Yields of glyoxal, methylglyoxal, and biacetyl were 8, 23, and 10% (mole/mole) of *o*-xylene consumed, respectively. Yields of glyoxal and methylglyoxal were 13 and 42% in the case of *m*-xylene, and 24 and 12% in the case of *p*-xylene. These yields could be explained by the ring cleavage of 6,7-dioxabicyclo[3.2.1]octane compounds of OH-aromatics-O_2 adduct. Formations of maleic anhydride was observed in the case of *o*-xylene and it is suggested that maleic anhydride is produced from *cis*-2-butenedial. Formation of 3-hexene-2,5-dione (unsaturated γ-dicarbonyl) was observed from *p*-xylene. The ring-cleavage process accounts for 41, 55, and 36% of the total reaction in *o*-, *m*-, and *p*-xylenes, respectively.

The studies of the mechanism of the ring-cleavage reactions in the photooxidation of benzene and toluene described in part I, are extended to *o*-, *m*-, and *p*-xylenes in the present work. The initial reaction of OH with xylenes also proceeds mainly by addition to aromatic ring (80—98% of the total reaction).[1–4] Also *m*-xylene reacts faster[1,4,5] than either *p*- or *o*-xylene with OH at 298K since meta substitution of the ring enhances electrophilic addition. The formation of α-dicarbonyls, glyoxal, methylglyoxal, and biacetyl (only in the case of *o*-xylene), by xylene-ring-cleavage reaction has been reported.[2,6,7] However, the yields of α-dicarbonyls reported are scattered. For example, in the case of *o*-xylene, the yields of glyoxal, methylglyoxal, and biacetyl per *o*-xylene consumed reported by Nojima *et al.*[6] are 0.2, 4.0, and 1.2%, respectively, the values by Takagi *et al.*[2] are 85, 14, and 26%, respectively, and those by Shepson *et al.*[7c] are 3.4, 11.6, and 8.5%, respectively. Darnall *et al.*[7a] measured only the yield of biacetyl and reported it to be 18% of *o*-xylene consumed. Very large spread of these results might be mainly due to difficulty of handling of α-dicarbonyls. In the previous studies, GC analyses were carried out after a pre-collection of gas-phase products in a solution[6,7c] or by combining with a photoionization mass spectrometer as a detector.[2] The former represents a rather complicated procedure, while the latter requires concentration of a large amount of products, in compensation for the low detectivity of the compounds. Therefore, the direct observation of gaseous products by FT-IR should provide more reliable data on the yield and the ring-cleavage-reaction mechanisms of xylenes.

Experimental

The apparatus and experimental procedures were the same as those mentioned in part I.[8] The experimental conditions were xylene(4 ppm), NO(1.5 ppm), NO_2(0.5 ppm), and air (1 atm=101 kPa) system. Three experiments were carried out for each xylene isomer.

Results

Formaldehyde, formic acid, glyoxal, methylglyoxal, PAN, and tolualdehydes were observed as reaction products in the photooxidation of *o*-, *m*-, and *p*-xylenes. Formation of biacetyl and maleic anhydride was observed only from *o*-xylene. Product spectra (spectra, from which spectra of reactants, xylenes, NO, NO_2, and H_2O were subtracted) and residual spectra (spectra, from which spectra of products mentioned above were subtracted) are shown in Fig. 1 for each of *o*-, *m*-, and *p*-xylenes. Product spectra shown in Fig. 1, (a), (c), and (e), were obtained under the same conversion of xylenes (xylene consumed was about 20%).

Concentrations of each product from *o*-xylene as a function of irradiation time are shown in Fig. 2. Characteristic absorption bands used to determine the absolute concentrations of products are the same as for toluene (Table 1 in part I). The concentration of biacetyl was determined by absorption at 1120 cm^{-1} (in the region of skeletal vibrations), and that of tolualdehydes by absorption at 2730 cm^{-1} which corresponds to the C-H stretching mode of -CHO. The time profiles of formic acid and PAN show that both molecules are secondary products as in the case of toluene. From the slopes of the plots of the concentrations of products formed *versus* *o*-xylene consumed, shown in Fig. 3, yields of products listed in Table 1 were calculated. Yields shown in each run are obtained by the least-square fit of five initial points of each run (as shown in Fig. 3) except the case of tolualdehydes. For tolualdehydes, the least-square fit was done for three initial points. The indicated errors are one standard deviation of three runs.

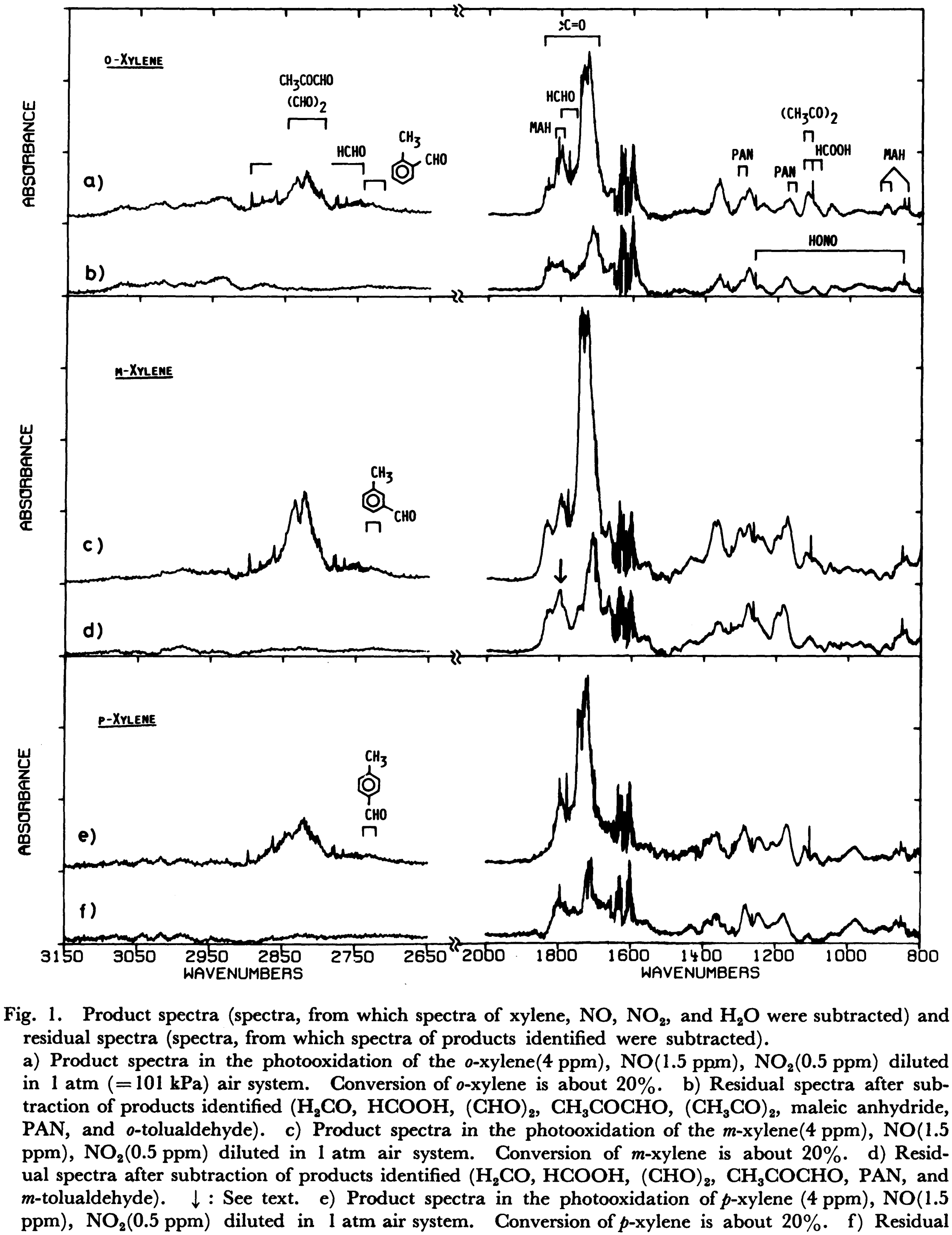


Fig. 1. Product spectra (spectra, from which spectra of xylene, NO, NO_2, and H_2O were subtracted) and residual spectra (spectra, from which spectra of products identified were subtracted).
a) Product spectra in the photooxidation of the *o*-xylene(4 ppm), NO(1.5 ppm), NO_2(0.5 ppm) diluted in 1 atm (=101 kPa) air system. Conversion of *o*-xylene is about 20%. b) Residual spectra after subtraction of products identified (H_2CO, HCOOH, $(CHO)_2$, CH_3COCHO, $(CH_3CO)_2$, maleic anhydride, PAN, and *o*-tolualdehyde). c) Product spectra in the photooxidation of the *m*-xylene(4 ppm), NO(1.5 ppm), NO_2(0.5 ppm) diluted in 1 atm air system. Conversion of *m*-xylene is about 20%. d) Residual spectra after subtraction of products identified (H_2CO, HCOOH, $(CHO)_2$, CH_3COCHO, PAN, and *m*-tolualdehyde). ↓ : See text. e) Product spectra in the photooxidation of *p*-xylene (4 ppm), NO(1.5 ppm), NO_2(0.5 ppm) diluted in 1 atm air system. Conversion of *p*-xylene is about 20%. f) Residual spectra after subtraction of products identified (H_2CO, HCOOH, $(CHO)_2$, CH_3COCHO, PAN, and *p*-tolualdehyde).

Discussion

A. Yields of α-Dicarbonyls and Reaction Mechanism of Ring-cleavage Reaction. As shown in Table 1, product yields of each α-dicarbonyl are varying among the xylenes. For example, the yield of methylglyoxal is the largest for *o*- and *m*-xylene, and that of glyoxal is the largest in the case of *p*-xylene. It is very interesting if the significant variations in yield of α-dicarbonyls among the xylenes can be explained by a unique and simple ring-cleavage mechanism. If such a mechanism will be proved to be applicable as a general rule to other aromatic compounds, it would be very useful for modeling

Table 1. Yield of products[a] (amount of product formed/amount of xylene consumed) in the photooxidation of *o*-, *m*-, *p*-xylene–NO_x–air system[b]

Run	*o*-Xylene				*m*-Xylene				*p*-Xylene			
Product	1	2[c]	3	Ave.[d]	4	5	6	Ave.[d]	7	8	9	Ave.[d]
HCHO	0.18	0.13	0.22	0.18±0.04	0.14	0.17	0.19	0.17±0.02	0.19	0.16	0.16	0.17±0.02
$(HCO)_2$	0.07	0.08	0.09	0.08±0.01	0.11	0.12	0.16	0.13±0.03	0.26	0.22	0.23	0.24±0.02
CH_3COCHO	0.23	0.20	0.25	0.23±0.03	0.37	0.44	0.47	0.42±0.05	0.13	0.11	0.14	0.12±0.02
$(CH_3CO)_2$	0.10	0.08	0.12	0.10±0.02								
Maleic anhydride	0.04	0.03	0.05	0.04±0.01								
Tolualdehyde	0.04	0.05	0.05	0.05±0.01	0.03	0.04	0.05	0.04±0.01	0.08	0.08	0.07	0.08±0.01
Total yield of α-dicarbonyls				0.41±0.04				0.55±0.07				0.36±0.03

a) Values were calculated by the least-square fit of five initial points of each run except the case of tolualdehydes (least-square fit of three points). b) Initial conditions of reactants were 4 ppm of xylene, 1.5 ppm of NO, and 0.5 ppm of NO_2 in 1 atm (=101 kPa) air in all runs except run number 2. c) Initial conditions of reactants was 8 ppm of *o*-xylene, 1.5 ppm of NO, and 0.5 ppm of NO_2 in 1 atm air. d) The indicated errors are one standard deviation of three runs.

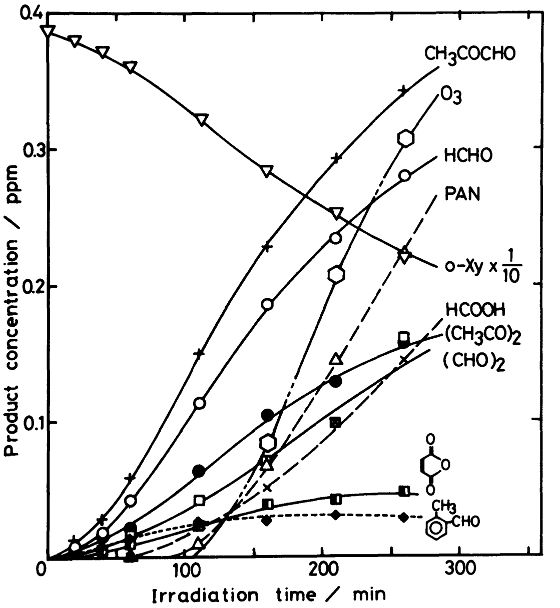


Fig. 2. Concentrations of each product as functions of irradiation time in the case of *o*-xylene.

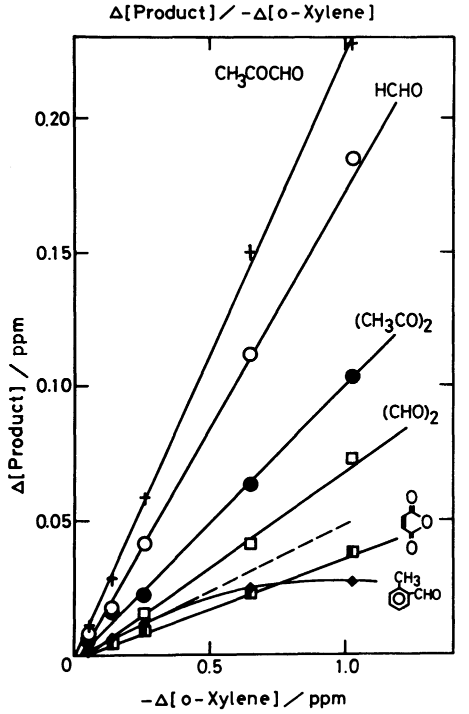
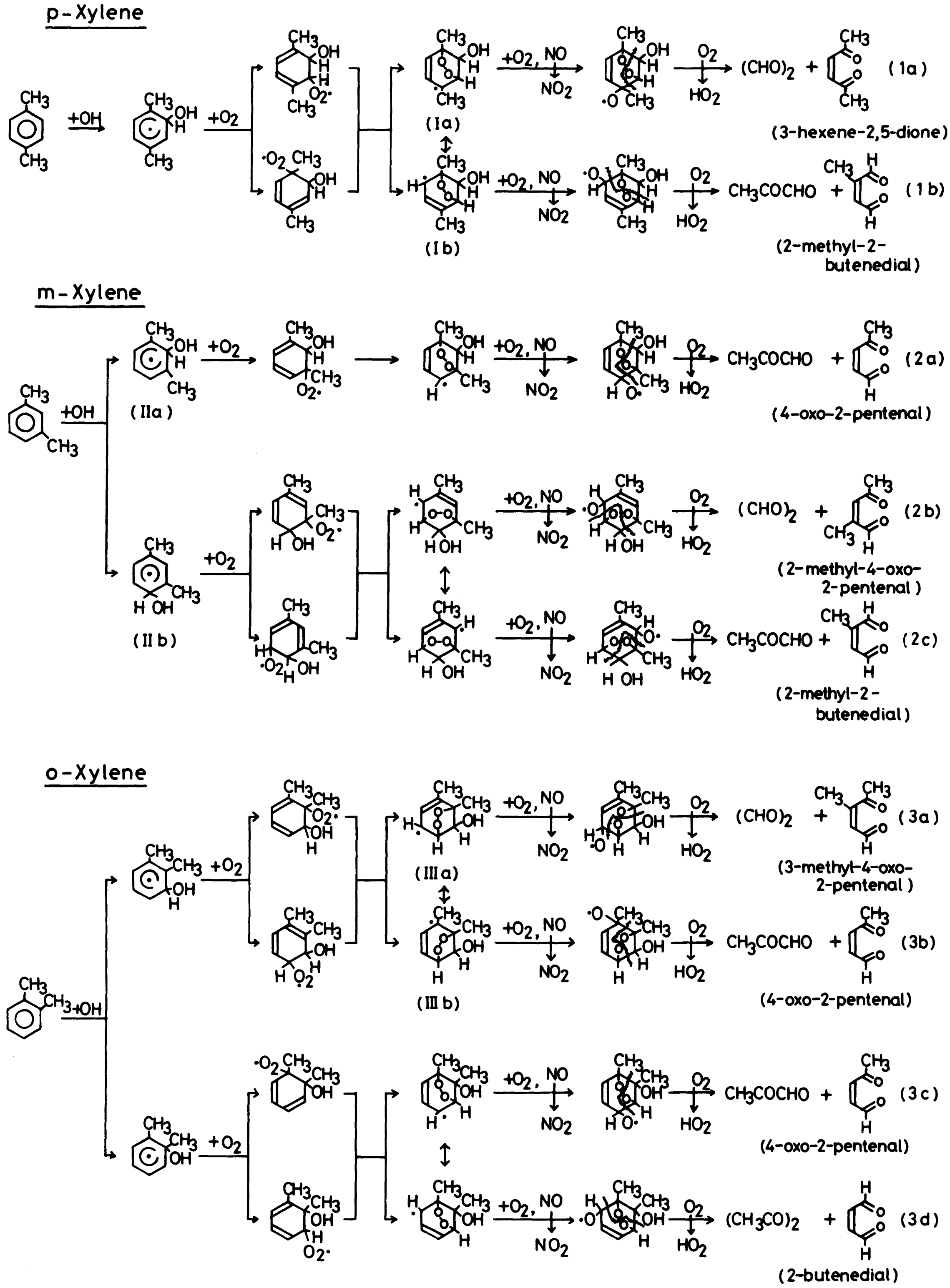


Fig. 3. Concentrations of products are plotted against the concentration of *o*-xylene consumed.

studies of the photooxidation of aromatic compounds.

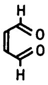
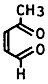
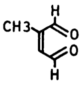
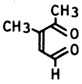
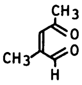
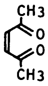
First, we assume [Assumption I] that the addition of OH to xylene is predominantly at the ortho position.[9] According to the cyclization mechanism described for the ring-cleavage reaction of toluene,[8] the reactions of xylenes are considered to proceed as shown in Scheme 1. In this scheme, allyl-type radicals, 6,7-dioxabicyclo[3.2.1]octane compounds which are produced by bicyclo[3.2.1] cyclization from OH-aromatics-O_2 adducts, are represented by their resonance structures, for example, **Ia**↔**Ib** in the case of *p*-xylene. We consider the example of *p*-xylene first since it is the simplest to follow. Glyoxal and methylglyoxal can be produced with 3-hexene-2,5-dione and 2-methyl-2-butenedial, respectively, and the ratio of the formation of glyoxal and methylglyoxal is governed by the ratio between Reactions 1a and 1b. In the case of *p*-xylene, the formation ratio of glyoxal to methylglyoxal obtained by experiment (see Table 1) is two to one. Therefore, if one takes the bicyclo[3.2.1] cyclization mechanism as the reaction path to yield α-dicarbonyls, the branching ratio of Reaction 1a to 1b should be two to one, that is, the probability of O_2 addition to **Ia** (resonance structure with tertiary radical) and **Ib** (that with secondary radical) of the allyl radicals should be



Scheme 1.

two to one. On the other hand, when the resonance structures of the allyl radicals are both secondary radicals, the probability of O_2 addition to the alternate radical points is expected to be the same judging from the case of toluene.[8] This consideration leads us to the second assumption [Assumption II] that the probability of O_2 addition to the resonance structure with tertiary radical is twice as that with secondary radical when the resonance structures of 6,7-dioxabicyclo[3.2.1]octane com-

Table 2. Experimental and calculated[a)] values of the ratio of the formation yields of α- and unsaturated γ-dicarbonyls

	$(CHO)_2$	CH_3COCHO	$(CH_3CO)_2$						
o-Xylene									
Exp.	0.20	0.56	0.24						
Calcd	0.17	0.58	0.25	0.25	0.58	—	0.17	—	—
m-Xylene									
Exp.	0.24	0.76	—						
Calcd	0.25	0.75	—	—	0.50	0.25	—	0.25	—
p-Xylene									
Exp.	0.67	0.33	—						
Calcd	0.67	0.33	—	—	—	0.33	—	—	0.67

a) Calculated by using Assumptions I—III (see text).

pounds consist of both secondary and tertiary radicals, otherwise the probability is the same.

In the case of *m*-xylene, the formation mechanism of glyoxal and methylglyoxal according to Assumption I is also shown in Scheme 1. In the OH–aromatics adducts, **IIa** and **IIb**, the compound **IIa** is produced by the addition of OH to *m*-xylene at the 2-position. The compound **IIb** can be produced by the addition of OH at either the 4- or the 6-position of *m*-xylene. Therefore, if the addition of OH occurs with equal probability, the formation ratio of the compounds **IIa** and **IIb** is one to two. With the assumption of the equal probability of Reactions 2b and 2c under Assumption II the formation ratio of glyoxal to methylglyoxal can be calculated to be 0.33 to 0.67. The experimentally observed formation ratio of glyoxal to methylglyoxal, 0.23 to 0.77, can be explained by introducing the third assumption [Assumption III]: the probability of addition of OH at the 2-position is two times larger than at the other ortho position when the aromatics have methyl groups at 1- and 3-positions simultaneously (*e.g. m*-xylene, 1,2,3- and 1,3,4(=1,2,4)-trimethylbenzenes), otherwise the probability is the same. According to Assumption III, the formation ratio of compound **IIa** to **IIb** is one to one and the formation ratio of glyoxal and methylglyoxal was calculated to be 0.25 to 0.75. The value obtained including Assumption III is much closer to the experimental results and assumption III is important to explain the results in cases of trimethylbenzenes as will be described in part III. The formation ratio of α-dicarbonyls obtained by experiments and estimated from Assumptions I—III are listed in Table 2 with estimated yields of unsaturated γ-dicarbonyls.

Reaction mechanisms for the ring-cleavage processes for *o*-xylene are shown also in Scheme 1, and the formation ratios of dicarbonyls obtained by experiments and calculations are listed in Table 2. In the case of *o*-xylene, Assumption II was used to determine the branching ratio of Reactions 3a and 3b (1:2). Table 2 clearly shows that using the same reaction mechanism and the same assumptions which have been introduced to explain the formation ratio of α-dicarbonyls from toluene and *m*- and *p*-xylenes, the ratio from *o*-xylene can be also reproduced well.

The fractions of the ring-cleavage process in the total reaction were 41, 55, and 36% in cases of *o*-, *m*-, and *p*-xylenes, respectively. These values are larger than those of toluene and benzene. The largest fraction from *m*-xylene is reasonable because the addition reaction of OH to the ring is enhanced. This is also evident from the fact that the yields of tolualdehydes which are produced *via* competitive reaction, H-atom abstraction from methyl side chain, are in the reverse order, *i.e. p*->*o*->*m*-, as will be discussed later. The reason for the yield of the ring cleavage being larger in *o*-xylene than in *p*-xylene is not clear. However, if the cleavage of the ring occurs in the 6,7-dioxabicyclo[3.2.1]octyloxyl radicals, the distortion energy of the rings should have an effect on the ring cleavage as demonstrated in the photooxidation of C_5–C_7 cycloalkanes.[11)] In those molecules, the ring rupture in the vibrationally hot cycloalkyloxyl radicals occurs in order of $C_5 > C_7 > C_6$ following the order of the strain energy of rings. It is very probable that the distortion energy of the bicyclo compound is larger in the case of *o*-xylene which has adjacent methyl side groups, than in the case of *p*-xylene. Discussions on the distortion energy are given again in paper III.

Yields of α-dicarbonyls obtained in the present study disagree with those obtained in the previous studies by GC analysis.[2,6,7a)] In *o*-xylene, for example, reported yields of glyoxal, methylglyoxal and biacetyl by Takagi *et al.*[2)] are 0.85, 0.14, and 0.26, respectively. Calculated values from the data by

Nojima *et al.*⁶⁾ are 0.002, 0.040, and 0.012, respectively. These data showed quite poor agreement in the yield. Recently, Shepson *et al.*⁷ᶜ⁾ have carried out an extensive analysis of ring-cleavage products in toluene and *o*-xylene photooxidation. Their reported yields of glyoxal, methylglyoxal and biacetyl are 0.034, 0.116, and 0.085, respectively. Also, Atkinson *et al.*¹²⁾ reported the yield of biacetyl (0.137 at 740 torr of air) formed in the NO_x photooxidation of *o*-xylene. The values obtained in the present study (0.08±0.01, 0.23±0.03, and 0.10±0.02 for glyoxal, methylglyoxal and biacetyl, respectively) are in good agreement with those of Shepson *et al.*⁷ᶜ⁾ and Atkinson *et al.*¹²⁾ We believe the direct measurement such as in the present study gives more reliable data of the yield. In *m*- and *p*-xylenes, very low yields of glyoxal, one tenth and one fifth of methylglyoxal, respectively, and the very low absolute yields , only a few percent of the xylene consumed, were reported by Nojima *et al.*⁶⁾

The yield of the high-boiling-point products has been reported only for the photooxidation of *o*-xylene by the use of the GC analysis.²⁾ The yield of the total high-boiling-point products analyzed was about 17% of *o*-xylene consumed. Therefore, 58% of the total products were accounted for in the case of *o*-xylene; total high-boiling-point products (17%), glyoxal (8%), methylglyoxal (23%), and biacetyl (10%).

B. Residual Spectra of Products and Unsaturated γ-Dicarbonyls. The spectra of unidentified products are shown in the residual spectra (b, d, and f) in Fig. 1. In these, absorptions appearing in the frequency region of 2850—3010 cm^{-1} are due to C–H stretching of hydrocarbons. The absorptions around 1800 cm^{-1} corresponds to the C=O stretching of carboxylic acids, anhydrides, and peroxyacyl nitrates as described in paper I. Formation of maleic anhydride was observed in the case of *o*-xylene. Although Fig. 2 shows a linear increase of maleic anhydride to *o*-xylene consumption, maleic anhydride is considered to be a secondary product produced from *cis*-2-butenedial as proposed in the case of toluene.⁸⁾ Under the reaction mechanism mentioned above, only *o*-xylene can yield *cis*-2-butenedial (see Table 2). This also suggests that maleic anhydride is produced from *cis*-2-butenedial. If maleic anhydride is produced from *cis*-2-butenedial, methylmaleic anhydride can be produced from 2-methyl-2-butenedial. However, no significant IR absorption¹³⁾ of methylmaleic anhydride was observed. In *m*-xylene, a strong absorption (shown by an arrow) appears at the low frequency side of the absorption around 1800 cm^{-1}. This absorption was always prominent in cases of *m*-xylene and 1,3,5-trimethylbenzene (will be described in part III), and increases strongly upon prolonged irradiation. Although the compounds for this absorption were not identified, it is suggested that more carboxylic acids and/or anhydrides are produced in the photooxidation of *m*-xylene and 1,3,5-trimethylbenzene.

A strong absorption in the frequency region of 1700—1750 cm^{-1} corresponds to the C=O stretching of aldehyde, ketone, dialdehyde, and diketone. If unsaturated γ-dicarbonyls shown in Scheme 1 are present, these compounds should have strong absorption in this region. The noise appearing in the region of 1600—1650 cm^{-1} is caused by the subtraction of the absorption of NO_2. Organic nitrates, which should absorb around 1670, 1280, and 850 cm^{-1}, were not observed as major products.

Absorptions appearing in the frequency region of 1400—800 cm^{-1} are attributable to skeletal vibrations. As described in paper I, absorptions by HONO can also be seen. Spectra in the frequency region of 1400—900 cm^{-1} are expanded and shown in Fig. 4. Spectra (a), (b), and (c) in Fig. 4 are residual spectra of *o*-, *m*-, and *p*-xylene, respectively. In these, the absorption spectrum of HONO was subtracted. Among unsaturated γ-dicarbonyls shown in Scheme 1

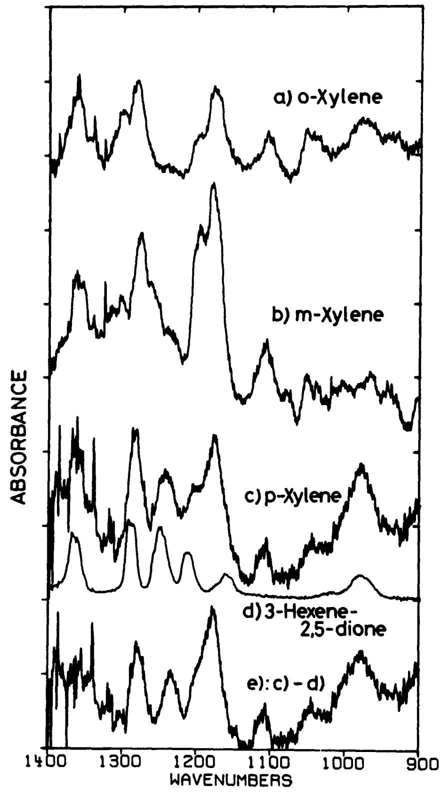
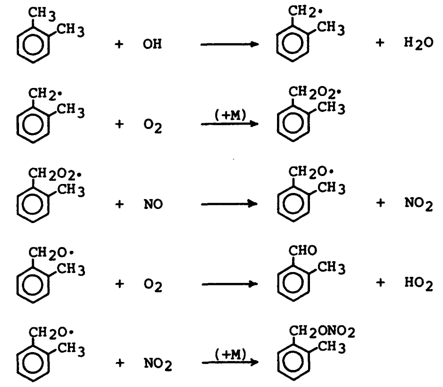


Fig. 4. Residual spectra in the frequency region of 1400—900 cm^{-1}. Conditions are the same as the case in Fig. 1.
a), b), and c) are residual spectra in cases of *o*-, *m*-, *p*-xylenes, respectively. d) Standard spectrum of *trans*-3-hexene-2,5-dione. e) Difference spectrum of c) − d).

and Table 2, 3-hexene-2,5-dione is expected to be the least reactive against OH attack because of an absence of aldehydic hydrogens, taking into account that the loss of unsaturated γ-dicarbonyls is partly due to hydrogen-atom abstraction from –CHO by OH radicals. Takagi *et al.*[14] reported the observation of 3-hexene-2,5-dione by GC/MS method among the compounds collected in a trap at liquid nitrogen temperature from gaseous mixtures of both 1,2,4-trimenthylbenzene and *p*-xylene photooxidation. Thus, in the present study, *in-situ* observation of 3-hexene-2,5-dione was attemped. The standard spectrum of 3-hexene-2,5-dione synthesized by the reaction of acetonylacetone with selenious acid[14,15] is shown in Fig.4(d). Only in the *p*-xylene, spectrum(c), the absorption by 3-hexene-2,5-dione was apparent. Spectrum (e) shows the (c)–(d) difference spectrum. By substraction of the spectrum of 3-hexene-2,5-dione, the yield of 3-hexene-2,5-dione was estimated to be about 8% of the *p*-xylene consumed. The uncertainty of the value is ±100% because of ambiguity of the subtraction. Recently, Tuazon *et al.*[16] investigated the atmospheric chemistry of *cis*- and *trans*-3-hexene-2,5-dione. They report the existence of photoisomerization between the two isomers, and the isomerization was found to account for ≥80% of the total photolysis rate with a photoequilibrium [trans]/[cis] ratio of 0.55±0.05 under their irradiation conditions (25-kW xenon arc solar simulator, NO_2-photolysis rate of $2.1\times10^{-3}\ s^{-1}$). According to the vapor-phase IR spectra of the two isomers reported in their study, the spectrum shown in Fig. 4 (d) is *trans*-3-hexene-2,5-dione. In the ring cleavage of *p*-xylene formation of cis isomer is expected primarily, and the cis isomer shows only one strong IR absorption at around 1160 cm^{-1} [16] in the skeletal vibration region. Unfortunately the existence of *cis*-3-hexene-2,5-dione can not be confirmed from Fig. 4(e). It can be, however, assumed that in the present study light intensity is strong enough to establish the photoequilibrium of [trans]/[cis]≈0.5 in 3-hexene-2,5-dione within a few tens min, judging from their data[16] and the NO_2 photodecomposition rate of the present study ($3.7\times10^{-3}\ s^{-1}$) although the dependence of the photoisomerization rate on wavelength is uncertain. If we take the photoequilibrium into account, the total yield of 3-hexene-2,5-diones should be about three times larger than that of the trans isomer. The yield thus estimated is comparable to that of glyoxal (24±2%), which is a counterpart of 3-hexene-2,5-dione in the ring cleavage of *p*-xylene in Scheme 1.

Syntheses of other unsaturated γ-dicarbonyls, *e.g.* 2-butenedial[17] and 4-oxo-2-pentenal,[18] were attempted. However these compounds were glassy and easily polymerized. Since the purification of these compounds was very difficult, standard spectra of these compounds were not obtained although the residual spectra show the possibility of the presence of unsaturated γ-dicarbonyls.

C. Yields of Tolualdehydes. The formation of *o*-, *m*-, and *p*-tolualdehydes was observed in the photooxidation of *o*-, *m*-, and *p*-xylene, respectively. Since *o*-, *m*-, and *p*-tolualdehydes are formed from *o*-, *m*-, and *p*-methylbenzyl radicals produced by the side-chain hydrogen abstracion by OH radicals, Reactions 4—7, the fractions of the side-chain abstraction channel in the total reaction can be estimated from the yields of tolualdehydes.



(4)

(5)

(6)

(7)

(8)

Results are listed in Table 3 together with literature values. The values in the present study were obtained from the yields of tolualdehydes only, and are therefore lower limit, because the amount of other products produced from methylbenzyl radicals such as *o*-, *m*-, *p*-methylbenzyl nitrates (Reaction 8) should account for up to 10%[2] of tolualdehydes produced.

D. Atmospheric Implication. From the photochemical reactivity point of view, ring-cleavage products are important among the compounds produced in the photooxidation of aromatic hydrocarbon. The ring-cleavage products are produced through rather long sequences of reactions involving organic radicals and are often more reactive against photolysis and OH radical attack, which bring forth other radical reaction sequences, than the parent aromatic hydrocarbons. Therefore, the yield of ring-cleavage products such as α-dicarbonyls and unsaturated γ-dicarbonyls is a key for atmospheric photooxidation of aromatic hydrocarbons. Nevertheless, there have been few systematic studies[6,7b] on the yield of α-dicarbonyls from alkylbenzenes, and there is no generalized mechanism for the ring-cleavage reactions so far. This has enforced one to include many branches of reactions and thus to introduce many parameters in model simulation studies of aromatic hydrocarbon photooxidation.

The yield of α-dicarbonyls has been determined systematically for toluene and xylenes in paper I and

Table 3. Fractions of side-chain-abstraction channel in the total reaction of OH+xylenes

	Perry *et al.* (Ref. 1)	Nicovich *et al.* (Ref. 4)	Takagi *et al.* (Ref. 2)	Kenley *et al.* (Ref. 3)	This work
o-Xylene	$0.20^{+0.15}_{-0.10}$	0.04	0.08—0.13		0.05±0.01
m-Xylene	$0.04^{+0.04}_{-0.02}$	0.02			0.04±0.01
p-Xylene	$0.07^{+0.07}_{-0.03}$	0.04		0.15±0.02	0.08±0.01
Method	Temperature dependence of rate constants.	Temperature dependence of rate constants.	GC analysis of tolualdehyde and nitrate.	GC analysis of products.	FT-IR analysis of tolualdehydes.

the present study, and the observed data could be explained by the mechanism depicted as Scheme 1 with Assumptions I—III. Although it is extremely simplified and its validity is still uncertain, the authors believe that it is very useful for predicting the product distribution of the ring-cleavage products and it can provide the most appropriate basis at present of the complex ring-cleavage processes for modeling studies. Indeed, the mechanism seems applicable to other aromatic hydrocarbons as will be demonstrated in the following report, paper III. However, in order to establish more realistic reaction mechanism for the ring-cleavage reactions, extensive analysis of ring-cleavage products is needed including unsaturated γ-dicarbonyls. Further the thermochemical information of the radicals which might involve in the photooxidation of aromatic compounds, such as 6,7-dioxabicyclo[3.2.1]octane and 2,3-dioxabicyclo[2.2.2]octane compounds and their oxygenated radicals, is also needed.

References

1) R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., *J. Phys. Chem.*, **81**, 296 (1977).

2) H. Takagi, N. Washida, H. Akimoto, K. Nagasawa, Y. Usui, and M. Okuda, *J. Phys. Chem.*, **84**, 478 (1980).

3) R. A. Kenley, J. E. Davenport, and D. G. Hendry, *J. Phys. Chem.*, **85**, 2740 (1981).

4) J. M. Nicovich, R. L. Thompson, and A. R. Ravishankara, *J. Phys. Chem.*, **85**, 2913 (1981).

5) A. R. Ravishankara, S. Wagner, S. Fisher, G. Smith, R. Schiff, R. T. Watson, G. Tesi, and D. D. Davis, *Int. J. Chem. Kinet.*, **10**, 783 (1978).

6) K. Nojima, K. Fukaya, S. Fukui, and S. Kanno, *Chemosphere*, **3**, 247 (1974).

7) a) K. R. Darnall, R. Atkinson, and J. N. Pitts, Jr., *J. Phys. Chem.*, **83**, 1943 (1979).

b) E. C. Tuazon, R. Atkinson, H. MacLeod, H. W. Biermann, A. M. Winer, W. P. L. Carter, and J. N. Pitts, Jr., *Environ. Sci. Technol.*, **18**, 981 (1984).

c) P. B. Shepson, E. O. Edney, and E. W. Corse, *J. Phys. Chem.*, **88**, 4122 (1984).

8) H. Bandow, N. Washida, and H. Akimoto, the preceding paper (Part I) in this volume.

9) There is no direct experimental proof that the addition of OH to xylene is predominantly at *o*-position. However, in the case of $O(^3P)$+xylene, Grovenstein and Mosher[10] suggested that the addition of O atoms to xylene is predominantly at *o*-position. Kenley *et al.*[3] reported the formation of $C_6H_3(OH)(CH_3)_2$[2,1,4-] in the reaction of OH+*p*-xylene.

10) E. Grovenstein, Jr. and A. J. Mosher, *J. Am. Chem. Soc.*, **92**, 3810 (1970).

11) H. Takagi, N. Washida, H. Bandow, H. Akimoto, and M. Okuda, *J. Phys. Chem.*, **85**, 2701 (1981).

12) R. Atkinson, W. P. L. Carter, and A. M. Winer, *J. Phys. Chem.*, **87**, 1605 (1983).

13) Since methylmaleic anhydride is commercially available, a standard absorption spectrum can be obtained.

14) H. Takagi, N. Washida, H. Akimoto, and M. Okuda, *Spectrosc. Lett.*, **15** 145 (1982).

15) M. W. Goldberg and P. Müller, *Helv. Chim. Acta*, **21**, 1699 (1938).

16) E. C. Tuazon, R. Atkinson, and W. P. L. Carter, *Environ. Sci. Technol.*, **19**, 265 (1985).

17) K. Alder, H. Betzing, and K. Heimbach, *Liebig's Am. Chem.*, **638**, 187 (1960).

18) J. A. Hirsch and A. J. Szur, *J. Heterocycl. Chem.*, **9**, 523 (1972).