Bull. Chem. Soc. Jpn., 58, 2549—2555 (1985)

Ring-cleavage Reactions of Aromatic Hydrocarbons Studied by FT-IR Spectroscopy. III. Photooxidation of 1,2,3-, 1,2,4-, and 1,3,5-Trimethylbenzenes 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, Ibaraki 305

(Received February 12, 1985)

Photooxidation of 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzenes was carried out in the NO_x–air system. Formation of glyoxal, methylglyoxal and biacetyl was observed in the cases of 1,2,3- and 1,2,4-trimethylbenzenes, and only methylglyoxal was observed from 1,3,5-trimethylbenzene. Yields of glyoxal, methylglyoxal and biacetyl were 7, 18, and 45% and 8, 37, and 11% of trimethylbenzene consumed in cases of 1,2,3- and 1,2,4-trimethylbenzenes, respectively. The reaction mechanism which was used to explain the yields of α-dicarbonyl compounds from toluene and *o*-, *m*-, *p*-xylenes in the preceding paper (part II) has been applied to explain these yields, and has been found to reproduce these yields well. Formation of 3-hexene-2,5-dione was observed only from 1,2,4-trimethylbenzene. The fractions of the ring-cleavage process in the total reaction were 70, 56, and 64% in cases of 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzenes, respectively. The yields of the ring-cleavage process are discussed.

In the final paper of this series,[1,2] quantitative analysis of ring-cleavage products in the photooxidation of 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzenes is reported. The rate constants for the reactions of OH+trimethylbenzenes are reported to be very large[3,4,5] (as large as OH+butenes), and the branching ratios for side-chain hydrogen abstractions (estimated to be 2—3% of total reaction[4,6]) are much smaller than in the cases of toluene and xylenes.

The questions addressed in this study are as follows: (1) How large is the fraction of the ring-cleavage process in the total reaction of trimethylbenzenes? (As described in papers I and II, fractions of the ring-cleavage process were in order of *m*-xylene (55%)>*o*-xylene (41%)>*p*-xylene (36%)>toluene (29%)> benzene (15—20%)): (2) Can the formation ratio of α-dicarbonyls (glyoxal, methylglyoxal, and biacetyl) be explained by the cyclization mechanism with three assumptions used in cases of toluene and *o*-, *m*-, *p*-xylenes?: (3) Can formation of unsaturated γ-dicarbonyls be observed? (In the case of 1,2,4-trimethylbenzene, formation of 3-hexene-2,5-dione has been observed by the GC analysis[7]): (4) Are there new specific ring-cleavage products in the photooxidation of trimethylbenzenes?: (5) How consistent are the results for the photooxidation of aromatic hydrocarbons (from benzene to trimethylbenzenes)?

Results

A mixture of trimethylbenzene (4 ppm), NO (1.5 ppm), and NO_2 (0.5 ppm), diluted in 1 atm (=101 kPa) air was irradiated in the reaction chamber as described in paper I.[1] Three experiments were carried out for each 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzenes.

Product spectra (spectra of reactants and H_2O were subtracted) of each trimethylbenzene are shown by spectrum (a), (c), and (e) in Fig. 1. Residual spectra (spectra of identified products were subtracted from spectrum (a), (c), and (e)) of each trimethylbenzene are shown by spectrum (b), (d), and (f) in Fig. 1. These spectra were obtained under nearly equal (about 20%) conversions of trimethylbenzenes. In all cases, formation of formaldehyde, formic acid, and PAN was observed. α-Dicarbonyls observed are

Table 1. Yield of products[a)] (Δproduct/−Δtrimethylbenzene) in the photooxidation of trimethylbenzenes[b)]

Product \ Run	1,2,3-Trimethylbenzene				1,2,4-Trimethylbenzene				1,3,5-Trimethylbenzene			
	1	2	3	Ave.[c)]	4	5	6	Ave.[c)]	7	8	9	Ave.[c)]
HCHO	0.17	0.18	0.17	0.17 ±0.01	0.18	0.18	0.17	0.18 ±0.01	0.15	0.15	0.16	0.15±0.01
$(CHO)_2$	0.073	0.071	0.071	0.072±0.001	0.072	0.081	0.081	0.078±0.005	—	—	—	—
CH_3COCHO	0.17	0.18	0.19	0.18 ±0.01	0.38	0.37	0.36	0.37 ±0.01	0.67	0.63	0.63	0.64±0.03
$(CH_3CO)_2$	0.44	0.45	0.47	0.45 ±0.02	0.09	0.11	0.11	0.11 ±0.01	—	—	—	—
Total yield of α-dicarbonyls				0.70 ±0.02				0.56 ±0.02				0.64±0.03

a) Values were calculated by the least-square fit of six initial points of each run. b) Initial concentrations of reactants were 4 ppm trimethylbenzene, 1.5 ppm NO, and 0.5 ppm NO_2 in 1 atm (=101 kPa) air in all runs. c) The indicated errors are one standard deviation of three runs.

glyoxal, methylglyoxal, and biacetyl in cases of 1,2,3- and 1,2,4-trimethylbenzenes, and only methylglyoxal is produced from 1,3,5-trimethylbenzene. Maleic anhydride, which is produced in the reactions of benzene, toluene, and *o*-xylene, was not observed as products of the trimethylbenzenes in significant amounts. Dimethylbenzaldehydes are probably produced, but were not analyzed because of too small yields.

The profile of the product concentrations *versus* irradiation time in the case of 1,2,4-trimethylbenzene is shown in Fig. 2 as an example. Among the products identified, formic acid and PAN were found to be secondary products, like in the cases of toluene and xylenes. As described in paper I,[1] amounts of products formed were plotted against trimethylbenzene consumed. From the slopes of these plots, the yield of each product was determined. Yields of products except formic acid and PAN (secondary products) are listed in Table 1. Values of yield were

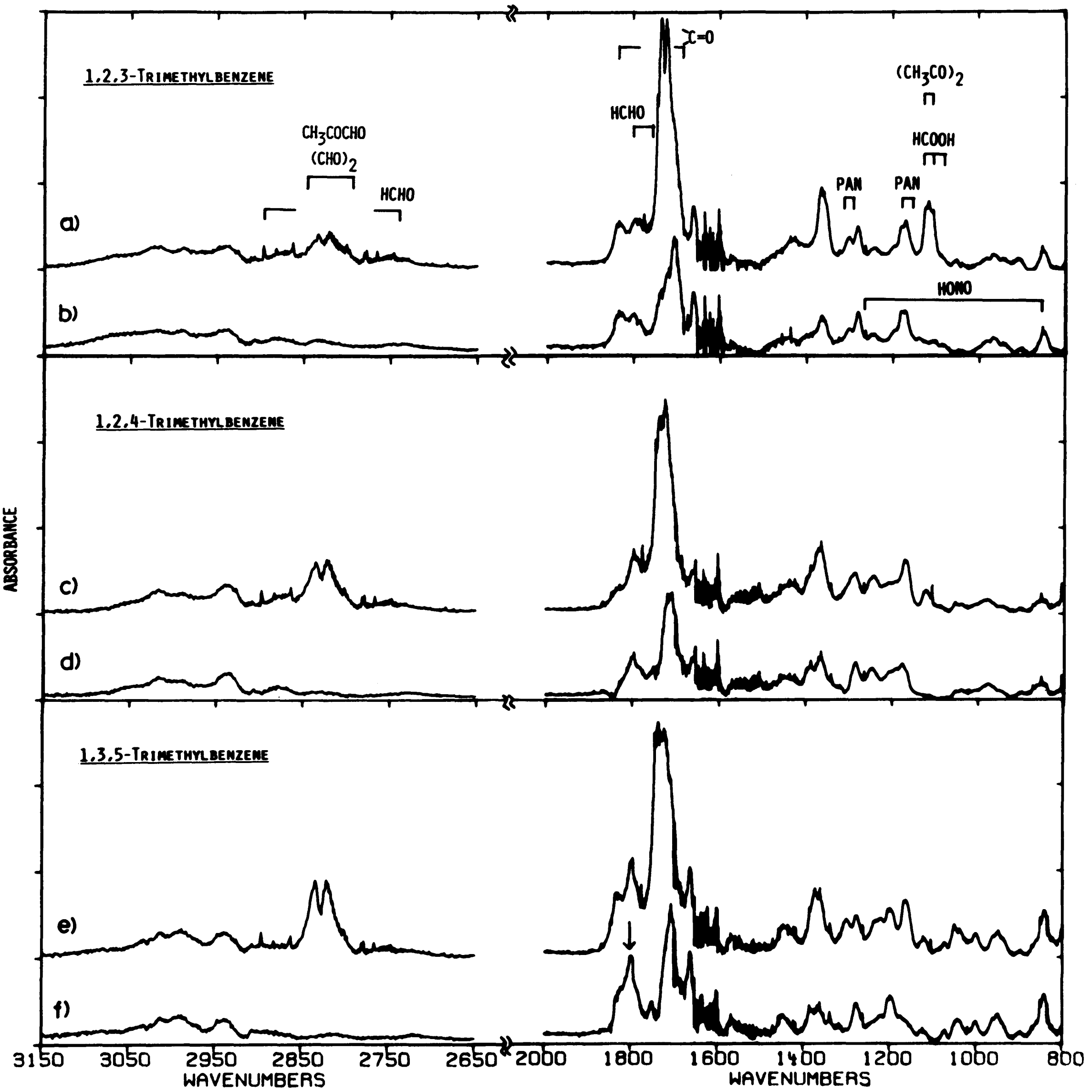


Fig. 1. Product spectra (spectra of reactants were subtracted) and residual spectra (spectra of products identified were subtracted). The initial conditions: [trimethylbenzene]=4 ppm, [NO]=1.5 ppm, and [NO_2]=0.5 ppm in 1 atm (=101 kPa) air.

a) Product spectra in the photooxidation of 1,2,3-trimethylbenzene after 80 min irradiation. Conversion of 1,2,3-trimethylbenzene is 19%. b) Residual spectra after subtraction of products identified (H_2CO, $(CHO)_2$, CH_3COCHO, $(CH_3CO)_2$, PAN, and HCOOH). c) Product spectra in the photooxidation of 1,2,4-trimethylbenzene after 66 min irradiation. Conversion of 1,2,4-trimethylbenzene is 19%. d) Residual spectra after subtraction of products identified (H_2CO, $(CHO)_2$, CH_3COCHO, $(CH_3CO)_2$, PAN, and HCOOH). e) Product spectra in the photooxidation of 1,3,5-trimethylbenzene after 50 min irradiation. Conversion of 1,3,5-trimethylbenzene is 18%. f) Residual spectra after subtraction of products identified (H_2CO, CH_3COCHO, PAN, and HCOOH). ↓ : See text.

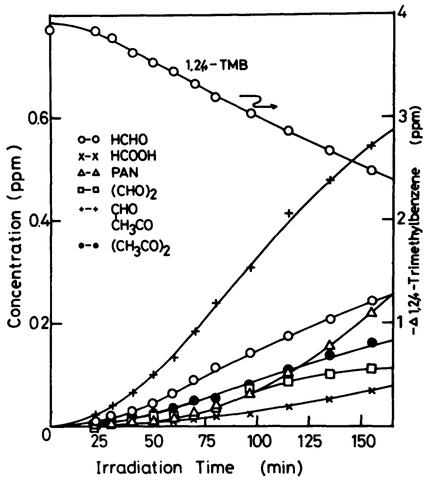


Fig. 2. Concentration of each product as a function of irradiation time in the case of 1,2,4-trimethylbenzene.

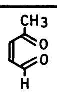
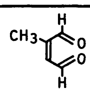
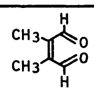
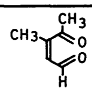
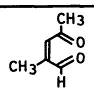
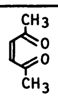
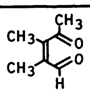
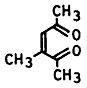
calculated by the least-square fit of six initial points of each run. The indicated errors are one standard deviation of three runs. Yields of α-dicarbonyls are fairly large in cases of 1,2,3- and 1,3,5-trimethylbenzenes compared with those of xylenes.

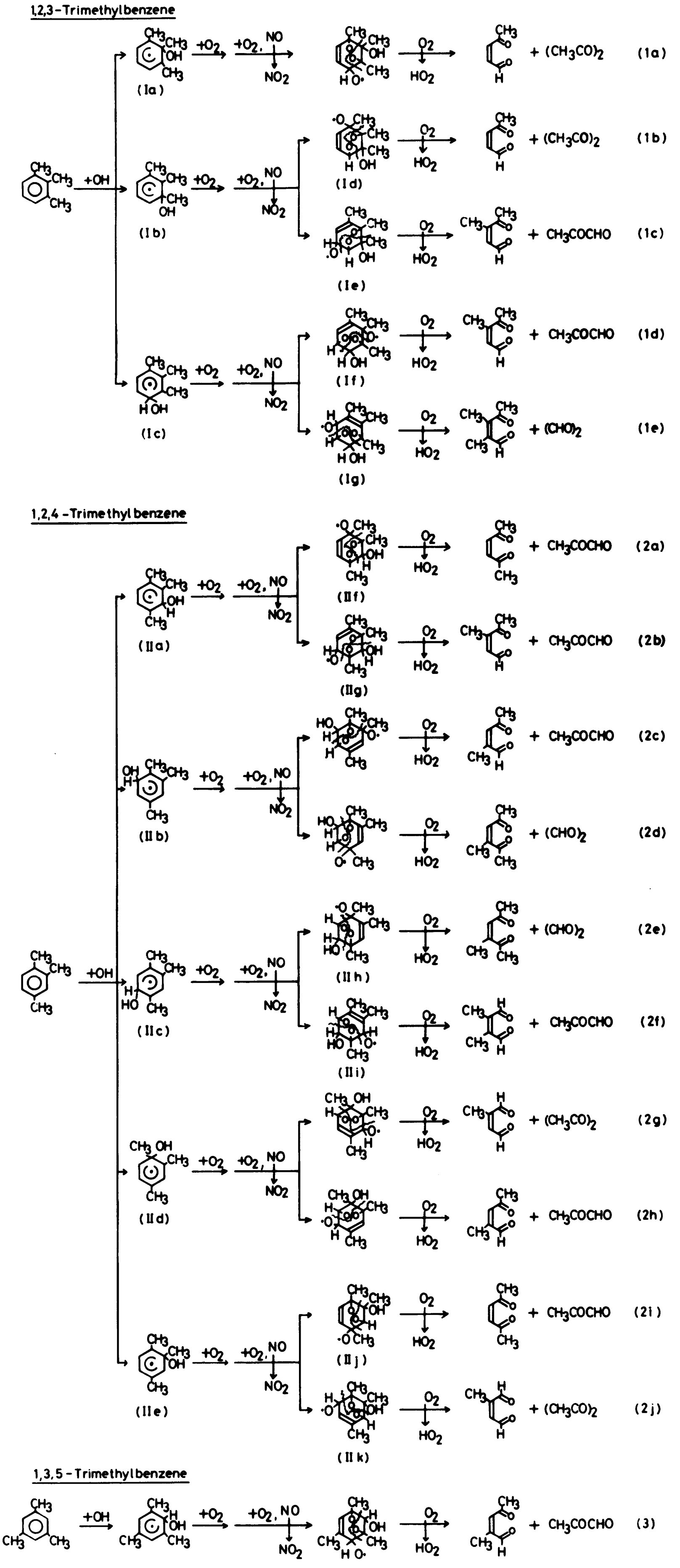
Discussion

A. Yields of α-Dicarbonyls and Reaction Mechanisms. It should be examined whether the yields of α-dicarbonyls shown in Table 1 can be explained by the cyclization mechanism with the assumptions used in cases of toluene and xylenes, as described in paper II.[2] The rules in the reaction mechanism used in paper II are as follows: (1) OH radicals add primarily to the ortho position of each side chain ([Assumption I] in paper II): (2) When the aromatics have side chains ($-CH_3$) at 1- and 3-positions (*e.g.* in *m*-xylene, 1,2,3- and 1,3,4(=1,2,4)-trimethylbenzenes), the probability of OH addition at the 2-position is two times larger than at other ortho position, otherwise the probability is the same ([Assumption III] in paper II): (3) Addition of O_2 to the OH-aromatics adduct occurs predominantly at a position which yields conjugated double bonds (see Reactions 6a and 6b in paper I[1]): (4) The OH-aromatics-O_2 adduct primarily undergoes a cyclization reaction forming a bicyclo(-O-O-bridge) compound. In this case, formation of 6,7-dioxabicyclo[3.2.1]octane compound (allyl-type radical) is dominant. (In the case of 2,3-dioxabicyclo[2.2.2]octane compound, a radical point and a double bond are not conjugated): (5) The probability of O_2 addition to resonance structure with tertiary radical is two times larger than that to resonance structure with secondary radical when the resonance structures of the allyl-type radical consist of both secondary and tertiary radicals, otherwise the probability of O_2 addition to resonance structures of allyl-type radical is the same ([Assumption II] in paper II): (6) After addition of O_2 to the bicyclo[3.2.1] radical, an alkoxyl-type radical is produced by the abstraction of an O atom by NO: (7) The resulting alkoxyl-type radical undergoes cleavage of the ring, and a 1-hydroxyl-2-oxoalkyl radical ($R-\dot{C}(OH)-CR'=O$) and an unsaturated γ-dicarbonyl are produced: (8) The 1-hydroxy-2-oxoalkyl radical undergoes hydrogen abstraction by O_2, and an α-dicarbonyl is produced.

Ring-cleavage reactions of the trimethylbenzenes according to the above rules are shown in Scheme 1. The process of O_2 addition to the OH-aromatics adduct and the formation of 6,7-dioxabicyclo[3.2.1]-octane compound are excluded just for avoiding complication. Formation ratios of α-dicarbonyls obtained by experiments and of α- and unsaturated γ-dicarbonyls calculated using the above rules are listed in Table 2. Branching ratios used in the calculations are as follows: Compound **Ia**:**Ib**:**Ic**=1:1:1 and **IIa**:**IIb**:**IIc**:**IId**:**IIe**=2:1:1:1:1, according to the number of equivalent positions and Assumptions I and III: Compound **Id**:**Ie**=2:1, **If**:**Ig**=2:1, **IIf**:**IIg**=2:1, **IIh**:**IIi**=2:1, and **IIj**:**IIk**=2:1, according to Assumption II in paper II: One to one is used for all other branching ratios. Yields of α-dicarbonyls obtained by the calculations are in excellent agreement with experimentally observed values. In the

Table 2. Experimental and calculated relative yields of α- and unsaturated γ-dicarbonyls

	$(CHO)_2$	CH_3COCHO	$(CH_3CO)_2$								
1,2,3-Trimethylbenzene											
Exp.	0.10	0.26	0.64								
Calcd	0.11	0.33	0.56	0.56	—	—	0.33	—	—	0.11	—
1,2,4-Trimethylbenzene											
Exp.	0.14	0.66	0.20								
Calcd	0.19	0.67	0.14	—	0.14	0.06	0.11	0.17	0.33	—	0.19
1,3,5-Trimethylbenzene											
Exp.	—	1.0	—								
Calcd	—	1.0	—	—	—	—	—	1.0	—	—	—


1,2,3-Trimethylbenzene
+OH
+O2
+O2, NO
NO2
O2
HO2
(Ia)
(Ib)
(Ic)
(Id)
(Ie)
(If)
(Ig)
+ (CH3CO)2 (1a)
+ (CH3CO)2 (1b)
+ CH3COCHO (1c)
+ CH3COCHO (1d)
+ (CHO)2 (1e)
1,2,4-Trimethylbenzene
(IIa)
(IIb)
(IIc)
(IId)
(IIe)
(IIf)
(IIg)
(IIh)
(IIi)
(IIj)
(IIk)
+ CH3COCHO (2a)
+ CH3COCHO (2b)
+ CH3COCHO (2c)
+ (CHO)2 (2d)
+ (CHO)2 (2e)
+ CH3COCHO (2f)
+ (CH3CO)2 (2g)
+ CH3COCHO (2h)
+ CH3COCHO (2i)
+ (CH3CO)2 (2j)
1,3,5-Trimethylbenzene
+ CH3COCHO (3)

Scheme 1.

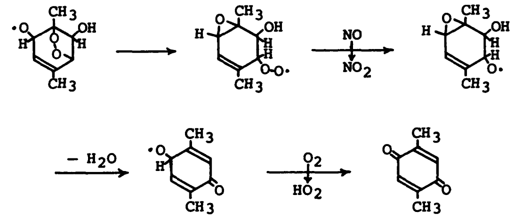
calculations, Assumption III in paper II is crucial. Without this assumption less satisfactory agreement of calculations with experimental values was obtained.[8]

B. Yield of the Ring-cleavage Process. The fractions of the ring-cleavage process in the total reaction are 70, 56, and 64% in cases of 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzenes, respectively. The percentages in 1,2,3- and 1,3,5-trimethylbenzenes are larger than in the cases of benzene, toluene and xylenes. The value of 56% in 1,2,4-trimethylbenzene is close to 55% in the case of *m*-xylene which shows the largest value of all xylenes. Factors governing the extent of ring cleavage are as follows: 1) The branching ratio between OH addition to the aromatic ring and side-chain hydrogen abstraction: 2) The branching ratio between cyclization of the OH–aromatics–O_2 adduct and the formation of phenols by hydrogen abstraction from the ring by O_2, and the formation of aromatic nitro compounds by the addition of NO_2:[9] 3) The distortion energy of 6,7-dioxabicyclo[3.2.1]octane compound (the alkoxyl-type radical).

As to factor 1, 100%, 85—90%, 90—95%, and 97—98% of total reactions are estimated to proceed through addition in the cases of benzene (no side chain), toluene, xylenes, and trimethylbenzenes, respectively.[4] Therefore, side-chain abstraction might have a slight effect on the yield of ring cleavage, except the case of benzene. Factor 1 alone seems not to explain the large variations of the ring-cleavage yields (15—20% in benzene, 29% in toluene, 36% in *p*-xylene, 41% in *o*-xylene, 55% in *m*-xylene, 56% in 1,2,4-trimethylbenzene, 64% in 1,3,5-trimethylbenzene, and 70% in 1,2,3-trimethylbenzene).

Factor 2 is likely to be important. The probability of cyclization might be governed by the reactivity to electrophilic attack of the carbon with which the end oxygen of the OH–aromatics–O_2 adduct forms a bond. Presumably increase of the number of methyl side chains enhances the probability of cyclization, meta substitution being particularly favorable for electrophilic attack leading to cyclization. The increasing extent of ring cleavage in the order of benzene<toluene<xylenes<trimethylbenzenes, and the large extent of ring cleavage in the cases of *m*-xylene and 1,3,5-trimethylbenzene, might reflect the reactivity of the aromatic ring to electrophilic attack.[10]

After the formation of the 6,7-dioxabicyclo[3.2.1]-octane compound, the distortion energy of this compound would affect the occurrence of the ring cleavage as mentioned in paper II.[2] Although distortion energies of the bicyclo[3.2.1] compounds are not known, the distortion energy is probably larger in the case that the side chains are located adjacent to each other than in the case that side chains are located separately in good symmetry. The larger extent of the ring-cleavage process in the case of 1,2,3-trimethylbenzene as compared with 1,3,5-trimethylbenzene and also in the case of *o*-xylene as compared with *p*-xylene, might be partly due to differences in distortion energy. The fate of the bicyclo compounds when the ring cleavage does not occur is not clear. One possible route is the formation of quinones after rupture of the –O–O– bridge in 6,7-dioxabicyclo[3.2.1]octyloxyl radicals. For example, in the case of *p*-xylene:



(4)

Formation of small amounts of dimethyl-*p*-benzoquinones have been reported in the photooxidation of *o*-, *m*-, and *p*-xylenes.[11,12] The relative yield of dimethyl-*p*-benzoquinone is the largest for *p*-xylene.[12]

As discussed above, the yield of the ring-cleavage process and the ratio of the α-dicarbonyls formed are governed by several factors. Some features of the ring-cleavage reaction can be explained, although a quantitative evaluation of all factors is not possible at present.

C. 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. Absorptions appearing in the frequency region of 2850—3010 cm^{-1} (C–H stretching of hydrocarbons) are stronger than in the case of xylenes. This is probably due to larger yields of unsaturated γ-dicarbonyls (*cf.* Table 2 and Scheme 1) which have more methyl groups.

Residual absorption around 1800 cm^{-1} can be accounted for by C=O stretching of carboxylic acids, anhydrides, and peroxyacyl nitrates. A sharp absorption at 1800 cm^{-1} observed in the case of *m*-xylene is also apparent for 1,3,5-trimethylbenzene (marked by an arrow). No absorptions of maleic anhydride, methylmaleic anhydride, and dimethylmaleic anhydride were observed in this frequency region. Absorption around 1700 cm^{-1} (C=O stretching of aldehyde, ketone, dialdehyde, and diketone) is also present. The large number of overlapping bands in the frequency region of 1700—1850 cm^{-1} shows that there should be a variety of carbonyls present. Sharp absorption at 1670 cm^{-1} is due to organic nitrates which have accompanying bands at 1280 and 850 cm^{-1}.

Absorptions in the region of skeletal vibrations (1400—900 cm^{-1}) are shown on an expanded scale in

Fig. 3. The spectra shown in Fig. 3 are arranged in order of 1,2,3-, 1,3,5-, and 1,2,4-trimethylbenzene: (Note that the order differs from the order in Fig. 1). Spectrum (d) in Fig. 3 shows a standard spectrum of *trans*-3-hexene-2,5-dione. Formation of 3-hexene-2,5-dione in the photooxidation of 1,2,4-trimethylbenzene has been reported in the previous work using the method of GC/MS analysis.[7] In this study, also the formation of 3-hexene-2,5-dione was observed in the case of 1,2,4-trimethylbenzene (spectrum (c) in Fig. 3). Subtraction of the spectrum of *trans*-3-hexene-2,5-dione from spectrum (c) led to an estimated yield of 6% for *trans*-3-hexene-2,5-dione to 1,2,4-trimethylbenzene consumed. According to the study on atmospheric chemistry of *cis*- and *trans*-3-hexene-2,5-dione by Tuazon *et al.*[13] cis and trans isomers of the compound is expected to establish a photoequilibrium with the ratio of [trans]/[cis]≃0.5 under the present experimental conditions.[2] The estimated total yield of 3-hexene-2,5-diones is thus about 18%. The uncertainty of this estimate is ±100% because of the ambiguity of the subtraction. Spectrum (e) shows the difference spectrum (c)−(d).

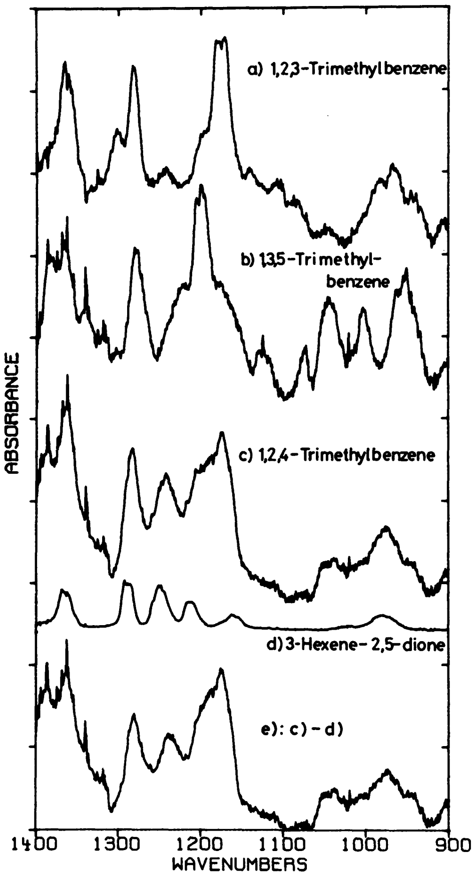


Fig. 3. Residual spectra in the frequency region of 1400—900 cm^{-1}. Conditions are the same as in Fig. 1. a), b), and c) are residual spectra in the cases of 1,2,3-, 1,3,5-, and 1,2,4-trimethylbenzenes, respectively. d) Standard spectrum of *trans*-3-hexene-2,5-dione. e) Difference spectrum of c)−d).

Although no further products except 3-hexene-2,5-dione could be identified in the residual spectra, remaining of C–H stretching vibrations (2850—3010 cm^{-1}), strong absorption around 1700 cm^{-1}, and numerous bands in the region of skeletal vibrations (800—1400 cm^{-1}), suggests the presence of unsaturated γ-dicarbonyls (shown in Table 2 and Scheme 1) in considerable amounts. No unique products of the trimethylbenzenes could be identified.

D. General Conclusions: *The Photooxidations of Aromatic Hydrocarbons.* This study of eight aromatic hydrocarbons (benzene, toluene, *o*-, *m*-, and *p*-xylenes, 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzenes) and the conclusions drawn from it may be summarized as follows:

1) Products formed by the ring-cleavage reaction in the photooxidation of aromatic hydrocarbons were analyzed by long-path FT-IR spectroscopy. The advantage of this technique is that products can be observed *in situ*, without the sampling and preconcentration processes which are needed generally in GC and GC/MS analysis. The FT-IR is particularly useful for the quantitative analysis of α-dicarbonyls which cannot be analyzed with reasonable sensitivity by GC even with flame ionization detection.[11] Therefore, reliable yields of α-dicarbonyls were determined for the first time in the present study.

2) The α-dicarbonyls observed in the photooxidation of aromatic hydrocarbons are glyoxal, methylglyoxal, and biacetyl. The relative yields of these products can be explained by a cyclization mechanism of OH-aromatics-O_2 adducts, and cleavage of 6,7-dioxabicyclo[3.2.1]octane compounds. It is suggested that an α-dicarbonyl and an unsaturated γ-dicarbonyl are produced in this process.

3) 3-Hexene-2,5-dione was observed as an unsaturated γ-dicarbonyl in the photooxidation of *p*-xylene and 1,2,4-trimethylbenzene. Formation of maleic anhydride observed in the photooxidation of benzene, toluene, and *o*-xylene is considered as an indirect evidence of the formation of *cis*-2-butenedial (an unsaturated γ-dicarbonyl). Other unsaturated γ-dicarbonyls could not be identified.

4) The fractions of the ring-cleavage process are: 15—20% (benzene); 29% (toluene); 36% (*p*-xylene); 41% (*o*-xylene); 55% (*m*-xylene); 56% (1,2,4-trimethylbenzene); 64% (1,3,5-trimethylbenzene); and 70% (1,2,3-trimethylbenzene). It is suggested that the extent of ring cleavage is governed by the reactivity to electrophilic attack of the OH-aromatics-O_2 adduct, and by the distortion energy of the resulting 6,7-dioxabicyclo[3.2.1]octane compound.

5) Since the formation of fairly large amounts of α- and unsaturated γ-dicarbonyls are expected in the urban atmosphere, studies of the mechanisms of both photolysis and photooxidation of α- and γ-dicar-

bonyls are necessary to develop the chemical models of photochemical air pollution, although the rate constants of the photolysis and OH radical reactions of α-dicarbonyls[14)] and 3-hexene-2,5-diones[13)] were reported recently.

Throughout this series of investigations, the authors wish to thank Prof. U. Schurath of University of Bonn in Germany and Dr. C. J. Howard of National Oceanic and Atmospheric Administration for helpful suggestions and discussions. We also thank Dr. S. Hatakeyama in our laboratory for helpful discussions. The assistance of H. Takagi in the early stage of this work is gratefully acknowledged.

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8) The ratios among glyoxal, methylglyoxal and biacetyl were 0.13:0.40:0.47 and 0.23:0.60:0.17 in cases of 1,2,3- and 1,2,4-trimethylbenzene, respectively, when Assumption III in paper II was not used.

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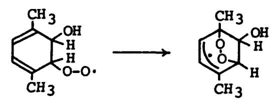
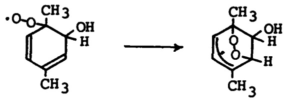
10) Assuming that the probability of forming the 6,7-dioxabicyclo[3.2.1]octane compound increases when the -O-O· attacks the carbon at the ipso position [Assumption IV], the yield of the bicyclo[3.2.1] compound should increase in the cases of *m*-xylene and 1,3,5-trimethylbenzene. For example, in the cases of *o*-, *m*-, and *p*-xylene, the total yield of α-dicarbonyls can be explained if the ratio of the rate of Reactions A to B is 8:1. In the case of *p*-xylene:



ipso attack (A)



(B)

On this assumption (A:B=8:1), the ratio of the calculated yield of each α-dicarbonyl (Table 2 in paper II and Table 2 in paper III) according to the ring-cleavage mechanism shown in Scheme 1 in paper II and III would vary not more than 10—20%.

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

12) T. Katou and Y. Hanai, *Bull. Environ. Sci. Technol. Yokohama Natl. Univ.* **2**, 1 (1976).

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

14) C. N. Plum, E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. N. Pitts, Jr., *Environ. Sci. Technol.*, **17**, 479 (1983).