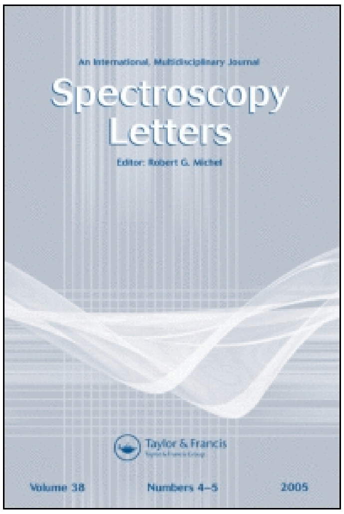

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Takagi, H. , Washida, N. , Akimoto, H. and Okuda, M.(1982) 'Observation of 3-Hexene-2,5-dione in the Photooxidation of 1,2,4-Trimethylbenzene in the NO-H_2 O-Air System', Spectroscopy Letters, 15: 2, 145 — 152

To link to this Article: DOI: 10.1080/00387018208062655

URL: http://dx.doi.org/10.1080/00387018208062655

SPECTROSCOPY LETTERS, 15(2), 145-152 (1982)

OBSERVATION OF 3-HEXENE-2,5-DIONE IN THE PHOTOOXIDATION OF 1,2,4-TRIMETHYLBENZENE IN THE NO-H_2O-AIR SYSTEM

Key Words: Aromatic Hydrocarbon, Photooxidation,
Dicarbonyl

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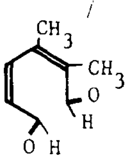
ABSTRACT

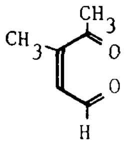
Formation of 3-hexene-2,5-dione (diacetylethylene) was observed in the photooxidation of 1,2,4-trimethylbenzene in the mixture of NO-H_2O-air. The 3-hexene-2,5-dione is a larger aromatic ring-ruptured compound than has been reported. Although the yield of 3-hexene-2,5-dione collected was very low, the formation of 3-hexene-2,5-dione showed that the formation of other large dicarbonyl compounds due to the cleavage reaction of aromatic ring is possible in the photooxidation of aromatic hydrocarbons. Formation of 3-hexene-2,5-dione was also observed in the photooxidation of the p-xylene system.

INTRODUCTION

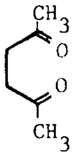
The occurrence of the cleavage reaction of the aromatic ring has been reported in the photooxidation of aromatic hydrocarbon-NO_x systems(1-3). Typical reaction products by ring cleavage are glyoxal from benzene1), glyoxal and methylglyoxal from toluene(1, 4) and glyoxal, methylglyoxal and biacetyl from o-xylene(2,3). In addition to these products, the possibility of the formation of larger dicarbonyl compounds (for example, compounds (A) and (B) in the case of o-xylene) has been suggested(3). However, evidence of these compounds has not been found by GC and GC/MS analyses because these compounds are probably thermally very unstable.



(A)



(B)



(C)

If the terminal hydrogens in compounds (A) and (B) are CH_3, the compounds are expected to be more stable. In this paper, the detection of 3-hexene-2,5-dione (diacetylethylene, compounds (C)) by the GC/MS is reported. This compound was observed in the photooxidation of 1,2,4-trimethylbenzene(5) in the NO-H_2O-air system and also in the photooxidation of p-xylene.

EXPERIMENTAL

The 67 m^3 Pyrex reaction chamber, pumping system, and xenon short arc light source are as described previously(3). The method for gas handling is also as described before(3). Since 3-hexene-2,5-dione dissolves easily in water, the reaction mixture was trapped in a Tenax GC column (4 mm i.d., 20 cm length) and was fed into the GC/MS. The GC/MS analysis was made by using a 2-m column of PEG-20M. The experimental conditions of photooxidation were 1,2,4-trimethylbenzene (40-80 ppm), NO (10 ppm), H_2O (about 60% relative humidity), and air (1 atm). 3-Hexene-2,5-dione (diacetylethylene), used as the standard sample, was synthesized by the reaction of acetonylacetone with selenious acid(6,7).

RESULTS AND DISCUSSION

The gas mixture was photolyzed and the reaction products were analyzed by the GC/MS. Figures (a)-(j) in Figs 1(a) and 1(b) show the mass fragment chromatograms [(a)-(g)], the TIC chromatogram of the reaction products [(h)], and the mass spectra of two peaks (I and J) shown by arrows [(i) and (j)]. Two products were observed on the tail of the large signal of 1,2,4-trimethylbenzene. In the mass spectra shown in (i) and (j) in Fig. 1(b), signals of the mass fragmentation pattern of 1,2,4-trimethylbenzene are subtracted.

The product obseved at peak I is 3-hexene-2,5-dione. The mass spectrum shown in Fig. 1(b) (i) and the retention time agreed well with those of the synthesized standard sample, and also with the mass spectrum shown in the registered mass spectral data(8). Major ions observed in 3-hexene-2,5-dione by 70-eV electron impact were $CH_3COCHCHCOCH_3^+$ (m/e = 112, parent ion), $CH_3COCHCHCO^+$ (m/e = 97), $CH_3COCHCH^+$ (m/e = 69), and CH_3CO^+ (m/e = 43).

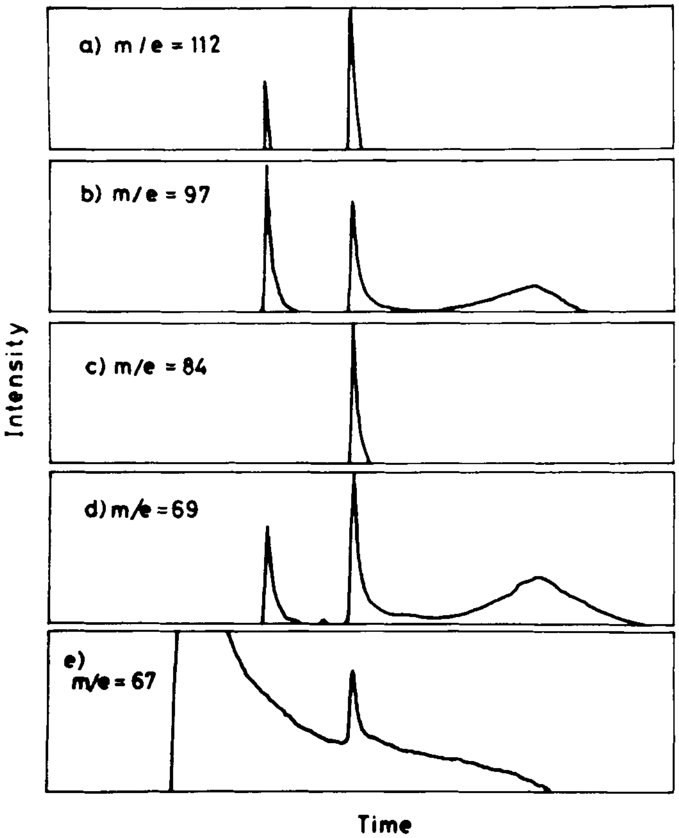


FIG. 1(a). GC/MS analysis of the reaction products in the photooxidation of 1,2,4-trimethylbenzene (76 ppm) - NO (10 ppm) - H_2O - air system: (a) - (e) mass fragment chromatogram for each m/e.

Another product observed at peak J could not be identified, although ions at m/e = 111, 84, 67, 58, 41 were observed in addition to the ions observed in 3-hexene-2,5-dione. Them mass spectrum of peak J appears to be that of 3-methyl-3-hexene-2,5-dione, $CH_3COC(CH_3)CHCOCH_3$. However, signals of the parent ion at m/e = 126 and of $CH_3COC(CH_3)CH^+$ at m/e = 83 were not observed (a signal at m/e = 84 was observed).

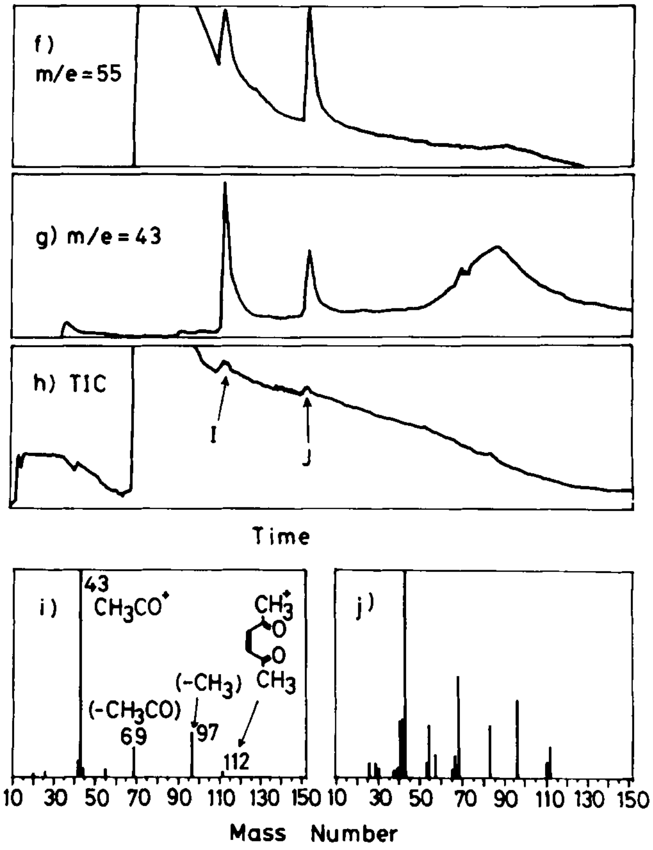


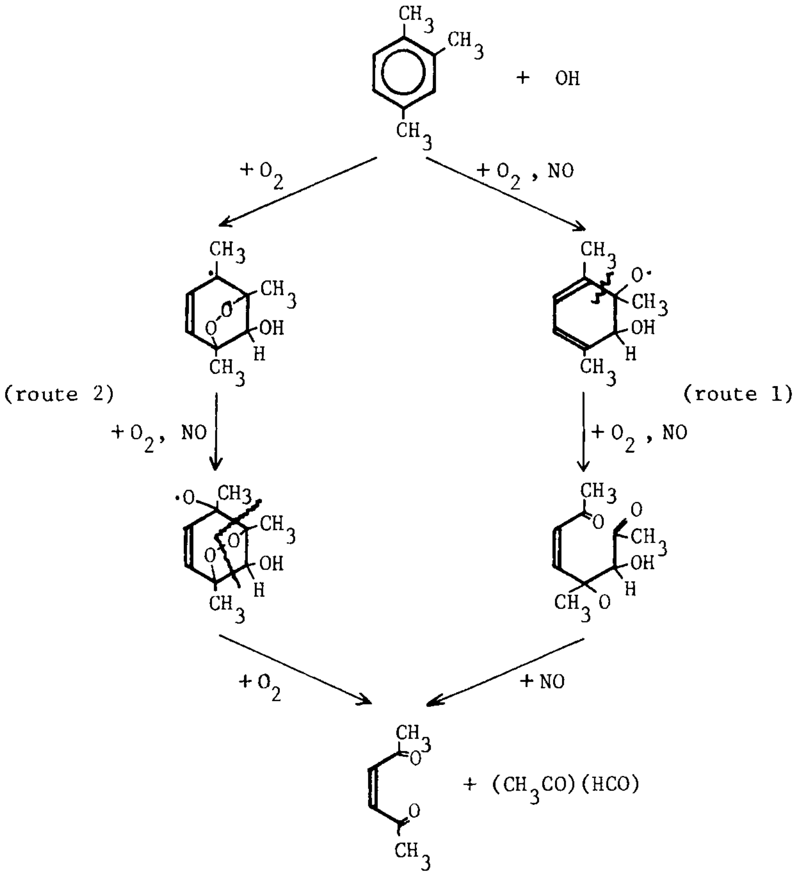
FIG. 1(b). GC/MS analysis of the reaction products in the photooxidation of 1,2,4-trimethylbenzene (76 ppm) - NO (10 ppm) - H_2O - air system: (f) and (g) mass fragment chromatogram for each m/e; (h) TIC chromatogram; (i) and (j) mass spectrum for each peak (mass fragment signals by 1,2,4-trimethylbenzene are subtracted).

Products analysis was made by using the FID GC. Methylglyoxal and acetic acid were observed as low boiling point products when a 2-m column of Porapak-T was used.

The yield of 3-hexene-2,5-dione (ratio of 3-hexene-2,5-dione produced to 1,2,4-trimethylbenzene consumed during the irradiation) was calculated by using the sensitivity of 3-hexene-2,5-dione to the GC/MS. The yields calculated in the two different experiments (initial concentrations of 1,2,4-trimethylbenzene were 42 and 76 ppm) were 0.002 and 0.001, respectively. In both cases, the 1,2,4-trimethylbenzene consumed was about 40% of the initial concentration. The yields obtained above should be the lower limits of the formation of 3-hexene-2,5-dione because the subsequent reactions of 3-hexene-2,5-dione (photodecomposition, and reactions with radicals and ozone) and loss of 3-hexene-2,5-dione on the surface of the reactor and the Tenax GC column can not be neglected.

Although the yield of 3-hexene-2,5-dione collected was very low, it is very interesting that the formation of a ring-ruptured compound larger than $(CH_3CO)_2$, $(CH_3CO)(CHO)$, and $(CHO)_2$ was observed. This fact shows that large dicarbonyl compounds can be produced by ring cleavage in the aromatic ring. Therefore, compounds such as A and B might be produced in the case of o-xylene and these compounds will not be observed due to their instability. Formation of 3-hexene-2,5-dione can be explained by mechanisms proposed by Takagi et al.(3) and Darnall et al.(2) in the case of o-xylene. These mechanisms in the case of 1,2,4-trimethylbenzene are shown in the following scheme (route 1 is from Takagi et al. and route 2 from Darnall et al.).

There should be other reactions which produce $(CHO)_2 + (CHO)(CH_3CO) + (CH_3CO)_2$, $3(CHO)(CH_3CO)$, C_6-dicarbonyls $+ (CHO)(CH_3CO)$, and C_5-dicarbonyl $+ (CH_3CO)_2$ because the amount of methylglyoxal observed was about two orders of magnitude larger than that of the 3-hexene-2,5-dione collected.



Formation of 3-hexene-2,5-dione was also observed in the photooxidation of the p-xylene (40 ppm) - NO - H_2O - air system. The yield of the formation of 3-hexene-2,5-dione was nearly equal to that obtained in the case of 1,2,4-trimethylbenzene.

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Received: April 2, 1981
Accepted: January 4, 1982