CHEMISTRY LETTERS, pp. 1303-1306, 1973. Published by the Chemical Society of Japan

STRUCTURE AND REACTIVITY OF ORGANIC IONS IN GAS-PHASE RADIOLYSIS.
IV. THE $C_7H_7^+$ ION FROM CYCLOHEPTATRIENE

Setsuo TAKAMUKU, Katsuyoshi NAKAMURA, Kenji NAGAOKA, and Hiroshi SAKURAI
The Institute of Scientific and Industrial Research, Osaka University,
Yamadakami, Suita, Osaka 565

The structure of the $C_7H_7^+$ ion formed by γ radiolysis of cycloheptatriene vapor has been investigated by an ion-trapping with toluene-d_8 or dimethylamine. The $C_7H_7^+$ ion was shown to be mainly a rearranged benzyl type while a tropylium ion was also trapped with dimethylamine in a low yield.

Recently, much attention has been paid to the structure and reactivity of the $C_7H_7^+$ ion observed in abundance in the mass spectrum of toluene as well as in the spectra of higher alkylbenzenes and cycloheptatriene (CHT) since the ion has been shown to have a symmetrical tropylium structure rather than a benzyl by the classical studies of Meyerson.[1] In a series of investigations[2,3] we have attempted to focus attention on the structure and reactivity of the $C_7H_7^+$ ion formed in the gas-phase radiolysis of alkylbenzenes and CHT through the technique of an end-product analysis.

In the γ radiolysis of CHT vapor,[4] however, the fate of the $C_7H_7^+$ ion, which might be expected to be formed in the radiolytic system,[5] has not been clarified because the reaction products via the $C_7H_7^+$ ion could not be identified. Thus, it was presumed that the $C_7H_7^+$ ion, if formed, may be consumed by the initiation of the ionic polymerization of CHT. On the other hand, it has been shown that the $C_7H_7^+$ ion produced by the gas-phase radiolysis of alkylbenzene such as toluene, ethylbenzene, and m-xylene reacts with the respective aromatic-ring, finally forming benzylated products predominantly at a meta position to the resident alkyl group.[2a,2c]

On the basis of these observations, it appeared promising to investigate such an electrophilic reaction of the $C_7H_7^+$ ion originating from CHT with an aromatic compound. Furthermore, the trapping of the $C_7H_7^+$ ion by more basic dimethylamine (DMA) was also undertaken.

1. Radiolysis of a CHT-Toluene-d_8-NO Mixture

It has been already reported that the methyldiphenylmethanes (MDPM) were formed as main products in the γ radiolysis of toluene via a $C_7H_7^+$ ion intermediate.[2] Therefore, in order to clarify whether the reactivity of the $C_7H_7^+$ ion originating from CHT is similar to that from toluene, the γ radiolysis of a CHT-toluene-d_8-NO (5:5:1 mmHg) mixture was carried out with ^{60}Co γ-rays to a dose of 3.9×10^{18} eV at room temperature. The isotopic distributions of MDPMs formed were analyzed by GC-MS. If the $C_7H_7^+$ ion has an identical reactivity with that from toluene, two types of isotopic MDPMs ([I] and [II]) are expected as is suggested by the following scheme.

$$\text{Toluene-}d_8 \rightsquigarrow C_7D_7^+ + D \qquad (1)$$

$$\text{CHT} \rightsquigarrow C_7H_7^+ + H \qquad (2)$$

$$C_7D_7^+ + C_6D_5CD_3 \xrightarrow{-D^+} \underset{\text{[I] m/e 196}}{C_6D_5CD_2C_6D_4CD_3} \qquad (3)$$

$$C_7H_7^+ + C_6D_5CD_3 \xrightarrow{-D^+} \underset{\text{[II] m/e 189}}{C_6H_5CH_2C_6D_4CD_3} \qquad (4)$$

The results are shown in Fig. 1. The meta isomer of MDPM, which is the main product, does not separate completely from ortho and para isomers in the present gas chromatographic condition. Furthermore, it is known that the more deuterated a compound the shorter the retention time.[6] Then, the mass spectrum was measured at three different points of a gas chromatographic peak of MDPMs. The results obviously indicate the formation of both I and II though the relative yields are varied among the three measurements. Thus, one might conclude that the $C_7H_7^+$ ion from CHT also has a similar reactivity towards toluene as well as that from toluene and the structure of the ion is reasonably suggested as a benzyl type.[2a]

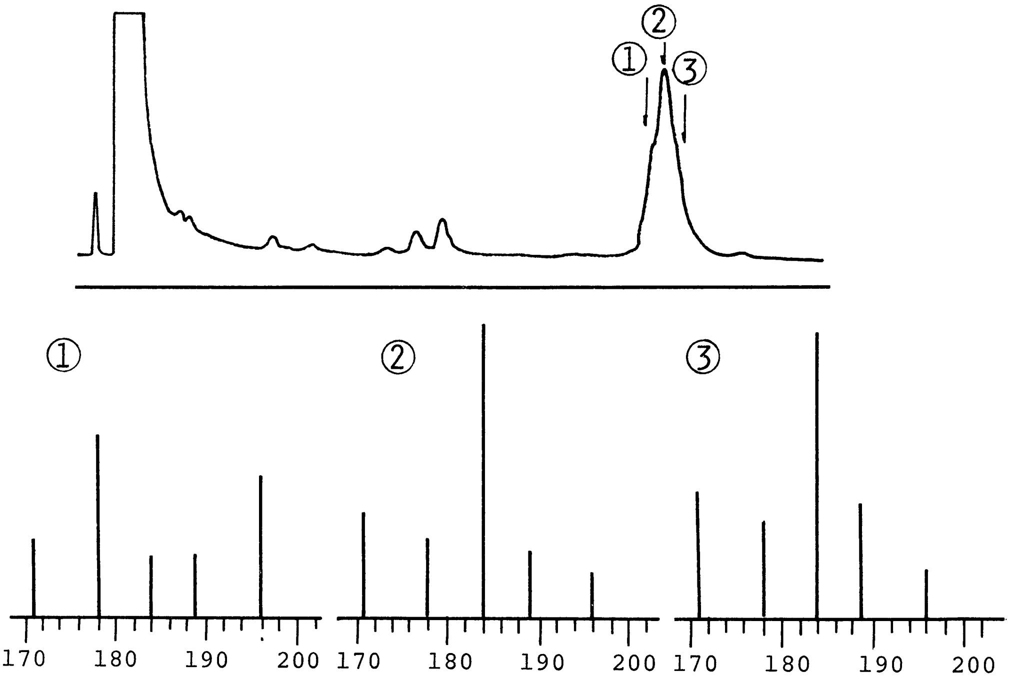
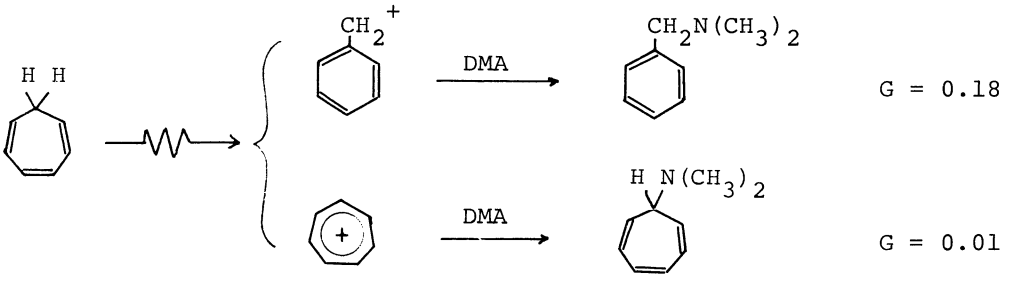


Fig. 1. Gas chromatograph and mass spectra of MDPMs produced by γ irradiation of a CHT-toluene-d_8-NO mixture (SE 30, 3m at 80°C).

2. Radiolysis of a CHT-Dimethylamine-O_2 Mixture

The formation of benzyl ion is suggested by an electrophilic aromatic reaction of the $C_7H_7^+$ ion from CHT as presented above. However, there is still uncertainty with the formation of tropylium ion because such a less electrophilic ion may hardly react with aromatics, even if produced in the γ radiolysis of CHT vapor. Thus, the trapping of the $C_7H_7^+$ ion with DMA was undertaken. Dimethylamine has higher basicity than that of toluene and is known to react with tropylium ion forming N,N-dimethyltropylamine in liquid phase.[7] A gaseous mixture of CHT-DMA-O_2 (10:20:1 mmHg) was irradiated with ^{60}Co γ-rays to a dose of 1.1×10^{19} eV. The formation of N,N-dimethylbenzylamine and a small amount of N,N-dimethyltropylamine were observed by comparisons of glc and mass spectra with those of authentic samples, respectively.



Since the yields of these products did not increase with increasing DMA pressure, the precursor ions are assumed to be one formed from CHT and not from DMA. The formation of N,N-dimethyltropylamine, though the yield was low, is of importance because it shows the possibility of the trapping of tropylium ion if formed in gas phase. Further work is in progress on the reactivity of tropylium ion from CHT and also from 7-methylcycloheptatriene and will be reported in the near future.

References

1) H. M. Grubb and S. Meyerson in Mass Spectrometry of Organic Ions, F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 10.

2) Y. Yamamoto, S. Takamuku, and H. Sakurai; (a) J. Amer. Chem. Soc., 91, 7192 (1969), (b) ibid., 94, 661 (1972), (c) J. Phys. Chem., 74, 3325 (1970), (d) Bull. Chem. Soc. Japan, 44, 574 (1971), (e) ibid., 44, 2104 (1971).

3) S. Takamuku, N. Sagi, K. Nagaoka, and H. Sakurai, J. Amer. Chem. Soc., 94, 6217 (1972).

4) K. Nakamura, S. Takamuku, and H. Sakurai, Bull. Chem. Soc. Japan, 44, 2090 (1971).

5) S. Meyerson, J. Amer. Chem. Soc., 85, 3340 (1963).

6) T. Gaumann in Aspects of Hydrocarbon Radiolysis, T. Gaumann and J. Hoigne, Ed., Academic Press, London, 1968, Chapter 5.

7) W. von E. Doering and L. H. Knox, J. Amer. Chem. Soc., 79, 352 (1957).

(Received October 16, 1973)