BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1580—1581 (1970)

# Studies of the Electric Discharge of Organic Compounds. III. The Decomposition of Methylcyclohexane in 10-MHz and 2450-MHz Discharges

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(Received October 16, 1969)

In the electric discharge of the methyl-substituted benzene homologue,[1,2] methyl migration has been found to be a main process. In this paper the methyl-group migration on methylcyclohexane in the high-frequency electric discharge was examined. Methylcyclohexane was chosen as a representative of saturated hydrocarbons. As has been shown previously,[1] radical and electron scavengers were used to investigate the reaction process, and the product distributions were described. Methylcyclohexane (Tokyo Kasei Kogyo Co., Ltd.) was purified by repeated distillation so as to make it gas-chromatographically pure.

## Results and Discussion

The gaseous products were methane, ethane, ethylene, acetylene, propane, methylacetylene, allene, isobutane, butadiene, and seven unidentified products, while the liquid products were 1-methylcyclohexene, 4-methylcyclohexene, cyclohexane, and ten unidentified products. It was confirmed that ethylcyclohexane*1 is not formed in the present work, while in the case of toluene ethylbenzene is one of the major products. The yields of the products are shown in Table 1. Figures 1 and 2 show the effects of added oxygen and nitrous oxide on the yields of 1-methylcyclohexene and 4-methylcyclohexene.

From these data, the effects of additives can be summarized as follows: The yields of 1-methylcyclohexene and 4-methylcyclohexene decrease with an increase in the quantity of $O_2$ and $N_2O$ scavengers in both the discharges, but the effect seems to be a little larger in the case of the $O_2$ scavenger. Moreover, the formation of ethane is inhibited by $O_2$, but not by $N_2O$, in both the discharges. The formation of cyclohexane is inhibited by both the scavengers; no striking difference in effect between the two additives is observed. The main products, 1- and 4-methylcyclohexenes, may be formed by the dehydrogenation, of the cyclohexane ring. Arnold[3] reported that the decomposition of cyclohexane in an electric discharge can be explained quantitatively by a radical mechanism.

The formation of cyclohexane and ethylcyclohexane involves the cleavage and recombination of the methyl group from methylcyclohexane, but ethylcyclohexane was not obtained in the discharges. The migration of the methyl group is quite different from that of toluene and xylene. The reason for this is not clear, but it may be explained by the stability of the benzene ring. Moreover, the fact that nitrous oxide does not inhibit the formation of 1- and 4-methylcyclohexenes so greatly as toluene decomposition[1] may be explained by assuming that the compounds having an electron network, such as toluene, behave differently from the saturated counterparts, such as methylcyclohexane, in the electron bombardment of an electric discharge.

The decomposition of methylcyclohexane gives many fragmented products in the discharges; this fact coincides with the result reported by Streitwieser and Ward.[4] The differences between the

1) K. Taki, This Bulletin, **43**, 1574 (1970).
2) K. Taki, *ibid.*, **43**, 1578 (1970).
*1 Authentic ethylcyclohexane was prepared by the reduction of ethylbenzene using a ruthenium carbon catalyser. The catalyser was kindly provided by Dr. Taya of this Institute.
3) G. Arnold, *Z. Naturforsch.*, *A*, **20**, 435 (1965).
4) A. Streitwieser, Jr., and H. R. Ward, *J. Amer. Chem. Soc.*, **85**, 539 (1963).

Table 1. The yield % of the products based on methylcyclohexane consumed

| | 10-MHz discharge | 2450-MHz dischage |
|---|---|---|
| Residence time | 0.21 sec | 0.009 sec |
| Methylcyclohexane % | 9.1% in He | 9.1% in He |
| Methane | 0.39 | 2.1 |
| Ethane | 1.25 | 1.7 |
| Ethylene | 4.1 | 3.7 |
| Acetylene | 0.73 | 4.5 |
| Propane | 0.57 | 0.93 |
| Methylacetylene + Allene | 2.62 | 8.4 |
| Isobutane + 1,3-Butadiene | 0.08 | 2.3 |
| | 5-Unidentified products | 7-Unidentified products |
| Cyclohexane | 0.95 | 0.9 |
| 4-Methylcyclohexene | 1.19 | 15.1 |
| 1-Methylcyclohexene | 15.1 | 11.5 |
| Benzene | —— | 0.2 |
| Toluene | 0.31 | 0.3 |
| | 6-Unidentified products | 5-Unidentified products |
| Polymer | 5.8 | 3.8 |

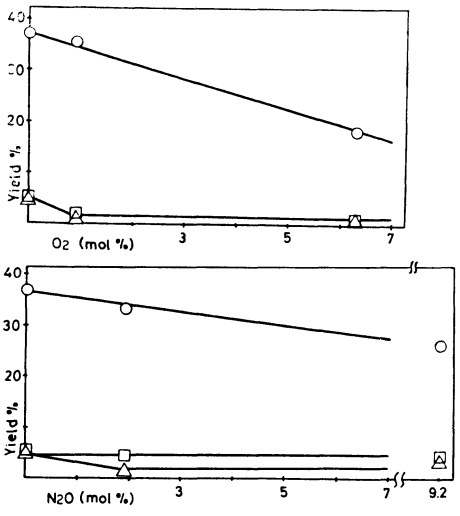


Fig. 1. 2450-MHz discharge of methylcyclohexane.
○ 1-Me-cyclohexene+4-Me-cyclohexene
△ Cyclohexane
□ Ethane

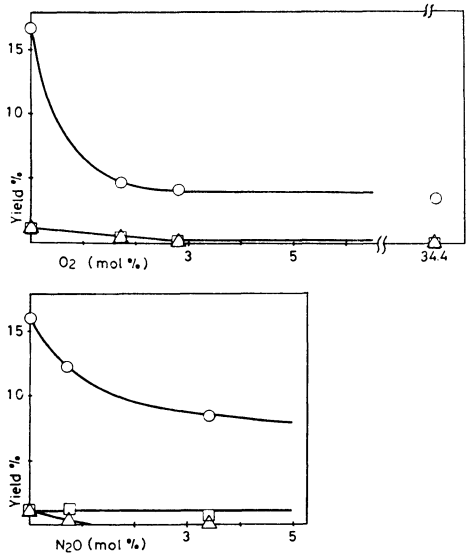


Fig. 2. 10-MHz discharge of methylcyclohexane.
○ 1-Me-cyclohexene+4-Me-cyclohexene
△ Cyclohexane
□ Ethane

two types of discharges, 10 and 2450 MHz, were not clear.

The author wishes to thank Professor S. Murahashi (Osaka University) for his useful suggestions and encouragement and Miss K. Motegi for her help with the analyses of the reaction products. He also wishes to thank Dr. M. Imamura and Dr. M. Matsui for their helpful discussions and suggestions.