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Gaseous Products from the Plasma Decomposition of Isomeric Xylenes

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Synopsis. The formation of methane and ethane on decomposition of the isomeric xylenes in Siemens-type discharges has been investigated. With increasing voltage the methane yield decreased, while the ethane yield increased; the C_2H_6/CH_4 mole ratios increased continuously but varied in the order *ortho*>*meta*>*para*.

A recent investigation[1] of the plasma decomposition of isomeric xylenes showed that ethane is the major gaseous product and that very little methane is formed in high-frequency (10—2450 MHz) electrical discharges. Under the experimental conditions extensive polymerization occurred.[1,2] Dimerization by elimination of hydrogen has been reported[3] to be the major reaction in low-frequency (50 Hz) electrical discharges in xylene vapors, but there is no published data on the gaseous products from such discharges.

In our preliminary investigations of isomeric xylene plasmas produced by low-frequency Siemens-type discharges significant amounts of methane and ethane were detected among the gaseous products.[4] Since methane was not a significant product in the high-frequency discharges,[1] it was desirable to re-investigate this aspect of the plasma chemistry of xylenes. In this paper we report on the yields of methane and ethane from 50 Hz xylene plasmas.

Experimental

Xylene vapor (99.9 per cent purity, Matheson Company) was pumped at a pressure of 7 Torr and a flow rate of 22 micromole s^{-1} through a 15 cm long Siemens co-axial-type Pyrex reactor with 5 mm inter-electrode separation. The plasma was produced by applying line frequency (50 Hz) high voltage from a transformer to electrodes which were (1) a thick copper wire dipping in salt solution inside the inner glass tube and (2) a thin copper wire wound outside the outer glass tube of the reactor. For the experimental conditions an approximate residence time of 0.75 s was calculated[5] for the xylene in the plasma zone where, depending on the applied voltage, 5—10 per cent of the input xylene was decomposed. The products were trapped at 77 K in a U-trap which was warmed to 215 K prior to the gas chromatographic analysis for CH_4 and C_2H_6. The analysis was performed *in situ* using a Gow-Mac chromatograph in conjunction with a 1.2 m long silica gel column at 273 K.

Results and Discussion

The yields of CH_4 and C_2H_6 found per mole of *o*-xylene entering the discharge tube are shown in Fig. 1. At the lower applied voltages the methane yield increased slightly to a maximum, but it then dereased almost linearly with increasing voltage while the ethane yield increased continuously. This behavior was less dominant in the case of the *meta* and *para* isomers than the *ortho* isomer. The CH_4 and C_2H_6 yields varied in the order *ortho*>*meta*>*para* suggesting that these product yields depend on the proximity of the two methyl groups in the xylene molecule.

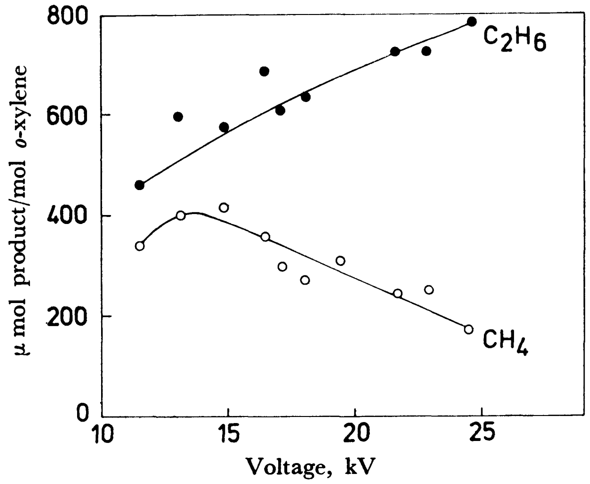

Fig. 1. Methane and ethane yields from *o*-xylene as functions of the applied voltage.

Some sort of xylene ion must form as a result of inelastic collisions between the electrons and xylene molecules in the plasma, but whether these ions or some derivative species are the reactive intermediates is not known. The energetics of xylene decomposition[6] suggests that both the C–H (*ca.* 77.5 kcal mol^{-1}) and C–C (87 kcal mol^{-1}) bonds in the xylene molecule may split under plasma conditions:

$$C_6H_4(CH_3)_2 \rightarrow CH_3C_6H_4CH_2^{\cdot} + {}^{\cdot}H \tag{1}$$

$$C_6H_4(CH_3)_2 \rightarrow CH_3C_6H_4^{\cdot} + {}^{\cdot}CH_3 \tag{2}$$

The formation of these free radicals is supported by the evidence from mass spectroscopy[7] and emission spectroscopy[8,9] of the xylene plasmas. If reaction (2) is the CH_3 radical source[10] and is followed only by the recombination reaction to form ethane

$$2\,CH_3^{\cdot} \rightarrow C_2H_6 \tag{3}$$

and the abstraction reaction to form methane

$$CH_3^{\cdot} + C_6H_4(CH_3)_2 \rightarrow CH_3C_6H_4CH_2^{\cdot} + CH_4 \tag{4}$$

then the fate of the methyl radicals produced in the xylene plasmas is somewhat exemplified by the C_2H_6/CH_4 mole ratios[11] shown in Fig. 2. The voltage dependence of the ratio suggests that reactions (2) and (3) are favored and reaction (4) is disfavored as the voltage is increased. The different ratios for the isomers at a given voltage indicate that the proximity of the two interacting methyl groups in the xylene molecule may be significant for methane production *via* reaction (4). This conclusion, however, excludes

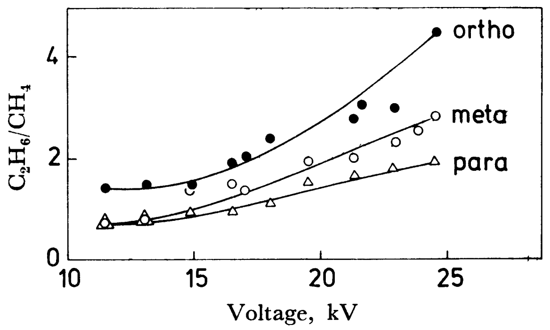

Fig. 2. Variation of the C_2H_6/CH_4 ratios with applied voltage for the three isomeric xylenes.

the loss of CH_3 radicals by their combination with $CH_3C_6H_4CH_2$ radicals to form the isomeric ethyltoluenes.

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4) Of course, H_2 is the most abundant gaseous product from xylene plasmas. For a given plasma conditions the product distribution varied in the order $H_2 > C_2H_6 > CH_4$.

5) This is an upper limiting value because the rate of flow through the plasma volume (*ca.* 44 cm^3) was assumed to be the molar rate of input of xylene vapor at room temperature. For the calculation of the residence time, see R. A. Jones, W. Chan, and M. Venugopalan, *J. Phys. Chem.*, **73**, 3695 (1969).

6) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworths Publications, London (1958), p. 184.

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10) Another source is the exchange reaction $H^{\cdot} + C_6H_4(CH_3)_2 \rightarrow C_6H_5CH_3 + CH_3^{\cdot}$ which is unlikely due to high activation energy requirement.

11) The ratio of product yields is sufficient for the type of comparison attempted here. Absolute considerations would require that the ratio $[C_2H_6]^{1/2}/[CH_4]$ be used.