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THE MERCURY-SENSITIZED PHOTOLYSIS AND RADIOLYSIS OF METHANE

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The radiation chemistry of pure methane[1] and the argon and krypton sensitized radiolysis of methane[2] have recently been described. These investigations were interpreted in terms of ion-molecule mechanism based upon mass spectrometer studies.[3,4] In the sensitized radiolysis studies the role of ion-molecule reactions was emphasized by charge transfer reactions of the following nature.

$$Ar^+ + CH_4 \longrightarrow CH_3^+ + Ar + H \qquad (1)$$

We have undertaken the study of the radiation chemistry of methane in the presence of a large excess of mercury vapor so that charge transfer reactions of the type

$$CH_4^+ + Hg \longrightarrow CH_4 + Hg^+ \qquad (2)$$

should effectively scavenge hydrocarbon molecule ions which survive neutralization for a period of the order of 10^{-9} seconds. The neutralization of Hg^+ results in the production of a variety of electronic excited states of mercury of which the most important are the 7^1S_0 and the 6^3P states. These excited states of Hg, which are produced by direct action of the radiation as well as

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by charge neutralization, sensitize the decomposition of the methane by chemical quenching reactions such as reaction (3).

$$Hg^{*}\,(^{3}P_{1}) + CH_{4} \longrightarrow CH_{3} + H + Hg \qquad (3)$$

We have investigated the radiolysis of methane in the presence and absence of mercury at 260° and the $^{3}P_{1}$ mercury sensitized photolysis of methane at 260°. The electron source used was a 4.5 Mev electron beam from a microwave linear accelerator. In each experiment the methane pressure was 10 mm measured at 25°.

The mass spectra of the products produced are shown in Fig. 1. These spectra represent the products formed when about 4% methane was reacted. The gross features of the spectra are identical, indicating the nature of the products formed to be the same. Analysis of the mass spectra and analysis of the products by gas chromatography confirm the identity of the products. The products from photolysis exhibit a somewhat larger proportion of higher hydrocarbons than is formed in either of the radiolysis experiments. This rapid build-up of higher hydrocarbons in the photolysis is probably due to the high local concentration of free radicals from the rapid extinction of the 2537 Å mercury resonance line at high mercury pressures. This occurred even though the mercury pressure in the photolysis was only 20 mm compared to 100 mm in the radiolysis.

The photolysis products must of necessity be described by processes not involving ions. Therefore we conclude that ion-molecule reactions are not necessary to account for the products of the radiolysis of methane at 260°C. Thus we cannot agree with the statement that free radical reactions cannot account for the formation of propane, butane, and pentane in the radiolysis of methane.[2] Recently, Yang and Manno[5] have reported their

studies on the nitric oxide inhibition of the radiolysis products of methane and concluded that 85% of the ethane and propane and 100% of the higher products arise from free radical reactions. Assuming an activation energy of 8 kcal/mole for the free radical processes and zero activation energy for non-free radical processes we conclude that non-free radical processes can account for less than 0.1% of the radiolysis products at 260°C. Our experimental results are in accord with this conclusion.

We are undertaking a more complete study of the radiolysis of pure methane and mercury sensitized radiolysis and photolysis of methane at 260°C. We shall report the results of these investigations in a later publication.

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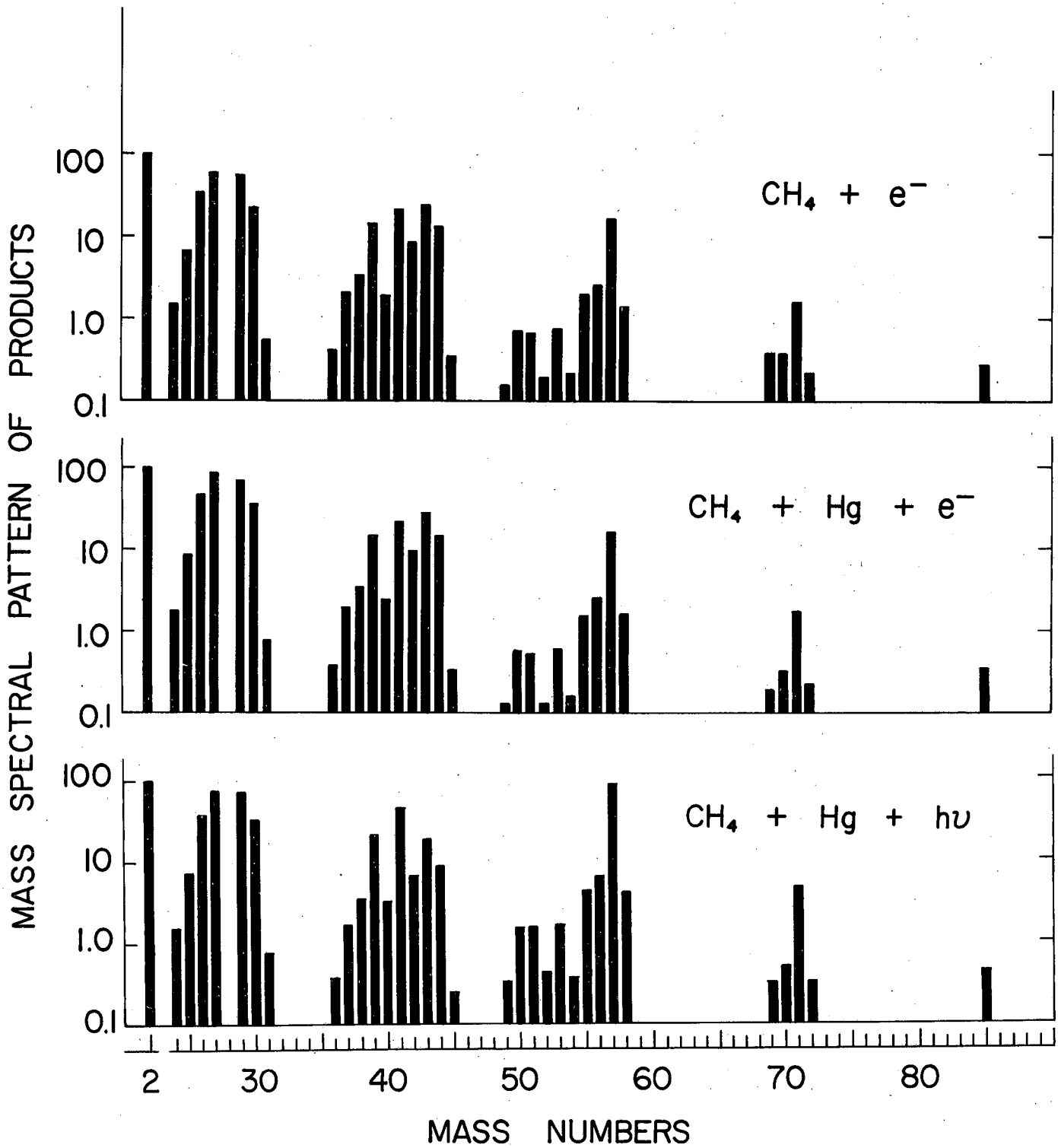
MASS SPECTRAL PATTERN OF PRODUCTS
100
10
1.0
0.1
$CH_4 + e^-$
$CH_4 + Hg + e^-$
$CH_4 + Hg + h\upsilon$
2
30
40
50
60
70
80
MASS NUMBERS

MUB-346

Fig. 1