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Use of an Ion Source with an Inhomogeneous Electric Field for Studying Processes Induced by Collisions of Electrons and Ions with Molecules

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The authors report mass-spectroscopic data on species obtained by electron impact in an ion source which contains a strong electric field, created around a thin metal filament. About half of the $C_7H_7^+$ fragments produced during ionization of toluene have formation times greater than 10^{-9} sec, but most of the decay processes terminate in less than 2.5×10^{-7} sec. The same filament-containing source was used as an ion trap to increase the dwell time of primary ions in the ion source; in studies of elementary processes, this technique offers several advantages over the conventional ion sources. The rate constants for the reactions $H_2^+ + H_2 = H_3^+ + H$ and $N^+ + O_2 = NO^+ + O$, obtained by the above technique, agree with those obtained by other methods. In addition, some data indicating a reaction of propane-derived ions with krypton have been obtained.

High-Temperature Reactions of Fluoromethanes. 1. Pyrolysis of Methyl Fluoride

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The kinetics of high-temperature decomposition of methyl fluoride were studied at 850°–1100°C in a flow apparatus. The rate constant of this first-order homogeneous reaction is

$$K = 7.41 \times 10^{13} \exp -(82{,}600/RT) \text{ sec}^{-1}$$

The products consist of hydrogen fluoride, ethylene and products of decomposition of ethylene, that is, hydrogen, methane, acetylene, and coke. These data, as well as thermochemical considerations, indicate that the first step of this reaction is splitting of CH_3F into the diradical CH_2 and HF.

Reactions of α-Oxides. XI. Kinetics of Reactions of Ethylene Oxide with Alcohols in the Presence of Boron Fluoride or Metal Halide Catalysts

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The reactions of ethylene oxide with methyl and octyl alcohols in the presence of BF_3 proved to be first order with respect to EtO and BF_3 while exhibiting a complex dependence on the alcohol concentration. The activity of various catalyst employed can be ordered as follows: $BF_3 > SbCl_5 > SnCl_4 > FeCl_3 > TiCl_4$. In solvents with low dielectric constants, protonated acids are less active than BF_3, but are more active in strongly dissociating media.

Activity of Catalysts in Concerted Polymerization

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The authors discuss the possibility of creating catalysts for the homogeneous polymerization of vinyl monomers. Comparison of homogeneous and heterogeneous catalysts would seem to indicate that no major mechanistic changes should result from the replacement of one catalyst by the other. During the stereospecific polymerization in the presence of a complexed metalorganic catalyst, the controlling factor is the compound formed by the transition metal. The latter will participate in the formation of an active site regardless of whether the catalyst as a whole is in the same or in another