

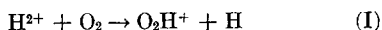
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**Effect of Relative Shifts in Kinetic Energy on
Cross-Sections of Molecular Ionic Reactions**

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The effect of a 3-20 ev shift in kinetic energy of H_2^+ ions on the reaction cross-section was determined for the processes below:



The results show that at the H_2^+ energy levels of over 15-20 ev, Reaction (I) practically does not occur. This is believed to be due to a decrease in the life-time of the intermediate complex ion, $(O_2H_2)^+$, because during formation of this ionic complex a significant portion of its kinetic energy is transformed into excitation energy in accordance with the reaction momentum principle. The effect of increasing kinetic energy of H_2^+ ions on the cross-sections of the reactions, $H_2^+ + D_2O \rightarrow D_2HO^+ + H$ and $H_2^+ + D_2 \rightarrow D_2H^+ + H$ is analogous.

The present study was carried out with the aid of a mass-spectrometer. The primary and secondary source-ions were formed in two separate chambers. Separation of these ions was effected by pulse ionization and extraction methods.

Analogy between Homogeneous and Heterogeneous Activators of Molecular Hydrogen (H_2)

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Assuming analogous action mechanisms of the homogeneous and heterogeneous activators of molecular hydrogen, the reaction mechanism proposed is based on the concept that the H_2 activation process of either type proceeds along identical elementary steps. This scheme is applicable to

electrochemical oxidation of hydrogen on metallic electrodes in an aqueous solution; it also helps to interpret the rate equation in reduction of Ag^+ and $Ag(NR)_2^+$ ions by gaseous hydrogen in aqueous solutions. Parallelism is shown to exist between the oxidation-reduction potential and the rate of hydrogen activation by homogeneous activators. Analogous to the linear relationship between activation energy and heat of reaction, discovered by Pol'yany, it is hypothesized that for related reactions a similar correlation exists between the free enthalpy of activation (the log of the rate constant) and a change in the standard free enthalpy due to the rate limiting step in each reaction. Validity of this hypothesis is demonstrated, for example, by reduction of complexes of the $Ag(NR_3)_2^+$ type, where the group, NR_3 , represents different aliphatic monoamines.

Two-Stage Combustion of Explosive Mixtures

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Experimental micro-kinetic parameters are listed for a two-stage auto-ignition of isooctane in the isooctane-air mixture when $\alpha = 0.8$. Two zones, differing in kinetic auto-ignition parameters, are observed at low temperatures: one zone extends from the minimum temperature to 320° ; the other one, from 320° to 450° . The values of E_{eff}^{CF} in the low- and the high-temperature zones are 27.1 and 12.2 kcal/mol, respectively. (In E_{eff}^{CF} , CF stands for "Cold Flame" and "eff," for "effective.") In the low temperature region, the value of E_{eff}^{HF} (HF = Hot Flame) is positive; in the high temperature region, it is negative. Comparative data of the kinetic auto-ignition parameters of isooctane and heptane at elevated pressures show that the pre-ignition oxidation rate of isooctane is slower in both kinetic zones of each stage of the auto-ignition process.