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The Kinetics of the Reaction between Fluorine and Ethylene in a Diffusion Flame

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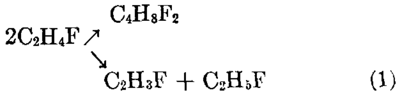
This reaction was studied between 25° and 157°C. The ethylene concentration in the flame exceeded that of fluorine by a factor of 1000. The analysis of the products and kinetic measurements have shown that the following reactions take place:

$$F_2 + C_2H_4 \rightarrow F + C_2H_4F$$
$$F + C_2H_4 \rightarrow C_2H_4F$$



$$2C_2H_4F \begin{cases} \nearrow C_4H_8F_2 \\ \searrow C_2H_3F + C_2H_5F \end{cases} \qquad (1)$$

The rate constant for reaction (1) is $8 \times 10^{-14}\, e^{-4600/RT}$ cm^3/sec.

Preflame Processes and Ignition of Various Hydrocarbons. II. The Intensity of the Cool-Flame Stage

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Data are presented on the intensity of cool flames as a function of temperature and compression of the fuel mixture. The intensity was measured in terms of the luminance of the glow ($I_{\text{cool flame}}$) and of the relative increment of pressure $\Delta P_{\text{cool flame}}/P_{\text{comp}}$. The authors tested stoichiometric mixtures of fuel and air by using the following hydrocarbons: *n*-hexane, isooctane, cyclohexane, cyclohexene, diisobutylene, and a 60:40 mixture of isooctane and *n*-heptane. The authors have shown that, for saturated hydrocarbons, the temperature functions of $\Delta P_{\text{cool flame}}/P_{\text{comp}}$ and of log $I_{\text{cool flame}}$ form a family of similar curves; furthermore, within the range of $T_{\text{comp}} =$ 400°–450°C, these quantities are related to the octane numbers of the fuels. The situation is very different with olefinic hydrocarbons: the cool flame appears while the mixture is still being compressed, and has a glow of very low intensity. This apparently is why unsaturated hydrocarbons do not exhibit a region of two-stage, low-temperature ignition. This also explains the high-temperature sensitivity and poor response to anti-knock substances exhibited by these hydrocarbons.

Two-Stage Burning of Explosive Mixtures. IV. The Rate of Pressure Increase during the Cool-Flame Stage of Combustion of Isooctane–*n*-Heptane Mixtures in Air

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The author relates the length of the induction period and of the period of pressure increase in the two-stage ignition of isooctane–*n*-heptane mixtures in air to the initial temperature and pressure of this process. He then uses these relations to calculate the following factors: the apparent activation energy, the apparent reaction order, and the rate of pressure increase during the cool-flame stage. The magnitudes of these factors differ in the various regions of the low-temperature ignition region.

The rate of pressure rise (measured in a bomb) during the first ignition stage decreases with the increase in the octane number of the mixture. The behavior of the intensity of the cool flames of these mixtures in internal combustion engines parallels the behavior of the pressure.

The Mechanism of Reactions of Epoxides with Carboxylic Acids

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The authors have studied the base-catalyzed reactions of monoepoxides with carboxylic acids.

It was shown that these epoxides can react with caproic acid via the following processes: (*a*) a noncatalytic reaction; and (*b*) reactions catalyzed by trihexylamine or bases, which go via a different mechanism. The authors have derived the kinetic equations for these reactions and have postulated mechanisms involving ring-type and linear transition complexes.

Kinetics and Mechanism of Catalytic Dimerization of Acetylene. I. The Effect of Proton Acidity

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The authors have investigated the effect of NH_4Cl, CuCl, and acetylene on the acidity (h_0) and the concentration of HCl in the solution during the catalytic synthesis of vinyl acetylene. They have derived an equation relating the role of the dimerization to steady-state acidity of HCl at constant activity of cuprous ions. They have also shown that the intermediate of this synthesis is a diacetylenide.

Photolysis of Frozen, Dilute Aqueous H_2O_2

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The ESR analysis of the photolysis of polycrystalline samples of rapidly frozen aqueous H_2O_2 ($[H_2O_2] < 10^{-2}$ moles/liter) at 77°K indicates the presence of a mixture of HO_2 and OH radicals. At $[H_2O_2] = 2 \times 10^{-2}$ mole/liter, only the HO_2 species is recorded. In the range of $10^{-2} - 1$ mole H_2O_2/liter, the quantum yield of stabilized radicals (Φ) is constant. Addition of isopropanol, which is not photolyzed under these conditions, increases Φ. Glass-like frozen samples containing 1.6×10^{-1} mole H_2O_2/liter plus some $NaClO_4$ indicate the presence of the OH species, but their Φ is lower. The authors conclude that the H_2O_2 exists in these frozen solutions as a separate microcrystalline phase and undergoes photolysis independently of the solvent. The increase in Φ upon addition of isopropanol and the decrease in Φ in the glass-like samples are related to the change in the cage effect present in the reaction $H_2O_2 \xrightarrow{h\nu} 2OH$.

Reactions of Atomic Hydrogen in the System, $H_2O + H_2SO_4 + FeSO_4$. V. Effect of Light on "Scavenger" Radicals

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The ESR technique was used to study the effect of light on the "scavenger" radicals of the $\dot{C}_6H_7$ type. It was shown that the ratio of the probabilities of rupture of the C–H and C–D bonds of the >CHD group is approximately the same (3 ± 1) in $\dot{C}_6D_6H$ and $\dot{C}_6H_6D$. The radicals formed by "adhesion" of atomic hydrogen to hydroquinone, pyrocatechol, or benzene sulfonic acid molecules undergo reversible conversions from one radical form to another under the influence of light of two similar wavelengths. The author has compared the long-wave cutoffs in the spectra of the starting molecules with those in the spectra of the radicals formed by "adhesion" and has concluded that the latter always exhibit a shift of the cutoff toward long wavelengths. The shift, $\alpha = \lambda_{\dot{R}}/\lambda_{mol.}$, varies from 1.1 to 2, depending on the structure of the radical.

Reactivity of Pt(IV) Complexes in the Oxidation of CO in Aqueous Solutions

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The authors have studied the reactivity of several Pt(IV) complexes (of the K_2PtX_6 type) in the oxidation of CO, and have found that the reactivity decreases in the following order: $PtI_6^{2-} > PtBr_6^{2-} > Pt(CNS)_6^{2-} > PtCl_6^{2-} > Pt(NO_2)_6^{2-} > Pt(OH)_6^{2-} > Pt(NH_3)_6^{4+} > Pt(CN)_6^{2-}$. This series is the exact opposite of the series formed when the ligands of these complexes are arranged in the order of strengths of the crystalline fields they generate.

Qualitative considerations indicate that apparently there is a reciprocal relationship between the reactivity of the complex and the strength of the Pt–X bond. However, no clear-cut relationship was detected between the reactivities and the stability constants of the above complexes.

Free Radicals Formed by Irradiation of Water and Methanol Adsorbed on Synthetic Zeolites

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The ESR technique was used to investigate the $\dot{H}$, $\dot{O}H$, and $\dot{C}H_2OH$ species formed by γ-irradiation (^{60}Co source, 77°K) of water and methanol adsorbed on type A and X synthetic zeolites.

The authors studied the rates of accumulation