JOURNAL OF CATALYSIS 4, 530–534 (1965)

Abstracts of Articles in "Kinetics and Catalysis"; Vol. V, Issue 5, Sept.–Oct., 1964; pp. 769–775. Edited by the Siberian Division of the Academy of Sciences of USSR

Investigation by EPR Method of Early Stages of Oxidation of Palmitic Acid and Its Derivatives

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The free radicals formed in vacuum at 77°K by irradiation of palmitic acid, potassium palmitate, and of tripalmitine were studied by EPR method. The radicals produced in the radiolysis differ in structure, yields, and in the kinetics of accumulation and extinction. These findings emphasize the importance of the role of the carboxyl group bonds in the radiolysis.

Increasing the temperature after the radiolysis results in partial extinction of the radicals and in their partial transformation; the latter, as a result of migration of the free valences in the carboxyl groups.

For potassium palmitate and tripalmitine, addition of oxygen at 77°K alters the free radical yields. However, for all three compounds, formation of the peroxide radicals occurs only at much higher temperatures. With potassium palmitate in short exposure periods, an early stage of oxygen-free radical interaction was uncovered, representing reversible disappearance of the radicals.

Effect of Ionizing Radiation on Oxidation-Reduction Transformations of Acceptors in Organic Solvents

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A study was made of the effect of X-rays upon dilute solutions of CrO_3 and $CrCl_3$ in acetone. The results show that for 0.01 *M* solutions reduction of Cr^6 to Cr^3 occurs with and without presence of oxygen and that the limiting yields are 10.5 and 3.5 equivalents per 100 electron volts, respectively.

The irradiative oxidation of Cr^3 occurs only in presence of oxygen. In this case, for 0.01 *M* solutions of $CrCl_3$, the yield is 2.0 eqv./100 ev. The results show that the Cr^6 in Cr^6-Cr^3 complexes is more resistant to the action by the acetone radiolysis products than a non-complexed Cr^6.

Formation of Free Radicals from Hydrogen Peroxide in Cyclohexanol

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The formation of free radicals was investigated during decomposition of hydrogen peroxide in cyclohexanol at 120°–140° by observing consumption of the α-naphthylamine in presence of inhibitors. The results show that the free radical formation occurs along the following routes:

$$2ROH \ldots H_2O_2 \rightarrow 2RO^{\cdot} + 2H_2O$$
$$k = 8.9 \times 10^9 \exp(-23{,}500/RT)\ \text{sec}^{-1};$$

$$2H_2O_2 \rightarrow HO^{\cdot}{}_2 + H_2O + \cdot OH$$
$$k = 6.8 \times 10^9 \exp(-29{,}100/RT)\ l/\text{mol-sec}$$

The value of the reaction rate constant, k, in the bimolecular hydrogen peroxide—α-naphthylamine interaction is $7.8 \times 10^{12} \exp(-32{,}800/RT)\ \text{sec}^{-1}$.

Reactions of α-Oxides: Reactivity of Carboxylic Acids with Ethylene Oxide

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In this work, a continuation of an earlier study of interaction of ethylene oxide with carboxylic acids, the reactivity of nine carboxylic acids was determined when catalyzed by undissociated molecules of the acids. The reaction rate increases with increasing acidity. This relationship is accurately described by Bronsted's equation. For aromatic and aliphatic acids the resulting correlations form a family of parallel straight lines.