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# Abstracts of Articles from "Kinetics and Catalysis," Vol. V, Issue 2, March–April, 1964; pp. 201–210. Edited by Siberian Division of the Academy of Sciences of USSR

## Determination of an Oxygen-Methane Reaction Rate Constant

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The rate constant of the reaction, $O + CH_4 = OH + CH_3$, was determined by measuring at 570°–660° the primary ignition limits of stoichiometric mixtures of $H_2 + O_2$ and $CO + O_2$, each containing various small amounts of methane. This was found to be

$$(0.94 \pm 0.4) \times 10^{-10} e^{-\frac{8700 \pm 800}{RT}}, \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1},$$

For the reaction, $H + CH_4 = H_2 + CH_3$, at a temperature of 610° the value of the rate constant is $4.9 \times 10^{-14}$ $\text{cm}^3$ $\text{mol}^{-1}$ $\text{sec}^{-1}$.

The mathematical expressions based on the assumed reaction mechanism agree well with the experimental data.

## EPR Spectra of $HO_2$ and $DO_2$ Radicals Frozen Out of Exhaust Gases at 77°K

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A study was made of the EPR spectra of $HO_2$ and $DO_2$ radicals produced in freezing combustion products at a temperature of 77°K. The results show that the individual component widths broaden with increasing concentration of the radicals. Appreciable broadening of the widths may significantly alter the appearance of the spectra. These observations provide the clue to the differences in the EPR spectra of $HO_2$ radicals as reported by various investigators.

## Quantitative Investigations of Radical Reactivity Using a Competing Reaction Method: Phenyl Radical Reactions with Phenol, Aniline, and Anisole

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The relative rate constants of the phenyl radical reactions with phenol, aniline, and anisole were determined by a competing reaction method. With phenol and aniline in hydrogen split-off reactions, effective values of the constants decrease with increasing concentration. This is due to the combination of molecules of these compounds at the expense of hydrogen bond formation.

The relative constants were also determined for the reactions of hydrogen split-off from the dissociated forms of phenol and aniline and from the associated form of phenol. A discussion covers the causes of high reactivity of hydrogen atoms in phenol and aniline.

## Formation of Soluble Complexes of Unsaturated Hydrocarbons with Metal Salts and Their Role in Catalytic Reactions: Thermodynamics of Formation of Soluble $\pi$-Complexes of Ethylene with $Ag^+$ and $Cu^+$ Ions

*By* O. N. T'YOMKEEN, A. G. GEENZBOORG, AND R. M. FLEED

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The thermodynamics of formation of soluble $\pi$-complexes of ethylene with $Ag^+$ and $Cu^+$ ions were studied potentiometrically at temperatures of 20° to 80°. The accuracy of this analytical method is demonstrated by good agreement between the experimental and literature data for ethylene-$AgNO_3$ complex formation in aqueous solutions. The thermodynamic characterization factors for ethylene-monovalent copper $\pi$-complex formation are entirely novel.

### Electron Paramagnetic Resonance of Products of Reaction of Dicyclopentadienyl of Magnesium Dichloride with Alkyl Aluminums

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A study was made of the EPR spectra of $(C_5H_5)_2VCl_2$ complexes with various alkyl- and halo-aluminums. The results show that the complexes formed with $Al(CH_3)Cl_2$, $Al(C_2H_5)Cl_2$, and also with $Al(OCH_3)Cl_2$, $AlCl_3$, $AlBr_3$, $AlI_3$—are of the donor-acceptor type, not involving reduction of the vanadium. By contrast, in the $(C_5H_5)_2VCl_2$ reactions with $Al(C_2H_5)_2Cl$, $Al(C_2H_5)_3$, $Al(CH_3)_3$ and $Al(C_6H_5)_3$, the vanadium is reduced without accompanying split-off of the cyclopentadienyl rings.

Polymerization of ethylene over the complexes of $(C_2H_5)_2VCl_2$ with $Al(CH_3)Cl_2$ and $AlBr_3$, Cn* $(C_6H_5)_4$, does occur provided small amounts of oxygen are added to the reaction mixture.

### Kinetics of Oxidation of Cyclohexanone and 3-Methyl Cyclohexanone by Ammonium Metavanadate in Acidic Media

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The kinetics of oxidation of cyclohexanone and of 3-methyl cyclohexanone by ammonium metavanadate dissolved in HCl were studied at a wide range of solution acidities. At the acidity function values, $H_0$, greater than 1.6, the rate of the reaction, is limited by the ketone enolization stage. In less-acid solutions, parallel oxidation of a ketone-like substrate is also possible. This affects the magnitude of the activation energy and the applicability limits of the kinetic equation which is adequately accurate for the reaction rate values at high acidities.

### Kinetics and Mechanism of Hydrogen Iodide Addition to Multiple Carbon-Carbon Bonds of Organic Solvents: Addition of Hydrogen Iodide to Cyclohexene Dissolved in Benzene

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The rate of HI addition to cyclohexene is defined by the following trimolecular kinetic equation: $-d[HI]/dt = k_3[C_6H_{10}][HI][I_2]$. At temperatures of 4° to 47.5°, the temperature-rate constant, $k_3$, relationship is complex: the maximum and the minimum values of $k_3$ occurring at 20° and at 25+°, respectively. This relationship is explained as due to the formation and decomposition of intermediate iodine and cyclohexene complexes. Apparently, this reaction occurs via the formation of 1,2-di-iodocyclohexane, which is subsequently reduced by HI to iodocyclohexane. The results show that decomposition of 1,2-di-iodocyclohexane is faster than the addition of HI to cyclohexene in presence of iodine dissolved in benzene.

### Study of Polycoordination Kinetics

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A study was made of poly-coordination of 4,4′-bis(acetoacetyl) diphenyloxide and a solution of berillium acetylacetone. This reaction is of bimolecular type. The rate constants of the forward and the reverse reactions were determined using dimethylformamide and dinyl as the solvents. The activation energies of the polycoordination—and of the reverse reaction, that of polymer destruction, were determined in dimethylformamide solutions. The results of this investigation agree closely with the collision theory of reaction rates.

### Mechanism and Kinetics of Hydrolysis of γ-Butyrolactam in Potassium Hydroxide Solutions

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A study of hydrolysis of γ-butyrolactam by widely varying concentrations of KOH and KOD shows that the singly- and the doubly-ionizable forms of lactam are the reactable forms. Interaction of these two forms with water molecules is the limiting stage of the process. The ionization—and the true hydrolysis rate constants for the singly- and the doubly-ionizable forms are: $K_r = 4$; $K_{true} = 4 \times 10^{-3}$ min$^{-1}$ *and* $K'_r = 190$; $K'_{true} = 2.62 \times 10^{-2}$ min$^{-1}$, respectively.

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* Apparently, a misprint. Translator.