INFLUENCE OF IRRADIATION ON OXYGEN-CONTAINING COMPOUNDS IN THE PRESENCE OF OLEFINS

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The relation between the structure of olefins and oxygen-containing compounds and their reactivity in radical addition, substitution and isomerization processes under γ-irradiation in a wide temperature range was examined. Correlation equations for the determination of elementary rate constants and their Arrhenius parameters are given. The compensation effect is discussed. A mechanism of product formation is proposed and the corresponding kinetic equations are derived from the steady-state principle.

Introduction

Oxygen-containing compounds especially ketones and acids are known to possess a good extracting ability. The majority of extractants is usually applied in combination with diluters mainly paraffins. A variety of reactions may occur under irradiation in systems "paraffin-oxygen-containing compound", addition to the double bond of the initial olefin or to those resulting from the radiolysis of paraffins being of special interest. Olefins are often used as radical scavengers when investigating radiolytic processes in extractants. In this paper a study of the mechanism and kinetics of telomerization\(^1\) and addition\(^2\) of oxygen-containing compounds to olefins, the correlation of reactivity and structure and its dependence upon the solvent is reported.

Results and discussion

The general scheme of interaction of olefins with oxygen-containing compounds under irradiation is given in Fig. 1. Here the right vertical column contains information on the steps of chain initiation and chain growth, namely the reactions of the initial radicals with the monomer (not indicated in the scheme), radicals containing 1, 2, ..., \(i\) olefinic molecules being formed. The horizontal lines on the right of the column designate chain transfer reactions, namely the interaction of radicals with oxygen-containing compounds (not indicated in the scheme). These reactions result in...
Fig. 1. Radical telomerization mechanism. S - telogen; S' - initiating radical; T_i - telomer of the "normal" series; T_i' and T_i'' - telomers of the rearranged series; T' - telomeric radicals in the formation of so-called telomeric products T_1, T_2, ..., T_i. The horizontal arrow on the left of the column indicates the process of isomerization, i.e., the unimolecular migration of the radical center from the end of the radical to its inner part, usually to the fifth position. The resulting isomerized radical participates in addition and chain transfer processes similar to those mentioned above, T_1', T_1'', ..., T_1''' isomers being formed. The principal reactions are illustrated further, using methyl isopropyl ketone and ethylene as reagents:

**Initiation:**

\[
\text{CH}_3\text{COCH(CH}_3)_2 \buildrel \longrightarrow \over \longrightarrow \text{CH}_3\text{COC(CH}_3)_2 + \text{H} \quad (1)
\]

**Chain propagation:** (1) Growth

\[
\text{CH}_3\text{COC(CH}_3)_2 + \text{C}_2\text{H}_4 \buildrel K_{go} \over \longrightarrow \text{CH}_3\text{COC(CH}_3)_2\dot{\text{C}_2\text{H}_4} \quad (2)
\]

\[
\text{CH}_3\text{COC(CH}_3)_2\dot{\text{C}_2\text{H}_4} + n\text{C}_2\text{H}_4 \buildrel K_{gn} \over \longrightarrow \text{CH}_3\text{COC(CH}_3)_2(\text{C}_2\text{H}_4)_n\text{H} \quad (3)
\]

(2) Transfer:

\[
\text{CH}_3\text{COC(CH}_3)_2(\text{C}_2\text{H}_4)_n + \text{CH}_3\text{COCH(CH}_3)_2 \buildrel K_{trn} \over \longrightarrow \text{CH}_3\text{COC(CH}_3)_2(\text{C}_2\text{H}_4)_n\text{H} + \text{CH}_3\text{COC(CH}_3)_2 \quad (4)
\]