PERBENZOYLALKYL(ARYL) CARBONATES

REPORT 1. INITIATORS OF THE POLYMERIZATION OF VINYL COMPOUNDS

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Substantial development of the chemistry of peroxide compounds has recently been observed [1, 2]. A whole series of peroxides, which are initiators of free radical processes, has been produced. In our laboratory, investigations of free radicals in the liquid phase have been conducted for many years. Benzoyl peroxide and peroxycarbonates have been the sources of free benzoate and alkyloxy radicals. In this work we are reporting on the syntheses of mixed acyl peroxides, which undergo thermal decomposition to give benzoate and alkyloxy radicals simultaneously. Nonsymmetrical peroxides of the type

\[ \text{R'} - \text{O} - \text{C} - \text{O} - \text{O} - \text{C} - \text{R}'' \]

where \( \text{R'} = \text{CH}_3; \text{C}_6\text{H}_5; \text{C}_6\text{H}_{11}; \text{R}'' = \text{C}_6\text{H}_5 \), were synthesized. It seemed to us that such compounds should be very effective initiators of radical polymerization. The method of synthesizing perbenzoylalkyl(aryl) carbonates that we used consisted of reacting the corresponding alkyl- or arylchloroformiates with salts of perbenzoic acid in ether solution with energetic mixing at a temperature of 10° according to the equation

\[ \text{R'} - \text{O} - \text{C} - \text{Cl} + \text{MetOOC} - \text{C}_6\text{H}_5 \rightarrow \text{R'} - \text{O} - \text{C} - \text{OO} - \text{C} - \text{C}_6\text{H}_5 + \text{MetCl}. \]

Perbenzoylcyclohexyl carbonate and perbenzoylphenyl carbonate represent white crystalline substances, Perbenzoylmethyl carbonate is a liquid. All the peroxides obtained are readily soluble in ether, benzene, acetone, hydrocarbons, alcohols, and insoluble in water; they liberate iodine quantitatively from solutions in the presence of KI. In spite of their low decomposition point, we observed no explosions of the peroxide upon melting; they are stored well in a refrigerator for several months.

After the synthesis and investigation of the initiating ability of these compounds, we learned of the English patent [3], in which the peroxide of percaprylisopropyl carbonate (\( \text{R'} = \text{C}_7\text{H}_{15}; \text{R}'' = \text{C}_9\text{H}_{19} \)) is proposed as an initiator of the process of polymerization of styrene and methylmethacrylate.

The patent cites constants for three peroxides: perlaurylmethyl carbonate (\( \text{R'} = \text{CH}_3; \text{R}'' = \text{C}_{12}\text{H}_{25} \)), and perlaurylisopropyl carbonate (\( \text{R'} = \text{C}_7\text{H}_{15}; \text{R}'' = \text{C}_{12}\text{H}_{25} \)) and perlauryl-3,5,5-trimethylhexyl carbonate. These peroxides were produced on the basis of perlauric acid and the corresponding alkylchloroformiate in the presence of pyridine. We should mention that we also made an earlier attempt to use such a method in the synthesis of perbenzoylalkyl(aryl) carbonates; however, in this case the isolation of the final product in the pure form is substantially hindered. Hence we developed a method of synthesizing these peroxides by the reaction of the barium salt of perbenzoic acid with the corresponding alkyl(aryl) chloroformiates. It was shown that the perbenzoylalkyl carbonates synthesized, with the exception of perbenzoylphenyl carbonate, are very effective initiators of the polymerization of vinyl chloride and methylmethacrylate.

The reactivity of the peroxides obtained in the polymerization reaction can be seen from the kinetic curves for vinyl chloride (Fig. 1) and methylmetacrylate (Fig. 2). As can be seen from Fig. 1, the rate of vinyl chloride
polymerization in the presence of perbenzoylalkyl carbonates at 35° is 10 times as great as in the case of polymerization with benzoyl peroxide. In the case of methylmethacrylate (Fig. 2), the initial rate in the presence of perbenzoylcyclohexyl carbonate at 45° is 6-7 times as great as in the use of benzoyl peroxide. We should note the fact that the perbenzoylalkyl carbonates synthesized actively produce polymerization at temperatures of 25-30°, which is of great significance in the production of certain polymers. Perbenzoylcyclohexyl carbonate and perbenzoylmethyl carbonate differ little in their initiating ability (see Fig. 1). The dependence of the initial polymerization rate on the temperature is described by the Arrhenius equation. The total activation energy, calculated for the initial rates, is equal to \( E = 13.9 \text{ kcal/mole} \) for the polymerization of methylmethacrylate in the presence of perbenzoylcyclohexyl carbonate (Fig. 3) and \( E \approx 12.8 \text{ kcal/mole} \) for vinyl chloride. The dependence presented in Fig. 4 indicates that the rate of polymerization of vinyl chloride in the presence of perbenzoylcyclohexyl carbonate is proportional to the square root of the initiator concentration. The absence of an initiating ability of perbenzoylphenyl carbonate in the polymerization of vinyl chloride is apparently due to the fact that phenoxy radicals, which are inhibitors of radical processes, can be formed when this peroxide decomposes.

**EXPERIMENTAL**

*Synthesis of peroxides.* The synthesis of the barium salt of perbenzoic acid was conducted according to the method described earlier [4]. The 50% barium salt of perbenzoic acid (14.8 g) and 75 ml dry ether were loaded into a reactor equipped with a mechanical mixer, dropping funnel, and thermometer. Then 6 g of cyclohexylchloroformiate, dissolved in 25 ml of ether, was added dropwise with cooling to 0-5°. Mixing was conducted for 16 h at 10°. Then