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Chemistry

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Abstract

Full Text

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Addition of Isopropyl Alcohol to Maleic Acid Initiated by Percarbonates

Pitts and coauthors recently showed ([1]) that radicals formed by abstraction of hydrogen from isopropyl alcohol by benzophenone under irradiation readily add to maleic acid, giving terebic acid. We decided to reproduce the reaction of the initiated addition of isopropyl alcohol to maleic acid, using percarbonates as the initiator. It was expected that in this way it would be possible to obtain some additional data on the mechanism of decomposition of percarbonates.

It turned out that, in the presence of dicyclohexyl and diisopropyl peroxydicarbonates at 50°, maleic acid reacts with isopropyl alcohol, giving terebic acid in high yield. In this case about 0.1 mole of percarbonate was taken per 1 mole of maleic acid. The use of C^{14}-labeled compounds made it possible to draw conclusions about the mechanism of the processes taking place.

In one series of experiments the reaction was carried out in isopropyl alcohol labeled at the secondary carbon atom. In another series the reaction was carried out in inactive alcohol, using diisopropyl peroxydicarbonate labeled at the secondary carbon atom. The activity values given below are measurement data recalculated to the labeled secondary carbon atom. Radiometric measurements were carried out with an internal-filling counter. The measurement error was ±3%. In the reaction of diisopropyl percarbonate (0.0016 mole) and maleic acid (0.0065 mole) in labeled isopropyl alcohol (0.19 mole; 39600 imp/min), the activity of the terebic acid (33779 imp/min) corresponded to 85.5% of the activity of the alcohol taken.

In the reaction of C^{14}-labeled diisopropyl percarbonate (0.0013 mole; 39600 imp/min) with maleic acid (0.0064 mole) in inactive isopropyl alcohol (0.18 mole), the activity of the terebic acid (252 imp/min) corresponded to only 0.6% of the activity of the peroxide taken. From this it may be concluded that the radicals

$$\begin{array}{c} \mathrm{CH_3} \\ \mathrm{CH-O} \\ \mathrm{CH_3} \end{array}$$

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formed during decomposition of the percarbonate do not add to maleic acid and do not isomerize into

$$\begin{array}{c} CH_3 - \dot{C} - CH_3 \\ OH \end{array}$$

radicals; otherwise they would be incorporated into the terebic acid. This conclusion is in agreement with previously obtained data on the mechanism of decomposition of percarbonates in isopropyl alcohol ([2]). The small activity found in the terebic acid is due to the fact that, as the peroxide decomposes, labeled isopropyl alcohol accumulates in the system.

On the basis of the data obtained, the following reaction scheme may be proposed:

$$\begin{aligned} (CH_3)_2CHOC(O)OOC(O)OCH(CH_3)_2 &\longrightarrow 2\,(CH_3)_2CHOC(O)O\cdot \\ &\longrightarrow 2\,(CH_3)_2CHO\cdot + 2CO_2; \end{aligned} \quad (1)$$

$$(CH_3)_2CHO\cdot + CH_3CHOHCH_3 \longrightarrow (CH_3)_2CHOH + CH_3{-}\dot{C}(OH){-}CH_3; \quad (2)$$

$$CH_3{-}\dot{C}(OH){-}CH_3 + HOOC{-}CH{=}CH{-}COOH \longrightarrow HOOC{-}\dot{C}H{-}CH[C(OH)(CH_3)_2]{-}COOH; \quad (3)$$

$$\begin{aligned} &HOOC{-}\dot{C}H{-}CH[C(OH)(CH_3)_2]{-}COOH + CH_3CHOHCH_3 \\ &\quad\longrightarrow HOOC{-}CH_2{-}CH[C(OH)(CH_3)_2]{-}COOH + CH_3{-}\dot{C}(OH){-}CH_3 \longrightarrow \text{chain} \\ &\quad\xrightarrow[-H_2O]{} \text{terebic acid.} \end{aligned} \quad (4)$$

Acetone is formed as a result of chain-termination reactions involving the radicals
$CH_3{-}\dot{C}(OH){-}CH_3$.

The 2,4-dinitrophenylhydrazone (333 imp/min) isolated in the reaction of maleic acid and labeled C^{14} diisopropyl percarbonate (39600 imp/min) in inactive isopropyl alcohol contained only 0.8% of the activity of the initial peroxide.

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CITED LITERATURE

1. J. N. Pitts, R. L. Letsinger et al., *J. Am. Chem. Soc.* **81**, 1068 (1959).
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Note: Figure translations are in progress. See original paper for figures.

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