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Magnetic-field Effect on the Thermal Decomposition of Dilauroyl Peroxide

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Synopsis. In the thermal decomposition of dilauroyl peroxide in octane, the yield of docosane increases by 3—6% in the presence of magnetic fields (0.15—1 T). The results are interpreted in terms of a radical-pair model.

Magnetic-field effects on photochemical reactions have been extensively and successfully studied in the last decade.[1,5] On the other hand, there have been few reports on the thermal reactions, since the first observation of the effect on the reaction of pentafluorophenylmethyl chloride with C_4H_9Li in hexane.[2] Recently, though, Imoto and Nomoto[3] studied the magnetic-field effect on the radical polymerization of methyl methacrylate initiated with poly(2-hydroxyethyl methacrylate). In the present paper, we have studied the magnetic-field effect on the thermal decomposition of dilauroyl peroxide in octane. In the presence of magnetic fields (0.15—1 T), the yield of docosane, a cage product, increases by 3—6%. The results are interpreted in terms of a radical-pair model.

Experimental

The octane solution (0.2 ml) of dilauroyl peroxide (0.05 mol dm^{-3}) in a NMR tube was placed in a home-made heat bath at the center of an electromagnet (JASCO, MCD-1BS). The temperature of the bath was kept at 97 °C by circurating ethylene glycol from a thermostat.

The decrease in dilauroyl peroxide was monitored by means of iodometric titration. Its half-lifetime was about 20 min. The reaction time was set at 90 min in order to decompose 96% of the peroxide.

The yields of the three products, docosane, undecane, and 1-undecene, were determined by means of vapor-phase chromatography VPC, using hexadecane as the external standard. Since undecane and 1-undecene showed the same retention time under our VPC conditions, the sum of the yields was measured.

Results and Discussion

In the thermal decomposition of dilauroyl peroxide, the yields of docosane, undecane, and 1-undecene have been reported to be 56, 36, and 9% in octane, and 58, 16, and 4% in *o*-dichlorobenzene, respectively.[4] Since *o*-dichlorobenzene is a radical scavenger, these facts imply that docosane is a cage product, while the larger amounts of undecane and 1-undecene are mainly formed *via* free-radical reactions. Figure 1 shows the magnetic-field dependence of the product yields in the decomposition of dilauroyl peroxide. The yield of docosane increases by 3—6% in the presence of magnetic fields. On the other hand, the yield of the undecane/1-undecene mixture is almost magnetic-field-independent, though the data points are rather scattered. This scattering is because the VPC peak of the mixture appears just after the intense peak of the solvent under our VPC conditions.

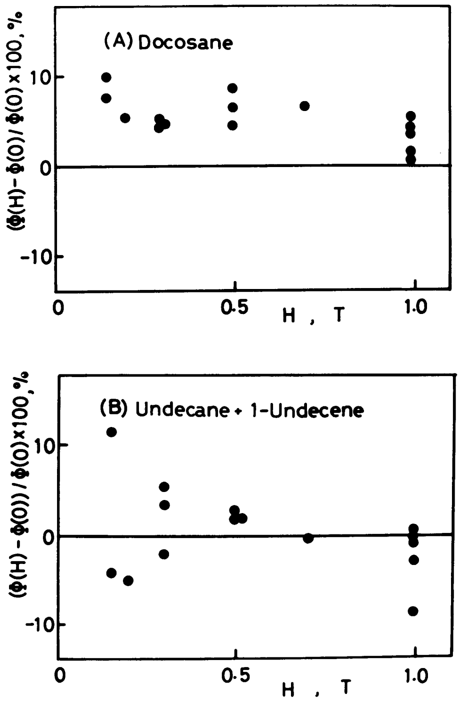

Fig. 1. Magnetic field dependence of the relative yields of (A) docosane and (B) the undecane/1-undecene mixture. Here, $\Phi(0)$ and $\Phi(H)$ represent the yields in the absence and presence of a magnetic field H, respectively.

TABLE 1. MAGETIC-FIELD EFFECT ON THE RELATIVE PRODUCT YIELDS (%) FOR THE THERMAL DECOMPOSITION OF DILAUROYL PEROXIDE AT 1 T

	Isopropyl iodide (mol dm^{-3})	
	0	1.5
Docosane	3.0±2.0	2.9±1.3
Undecane/ 1-undecene	−2.7±2.9	−0.7±3.5
No. of runs	5	11

To check the influence of a radical scavenger, isopropyl iodide is added into the solution. The VPC peak of the mixture remarkably decreases in intensity, while that of docosane is insensitive to the scavenger. This also implies that docosane and undecane/1-undecene are mostly a cage product and free-radical products respectively. The magnetic-field effects on the product yields in the absence and in the presence of the scavenger are shown in Table 1. The lack of any significant change in the magnetic-field effect by the scavenger supports the assignment of products presented above.

A proposed mechanism for the present thermal decomposition of dilauroyl peroxide is as follows:

$$\mathrm{C_{11}H_{23}COO_2COC_{11}H_{23}} \xrightarrow{\Delta} {}^{1}(\mathrm{C_{11}H_{23}COO\cdot\ \cdot OCOC_{11}H_{23}}) \tag{1}$$

$$^{1}(\mathrm{C_{11}H_{23}COO\cdot\ \cdot OCOC_{11}H_{23}}) \longrightarrow {}^{1}(\mathrm{C_{11}H_{23}\cdot\ \cdot C_{11}H_{23}}) + 2\mathrm{CO_2} \tag{2}$$

$$^{1}(\mathrm{C_{11}H_{23}\cdot\ \cdot C_{11}H_{23}}) \longrightarrow \mathrm{C_{22}H_{26}} \tag{3}$$

$$^{1}(\mathrm{C_{11}H_{23}\cdot\ \cdot C_{11}H_{23}}) \longrightarrow {}^{3}(\mathrm{C_{11}H_{23}\cdot\ \cdot C_{11}H_{23}}) \tag{4}$$

$$^{1,3}(\mathrm{C_{11}H_{23}\cdot\ \cdot C_{11}H_{23}}) \longrightarrow 2\mathrm{C_{11}H_{23}\cdot} \tag{5}$$

$$2\mathrm{C_{11}H_{23}\cdot} \longrightarrow \mathrm{C_{11}H_{24}} + \mathrm{CH_2{=}CH(CH_2)_8CH_3} \tag{6}$$

The initial step in the reaction is the homolysis of the oxygen–oxygen bond to generate a singlet radical pair of the lauroyloxyl radicals, (1). The decarboxylation of the lauroyloxyl radical, (2), is probably a very rapid process, since no appreciable amount of undecyl laurate, the product to be expected from the reaction of the radical, is detected.[4] The decarboxylation of lauroyloxyl radicals generates a singlet pair of the undecyl radicals. From the singlet radical pair, there are three processes; *i.e.*, a recombination into docosane, a cage product (3), an intersystem crossing to the triplet radical pair (4), and a diffusive separation into free radicals (5). The singlet-triplet intersystem crossing of the undecyl radical pair occurs *via* electron-nuclear hyperfine interaction. The rate is reduced in the presence of an external magnetic field because of the Zeeman splitting of the triplet sublevels (hfc mechanism). Therefore, this reduction in the intersystem-crossing rate leads to an increase in the yield of docosane, the cage product, in magnetic fields. Although an external magnetic field is also expected to decrease the yield of the free-radical products, the undecane/1-undecene mixture, this decrease is not so clear as that of the cage product because of the experimental error.

In the singlet-sensitized photolysis of dibenzoyl peroxide,[5] phenyl benzoate is detected as a cage product, and its magnetic-field effect (an 8% decrease at 4.3 T) is interpreted in terms of the Δg mechanism, in which the singlet-triplet intersystem crossing of the benzoyloxyl-phenyl radical pair is enhanced because of the difference in the g values of the component radicals. In the present reaction, the yield of docosane increases in the presence of relatively weak magnetic fields (0.15—1 T). Therefore, the magnetic-field effect observed here is mostly attributable to that on the undecyl radical pair by the hfc mechanism. The difference between dibenzoyl peroxide and dilauroyl peroxide reactions might be attributable to that in the decarboxylation rate of the intermediate radicals.

References

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