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Decomposition of Propionyl Peroxide over Cerium-Exchanged Y Zeolite

Diacyl peroxides are useful as the source of some radicals and the decomposition of diacyl peroxides in the gas phase or in the liquid phase has been frequently investigated (*1*). It is well known that radicals on solids are more stable than those in the gas phase or in the liquid phase. A remarkable example is radicals on zeolites obtained from some olefins, which are stable even at room temperature (*2*). The radicals formed from diacyl peroxides on zeolites may be easily observed by the ESR method. In the present paper the products from propionyl peroxide over cerium-exchanged Y zeolite and the plausible decomposition mechanism in connection with the ESR spectra are reported.

Cerium-exchanged Y zeolite (91.8% exchanged) was prepared by ion exchange of the sodium ions of Y-type zeolite with 10% aqueous solution of cerous chloride. The sodium type of Y zeolite (SK-40) was obtained from Union Carbide, Linde Division. The specific surface area estimated from nitrogen adsorption was 880 m^2/g. Propionyl peroxide (PP) was prepared by the method of Clover and Richmond (*3*) and it was kept at dry ice temperature to avoid decomposition. The ESR measurements were carried out with a Japan Electron Optics X-band spectrometer (JES PE-3X), using 100-kHz field modulation of 4.0-G width. The ESR sample tube was quartz (10 mm in diameter) with a stopcock at the top. Gas analyses were performed by gas chromatography with a 5-m column of propylene carbonate at 0°C. Helium was used as a carrier gas and its flow rate was about 40 cm^3/min.

After 3.1 g of the zeolite was degassed in a Pyrex reactor at 450°C for 2 hr, it was exposed to the vapor of PP kept at 0°C for 5 hr at dry ice temperature. Then, the reactor was soaked in a water bath maintained at 53°C for a desired time. The evolved gases were trapped with a liquid nitrogen trap for 12 min, allowing the gases to refill a bulb to measure the pressure. A small portion of the gases was analyzed by gas chromatography and the rest was returned onto the zeolite cooled at liquid nitrogen temperature. Thereafter, the PP-zeolite was soaked again in the water bath maintained at 53°C and these procedures were repeated. Ethylene, ethane, butane, formic acid, and carbon dioxide were obtained and the changes in the amount of these products are shown in Fig. 1.

Smid *et al.* (*4*) suggested the following decomposition mechanism for PP in solvents.

$$(C_2H_5COO)_2 \rightarrow 2\,C_2H_5COO\cdot, \quad (1)$$

$$C_2H_5COO\cdot \rightarrow \dot{C}_2H_5 + CO_2, \quad (2)$$

$$2\,\dot{C}_2H_5 \rightarrow C_2H_6 + C_2H_4, \quad (3)$$

$$\dot{C}_2H_5 + RH \rightarrow C_2H_6 + R, \quad (4)$$

where RH is a solvent.

$$(C_2H_5COO)_2 \rightarrow C_2H_5COOH + CO_2 + C_2H_4, \quad (5)$$

$$2\,\dot{C}_2H_5 \rightarrow C_4H_{10}. \quad (6)$$

Ethylene, ethane, butane, and carbon dioxide were obtained here; therefore, reactions (1), (2), (3), and (6) might have occurred. Propionic acid, C_2H_5COOH, was not obtained here and formic acid might have formed from propionic acid in the reaction

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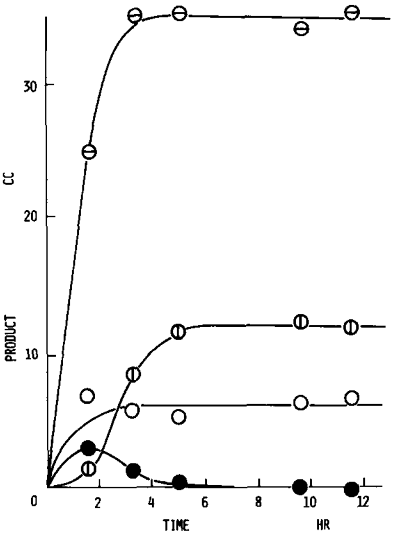

FIG. 1. Products in the decomposition of PP over Ce-exchanged Y zeolite at 53°C as a function of time. ⊖, CO_2; ⦶, C_4H_{10}; ○, $C_2H_4 + C_2H_6$; ●, HCOOH.

$$C_2H_5COOH \rightarrow C_2H_4 + HCOOH. \quad (7)$$

Then, reaction (5) might have occurred here.

When the zeolite was exposed to PP at −80°C and the temperature was raised to −60°C, an asymmetric ESR spectrum was observed and it may be identified with a peroxide such as $C_2H_5COO\cdot$. Thereafter, the spectrum changed gradually into a symmetric one as the temperature was raised, as shown in Fig. 2. This spectrum consists of five lines and their splitting is 21.8 G. In radicals formed from saturated molecules only α- and β-hydrogens will interact with the unpaired electron. The splitting caused by α-hydrogen does not differ very much from that by β-hydrogen. The components arising from this hyperfine interaction are then broadened by the dipolar interaction. This broadening is averaged to zero in liquids by the Brownian motion in the surrounding molecules. The ESR spectrum obtained on the solid surface are, however, usually of relatively poor resolution due to the lack of such "motional narrowing." Then this spectrum, shown in Fig. 2, may be ascribed to a radical in which an unpaired electron interacts with four nearly equivalent hydrogens, either α- or β-hydrogen.

In general, secondary radicals are more stable than primary radicals and the observed radical may be ascribed to a secondary one. The plausible secondary radical having four hydrogens, either α- or β-hydrogens, is $CH_3\dot{C}HCOOOOC_2H_5$ or $CH_3\dot{C}HCOOH$. Here the three hydrogens on the β-carbon would be equally coupled to the electron, while the one hydrogen on the α-carbon would be slightly differently coupled. The slight difference between the splitting by α-hydrogen and that by β-hydrogen have somewhat broadened the resulting spectrum. The five-line ESR spectrum similar to that in Fig. 2 had been obtained from the γ-ray irradiation (*5*) of ethanol at 77 K or from the photolysis (*6*) of ethanol adsorbed on Al_2O_3 at −140°C. These ESR spectra were identified with $CH_3\dot{C}HOH$ and with $CH_3\dot{C}HOAl$, respectively, which supports the identification of the radical obtained here.

Saturated hydrocarbons such as methane and ethane or saturated carboxylic acid such as acetic acid did not give any ESR signal on the zeolite at $g = 2.00$. Then, the radical obtained here may be formed by the

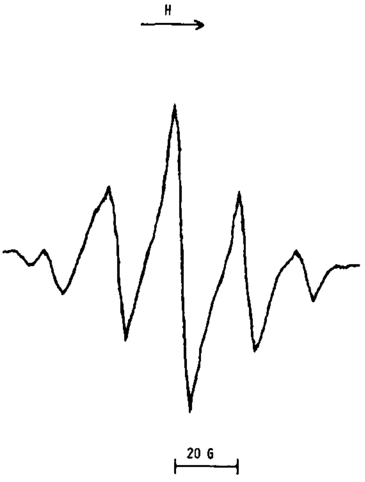

FIG. 2. ESR spectrum obtained from PP over cerium-exchanged Y zeolite at 25°C.

hydrogen abstraction with a radical formed from the decomposition of PP such as $\dot{C}_2H_5$ as follows:

$$C_2H_5COOOOC_2H_5 + \dot{C}_2H_5 \rightarrow CH_3\dot{C}HCOOOOC_2H_5 + C_2H_6 \quad (8)$$

or

$$C_2H_5COOH + \dot{C}_2H_5 \rightarrow CH_3\dot{C}HCOOH + C_2H_6. \quad (9)$$

This speculation is consistent with the change in the amount of the products decomposed from PP over the zeolite. In the initial stage when a large amount of PP or propionic acid was present on the zeolite surface, most of the ethyl radicals were consumed with the reactions with PP or with propionic acid (Eqs. (8) or (9)). As the PP or propionic acid decreased and the formation of ethane, ethylene, and carbon dioxide nearly ended, the recombination of the ethyl radical to form butane by Eq. (6) became predominant.

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