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THE EFFECT OF WATER ON THE PHOTO-REACTION OF TOLUENE WITH IRON(III) CHLORIDE

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The photo-reaction of toluene with iron(III) chloride is found to be controlled by the presence of water to lead to either nuclear or side-chain attack.

The photo-reaction of organic substrates with iron(III) chloride which is the photochemically active species has been of recent interest in our laboratory.[1] We now report that the photo-reaction of toluene with iron(III) chloride results in the nuclear and side-chain attack of reactive species and the reaction course is satisfactorily controlled by small quantities of water added.

$$C_6H_5CH_3 \xrightarrow[H_2O]{FeCl_3/h\nu} \underset{\mathrm{I}}{C_6H_5CH_2C_6H_4CH_3} + \underset{\mathrm{II}}{ClC_6H_4CH_3} + \underset{\mathrm{III}}{C_6H_5CH_2Cl}$$

In a rigorously anhydrous system, irradiation of a homogeneous solution of iron (III) chloride in toluene[2] yielded 98% phenyltolylmethanes (I) with an isomer ratio o : p = 46 : 54, plus a small amount of m-isomer and bibenzyl.[3] The isomer distribution coincided with that of I obtained from the thermal reaction of benzyl chloride and toluene in the presence of iron(III) chloride. When iron(III) chloride was dispersed in toluene, however, the isomeric chlorotoluenes [o : (m+p) = 13 : 87] (II) were produced in addition to the formation of I (Fig. 1). The fractional yield of II increased with increase of the amount of iron(III) chloride dispersed. During the reaction, iron(III) chloride was converted to iron(II) chloride.

In contrast, the addition of water to the dispersed iron(III) chloride system altered the reaction pathway.[3] In the water/iron(III) chloride ratio of 1.7, the reaction yielded I along with the small amount of II. This phenomenon was similar to the results in the thermal toluene-copper(II) bromide reaction.[4] However, the course of the reaction which is proceeding by side-chain attack is again altered in the direction of nuclear chlorination by further addition of water, as Fig. 1 shows. In addition, benzyl chloride (III) was obtained. In the water/iron(III) chloride ratio of 3, the maximum selectivity for nuclear chlorination was observed, and the nuclear chlorination resulted in the predominance of o-position [o : (p+m) = 67 : 33]. When the molar ratio became higher than 3, the yields of I and II decreased, and that of III increased. The maximum yield of III was observed in the molar ratio of 4-5. Thus, the presence of water in the iron(III) chloride system gives an important effect on the reaction course, that is, the reaction proceeds either by nuclear chlorination with the predominance of o-position or by side-chain attack leading to the formation of I and III which suggests the intermediacy of benzyl radical.[4,5]

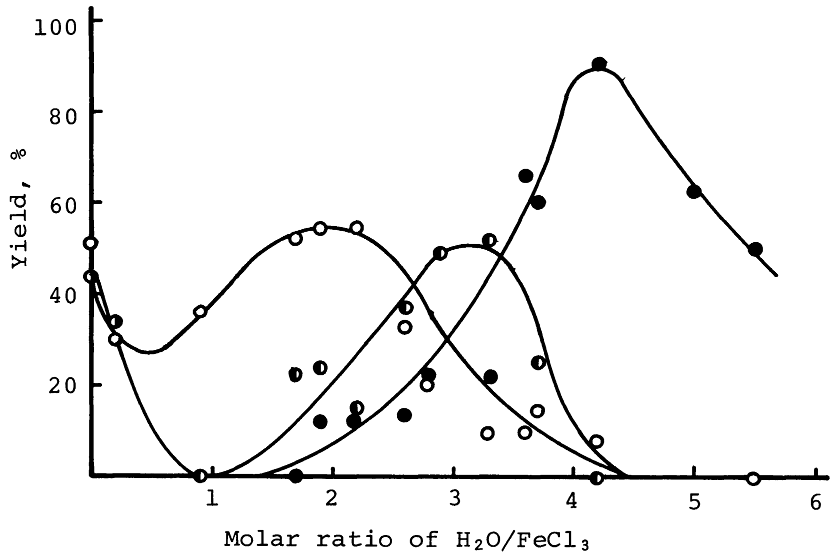

Fig. 1. Photo-reaction of toluene with iron(III) chloride in the presence of water. —○— I, —◑— II (p > o), —◐— II (o > p), and —●— III. Experiments were normally carried out by irradiating under stirring 10 ml of toluene in the presence of water and iron(III) chloride (0.22-0.25 g) at room temperature under a nitrogen atmosphere at the distance of 6 cm from a Pyrex-covered 100-W high pressure mercury lamp for 70 hr. Anhydrous iron(III) chloride was prepared by sublimation of the commercial iron(III) chloride (300°C at 1 mmHg). The amounts of the products were determined by the glc analysis. The yields were calculated from 2 x (the number of moles of the products/that of $FeCl_3$) x 100.

References and Notes

1) H. Inoue, N. Komakine, and E. Imoto, Bull. Chem. Soc. Japan, 41, 2726 (1968); H. Inoue, M. Sakata, and E. Imoto, ibid., 44, 3490 (1971).
2) Iron(III) chloride is reported to exist as a dimer in non-polar solvents; cf. A. F. Wells, "Structural Inorganic Chemistry", Oxford University Press, London (1950), p. 110.
3) In the dark reaction the products were not obtained at all.
4) P. Kovacic and K. E. Davis, J. Amer. Chem. Soc., 86, 427 (1964).
5) J. K. Kochi, J. Amer. Chem. Soc., 84, 2121 (1962); A. I. Kryukov and S. A. Ivanitskaya, Ukr. Khim. Zh., 34, 3 (1968); Chem. Abstr., 69, 35599 (1968).

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