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REACTION OF TRIPHENYLHYDRAZINE WITH tert-BUTYL HYDROPEROXIDE

Kazuhiro Maruyama and Tetsuo Otsuki
Department of Chemistry, Faculty of Science,
Kyoto University, Kyoto, Japan

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Recently the reaction of diphenylpicrylhydrazyl (DPPH) with tert-butyl hydroperoxide has been studied by E.S.R. technique(1) and it was supposed by Möbius and Schneider(2) that DPPH might be decomposed through the N-N bond scission, but no reaction products were isolated. The present authors studied reaction of triphenylhydrazine(3) with tert-butyl hydroperoxide and of tetraphenylhydrazine(4) with tert-butyl hydroperoxide. The reaction was followed by way of the E.S.R. technique(a 3BX-type spectrometer with 100 kc. modulation manufactured by Japan Electron Optics Lab. was used) and the reaction products were isolated and identified.

Triphenylhydrazine reacted with tert-butyl hydroperoxide rapidly, but tetraphenylhydrazine did not.

Triphenylhydrazine dissolved in benzene was treated with tert-butyl hydroperoxide in nitrogen atmosphere at 4°C for two hours. During the course of the reaction, the original colorless solution changed to violet, finally to dark brown. Out of the evaporated part of the reaction mixture under nitrogen atmosphere, nitrosobenzene was identified and determined (11 % yield) by electronic spectra. tert-Butyl alcohol and acetone were also identified by gas liquid partition chromatography from the evaporated part. Diphenylamine was isolated and determined (69 % yield) through a column chromatography on silicic acid. Of the above reaction products, nitrosobenzene and diphenylamine were considered as the main reaction products. On the other hand, it was found that tetraphenylhydrazine did not react with tert-butyl hydroperoxide at 4°C. Almost all part of tetraphenylhydrazine used was recovered after two hours.

On the other hand, reaction of triphenylhydrazine with tert-butyl hydroperoxide was followed by E.S.R. technique using a vessel furnished with a breakable seal containing tert-butyl hydroperoxide. In the course of the reaction, three different kinds of signal indicating the progressive appearance of three different kinds of radical were detected. The first strong signal decayed immediately and the spectrum of the radical could not be resolved. The other radicals, however, gave well resolved spectra and the second radical was assigned to $C_6H_5\dot{N}OH$ radical(FIG. 1)(5) and the third one to diphenyl nitric oxide(DPNO) radical(FIG. 2)(6).

From the results mentioned above, the present authors conclude that reaction of triphenylhydrazine with tert-butyl hydroperoxide proceeds through a radical mechanism starting with the scission of N-N bond.

Reaction of hydrazine derivatives with tert-butyl hydroperoxide are now under investigation and the complete mechanism will appear in a subsequent paper.

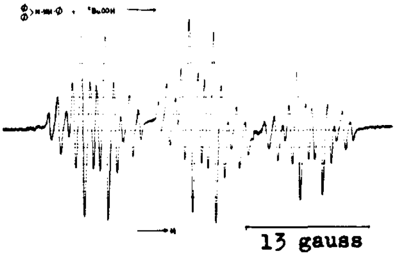

FIG. 1 E.S.R. spectrum of $C_6H_5\dot{N}OH$ radical obtained in reaction of triphenylhydrazine with tert-butyl hydroperoxide

(a_N= 11.1 g. $a_{Ho,p}$= 2.5 g. a_{Hm}= 0.9 g.)

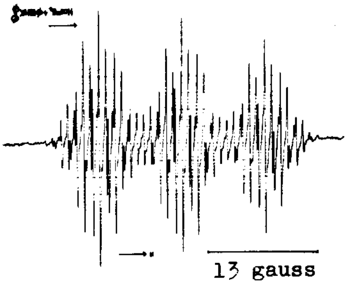

FIG. 2 E.S.R. spectrum of DPNO radical obtained in reaction of triphenylhydrazine with tert-butyl hydroperoxide

($a_N = 9.9$ g. $a_{Ho,p} = 1.8$ g. $a_{Hm} = 0.9$ g.)

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