The Appearance of Free Radicals during the Photo-decomposition of Nitrosobenzenes

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It has been reported that azoxybenzene, *p*- and *o*-hydroxyazobenzene, nitrobenzene, aniline and other minor amounts of hydroxyazoxybenzenes were formed by the photochemical decomposition of nitrosobenzene.[1] The present authors examined the process of the photochemical decomposition of several nitrosobenzene derivatives by using the ESR technique.

The subject of this investigation is the decomposition of nitrosobenzene, *o*-, *m*-, and *p*-methylnitrosobenzene, and *o*-, *m*-, and *p*-chloronitrosobenzene. Pure nitrosobenzene derivatives were dissolved in dry pure tetrahydrofuran and completely degased and illuminated by a 400-W. high pressure mercury-arc lamp at room temperature. These nitrosobenzene derivatives without exception produce free radicals from the beginning of decomposition. As the decomposition proceeds, the

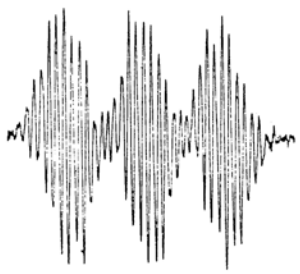

Fig. 1(a) ESR spectrum of free radicals produced by the photo-decomposition of nitrosobenzene.

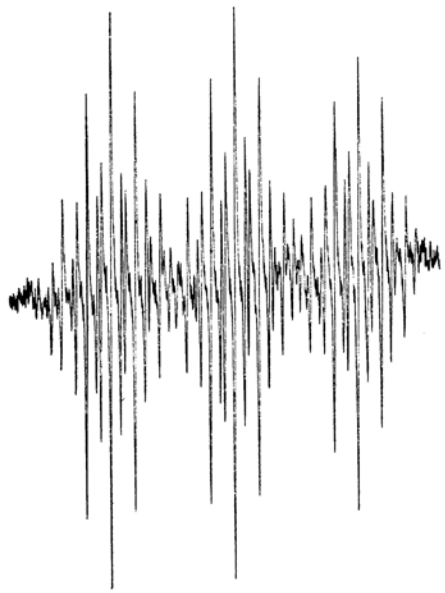

Fig. 1(b) ESR spectrum of free radicals produced by the photo-decomposition of *m*-chloronitrosobenzene.

1) E. Bamberger, *Ber.*, 35, 1606 (1902).

color of the solutions changed from green to brown. The free radicals produced were identified as the derivatives of diphenylnitroxide by the hyperfine structures of their ESR spectra; some of them are reproduced in Fig. 1.

It is noteworthy that the radicals produced from *o*-, *m*-, and *p*-substituted derivatives of nitrosobenzene were highly position-specific; *o*-methylnitrosobenzene decomposed to *o*, *o*'-dimethyldiphenylnitroxide, *m*-nitrosobenzene to *m*, *m*'-dimethyldiphenylnitroxide, *p*-methylnitrosobenzene to *p*, *p*'-dimethyldiphenylnitroxide, *o*-chloronitrosobenzene to *o*, *o*'-dichlorodiphenylnitroxide, *m*-chloronitrosobenzene to *m*, *m*'-dichlorodiphenylnitroxide, *p*-chloronitrosobenzene to *p*, *p*'-dichlorodiphenylnitroxide, and so on. Their ESR spectra show well-resolved hyperfine structures. Diphenylnitroxide, *m*, *m*'-dimethylnitroxide, and *p*, *p*'-dimethyldiphenylnitroxide were identified by a comparison of their ESR spectra with those of known samples. *p*, *p*'-Dichlorodiphenylnitroxide, *m*, *m*'-dichlorodiphenylnitroxide and *o*, *o*'-dichlorodiphenylnitroxide were clearly identified from the analysis of the ESR spectra obtained. Only *o*, *o*'-dimethyldiphenylnitroxide remains to be clarified completely; its spectrum shows a rather broad hyperfine structure.

Experimental.—*Derivatives of Nitrosobenzene.* —All the nitosobenzenes described above were synthesised from the corresponding nitro-derivatives. Nitro-derivatives were reduced to the corresponding hydroxylamine derivatives and oxidized to the nitroso-derivatives by a ferric chloride solution. The nitroso-derivatives obtained were carefully recrystallized from ethanol until their solutions in tetrahydrofuran became free from any ESR signal. Their physical constants were: nitrosobenzene, m. p. 68°C; *o*-methylnitrosobenzene, m. p. 72.5°C; *m*-methylnitrosobenzene, m. p. 53.5°C: *p*-methylnitrosobenzene, m. p. 49.0°C; *o*-chloronitrosobenzene, m. p. 56.5°C; *m*-chloronitrosobenzene, m. p. 72.0°C; *p*-chloronitrosobenzene, m. p. 89.5～90.0°C.

The ESR measurements were carried out by using a JEOL-3X spectrometer manufactured by the Japan Electron Optics Laboratory.

We are now performing the chemical analysis of the photo-decomposition products of nitrosobenzene derivatives, along with an ESR study to find the precise mechanism of the photochemical decomposition of nitrosobenzene derivatives.

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