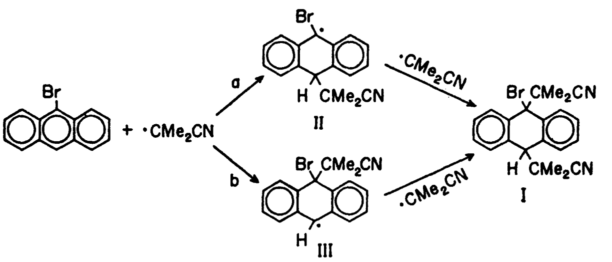
Chronology of the Addition of 1-Cyano-1-methylethyl Radicals to 9-Bromoanthracene Studied by CIDNP

Hiizu Iwamura, Michiko Iwamura,* Shiro Sato,** and Katsuhiko Kushida**
Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo
* *Department of Chemistry, Faculty of Science, Toho University, Narashino-shi, Chiba*
** *Nippon Electric Varian, Ltd., Azabu, Tokyo*

(Received January 21, 1971)

In previous papers we suggested a possible application of chemically induced dynamic nuclear polarization (CIDNP) for the determination of chronology of free radical addition reactions.[1] A typical example has now been found in the addition reaction of 1-cyano-1-methylethyl radicals to the *meso* positions of 9-substituted anthracenes.

The NMR spectrum of adduct I of 9-bromoanthracene, for example, has a doublet for the C-methyl protons at 0.86 and 0.78 ppm from the internal hexamethyldisiloxane. When 0.4 m*l* aliquot of a solution of 85 mg of 9-bromoanthracene and 112 mg of α,α'-azobisisobutyronitrile in 1.3 m*l* of tetrachloroethane was heated at 120°C in an NMR probe of a Varian HA-100 D spectrometer, it was the signal at the lower applied magnetic field (0.86 ppm) which showed an emission pattern. On the contrary, the intensity of the absorption peak at 0.78 ppm increased smoothly as expected for a normal growth of I as the reaction proceeded (see Fig. 1). Based on the empirical rule that the electronegative β-bromo substitution shifts the methyl proton resonance to the lower field by *ca.* 0.1 ppm,[2] it can be assumed that the emission signal corresponds to the methyl protons of $C_{(9)}$-CMe_2CN in I. Since the nuclear spin relaxation time T_1 of the intermediate radicals is usually short compared to their life-time, it is more probable that the nuclear spin polarization which was developed in the last step of the radical addition was detected in I. Thus the observation provides direct evidence for path a in Scheme 1 as the sequence of the addition reaction. The chronology is compatible with the knowledge that the addition proceeds through formation of a more stable intermediate radical in free radical chemistry. In the present case, II is considered to be more stable than III by additional resonance contribution of the bromine atom.



Scheme 1

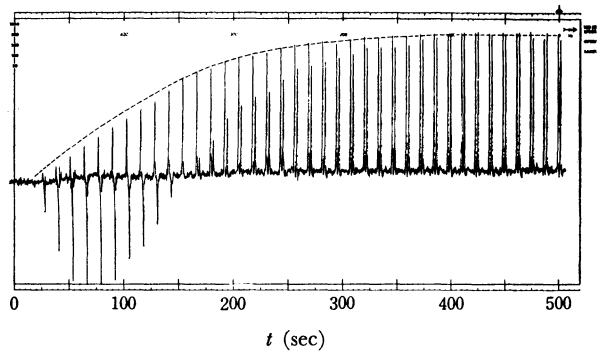


Fig. 1. Time dependence of the amplitude of the two C-methyl signals at 0.86 ppm (the upper envelope) and 0.78 ppm (the lower envelope) of I during the reaction. The dotted curve represents a theoretical increase in the concentration of I.[3]

A closer examination of the time dependence curve of the amplitude of the two C-methyl signals (Fig. 1) revealed, however, that the upper envelope representing the absorption peak at δ 0.78 ppm is not simply convex as expected for normal increase in the concentration of I as the reaction proceeds, but deviates slightly from the theoretical curve[3] in the 0—150 sec interval. The phenomenon seems to indicate that the curve could be an overlap between the normal exponential curve and a sigmoidal curve characteristic of the emission signals. The anomaly can be interpreted as a manifestation of the dual pathway of the addition reaction in which path b also contributes slightly.[4] The conclusion is consistent with that derived from the kinetic study of the reaction by Kooyman;[3] the partial rate factors at $C_{(10)}$ and $C_{(9)}$ of 9-bromoanthracene at 70°C are given as 1.37 and 0.07, respectively.[5]

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[1] H. Iwamura and M. Iwamura, *Tetrahedron Lett.*, **1970**, 3723; H. Iwamura, M. Iwamura, M. Tamura, and K. Shiomi, This Bulletin, **43**, 3638 (1970).

[2] L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed. Pergamon Press, Oxford (1969), p. 164; Ph. D. Thesis of Thomas Curphey, Harvard University.

[3] Given by Equation I in E. Farenhorst and E. C. Kooyman, *Rec. Trav. Chim. Pays-Bas*, **81**, 816 (1962).

[4] This effect is less conspicuous for the lower envelope representing the emission signals at 0.86 ppm in Fig. 1.

[5] Reactivity at $C_{(9)}$ is calculated to be *ca.* 10% at 120°C of the present experimental conditions.