

THE MECHANISM OF THE REACTION OF PICOLINE N-OXIDES WITH CARBOXYLIC ANHYDRIDES STUDIED BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY. III.<sup>1</sup>  
CHEMICALLY INDUCED <sup>13</sup>C POLARIZATION SPECTRA OF 4-ETHYLPYRIDINE

Hiizu Iwamura, Michiko Iwamura,\* Mamoru Imanari,\*\* and Makoto Takeuchi\*\*

Department of Chemistry, Faculty of Science, The University of Tokyo,

Bunkyo-ku, Tokyo, \*Department of Chemistry, Faculty of Science, Toho

University, Narashino, Chiba, and \*\*Japan Electron Optics Laboratory

Co. Ltd. (JEOL), Akishima, Tokyo, Japan

(Received in Japan 14 April 1973; received in UK for publication 18 May 1973)

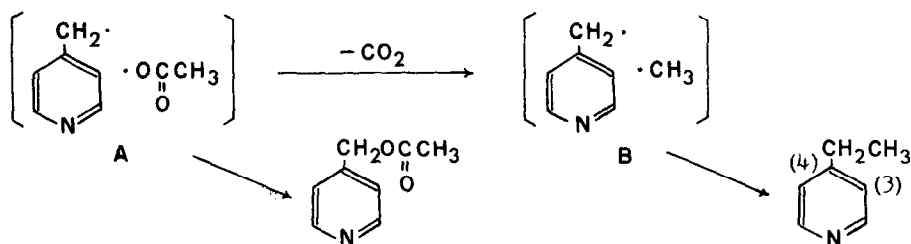
While the chemically induced <sup>13</sup>C polarization spectra are expected to give valuable information on the nature of radical pair intermediates, the experimental study has been hampered by the technical difficulty in short sampling time of the signals over the whole region of <sup>13</sup>C chemical shifts in the course of fast free radical reactions.<sup>2</sup> We wish to report on the chemically induced dynamic <sup>13</sup>C polarization spectra obtained with the aid of a Fourier transform pulsed nmr spectroscopy during the reaction of 4-picoline N-oxide with acetic anhydride.

A 3M solution of 4-picoline N-oxide in acetic anhydride was allowed to react in a sample tube of 8 mm O.D. which was heated at 110° in the nmr cavity of a JNM-PS-100 spectrometer (25.15 MHz). The Fourier transform pulsed nmr spectra were taken on a JNM-PFT-100 FT NMR System. A short radiofrequency 40° pulse of 8 usec width was applied with the repetition time of 1.1 sec over the <sup>13</sup>C spectrum width of 6.25 kHz. Nine scans on 2048 data points were accumulated in a magnetic drum of 16 kW which allowed us to obtain four separate spectra in the course of a single run of the reaction. After completion of the sampling, each accumulated time domain signal was Fourier transformed. Under these conditions, the signal to noise ratios of the

spectra were such that no signal except those of the solvent was detected before the start and after the end of the reaction. The signals of individual  $^{13}\text{C}$  were obtained as the v-mode single line with the aid of wide-band proton decoupling technique and were phase corrected by a computer calculation.

In 100 sec after the start of the reaction, we observed a pair of emission lines at 15.8 and 154.4 ppm and growth of a pair of absorption signals at 29.6 and 125.0 ppm (TMS-based). The intensity of these peaks increased until ca. 140 sec (Figure 1a), when it started to decay and disappeared in 300 sec. Time development of the polarization during the reaction is summarized in Figure 2. At the end of the reaction, we found signals due mainly to 4-picolyyl acetate on a chart of 100 scan accumulation, but no signal could be seen at the chemical shifts where the polarized signals appeared (Figure 1b). By comparison with the  $^{13}\text{C}$  spectrum of the authentic sample (Figure 1c), the emission signals were assigned to the methyl carbon and ring  $\text{C}_{(4)}$ , while the enhanced absorption signals corresponded to the methylene carbon and ring  $\text{C}_{(3)}$  of 4-ethylpyridine.

Examination of the polarization pattern in terms of the current radical pair theory of the chemically induced dynamic nuclear polarization<sup>3</sup> enables us to deduce the mechanism of formation of 4-ethylpyridine. Since 4-picolyyl and methyl radicals are both carbon radicals and differ only slightly in g factors ( $\Delta g \approx 0.0001$ ), the observed net polarization must have arisen in the precursor 4-picolyyl - acetoxy radical pairs (A), in which the acetoxy radical decarboxylated before recombination. The 4-picolyyl - methyl radical pair (B) thus formed can, in principle, superimpose the multiplet effect on the net polarization already present in the radical pair. The former effect can not be observed in the present example owing to the wide-band proton decoupling and to low statistical probability of  $^{13}\text{C} - ^{13}\text{C}$  coupling. In radical pair A, the acetoxy



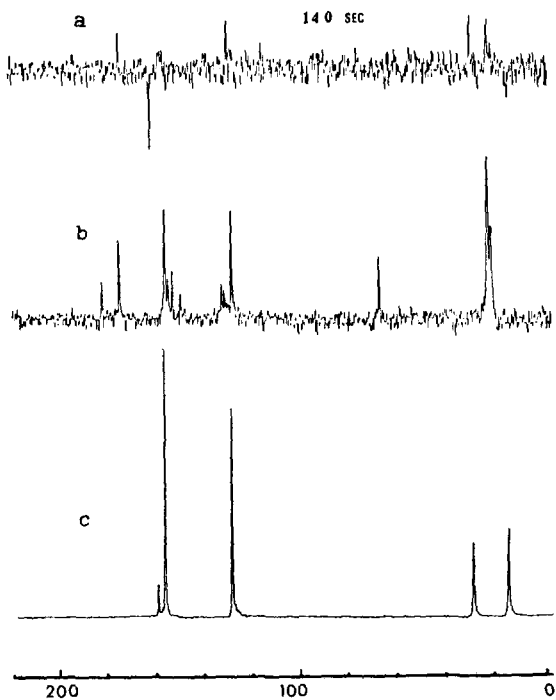


Figure 1.  $^{13}\text{C}$  spectra obtained (a) at 140 sec and (b) after the end of the reaction of 4-picoline N-oxide in acetic anhydride at  $110^\circ$ . (c)  $^{13}\text{C}$  spectrum of authentic 4-ethylpyridine.

acetoxyl radicals ( $10^{-9}$  sec)<sup>7</sup> could well be shorter than its relaxation time, giving polarization pattern of radical pair A in 4-ethylpyridine.

Turning now to a comparison with the proton polarization spectra in which net emission is observed at  $\delta$  4.98 for  $\text{CH}_2$  of 4-picolyl acetate and a pair of E/A multiplets is eminent for the ethyl signals of 4-ethylpyridine,<sup>1</sup> we note the strong contrast that net polarization is detected for the latter but no polarization due to 4-picolyl acetate is discernible under the S/N of the present  $^{13}\text{C}$  study. The difference may be derived from the slightly higher temperature

radical undoubtedly has the larger  $g$  value by ca. 0.003 due to the presence of the oxygen atom. In reference to the simple rules on the pattern of the polarization spectra,<sup>4</sup> the ring  $\text{C}_{(4)}$  in 4-picolyl radicals which carries negative hyperfine coupling constant<sup>5</sup> is expected to give net emission in the cage recombination product. Positive signs in hyperfine coupling of the  $\text{CH}_2$  carbon (35~40 G)<sup>6</sup> and the ring  $\text{C}_{(3)}$  should correspond to net absorption. The polarity of the polarized signals with respect to the sign of hyperfine coupling constants is reversed in acetoxyl radicals. The prediction is exactly what was observed in 4-ethylpyridine (Figure 1a). Nuclear relaxation times of radicals are usually in the range  $10^{-5} \sim 10^{-4}$  sec, so that the life-time of

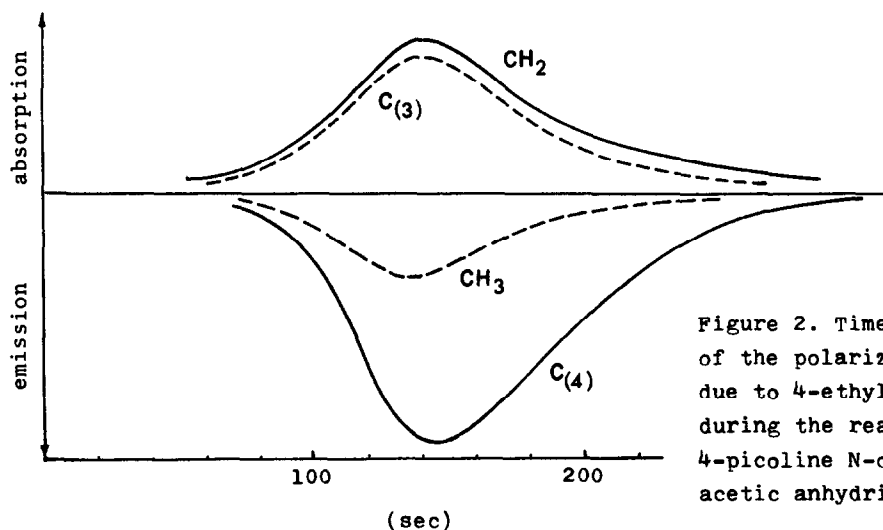


Figure 2. Time development of the polarization signals due to 4-ethylpyridine during the reaction of 4-picoline N-oxide in acetic anhydride at 110°.

(110°) employed in the present experiment compared to the previous  $^1\text{H}$  study (95°).<sup>1</sup> The intensity of net polarization in 4-ethylpyridine relative to that of 4-picolyl acetate, both originating from radical pair A, is reasonably expected to increase with increasing rate of the reaction.

#### References

1. Part II; H. Iwamura, M. Iwamura, T. Nishida, and S. Sato, J. Amer. Chem. Soc., 92, 7474 (1970).
2. S. Berger, S. Hauff, P. Niederer, and A. Rieker, Tetrahedron Lett., 2581 (1972).
3. G. L. Closs and A. D. Trifunac, J. Amer. Chem. Soc., 92, 2183, 2186 (1970); R. Kaptein and L. J. Oosterhoff, Chem. Phys. Lett., 4, 195 (1969); R. Kaptein, J. Amer. Chem. Soc., 94, 6251 (1972); and papers cited therein.
4. R. Kaptein, Chem. Commun., 732 (1971); R. Kaptein and J. A. den Hollander, J. Amer. Chem. Soc., 94, 6269 (1972).
5. M. Karplus and G. K. Fraenkel, J. Chem. Phys., 35, 1312 (1961).
6. R. W. Fessenden, J. Phys. Chem., 71, 74 (1967).
7. W. Braun, L. Rajbenbach, and R. F. Eirich, J. Phys. Chem., 66, 1591 (1962).