(2) (a) P. J. Wittek and T. M. Harris, *J. Am. Chem. Soc.*, **95**, 6865 (1973); (b) T. M. Harris and P. J. Wittek, *ibid.*, **97**, 3270 (1975).

(3) Several heterocyclic ring closures could also occur.

(4) T. T. Howarth, G. P. Murphy, and T. M. Harris, *J. Am. Chem. Soc.*, **91**, 517 (1969).

(5) Prepared by condensation of ethylene glycol with the keto diester in refluxing benzene (H_2SO_4 catalyst); water was removed azeotropically.

(6) The empirical formula was established by elemental analysis and mass spectrometry.

(7) Compound **9:** mp 162–164 °C dec (vacuo); ir (KBr) 1737, 1702 cm^{-1}; NMR (Me_2SO-d_6) δ 1.96 and 2.5 (2 CH_3's), 3.52 (CH_2), 3.75 and 3.96 (m, CH_2CH_2), 6.3, 6.4, and 6.57 (3 aromatic H's).

(8) Compound **8:** mp 143–144 °C dec (vacuo); ir (KBr) 1710, 1687, 1640 cm^{-1}; NMR ($CDCl_3$) δ 2.25 and 2.6 (2 CH_3's), 2.98 and 3.17 (ring CH_2's), 3.83 (chain CH_2), 4.01 (ketal CH_2CH_2), 6.59 (aromatic H), 13.97 (phenolic OH).

(9) Compound **10:** mp 201–202 °C; ir (KBr) 1630 cm^{-1}; NMR (acetone-d_6) δ 1.44 (CH_3), 2.75 (OH), 2.85 (*m*, CH_2), 3.1 (s, CH_2), 3.96 and 4.21 (m, ketal CH_2CH_2), 6.5, 6.79, 7.0 (3 aromatic H's), 9.82 (OH).

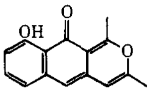
(10) Closely related natural products are known; they also dehydrate more readily with pyridine than with hydroxide ion: D. L. Dreyer, I. Arai, C. D. Bachman, W. R. Anderson, R. G. Smith, and G. D. Daves, *J. Am. Chem. Soc.*, **97**, 4985 (1975), and references cited therein.

(11) W. Karrer, "Konsitution und Vorkommen der organischen Pflanzenstoffe", Birkhäuser, Basel, 1958; R. H. Thomson, "Naturally Occurring Quinones", 2d ed, Academic Press, New York, N.Y., 1971.

(12) Aldrich Chemical Co.

(13) *Compound* **21:** mp 209–210 °C *dec*; ir ($CHCl_3$) 1720, 1695 sh, 1632 cm^{-1}; NMR (acetone-d_6/Me_2SO-d_6) δ 2.06 and 2.48 (2 CH_3's), 3.76 (CH_2), 6.72–7.34 (4 aromatic H's).

(14) The condensation also gave 12% of pyran i; diketone **21** with heating or acid catalysis gives i. The corresponding cyclization has also been observed with **9**.



i

(15) Compound **22:** mp 203–206 °C; ir (Nujol) 1620 cm^{-1}; NMR ($CDCl_3$/Me_2SO-d_6) δ 1.40 (CH_3), 2.86 and 3.08 (2 CH_2's), 4.68 (OH), 6.72–7.70 (4 aromatic H's), 9.84 and 16.04 (2 OH's).

(16) A. J. Birch, *Proc. Chem. Soc.* (*London*), 3 (1962); A. J. Birch, *Fortschr. Chem. Org. Naturst.*, **14**, 186 (1957).

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Nuclear Magnetic Resonance in Pulse Radiolysis. Chemically Induced Dynamic Nuclear Polarization[1]

Sir:

We wish to report here the first application of nuclear magnetic resonance spectroscopy and chemically induced dynamic nuclear polarization (CIDNP) to the study of pulse radiolysis.

The major part of radiation chemistry involves radicals produced by ionizing radiation.[2] The study of radicals themselves by time—resolved EPR spectroscopy[3] or the study of products of reactions of these radicals by nuclear magnetic resonance spectroscopy can yield useful details of reaction mechanisms. While the study of radical reaction mechanisms in photolysis and thermolysis by CIDNP-NMR methods has been common[4] there has been no successful application of CIDNP or NMR in pulse radiolysis.

Since direct irradiation of NMR samples with the electron beam does not appear feasible at this time we irradiate with the 3-MeV electron beam from the Argonne Van de Graaff accelerator in our EPR magnet (~4000 G) which has axial holes for beam access.[3]

A fast flow system, with transfer speeds of ~1 m/s (pump pressure ~60 psi) transfers the irradiated solution to the rotating 5-mm NMR sample tube in the probe of our Varian A56/60A NMR spectrometer.[5]

We have been able to observe CIDNP in numerous products of radicals in aqueous systems. Large radical concentrations can be produced either by the OH· abstraction reaction or the e_{aq}^- reaction with suitable compounds.

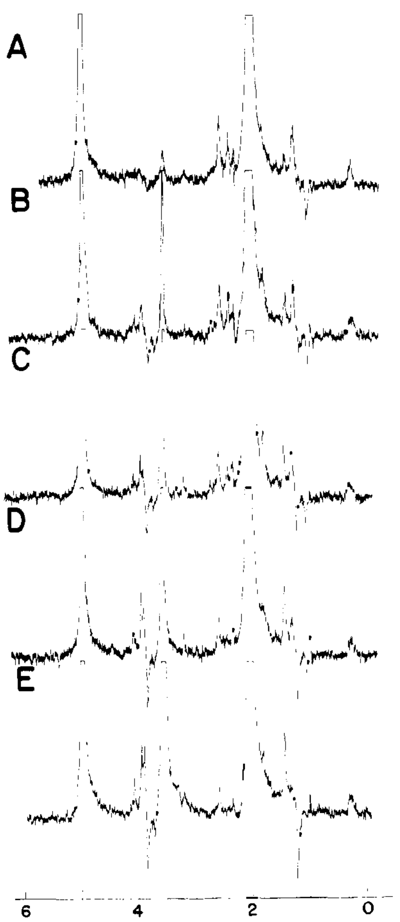

Figure 1. (A) The partial XL-100-15 ^{1}H NMR spectrum of **6a**, in $CDCl_3$, showing the signals derived from the $C_{11}H_8$ moiety. The inset displays H_g, H_b, and H_d at 270 MHz.[12] (B) The partial XL-100-15 ^{1}H NMR spectrum of **6b**, in $CDCl_3$, showing the signals derived from the $C_{11}H_4D_4$ moiety.

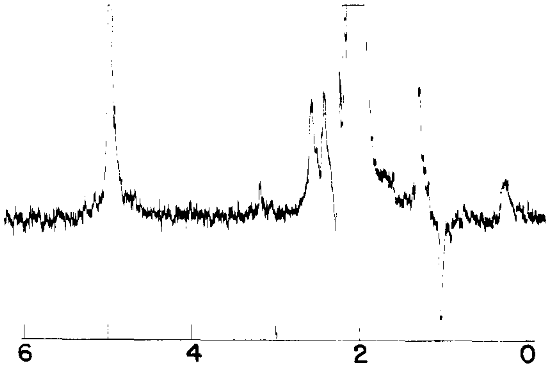

Figure 2. Pulse radiolysis of sodium acetate in D_2O. H_2O in D_2O is at ~5 ppm, and sodium acetate is at 2.1 ppm.

We illustrate some of the features of the CIDNP in pulse radiolysis of mixtures of sodium acetate and methanol. Figure 1 shows the CIDNP in various products in this system. The principal radicals produced are $\cdot CH_2OH$, $\cdot CH_2COO^-$, $\cdot CH_3$ (and ·D). Products corresponding to all possible combinations of these radicals are observed. Assignment is easy since by changing the relative concentrations of methanol vs. acetate different products are brought into prominence.

Irradiation of acetate alone (Figure 2) gives rise to two radicals, $\cdot CH_2COO^-$ and $\cdot CH_3$ (and ·D), and the principal product is propionic acid ($CH_3CH_2COO^-$) with polarized NMR peaks with enhanced absorption-emission (AE) triplet

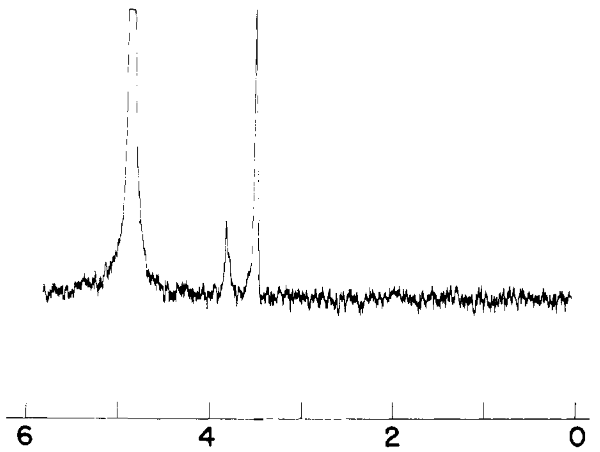

Figure 3. Pulse radiolysis of methanol in D_2O. Methanol is at 3.5 ppm.

at 1.15 ppm (Me_4Si) and AE quartet at 2.3 ppm. Methane (actually CH_3D) is seen at ~0.2–0.3 ppm and is in enhanced absorption (A), since in this system it is the radical with the smallest g factor.[6] Combination of two acetate radicals gives succinic acid which is seen at 2.6 ppm, and is weakly polarized. In the pulse radiolysis of methanol alone (Figure 3) only ethylene glycol can be seen at 3.7 ppm in enhanced absorption (A).[7]

A mixture of methanol and acetate yields, in addition to the products mentioned above, ethanol and β-hydroxypropionic acid ($OHCH_2CH_2COO^-$). Ethanol has AE triplet at 1.25 ppm and AE quartet at 3.7 ppm, and $OHCH_2CH_2COO^-$ has two AE triplets at ~3.7 and ~2.4 ppm. As more methanol is added to acetate solutions, propionate is displaced by ethanol (Figure 1 A–E) as the dominant polarized product.

While this example deals with radicals produced by the OH· abstraction reaction, we have also studied examples of the e_{aq}^- reaction in the CH_3I-CH_3OH system. Details of this and numerous other systems that exhibit CIDNP in pulse radiolysis will be discussed elsewhere.[8]

Several important features of pulse radiolysis NMR-CIDNP experiments should be mentioned. The intensities of polarized NMR signals are dominated by the nuclear spin lattice relaxation time (T_1) of the products in question. Thus products with very short T_1 may not be seen at all if the transfer time between the irradiating magnet and the NMR magnet is not comparable to the T_1 of that product. Substantial concentrations of radicals are produced by irradiation and the typical radical half-lives are in the range of microseconds or less.[9] This is considerably shorter than the nuclear T_1 in these radicals (~10^{-4} s) and sometimes it is shorter than the electron T_1 in some of these radicals. Under these conditions polarization transfer may be occurring.[10] This is being investigated.

The overall polarization pattern of NMR multiplets is AE (enhanced absorption low field lines and emission high field lines of the multiplet) as expected for independently generated radicals.[11] However, the relative signal intensities of the polarized NMR multiplets can be complex. The residence time of radicals in the irradiating magnet may affect the relative multiplet intensities.[12] The effect of flow rate on the NMR signal intensity should also be considered.[13] The CIDNP in varying magnetic fields can also be easily studied, and provides additional details on polarization in various products.

We hope to have illustrated how this novel application of nuclear magnetic resonance spectroscopy to pulse radiolysis can be used to study various radical products and their reaction mechanisms. The more detailed analysis of CIDNP can yield information on the radical-radical interaction in solution. We believe that CIDNP study in radiation chemistry will prove to be a simple and useful analytical tool.

References and Notes

(1) Work performed under the auspices of the USERDA.
(2) For general references see M. S. Matheson and L. M. Dorfman, "Pulse Radiolysis", The M.I.T. Press, Cambridge, Mass., 1969.
(3) A. D. Trifunac and M. C. Thurnauer, *J. Chem. Phys.*, **62**, 4884 (1975).
(4) A. R. Lepley and G. L. Closs, Ed., "Chemically Induced Magnetic Polarization", Wiley Interscience, New York, N.Y., 1973; G. L. Closs, *Adv. Magn. Reson.*, **7**, 157 (1974).
(5) A similar flow system has been described by R. G. Lawler and M. Halfon, *Rev. Sci. Instrm.*, **45**, 84 (1974). Flow systems have also been used to study CIDNP in the chemically produced OH· radical reaction products. M. Cocivera, C. A. Fyfe, S. P. Vaish, and H. E. Chen, *J. Am. Chem. Soc.*, **96**, 1611 (1974).
(6) G. L. Closs and A. D. Trifunac, *J. Am. Chem. Soc.*, **92**, 2183 (1970).
(7) This unusual polarization (A) has also been observed in other systems,[8] and remains to be explained.
(8) A. D. Trifunac, to be submitted for publication.
(9) These estimates of radical half-lives are based on our measurements of the $\cdot CH_2COO^-$ radical half-life at somewhat lower electron beam intensities. A. D. Trifunac, *J. Am. Chem. Soc.*, in press.
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(12) R. Kaptein, Ph.D. Thesis, Leiden, 1971.
(13) D. W. Jones and T. F. Child, *Adv. Magn. Reson.*, **8**, 123 (1976).

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1,6-Methano[10]annulen-11-ylidene

Sir:

Due to the continuing interest in the phenylcarbene-cycloheptatrienylidene rearrangement,[1] we undertook a study of 1,6-methano[10]annulen-11-ylidene (**2**), a relative of cycloheptatrienylidene. We now wish to report the successful generation of the carbenoid equivalent of **2** and the trapping of a novel intermediate.

When 11,11-dichloro-1,6-methano[10]annulene (**1**)[2] was treated with either n-butyllithium or methyllithium in an ether solvent, $C_{22}H_{16}$ hydrocarbons[3,4] were isolated. Due to their instability and the complex nature of their ^1H NMR spectrum, these $C_{11}H_8$ dimers were neither separated nor fully characterized. However, since the ^1H NMR spectrum revealed the presence of only vinyl and allylic protons, it was clear that rearrangement to 2,3-benzocycloheptatrienylidene or α-naphthylcarbene had not occurred.

Our efforts were then directed towards intercepting the $C_{11}H_8$ intermediate prior to dimerization in order to both enhance the stability and simplify spectral analysis of the product. Trapping by furan,[1a,5] cyclohexene,[6] mercaptide anion,[7] bis(triphenylphosphine)(ethylene)platinum,[8,9] anthracene, buta-1,3-diene, or 1-methoxybuta-1,3-diene proved unsuccessful. However, when **2** was generated in the presence of 1,3-diphenylisobenzofuran[10] (DPIBF), a 1:1 adduct,[11] mp 187–189 °C with decomposition, was obtained in 65% yield. The ^1H NMR spectrum of this compound is partially reproduced in Figure 1A. Extensive proton decoupling experiments[12] permitted us to obtain the chemical shift and coupling constant data displayed in Table I. This information, in conjunction with the ^{13}C NMR and the uv spectrum [λ_{max} (in acetonitrile) 303 nm (ϵ 3450)], still did not allow an unambiguous structural assignment.

Clear crystals of the 1,3-diphenylisobenzofuran adduct **6a** were grown by slow evaporation of an EtOAc solution at 4 °C. Diffraction symmetry was orthorhombic with accurate cell constants of $a = 8.792$ (2), $b = 17.037$ (5), and $c = 14.493$ (4) Å. Systematic absences indicated the chiral space group $P2_12_12_1$ and a calculated density suggested one molecule of $C_{31}H_{22}O$ per asymmetric unit.[13] All diffraction maxima with $2\theta \leq 114°$