

NMR SPECTRA OF TRANSIENT RADICALS*

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INTRODUCTION

A time resolved method for the study of structure and spin dynamics of transient radicals in liquids is described. Pulsed electron beam or pulsed laser irradiation is used to create transient radicals in solution. Irradiation is carried out in the field of a variable electromagnet, and, within a time comparable to nuclear T_1 's, the diamagnetic products are transferred using a fast flow system to an NMR probe for examination. During the radical reaction, a 0.5-10 μ sec r.f. pulse is applied to the reacting sample at an appropriate frequency, corresponding to a nuclear energy level spacing of the given radical. High H_1 fields are achieved by compact coil design and a matching network. Nuclear spin level population changes in the radical are transferred to its reaction product and detected as intensity changes in their NMR spectra. The NMR computer (ASPECT 2000) controls the frequency sweep, r.f. coil match and FT NMR spectrometer operations including the automatic data handling.

RESULTS

Nuclear resonance spectra of many simple radicals have been obtained. Here we illustrate the method with a

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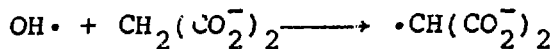
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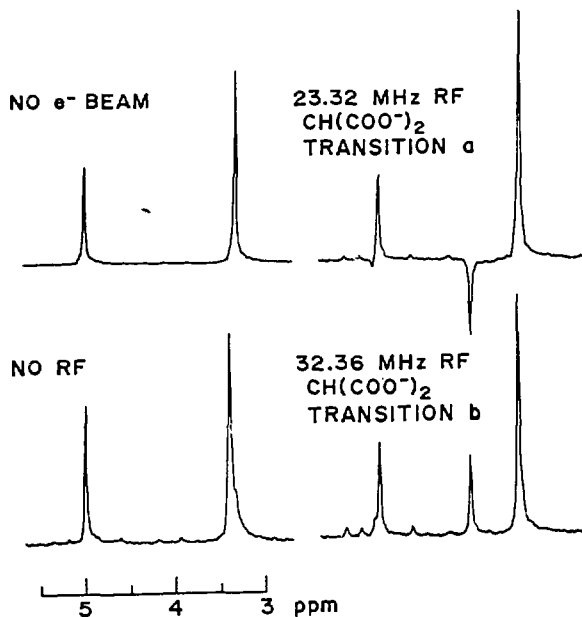
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simple one proton radical from the radiolysis of sodium malonate in D₂O:



MALONATE RADIOLYSIS
PROTON NMR SPECTRA
(N₂O, 100.0 mT)



In Fig. 1 the NMR spectral data are illustrated. At the magnetic field of irradiation (1000 g) used, no CIDNP of any products is seen. Application of r.f. at the appropriate frequencies indicated produced dramatic changes. When the intensities of the

coupling product (CH(CO₂⁻)₂)₂ are plotted as a function of nuclear frequency, Fig. 2 is obtained.

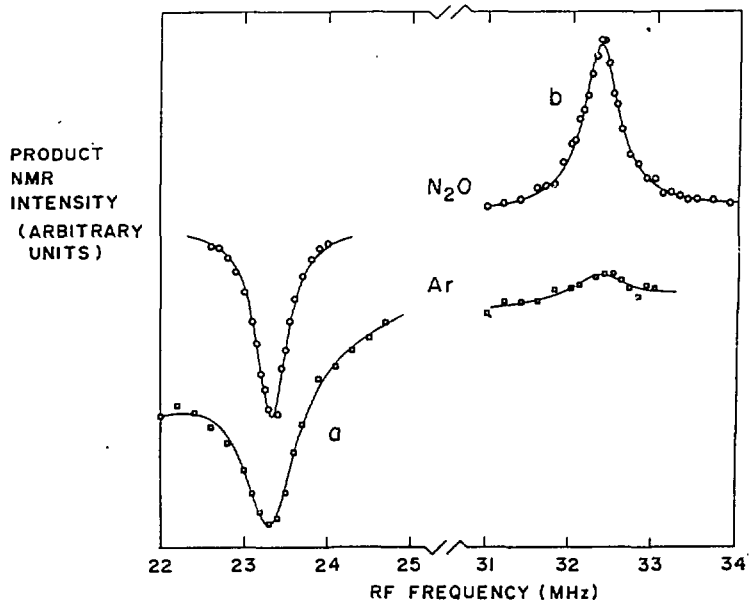
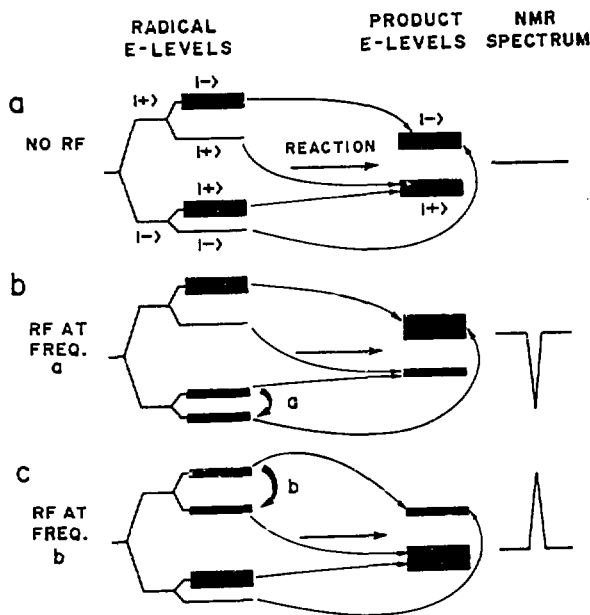


Fig. 2a illustrates the population distribution when e_{aq}⁻ is present and Fig. 2b when it is absent.



we obtain population of nuclear levels of the malonate radical by observing the r.f. induced change in the coupling product. The example illustrated is from Fig. 2b. The observed nuclear populations in the radical

can be explained by using the radical pair theory of chemically induced magnetic polarization, both electron (CIDEP) and nuclear (CIDNP) in the radicals!

In a more complicated spin system like $\cdot\text{CH}_2\text{X}$ additional peaks due to the double quantum transitions are observed. Since short ($0.5 \mu\text{sec}$) r.f. pulses can be used, kinetic information is also available. This is currently under active investigation.