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CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION, III[1]

^{13}C-POLARIZATION OBSERVED DURING REDUCTION OF DIAZONIUM SALTS, USING THE PULSE FOURIER TRANSFORM TECHNIQUE.

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There is a steady increase in the number of reactions in which the phenomenon of CIDNP is observed, providing evidence for the existence of radical pairs as precursors of diamagnetic species[2]. In proton magnetic resonance spectroscopy the CIDNP-effect can readily be observed with conventional NMR-spectrometer systems. For the organic chemist, the carbon atom is of even more importance. Unfortunately the magnetic carbon isotope ^{13}C is present only in 1 % natural abundance. Recently, however, Lippmaa and coworkers[3] have shown that the enhancement factor in ^{13}C polarization is high. Therefore, it should be possible to observe ^{13}C-CIDNP without ^{13}C enrichment in systems showing ^{1}H-CIDNP. For the interpretation of CIDNP effects ^{13}C measurements would have some advantages:

(i) By using complete proton decoupling multiplet effects will disappear. Furthermore, carbon-carbon coupling is not observed. Therefore one can expect simple line spectra in ^{13}C-CIDNP.

(ii) According to the experiments published so far[3], it seems that in a radical only few carbon atoms (those coupled with the free electron) are strongly polarized.

In fast reactions, however, the conventional continuous wave sweep technique permits one to accumulate the ^{13}C spectrum only within a small frequency range. Examples of such reactions are the reduction of diazonium[1] and iodonium[4] salts with $NaBH_4$, NaOH, amines, or $NaNO_2$. In these cases we observed ^{1}H-CIDNP (emission from the protons of the arenes formed). Since these reactions do not proceed exclusively via aryl radicals, the enhancement factors for ^{1}H-CIDNP are moderate (we could trap only 7 % in the case of phenyl diazonium salt and NaOH[1]). Indeed, we were not able to observe a well resolved ^{13}C-CIDNP signal using the normal continuous wave sweep technique. The great improvement in the signal-to-noise ratio obtained by using multi-channel excitation in Pulse Fourier Transform Spectroscopy enabled us, however, to observe the ^{13}C-CIDNP effect in the above reactions. In addition, this technique reveals the whole region of ^{13}C-chemical shifts within seconds.

The following experimental requirements should be taken into consideration:

(i) Since polarization of different signals varies distinctly with time, it is desirable to follow the reaction continuously. Consequently, the memory of the CAT should be divisable into several address groups. The reaction of diazonium salts with alkali, for instance, takes about 90 - 100 seconds (0.7 M solutions of $CH_3OC_6H_4N_2^{\oplus}\ BF_4^{\ominus}$ in CH_3CN/CD_3OD 1:1), so that in case of a fabritec signal average 1074 system, 3 accumulations (each of about 30 sec. length) may be performed.

(ii) Normally the phase must be corrected after each Fourier transformation. This phase correction is carried out before the addition of alkali to the diazonium salt solution, after which any change of spectrometer settings should be avoided.

(iii) The lock stability of the spectrometer must be very good, because of strong gas evolution (N_2) during all reactions of diazonium salts.

In figures 1 and 2, ^{1}H- and ^{13}C-CIDNP measurements taken during the reaction of p-methoxyphenyldiazonium tetrafluoroborate in CH_3CN with saturated methanolic NaOH solution are compared. In fig. 1a the ^{1}H-NMR spectrum (Varian A60A) of this diazonium salt is shown. Fig. 1b demonstrates the typical ^{1}H-CIDNP pattern, whereas fig. 1c shows the ^{1}H-NMR spectrum of anisole. It is apparent that the negative signals in 1b mainly correspond with the signals of anisole in 1c. No other polarized reaction product could be detected by proton resonance.

In fig. 2a the ^{13}C-PFT spectrum (Bruker HFX 90; 4096 scans) of the diazonium salt in a 1:1 CD_3OD/CH_3CN solution is depicted. The following assignment was adopted: $\underline{1}$: C-4, $\underline{2}$: C-3, $\underline{3}$: C-2, $\underline{4}$: CN group of acetonitrile, $\underline{5}$: C-1, $\underline{6}$: OCH_3, $\underline{7}$: CD_3OD, $\underline{8}$: CH_3 of acetonitrile, $\underline{9}$: TMS. As a consequence of the anisotropy of the NN-triple bond, carbon atom 1 absorbes at higher field than the other ring carbon atoms. Fig. 2b shows a 75 sec. (187 scans) ^{13}C-PFT-CIDNP spectrum of the above solution after the addition of NaOH. The spectrum after completion of the reaction is reproduced in fig. 2c (8192 scans, 1 hour recording), whereas fig. 2d represents the spectrum of anisole with the following assignment of lines:

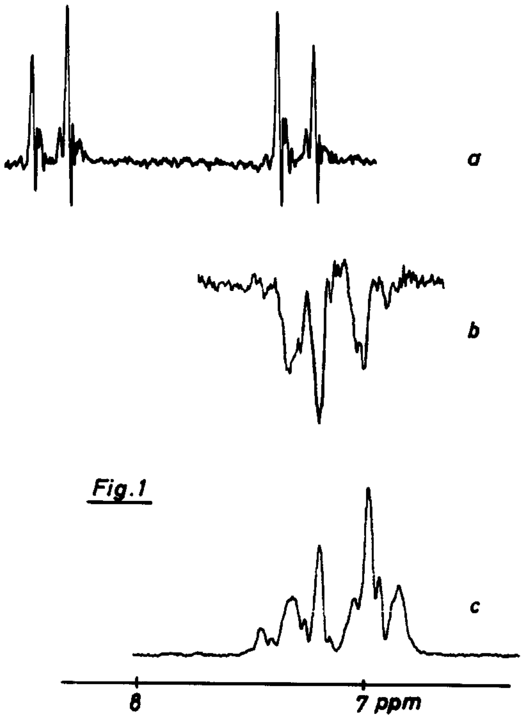


Fig.1

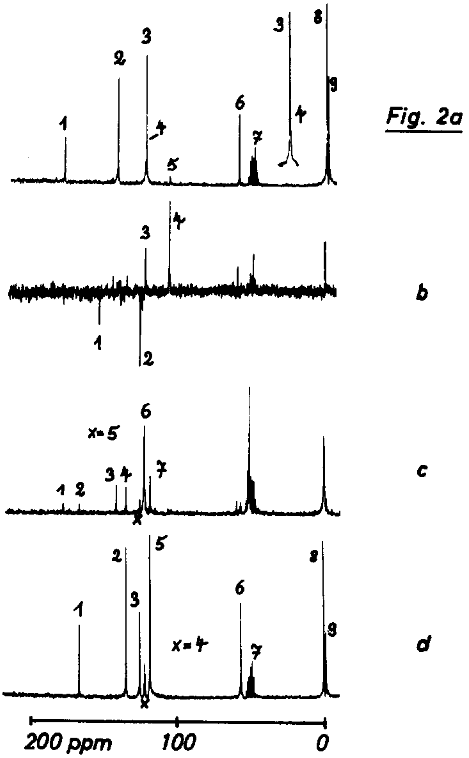
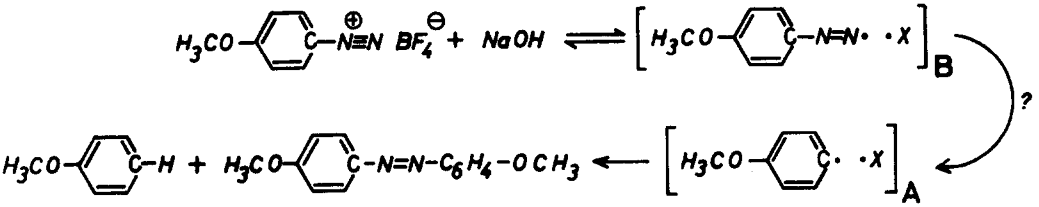


Fig. 2a

1: C-1, 2: C-2, 3: C-4, 4: CN of acetonitrile, 5: C-3, 6: OCH$_3$, 7: CD$_3$OD, 8: CH$_3$ of acetonitrile, 9: TMS.

Assignment of the lines in the CIDNP spectrum (fig. 2b): Line 3 belongs to the resonance of the CN group of acetonitrile, which is not polarized. The strongest negative line 2 corresponds to the carbon atom 4 in anisole (fig. 2d), as expected. It is apparent from the final spectrum, that anisole indeed is the main reaction product (lines 2, 4, 5 and 7 in fig. 2c). The other emission line 1 in the CIDNP spectrum has no counterpart in the anisole spectrum. This line should be assigned to the resonance of carbon atom 1 in 4,4'-dimethoxy-azobenzene, which can be isolated from the reaction mixture. Most remarkable, however, is the strong positive resonance 4 appearing exactly at the signal position of the carbon atom 1 of the original diazonium salt. In more than 75 % of our measurements this line was reproducible, depending on the concentration of the starting material and the velocity in mixing of the reactants. This line, therefore, should be attributed to polarized diazonium salt. We could not detect such enhanced absorption in the case of p-nitrophenyl- or phenyl-diazonium salts. From the polarization of the ring protons and of C-1 in anisole or azoanisole it must be concluded that radical pair A is of importance. Polarized diazonium salt may have been formed: (i) From pair B by electron transfer ($CH_3OC_6H_4{-}N{=}N\cdot$[5] + $\cdot X \longrightarrow CH_3OC_6H_4{-}N_2^{\oplus} + X^{\ominus}$) inside the cage. (ii) From pairs A or B, if $\cdot X$ is



$\cdot O{-}N{=}N{-}C_6H_4OCH_3$ (Rüchardt mechanism[6]). Then, polarized $\cdot O{-}N{=}N{-}C_6H_4OCH_3$ might be in equilibrium with the diazonium ion via the diazoanhydride $CH_3OC_6H_4{-}N{=}N{-}O{-}N{=}N{-}C_6H_4OCH_3$ (recombination in cage B) or the diazonium hydroxide $CH_3OC_6H_4{-}N{=}N{-}OH$ (escape from cage A and hydrogen uptake). According to the rules of Kaptein[2], the emission signals of ^1H and ^{13}C atoms of anisole can be interpreted in terms of a free radical encounter of $X\cdot = \cdot O{-}N{=}N{-}C_6H_4OCH_3$ and $CH_3OC_6H_4\cdot$ to form cage A $\left[a_{H\text{-ring}}\right.$ and $a_{^{13}C}$ for $CH_3OC_6H_4\cdot$ are taken > 0[2,3,7], $g_{CH_3OC_6H_4\cdot} \cong g_{C_6H_5\cdot} = 2.0024$; $g_{\cdot O-N=N-C_6H_4OCH_3} \cong g_{\cdot O-N=N-C_6H_5}$[6b] $\left. = 2.0017\right]$. However, Δg is very small, so that a singlet precursor of A (e.g. B) cannot be excluded definitely. A detailed discussion of the mechanism will be published elsewhere.

The main purpose of this paper[8] is to demonstrate the importance of the ^{13}C-Pulse Fourier Transform technique in CIDNP experiments as a powerful complement to the conventional ^1H continuous wave technique.

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