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STOPPED FLOW PULSE-FOURIER TRANSFORM NMR. OBSERVATION OF INTERMEDIATES IN THE TRICYANOVINYLATION OF N,N-DIMETHYLANILINE IN METHANOL

M.J.T. Robinson* and Stuart M. Rosenfeld
Dyson Perrins Laboratory, University of Oxford

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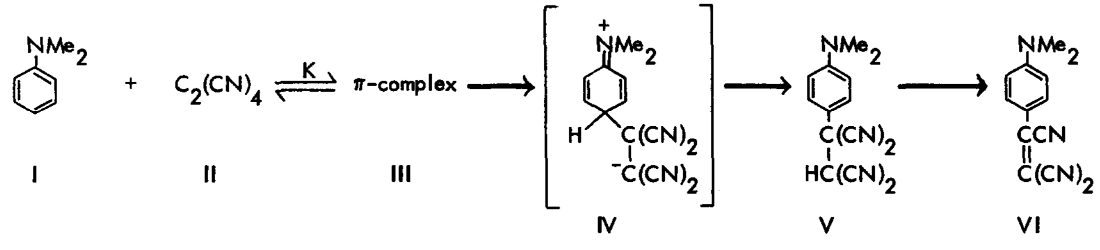
Pulse-Fourier transform (PFT) NMR has been widely used to achieve greater sensitivity than continuous wave (CW) NMR in a given time. Alternatively this method may be used to obtain a 10 ppm ^{1}H spectrum in as little as 2 s (for 4K points). Although slow compared with, e.g., UV methods for following chemical reactions PFT NMR has the advantage of giving structural information about intermediates formed at high concentrations of reactants, the most favourable conditions for the accumulation of intermediates formed by associative reactions. We now report preliminary results of a stopped flow ^{1}H PFT NMR[1,2] study on a moderately fast timescale (~30 s) of intermediates in the rapid reaction between N,N-dimethylaniline (I) and tetracyanoethylene (II) in CD_3OD.

It has been shown by Rappoport[3] that in solvents of moderate polarity such as $CHCl_3$ the reaction between I and II (see Scheme 1) involves rapid and reversible formation of a blue π-complex III. There follows a slow irreversible reaction via at least one colourless intermediate, to which we assign structure V (not IV[4]) in accordance with a study of a similar intermediate in the para-tricyanovinylation of 2,6-dimethylaniline[5] and our own CW NMR experiments on V and on the reaction between I and II in $CDCl_3$,[6] before the final red product VI. In V the chemical shift δ 3.02 (see Table) of the N-Me protons lies between the values for I and VI. In contrast the N-Me protons of the σ-complex IV should be at much lower field: compare the relative δs in the model compounds VII - IX.



$Me_2C{=}C\underset{\bullet}{H}.NMe_2$ VII

$Me_2C{=}CH.\overset{+}{N}HMe_2$ VIII

$Me_2CH.CH{=}\overset{+}{N}Me_2$ IX

SCHEME 1. Slow reaction in $CHCl_3$ and model compounds for chemical shifts.

TABLE. ^{1}H chemical shifts relative to $SiMe_4$ for solutions in CD_3OD ($CDCl_3$)

Signal	I	I-D$^+$	A (I I-D$^+$)	V	B (≡ XIII)	VI	VII	VIII	IX
N-Me	2.87	3.29	3.26-[a] 3.11	(3.02)	3.05	3.25	2.32	3.03	3.65 3.78
Aromatic	6.7 7.15	7.6	7.53-[a] 7.24	(6.87) (7.51)	6.86 7.47	7.0 8.15	-	-	-

[a] Chemical shift decreases with time (see text); values refer to first (at 4 s) and last (at 25 s) spectra in the Figure.

The reaction between I and II is greatly accelerated by very polar solvents but the colour changes mimic those in $CHCl_3$. Using, e.g., 0.15M solutions of I and of II in CD_3OD, the instantly formed, intensely blue π-complex III decays leaving a colourless solution after ~20 s which then develops a deep red colour during several minutes. The Figure shows the PFT NMR spectra during the first 25 s. Even at the first pulse (4 s) there is no signal for free I. The first intermediate A, which can not be III (see below and note 7), has signals that move upfield (see Table and Figure) as it decays to the second intermediate B, that shows a growth in the intensity complementary to the fall in intensity of A. After 1 min, when A has largely disappeared, the final product VI (N-Me at δ 3.25 superimposed on the CHD_2OD solvent signal) begins to show in the spectrum.

If we make plausible extrapolations from published[5] data for the association constant K and the molar extinction coefficient ε for III and assume that I and II are removed in a reaction that is first order in each of them, then the disappearance of the blue colour of III within ~20 s implies that the concentrations of I and II

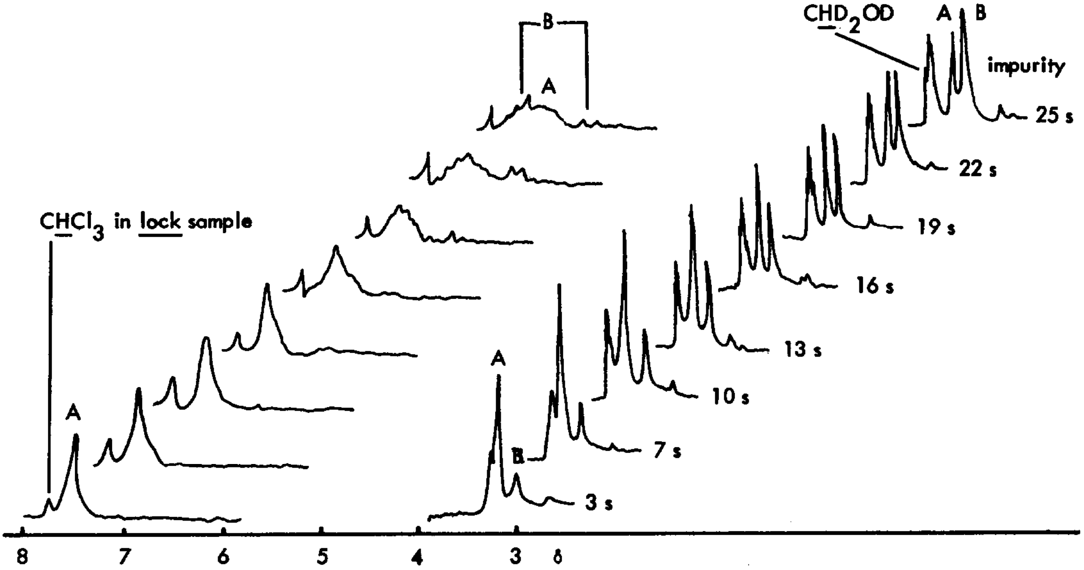
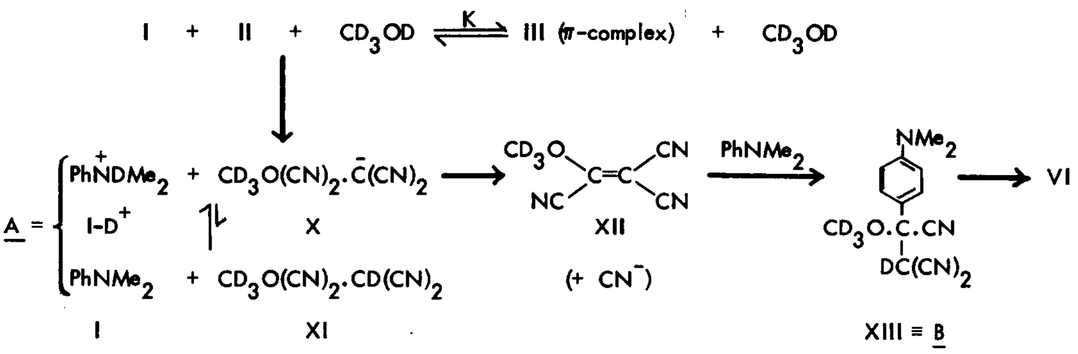


FIGURE. Successive spectra at 3 s intervals beginning 4 s after mixing 0.15M solutions of I and of II in CD_3OD ($CHCl_3$ at δ 7.54 in external lock sample)



SCHEME 2. Fast reaction in CD_3OD

must have fallen by < 90% before the first pulse at ~4 s. It is known[8] that II reacts very readily with ethanol in the presence of very weak bases to give ethoxytricyanoethylene, which, like II, reacts with I to give VI. The formation of methoxytricyanoethylene (XII) presumably goes via the weakly basic methoxytetracyanoethane anion (X) (see Scheme 2), which would not be expected to deprotonate $I\text{-}D^+$ to give the ethane XI and free I. The dissociation of X to XII, however, liberates the more strongly basic cyanide ion, which will deprotonate $I\text{-}D^+$ giving I. We therefore interpret intermediate A as the ion $I\text{-}D^+$ in mobile equilibrium with an increasing relative amount of the free base I, the concentration of which had fallen to a low value in the first very fast reaction giving $I\text{-}D^+$ and X. The intermediate B has not been isolated but the close similarity between the NMR spectra of B in CD_3OD and of V in $CDCl_3$ strongly suggests that B is XIII.

It has been suggested that π-complex formation between I and II is followed by electron transfer giving a radical anion-radical cation pair,[3] a situation which might give rise to CIDNP[9] under the conditions of this experiment. CIDNP was not observed. It should be noted, however, that 90° pulse angles were used so that multiplet effects would not be expected.[10] In any case absence of CIDNP does not eliminate the possibility of an electron transfer mechanism.

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References and notes

[1] The stopped flow system consisted of a simple T-mixer fed by two manually driven syringes giving equal flow rates for the reactant solutions, the mixed reactants being directed vertically into a 5 mm NMR tube concentrically positioned in a 10 mm tube, with a CDCl$_3$ lock sample in the annular gap, spinning in an unmodified probe. The reactants were stored and mixed at $\sim$2,000 Gauss, i.e., as close as possible to the high field of a Bruker WH 90 spectrometer. Successive FIDs, beginning $\sim$4 s after mixing to minimise relaxation effects and to allow the resolution to recover, were stored individually on disc for later processing.

[2] Stopped flow CW NMR on a fast timescale, but devoid of structural information, and stopped flow PFT NMR on a relatively long timescale for studying reactions have been described by J. Grimaldi, J. Baldo, C. McMurray, and B. D. Sykes, *J.Amer.Chem.Soc.*, **94**, 7641 (1972), and references therein. Continuous flow CW NMR has been used by C. A. Fyfe, M. Cocivera, and S.W.H. Damji, *J.C.S. Chem.Comm.*, 743 (1973).

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[6] We observed mp 117-119° dec (lit.[4] mp 118° dec.) and ^{1}H NMR spectrum in agreement with that published. The ^{13}C δ of the *N*-Me in V is at δ 40.1 ppm, compared with δ 41.4 in I (P. C. Lauterbur, *J.Chem.Phys.*, 38, 1415 (1963)).

[7] The formation of the π-complex III at high concentrations of I and II in CDCl$_3$ scarcely alters the NMR spectrum of I.

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