Chemical Polarisation of ^{15}N and ^{13}C Nuclei in Diazo Coupling Reactions*

E. Lippmaa, T. Pehk, T. Saluvere and M. Mägi
Institute of Cybernetics of the Estonian Academy of Sciences, Tallinn 200 001, *USSR*

(Received 13 February 1973; accepted 21 February 1973)

Abstract—Chemical polarisation of nitrogen and carbon nuclei in the decomposition and diazo coupling reactions of benzenediazonium fluoborate has been investigated. If homo- and heterolytic processes run in parallel in a multistage reaction sequence, then the nuclear polarisation created in a free-radical reaction can be nearly quantitatively carried over to products of rapid ionic reactions such as azo dyes.

INTRODUCTION

DIAZONIUM salts can undergo two types of reactions: ionic, such as hydrolysis in water, decomposition in alcohols with ether formation and diazo coupling; or free radical, producing various aromatic hydrocarbons. The free radical reactions proceed at higher pH values and in non-protonating solvents with diazotic acids and anhydrides as intermediates. Diazo coupling is known to be a typical ionic reaction and yet strong CIDNP effects on ^{1}H, ^{13}C and ^{15}N nuclei have been observed in the reaction of the benzenediazonium ion with sodium phenolate in acetone or dimethyl sulphoxide solution at room temperature (+15 to +35°C).[1,2,3] Additionally, free radicals have been proposed as intermediates in the diazo coupling reaction.[3,4] Such schemes are to some extent supported by the reported easy formation of free diazonium radicals on dithionite[5] or electrolytic reduction[6,7,8] of diazonium salts. The possible cryptoradical character of the diazo coupling reaction[3,4] is of considerable theoretical importance, and chemical polarisation of both ^{13}C and ^{15}N nuclei was used to establish the true mechanism of this reaction. At the same time special attention was paid to the problem whether, or to what extent, chemical polarisation can be considered a proof of the free radical character of the reaction involved. It appears that considerable caution is necessary, because polarised products can undergo rapid secondary ionic reactions ($k \gg T_1^{-1}$) and free radical pairs are necessary only for the formation of the primary polarised products. The situation is even more complicated if the starting material itself becomes polarised in some free-radical decomposition reaction proceeding in parallel with the observed ionic reaction. This appears to be the case with diazo coupling with phenols in basic media, where the dye formation is always accompanied by some decomposition (and chemical polarisation) of the diazo compound itself. Free radical formation during the decomposition of diazonium salts at room temperature is less pronounced in neutral or slightly acid media and indeed no polarisation of the benzenediazonium fluoborate itself or of the coupling product with aromatic amines was observed in experiments with ^{13}C and ^{15}N.

EXPERIMENTAL

The experiments were carried out at room temperature with moderate cooling (+15°C) of the 15 mm O.D. non-rotating sample tube. 2·0 ml of a 2M sodium phenolate solution in methanol were added with a syringe with long needle to a pre-cooled (+15°C) solution of 0·8 g benzenediazonium fluoborate in 2·5 ml of dimethyl sulphoxide and the resulting CIDNP signal was accumulated in the core memory of a 512-channel CAT (Nokia type LP 4050). Thorough mixing of the two solutions resulted from the turbulence created by the rapid injection (in about 2 s) of phenolate. The ^{13}C spectra were measured at 15·09 MHz and those of ^{15}N at 6·08 MHz on a frequency-swept and spin-stabilised universal double resonance NMR spectrometer.[9] Because of the negative nuclear Overhauser effect, only single resonance was used in the study of ^{15}N spectra, but double resonance with total proton decoupling was employed in the ^{13}C spectrometry. The ^{13}C chemical shifts were measured in ppm downfield from external tetramethylsilane and those of ^{15}N downfield from external NO_3^- (a saturated solution of 95% enriched $NaNO_3$ in water).

RESULTS AND DISCUSSION

^{15}N-experiments with benzenediazonium fluoborate having 44% ^{15}N-enrichment in either one or the other nitrogen position of the diazonium group revealed that both nitrogen resonances (N-1 at −61·0 ppm and N-2 at −142·3 ppm from external aqueous NO_3^-; diamagnetic shifts negative) show strong enhanced absorption in basic media, during both decomposition with alcoholates and the diazo coupling reaction with sodium phenolate. The same enhanced absorption of ^{15}N nuclei is retained in the stable coupling product, *p*-hydroxyazobenzene. During the reaction the resonance of N-1 (adjacent to the phenol ring) is shifted to +130·2 ppm and that of N-2 to +117·5 ppm (see Fig. 1). Another unidentified and very strongly polarised line appears at +83·9 ppm. No ^{15}N-resonance with this shift value could be detected even after prolonged accumulation in the stable reaction product. Only a very limited number of nitrogen-containing groups resonate in the region of +80 ppm from external NO_3^-. These are some nitroso compounds and unsaturated groups of the general structure —N=N—X, where X is an electronegative substituent. Taking into account the very transitory character of the polarised signal at +83·9 ppm, Ph—$\overset{*}{N}$=N—OH or the corresponding diazoether are the most logical choices and thus provide indirect proof for the proposed diazonium ion polarisation mechanism. It is not clear, however, why the other nitrogen atom does not show a similar signal with a shift value somewhere in the region between 80 and 100 ppm. Since gaseous nitrogen has a shift value close to that of N-1, pure argon and helium gas were bubbled through the reaction mixture in the sample tube. The passage of an inert gas during the decomposition and coupling reaction had no effect upon the N-1 polarisation, which is mainly a function of pH and the solvent.

---

*Paper presented at the International Symposium on Chemically Induced Dynamic Polarisation of Nuclei and Electrons, Tallinn, Estonian SSR, 13th to 16th August 1972.

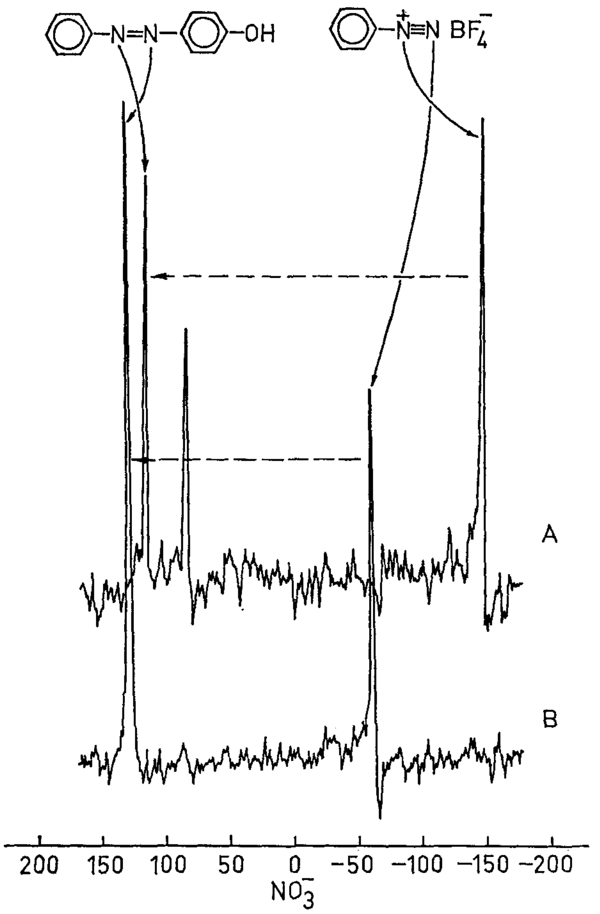
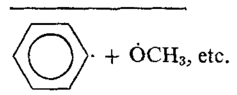


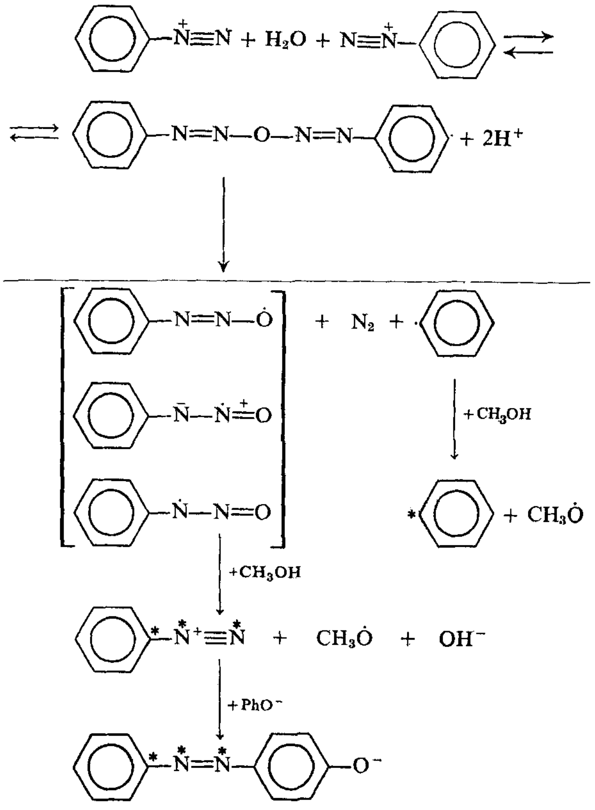
FIG. 1. (A) Diazo coupling at +15°C of labelled (44% ^{15}N-2) benzenediazonium fluoborate $C_6H_5{}^{15}N^+{\equiv}N\ BF_4^-$ (0·7 g in 2·5 ml of dimethyl sulphoxide) with 2·0 ml 2M sodium phenolate in methanol. (B) Diazo coupling at +15°C of labelled (44% ^{15}N-1) benzenediazonium fluoborate $C_6H_5N^+{\equiv}{}^{15}N\ BF_4^-$ (0·7 g in 2·5 ml of dimethyl sulphoxide) with 2·0 ml 2M sodium phenolate in methanol.

The enhanced absorption of N-1 and N-2 is absent during decomposition in a neutral solution, smaller in acetone and practically absent in acetonitrile or water.

The possible reaction sequence in basic media is given in Scheme 1 and is based on the Rüchardt mechanism.[10] For this reaction sequence catalytic amounts of water are necessary and were actually present. Various other products may result from free encounter pairs such as



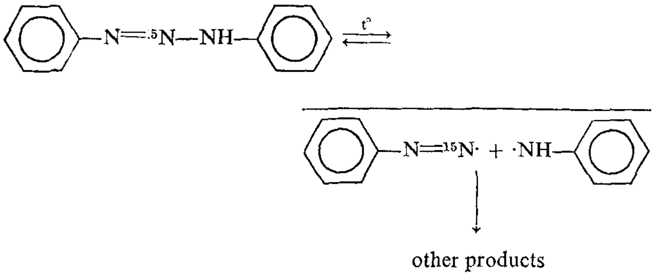
In this scheme the unstable diazoanhydride is formed initially. It is well known to decompose at room temperature with the formation of free radicals that must be of such a nature that some polarised benzenediazonium salt can be regenerated from it. Since the dye formation is practically quantitative and the reaction very fast, determined mainly by the efficiency of mixing, and both the ^{15}N and ^{13}C relaxation times are very long in these compounds, practically all nuclear polarisation that appears in the benzenediazonium ion is carried over to the diamagnetic dye molecule, even though the last reaction is a typical heterolytic process. The intermediate nitrogen-containing free radical is a highly hypothetical entity. The CIDNP data show that it must be strongly delocalised with practically equal hyperfine coupling constants to both nitrogen atoms. This contradicts the ESR data published by Cadogan, Paton and Thomson,[11] as well as those of Chalfont and Perkins,[12] for a closely related radical. In both cases the nitrogen hyperfine coupling constants differ by about an order of magnitude.



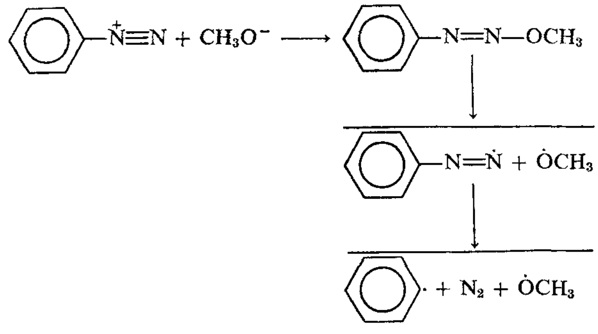
SCHEME 1

A diazonium radical has usually been proposed[1,2,3] as the intermediate nitrogen-containing radical according to Scheme 2.

A sequence of this type can certainly contribute to the overall chemistry of the reaction. Unfortunately the diazonium radical $PhN_2\cdot$ can hardly be the only intermediate nitrogen-containing radical, because it cannot ensure an equal polarisation of both N-1 and N-2 nitrogen atoms. In the thermal decomposition of labelled diazoaminobenzene, with the enriched nitrogen atom in the central position, the diazoaminobenzene is polarised alongside its decomposition products[13] according to the reversible reaction:



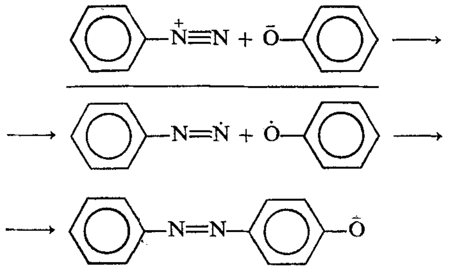
In a similar experiment, however, with material enriched in the nitrogen positions adjacent to the benzene rings, no polarisation of the starting material results. The hyperfine coupling constants with both nitrogens must be very dissimilar in this case and the two nitrogen-containing radicals formed in the thermal decomposition



SCHEME 2

of diazonium salts and diazoaminobenzene can hardly be identical. Since the diazonium radical is the only reasonable intermediate in a reversible decomposition of diazoaminobenzene, some other unsymmetrical free radical must be responsible for the polarisation of diazonium salts.

A very important question arises in connection with the scheme containing the diazonium radical and the phenmethylate in this reaction, then a free radical pathway appears for the diazo coupling reaction:[3]



oxide ion or radical. If one takes phenolate instead of

The question as to whether a phenolate ion or a phenoxide radical takes part in the coupling reaction can be answered with the use of ^{13}C CIDNP. The diazo coupling reaction was run as described for the experiments with ^{15}N, but with unenriched compounds. The results are given in Fig. 2 and the Tables 1 and 2.

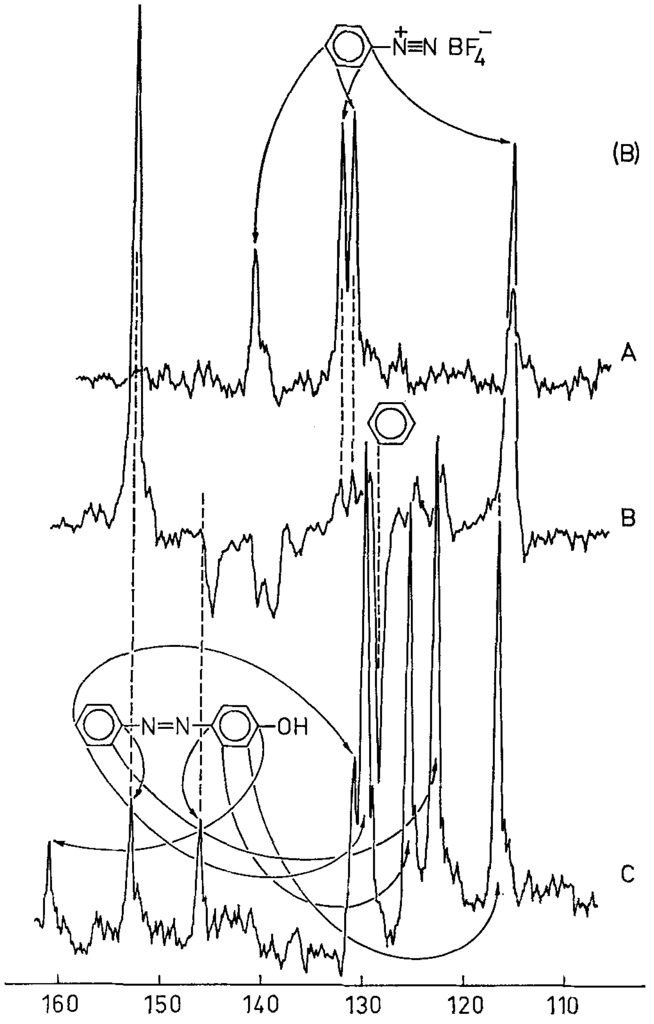


FIG. 2. (A) Unenriched (1·1% ^{13}C) benzenediazonium fluoborate (0·8 g) in a mixture of dimethyl sulphoxide (2·5 ml) and methanol (2·0 ml) at +35°C. Moderate decomposition with no chemical polarisation. (B) Diazo coupling at +35°C of unenriched (1·1% ^{13}C) benzenediazonium fluoborate $C_6H_5N^+{\equiv}N\ BF_4^-$ (0·8 g in 2·5 ml of dimethyl sulphoxide) with 2·0 ml 2M sodium phenolate in methanol. Accumulated spectra of five consecutive experiments. (C) ^{13}C spectrum of a solution of 1·0 g *p*-hydroxyazobenzene in a mixture of 2·5 ml dimethyl sulphoxide, 2·0 ml of methanol and 0·7 g of KBF_4. For ^{13}C chemical shifts see Tables 1 and 2.

TABLE 1. ^{13}C CIDNP IN THE DIAZO COUPLING REACTION OF BENZENEDIAZONIUM FLUOBORATE WITH SODIUM PHENOLATE AT +15°C

^{13}C chemical shifts, ppm		Assignment[a]	Polarisation sign	Remarks[b]
from ext. TMS	from ext. CS_2			
152·9	40·2	azo dye C-1′	A	s
145·2	47·9	?	E	w
140·8	52·3	?	E	w
139·1	54·0	?	E	w
132·8	(60·3)	diazo salt C-2,6?	A	p.n.
131·7	(61·4)	diazo salt C-3,5?	A	p.n.
128·5	64·6	benzene	E	s
124·9	68·2	azo dye C-2,6?	A	w, p.n.
122·6	70·5	azo dye C-2′,6′?	A	w
115·7	*77·4*	*diazo salt C-1*	A	s

[a] See Table 2.

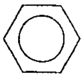
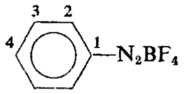
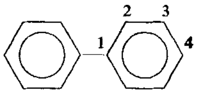
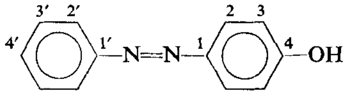
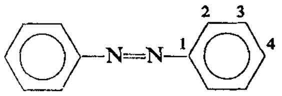
[b] s—strong, w—weak, p.n.—possibly noise.

It is immediately apparent that, just as it was the case with nitrogen spectra, C-1 in the benzenediazonium salt itself is polarised, showing enhanced absorption. The same atom retains its polarisation in the diazo coupling product, *p*-hydroxydiazobenzene. No other carbon atoms in the dye are polarised and, in particular, no polarised lines corresponding to the carbons of the phenol moiety can be found. The only polarised byproduct is benzene formed from radicals that have escaped from the primary cage(s). With this result in mind it is highly unlikely that the theoretically possible phenoxide radical will actually participate in any free-radical or cryptoradical reaction and thus diazo coupling may safely be considered to be a typical heterolytic ionic reaction, even in non-protonating solvents such as dimethyl sulphoxide, and even though the reaction product is polarised.

REFERENCES

1. E. Lippmaa, T. Pehk and T. Saluvere, *Ind. Chim. Belge* **36,** 1070 (1971).
2. A. Rieker, *Ind. Chim. Belge* **36,** 1078 (1971).
3. N. N. Bubnov, B. Ya. Medvedev, L. A. Polyakova, K. A. Bilevich and O. Yu. Okhlobystin, *Org. Magn. Resonance* **5,** 437 (1973).
4. S. Nagakura and J. Tanaka, *Bull. Chem. Soc. Japan* **32,** 734 (1950).

TABLE 2. ^{13}C CHEMICAL SHIFTS OF THE INITIAL DIAZO COMPOUND AND SOME POSSIBLE REACTION PRODUCTS

Compound	^{13}C chemical shifts[a]				Remarks
	C-1	C-2,6	C-3,5	C-4	
	128·5				
	115·9	132·8	131·7	141·5	
	140·3	126·6	128·3	126·6	
	146·0 152·9	125·1 122·6	116·4 129·5	161·1 130·6	Cl-6 Cl′-6′
	152·4	122·4	129·0	131·0	

---

[a] In ppm downfield from external TMS, measured at +35°C in a 5:4 mixture of dimethylsulphoxide and methanol.

5. W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.* 4857 (1964).
6. R. M. Elofson, R. L. Edsberg and P. A. Meckarly, *J. Electrochem. Soc.* **97**, 166 (1950).
7. R. M Elofson and F. F. Gadallah, *J. Org. Chem.* **34**, 854 (1969).
8. F. F. Gadallah and R. M. Elofson, *J. Org. Chem.* **34**, 3335 (1969).
9. E. Lippmaa, T. Pehk and J. Past, *Eest. NSV Tead. Akad. Toim. Füüs. Mat.* **16** (3) 345 (1967).
10. C. Rüchardt and E. Merz, *Tetrahedron Letters* 2431 (1969).
11. J. I. G. Cadogan, R. M. Paton and C. Thomson, *Chem. Commun.* 614 (1969).
12. G. R. Chalfont and M. J. Perkins, *J. Amer. Chem. Soc.* **89**, 3054 (1967).
13. E. Lippmaa, T. Saluvere, T. Pehk and A. Olivson, *Org. Magn. Resonance* **5**, 429 (1973).