Tetrahedron Letters No. 34, pp 2975 - 2978, 1974. Pergamon Press. Printed in Great Britain.

REACTION OF UNACTIVATED NITROGEN MOLECULES WITH PHENYL CATIONS IN 2,2,2-TRIFLUOROETHANOL[1]

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(Received in UK 31 May 1974; accepted for publication 11 June 1974)

Although reaction of molecular nitrogen with organic-inorganic systems is well known[3], in this communication we present what to our knowledge is the first evidence for a reaction of nitrogen molecules with a purely organic reagent in solution[4].

Recently, as part of our investigations of the reactivity and stability of arenediazonium ions[5], we found that the N_α-N_β rearrangement takes place to a significant extent when 2,2,2-trifluoroethanol (TFE) is used as solvent[1b]. The rate ratio of rearrangement (isotopic inversion) to solvolysis (k_r/k_s) is 0.072 ± 0.006 at 30°C and 0.079 ± 0.005 at 5°C. In addition, our value of $k_r/k_s = 0.016 \pm 0.001$ for the rearrangement in water at 35° confirms Lewis' result[6] (0.014; Swain et al.[7], 0.016). These results can be interpreted as evidence for the reverse reaction of phenyl cations[8] with the nitrogen molecule formed in the first step of an S_N1 dediazoniation[5]. A complete discussion of the influence of temperature, solvent and deuterium substitution on the N_α-N_β rearrangement reaction and the question of a common intermediate for solvolysis and rearrangement will be published later.

These results encouraged us to investigate the possibility of <u>external</u> exchange of nitrogen molecules with benzenediazonium tetrafluoroborate (containing 99.2 % ^{15}N in the β-position) in TFE. Solutions were kept in a glasslined autoclave for the appropriate time to get 62 to 73 % dediazoniation. The autoclave was pressurized with nitrogen of natural isotopic abundance (~0.4 % ^{15}N) as indicated in the following Table. The residual diazonium salt was reacted with 2-naphthol and the azo compound was analyzed by mass spectrometry for m/e 248 and 249 ($M^{+\cdot}$). The ratio of peak heights was compared with that found for the same azo dye after 0 % dediazoniation. Control experiments indicated that this technique afforded highly reproducible data.

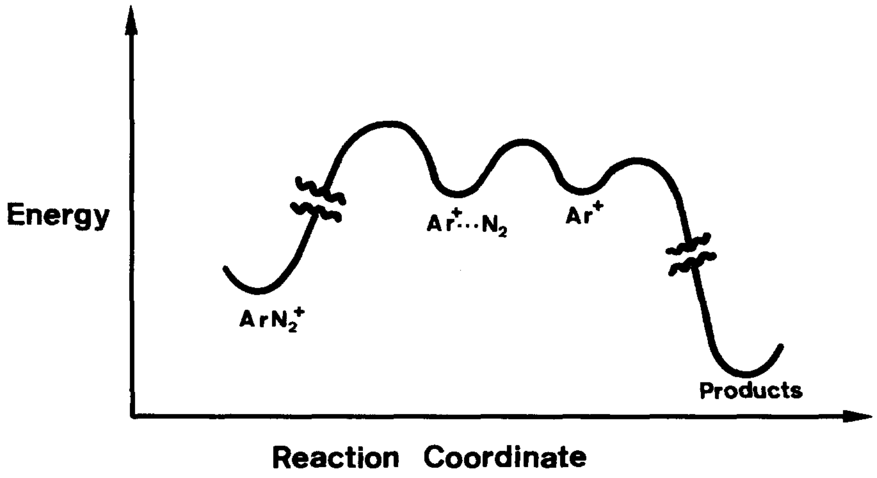
Table. Exchange of Diazonium Ions with External N_2 in TFE

Exp.No.	% Dediazoniation	Conditions (25°)	$^{15}N{=}^{14}N$ Content of Azo Dye (%)
1	0	1 atm, air	99.20[a]
2	70.4	1 atm, air	98.60 ± 0.44[b]
3	73.2	20 atm $^{14}N_2$	98.23 ± 0.48[b]
4	69.9	300 atm $^{14}N_2$	96.23 ± 0.47[b]
5	70.1	300 atm $^{14}N_2$	96.99 ± 0.26[b]
6	72.5	300 atm $^{14}N_2$	96.89 ± 0.27[b]
7	62.5	1000 atm $^{14}N_2$	94.71 ± 0.43[b]

[a] Reference Standard [b] 95 % Confidence Limits

The results of the Table demonstrate clearly that an exchange with external nitrogen molecules dissolved in TFE does take place. The average of 15 determinations from 3 independent experiments gives a value of 2.46 ± 0.40 % incorporation of external nitrogen at 300 atm. Considerably greater incorporation is found at 1000 atm. These results are consistent with the reaction of nitrogen molecules with a highly reactive species such as a phenyl cation.

Another experiment also indicates the formation of a phenyl cation intermediate. Under a pressure of 320 atm of carbon monoxide a solution of benzenediazonium tetrafluoroborate in TFE yielded 5.3 % 2,2,2-trifluoroethyl benzoate in addition to the normal products (fluorobenzene and 2,2,2-trifluoroethyl phenyl ether). Analogous experiments in water at lower pressure were not successful[6]. The results are consistent with the following energy diagram[9]:



We postulate that during the dissociation of the C-N bond of the arene diazonium ion and the subsequent reaction of the ion with nucleophiles, one or a sequence of <u>molecule-ion pairs</u> is present. Such species are analogous to the (cation-anion) ion pairs postulated by Winstein *et al.*[10] We will discuss the possibility of solvent assistance in the formation of these molecule-ion pairs and of competition between solvent capture and dissociation of the molecule-ion pairs in a later paper.

Acknowledgements. This work was supported by a grant of the Swiss National Foundation for Scientific Research (project 2.722.72). We are grateful to Prof. J. Seibl for helpful comments on the interpretation of our mass spectral data.

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