# 153. Dediazoniation of Arenediazonium Ions in Homogeneous Solution. Part IX. Spectral Evidence for a Homolytic Mechanism Involving Pyridine Complexes[1])

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*Summary.* The mechanism of dediazoniation of arenediazonium tetrafluoroborates in 2,2,2-trifluoroethanol (TFE) is strongly dependent on the concentration of added pyridine. The added base complexes with the diazonium ion and diverts it to a homolytic pathway. Complex formation is indicated by the disappearance of the $-\overset{\oplus}{N}\equiv N-$ stretching vibration and appearance of a new band at about 1640–1690 cm$^{-1}$ ascribed to the $-N{=}N-\overset{\oplus}{N}C_5H_5$ system. UV. and NMR. results support this conclusion.

Chemically induced dynamic nuclear polarization (CIDNP) experiments clearly implicate a radical-pair as an important intermediate in the decomposition of these complexes.

**1. Introduction.** – During the past few years there has been a considerable amount of interest in the application of chemically induced dynamic nuclear polarization (CIDNP) [2] techniques to demonstrate the intermediacy of radical species in a variety of chemical reactions. In particular, the field of diazonium ion chemistry has proven to be an area for application of this technique [3] [4].

We would like to disclose the results of our CIDNP studies of a dediazoniation reaction [5] involving the addition of pyridine to solutions of arenediazonium tetrafluoroborates in 2,2,2-trifluoroethanol (TFE) and in acetonitrile ($CH_3CN$). We recently reported our study of the effect of added pyridine on the kinetics and products of dediazoniation in TFE [6]. These results strongly implicate a second mechanism, in addition to normal heterolytic dediazoniation, which becomes increasingly dominant as the concentration of pyridine is increased. We now offer additional physical evidence of the homolytic nature of this second mechanism.

**2. Complex Formation.** – Since homolytic dediazoniations (*e.g.*, *Gomberg-Bachmann*) are thought to proceed by way of a complex of the type **1** or by electron transfer [7] we sought direct evidence that such a species was formed in our system on addition of pyridine.

$$Ar-N{=}N-X$$

**1**

2.1. *Infra-red spectroscopic* (*IR.*) *evidence.* Measurements were made on four different arenediazonium tetrafluoroborates in both TFE and in pyridine using a *Perkin-Elmer* Model 21 spectrophotometer. All measurements were made at −20°

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[1]) Part VIII: See [1].

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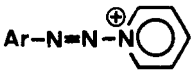
to minimize decomposition during the course of the measurement. The results are collocated in Table 1 along with literature data [8–11] for comparison.

The aromatic stretching vibrations and $-\overset{\oplus}{N}\equiv N$ stretching frequencies in TFE compare quite closely with literature values obtained on Nujol mulls. In pyridine, however, the diazonium stretching frequency absorption is decreased in intensity, and in the *p*-nitro-derivative it has completely disappeared. At the same time, all diazonium salts exhibit a new absorption between 1640 and 1690 cm$^{-1}$ in pyridine. We assign this new absorption to the N=N stretching mode of a complex formed between the diazonium ion and pyridine (**2**). Although this frequency range is higher than might be expected for a 'normal' –N=N– double bond (1444–1642 cm$^{-1}$) [8] many exceptions are known particularly for complexes of diazonium salts. In all cases, the exceptions are at higher frequency [8] as we observe. Although a completely reliable assignment is impossible, we consider it reasonable and consistent with the following data. Although it is likely that such a complex as **2** would be predominantly in the *trans*-configuration, our data are insufficient to make such an assignment. More careful examination of the 'normal' –N=N– stretching region particularly with isotopically labelled derivatives [12] was precluded by strong pyridine absorption.



**2**

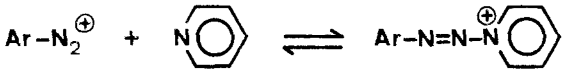
Table 1. *Infra-red absorption frequencies of* p-*substituted arenediazonium tetrafluoroborates*

| Substituent | $-\overset{\oplus}{N}\equiv N$ Stretching Vibration (cm$^{-1}$) | | | | N=N Stretching Vibration (cm$^{-1}$) | | Aromatic Stretching Vibration (cm$^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|
| | KBr | Nujol | TFE | Pyridine | TFE | Pyridine | DMSO[d] | TFE | Pyridine |
| $OCH_3$ | ~2260[a] | – | 2262 ± 10 | 2262 ± 10 | – | 1675 ± 5 | 1582 | 1575 ± 5 | 1575 ± 5 |
| H | – | 2296[b]<br>2283[c] | 2327 ± 14 | 2337 ± 20 | – | 1690 ± 5 | 1570 | 1572 ± 5 | 1575 ± 5 |
| Cl | – | 2252[c] | 2328 ± 10 | 2317 ± 20 | – | 1662 ± 5 | 1561 | 1567 ± 5 | 1560 ± 5 |
| $NO_2$ | – | 2306[b]<br>2294[c] | 2350 ± 10 | – | – | 1635 ± 5 | 1610 | 1580 ± 5 | 1590 ± 5 |

[a] Ref. [8]. [b] Ref. [9]. [c] Ref. [10]. [d] Ref. [11].

*2.2. Ultraviolet absorption (UV.) studies.* Arenediazonium salts exhibit medium to strong absorption at about 300 nm [13]. A solution of *p*-chlorobenzenediazonium tetrafluoroborate in TFE exhibits a similar absorption. On addition of pyridine a new absorption appears at about 350 nm. Using normal spectroscopic methods it proved difficult to gather quantitative data on the formation of a complex since the new absorption first grew in intensity and then began to decrease, indicating that reaction of the assumed complex was now competing favorably with formation of the complex. Consistent with this interpretation was the finding that the higher the temperature (–20, –10, 0°), the faster the maximal absorption was attained and likewise the consequent decrease was faster. Since the nature and amounts of the reaction products are not sufficiently determined [6], no compensation for their possible absorption could be applied to the observed spectra.

2.3. *Nuclear magnetic resonance (NMR.) studies.* Since the chemical shifts of the diazonium salts under investigation appeared to vary in a linear manner with added pyridine concentration, we sought to obtain quantitative data on the proposed equilibrium (eq. 1).



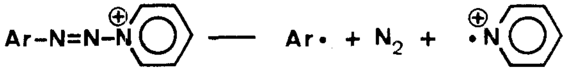
(1)

In order to apply NMR. methods, the equilibrium must be rapid (on the NMR. time scale) and it must be reversible. That this is the case is indicated by the typical case of *p*-chlorobenzenediazonium tetrafluoroborate in TFE deuteriated on the oxygen atom ($CF_3$–$CH_2OD$). Table 2 indicates that approximately the same shift is observed in $CF_3CH_2OD/Py\text{-}d_5$ 2:1, as is obtained by first preparing a 1:1 solution and then adding additional $CF_3CH_2OD$ to obtain a 2:1 solvent composition.

Other requirements of the NMR. method are that only a 1:1 complex is formed, that one species is held constant throughout a series and that the other species be present in relatively large excess. The first requirement is likely from the structure of the species involved and from the generally linear behavior of the change in chemical shift with added pyridine. The latter two requirements were carefully adhered to throughout the entire study.

Although the 95% confidence limits of $K_X$ are quite large (see Experimental Part) there seems little doubt that 1:1 complexes are indeed formed. Nothing can be said about relative complex stability among the *p*-chloro-, *p*-methoxy- and unsubstituted salts. However, it seems clear that the *p*-nitrobenzenediazonium salt forms a very much stronger complex than any of the other three salts. This result will be considered again in the next section.

2.4. *Chemically induced dynamic nuclear polarization (CIDNP) studies.* The foregoing studies provide reasonable qualitative evidence for complex formation. The composite of the IR., UV., and NMR. results provide strong support for the existence of a complex between arenediazonium salts and pyridine of structure **2** which possesses at least modest stability. By analogy with earlier work, it would therefore seem reasonable to expect such a complex to fragment in a homolytic fashion to provide the phenyl radical **3** (eq. 2). We therefore sought evidence for the formation of such radical species with the help of CIDNP studies.



**2** **3**

(2)

Using the procedure outlined in the Experimental Part, we investigated the behavior of four diazonium salts with a variety of bases including pyridine in a variety of solvents. The results are summarized in Tables 3 and 4.

Our studies in acetonitrile with added $NaOH/CH_3OH$ are an extension of *Rieker's* work [4] in which he used the pulse *Fourier* transform technique to study the $^{13}C$-polarization in the same reaction. Whereas the earlier study [4] detected CIDNP

Table 2. *Reversibility of complex formation between* p-*chlorobenzenediazonium tetrafluoroborate and pyridine-$d_5$ in TFE at 0° and 60 MHz*

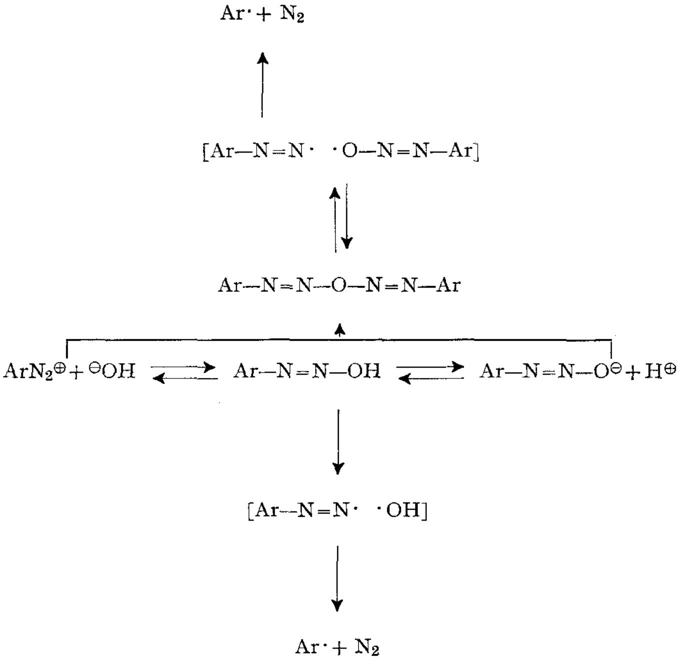
| Solution Number | Solution Composition | | | Chemical Shift, $\Delta$[a]), Hz |
|---|---|---|---|---|
| | $CF_3CH_2OD$ [ml] | Pyridine-$d_5$ [ml] | Diazo-Soln.[b]) [ml] | |
| 0 | – | 0.0 | 0.5 | 69 |
| I | 0.4 | 0.2 | 0.2 | 77 |
| II | 0.2 | 0.2 | 0.2 | 81 |
| III | 0.2 + Solution II | | | 78 |

[a]) The difference between the chemical shifts of the protons *ortho* to the diazonium group and those of chlorobenzene as internal standard.

[b]) Freshly prepared stock solution of the diazonium salt: 54 mg of *p*-chlorobenzene diazonium tetrafluoroborate in 0.5 ml $CF_3CH_2OD$.

signals only in the case of the *p*-methoxy derivative, we have found enhanced emission of the parent arene in all four salts studied. Furthermore, our results indicate that the base induced dediazoniation is slowest with the *p*-methoxy derivative. This finding coupled with *Rieker's* work [4] gives us confidence in the sensitivity of our technique.

Our work also offers some support of the *Rüchardt* mechanism [14] in this system. This mechanism involves the homolytic cleavage within a solvent cage of a 'classical' diazonium complex (eq. 3). We emphasize, however, that unfortunately, our results add little to our knowledge on the structure of the counter-radical in the radical pair cage.



(3)

The lower part of mechanism (3) is quite similar to the mechanism proposed for the dediazoniation in TFE in the presence of pyridine [6] which is supported by the work presented in this paper.

In TFE the less basic DABCO (1,4-diazabicyclo[2.2.2]octane) ($pK_a^{H_2O} = 9.08$) caused enhanced emission in all cases except the *p*-methoxy derivative. Benzene and nitrobenzene were identified as the polarized products of the corresponding diazonium salts. The *p*-chloro derivative produced an unidentified polarized intermediate (Chlorobenzene and 4,4′-dichlorobiphenyl were ruled out by standard techniques).

With the weakest base, pyridine ($pK_a^{H_2O} = 5.10$), only the *p*-nitrobenzenediazonium salt exhibited enhanced absorption. The *p*-methoxy derivative did not react appreciably under these conditions. The other two salts reacted, but did not produce any detectable polarized intermediates. However, on addition of small amounts of azobenzene (a possible radical scavenger) each of these two salts gave polarized intermediates attributable to the parent arenes. Possibly the azobenzene traps the counter-radical $X^{\cdot}(C_6H_5N^{\cdot\oplus}?)$ upsetting the equilibrium (eq. 5) and producing a net increase in arene radical concentration. Here again, more CIDNP and product information on the structure of the counter-radical and its consecutive products is desirable.

Since *p*-nitrobenzenediazonium tetrafluoroborate forms the strongest complex with pyridine and gives polarized intermediates under all conditions employed, it may be assumed that the complex formation is closely related to homolytic reactivity. The larger the equilibrium concentration of the complex, the higher is the average concentration of aryl radicals, and hence the easier it is to detect polarization. This interpretation assumes similar rates of homolytic cleavage of the complexes.

Table 3. *$^1$H-CIDNP results of dediazoniation in acetonitrile*

| Salt | Base | | | | | |
|---|---|---|---|---|---|---|
| | $OH^{\ominus}$ a) | | | $C_5D_5N$ | | |
| | Polarized Intermediate | Sign. b) | Product | Polarized Intermediate | Sign. b) | Product |
| $C_6H_5N_2BF_4$ | benzene | E | benzene | – | – | – |
| *p*-$ClC_6H_4N_2BF_4$ | chlorobenzene | E | chlorobenzene | chlorobenzene | A c) | chlorobenzene |
| *p*-$CH_3OC_6H_4N_2BF_4$ | anisole | E | anisole | – no reaction observed – | | |
| *p*-$NO_2C_6H_4N_2BF_4$ | nitrobenzene | E | nitrobenzene | nitrobenzene | E | – d) |

a) $CH_3OH$ saturated with NaOH.

b) E = emission; A = enhanced absorption.

c) The reaction mixture was not homogeneous at the end of the reaction.

d) Neither nitrobenzene nor 4,4′-dinitropiphenyl were detectable by NMR. The major product was not determined.

Table 4. *$^1$H-CIDNP results from dediazoniation in* $d_1$-*trifluoroethanol* ($CF_3CH_2OD$)

| Salt | Base | | | | | |
|---|---|---|---|---|---|---|
| | $OH^{\ominus}$ a) | | | DABCO | | |
| | Polarized intermediate | Sign. b) | Product | Polarized intermediate | Sign. b) | Product |
| $C_6H_5N_2BF_4$ | – | – | benzene | benzene | E | benzene |
| *p*-$ClC_6H_4N_2BF_4$ | chlorobenzene | A | chlorobenzene | unknown | E | chlorobenzene |
| *p*-$CH_3OC_6H_4N_2BF_4$ | – | – | anisole | – | – | anisole |
| *p*-$NO_2C_6H_4N_2BF_4$ | nitrobenzene | E | nitrobenzene | nitrobenzene | E | nitrobenzene |

| Salt | Base | | | | | | |
|---|---|---|---|---|---|---|---|
| | $C_5D_5N$ | | | | $C_5D_5N + C_6H_5N{=}NC_6H_5$ | | |
| | [DABCO]/ [$ArN_2BF_4$] | Polarized intermediate | Sign. b) | Product | Polarized intermediate | Sign. b) | Product |
| $C_6H_5N_2BF_4$ | 7.7–11.6 | – | – | benzene | benzene | E | benzene |
| *p*-$ClC_6H_4N_2BF_4$ | 6.5– 8.4 | – | – | chlorobenzene | chlorobenzene | E | chlorobenzene |
| *p*-$CH_3OC_6H_4N_2BF_4$ | 9.4–13.5 | – no reaction – | | | – | – | – |
| *p*-$NO_2C_6H_4N_2BF_4$ | $<3.4$ | nitrobenzene | E | nitrobenzene | – | – | – |

a) $CH_3OH$ saturated with NaOH.
b) E = emission; A = enhanced absorption.

We conclude therefore that the physical evidence provided by this study corroborates the initial interpretation [6] which was based solely on the kinetics and products of the reaction. Moreover, the suggestions of *Abramovitch et al.* [15] on the nature of the interaction of diazonium salts and pyridine now seem more secure.

Unfortunately, most homolytic dediazoniations yield diazo tars as major products. Exceptions are the *Gomberg-Bachmann* reaction and the formation of phenols in dimethylsulfoxide under carefully selected conditions as described in a previous paper of this series [1]. Unfortunately diazo tars have never been analysed with respect to their structure. Therefore they are a poor source of information of the consecutive steps of the formation of radical species in homolytic dediazoniations.

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**3. Experimental**[3]**.** – 3.1. *Materials.* Arenediazonium salts were prepared, purified and analysed according to standard procedures [6] [16]. Solvents were reagent grade. Deuteriated solvents were used as received from *Ciba-Geigy*. Trifluoroethanol (TFE) deuteriated on oxygen was prepared by distilling a mixture of TFE (*Fluka*) (b.p. 78°) and $D_2O$ 1:3. No OH-signal could be found in the NMR. spectrum. All bases used were reagent grade. DABCO (1,4-Diazabicyclo[2.2.2]octane) was sublimed prior to use.

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[3] For abreviations see [1].

3.2. *Spectral measurements.* IR. spectra were obtained with a *Perkin Elmer* Model 21 using an 'Amir' Dewar-insulated NaCl-cell equipped with Teflon spacers. This device provided low temperature spectra (– 20°) almost routinely. A commercial NaCl cell filled with the appropriate solvent, at RT. served as reference. UV. spectra were obtained with a *Beckman* Acta III spectrophotometer. Typical data are given in Table 5. NMR. spectra for stability constant measurements were obtained with a *Bruker* 90 MHz *Fourier*-Transform spectrometer. CIDNP studies were performed on a *Varian* T-60 spectrometer.

3.3. *Stability constant measurements.* Known volume aliquots of a deuteriated acetonitrile ($CD_3CN$) solution of the diazonium salt were added to solutions of $CD_3CN$ and $C_5H_5N$. The total volume in all cases was 0.5 ml.

For the mole fraction equilibrium constant, $K_x$ (eq. 4) in which $m_c$ is the number of moles of complex, $m_D$ the number of moles of diazonium salt, $m_p$ the number of moles of pyridine and $m_i$ the number of moles of species i, equation 5 may be derived to express the expected variation of observed chemical shift upon increasing the pyridine concentration.

$$K_x = \frac{m_c}{m_D \cdot m_p} \cdot \sum_i m_i \qquad (4) \qquad\qquad \frac{\Delta \cdot \sum_i m_i}{m_p} = \Delta_c^0 \cdot K_x - K_x \cdot \Delta \qquad (5)$$

In this expression, $\Delta$ is the difference in chemical shift of a given hydrogen atom in the diazonium salt and of the same hydrogen averaged between free and complexed in the presence of $m_p$ moles of pyridine. The *o*-hydrogen atom-signal was used in every case since it showed the greatest shift on addition of pyridine. In similar fashion, $\Delta_c^0$ is the difference in chemical shift between the pure, free diazonium salt and the pure complex. This latter quantity of course cannot be determined directly. Values of $K_x$ were then determined from the least squares slope of $\Delta \cdot \sum_i m_i/m_p$ *vs.* $\Delta$. The data are presented in Tables 6–14.

Table 5. *UV. Absorption of arenediazonium ions in 0.1* N *HCl* [6]

| Salt | $\lambda_{1\,max}$ (nm) | $\varepsilon_1$ $1 \cdot mol^{-1} \cdot cm^{-1}$ | $\lambda_{2\,max}$ (nm) | $\varepsilon_2$ $1 \cdot mol^{-1} \cdot cm^{-1}$ |
|---|---|---|---|---|
| $C_6H_5N_2BF_4$ | 263 | 13,200 | 298 | 2,100 |
| *p*-$ClC_6H_4N_2BF_4$ | 214 | 5,830 | 282 | 17,700 |
| *p*-$CH_3OC_6H_4N_2BF_4$ | 230 | 7,130 | 314 | 24,200 |
| *p*-$NO_2C_6H_4N_2BF_4$ | 261 | 15,100 | 312 | 2,200 |

Table 6. *Experimental data for the stability constant of benzenediazonium tetrafluoroborate and pyridine*-$d_5$ *in* $CD_3CN$ *at 0°*

| $CD_3CN$ ml | Py-$d_5$ ml | Py-$d_5$ M/l | $\sum_i m_i$[a]) mmol | $\delta$[b]) Hz | $\Delta$ Hz |
|---|---|---|---|---|---|
| 0.40 | – | – | – | 91 | – |
| 0.30 | 0.10 | 2.496 | 9.454 | 105 | 14 |
| 0.25 | 0.15 | 3.744 | 9.124 | 110 | 19 |
| 0.20 | 0.20 | 4.992 | 8.795 | 115 | 24 |
| 0.15 | 0.25 | 6.241 | 8.465 | 121 | 30 |
| 0.10 | 0.30 | 7.489 | 8.136 | 127 | 36 |

a) Each solution contained 0.1 ml of the diazonium salt stock solution = 94 mg diazonium salt + 1.0 ml $CH_3CN$ + 1 drop of benzene. Thus $\Sigma m_i$ is the sum of number of mmoles of the salt i + 0.1 ml $CH_3CN$ ($d^{20} = 0.7857$) + x ml of $CD_3CN$ ($d^{20} = 0.84$) + y ml of pyridine-$d_5$ ($d^{20} = 1.05$).

b) $\delta$ is the chemical shift of the protons *ortho* to the diazonio group from the reference of benzene.

Table 7. *Experimental data for the stability constant of* p-*chlorobenzenediazonium tetrafluoroborate*$^{a)}$ *and pyridine*-$d_5$ in $CD_3CN$ at 0°

| $CD_3CN$ ml | Py-$d_5$ ml | Py-$d_5$ M/l | $\sum_i m_i$ mmol | $\delta$$^{b)}$ Hz | $\Delta$ Hz |
|---|---|---|---|---|---|
| 0.40 | – | – | – | 98 | 0.0 |
| 0.30 | 0.10 | 2.496 | 9.434 | 111 | 13 |
| 0.25 | 0.15 | 3.744 | 9.104 | 117 | 19 |
| 0.20 | 0.20 | 4.992 | 8.775 | 123 | 25 |
| 0.15 | 0.25 | 6.241 | 8.445 | 134 | 36 |
| 0.10 | 0.30 | 7.489 | 8.116 | 138 | 40 |

$^{a)}$ Stock solution = 66 mg *p*-chlorobenzenediazonium tetrafluoroborate + 1.0 ml $CH_3CN$ + 1 drop of chlorobenzene.

$^{b)}$ $\delta$ of protons *ortho* to the diazonio group measured from the strongest peak of chlorobenzene.

Table 8. *Experimental data* (60 MHz) *for the stability constant of* p-*methoxybenzenediazonium tetrafluoroborate*$^{a)}$ *and pyridine*-$d_5$ *in* $CD_3CN$ at 0°

| $CD_3CN$ ml | Py-$d_5$ ml | Py-$d_5$ M/l | $\sum_i m_i$ mmol | $\delta$$^{b)}$ Hz | $\Delta$ Hz |
|---|---|---|---|---|---|
| 0.40 | – | – | – | 129.5 | 0.0 |
| 0.30 | 0.10 | 2.496 | 9.452 | 137 | 7.5 |
| 0.25 | 0.15 | 3.744 | 9.122 | 141 | 11.5 |
| 0.20 | 0.20 | 4.992 | 8.793 | 144 | 14.5 |
| 0.15 | 0.25 | 6.241 | 8.463 | 147 | 17.5 |
| 0.10 | 0.30 | 7.489 | 8.134 | 152 | 22.5 |

$^{a)}$ Stock solution = 102 mg *p*-methoxybenzenediazonium tetrafluoroborate + 1.0 ml $CH_3CN$ + 2 drops of methoxybenzene.

$^{b)}$ $\delta$ of protons *ortho* to the diazonio group measured from the strongest line of methoxybenzene.

Table 9. *Experimental data* (60 MHz) *for the stability constant of* p-*nitrobenzenediazonium tetrafluoroborate*$^{a)}$ *and pyridine*-$d_5$ *in* $CD_3CN$ *at 0°*

| $CD_3CN$ ml | Py-$d_5$$^{5)}$ soln. ml | Py-$d_5$ M/l | $\sum_i m_i$ mmol | $\delta$$^{c)}$ Hz | $\Delta$ Hz |
|---|---|---|---|---|---|
| 0.40 | – | 0.00 | 9.551 | 88 | – |
| 0.35 | 0.05 | 0.125 | 9.519 | 89 | 1.0 |
| 0.30 | 0.10 | 0.250 | 9.486 | 90 | 2.0 |
| 0.25 | 0.15 | 0.375 | 9.453 | 91 | 3.0 |
| 0.20 | 0.20 | 0.500 | 9.420 | 90.5 | 2.5 |
| 0.15 | 0.25 | 0.625 | 9.387 | 92 | 4.0 |
| 0.10 | 0.30 | 0.750 | 9.354 | 91.5 | 3.5 |
| 0.00 | 0.40 | 1.00 | 9.288 | 93 | 5.0 |

$^{a)}$ Stock solution = 4.00 mg *p*-nitrobenzenediazonium tetrafluoroborate + 1.0 ml $CD_3CN$ + 2 drops of nitrobenzene.

$^{b)}$ Stock solution of pyridine-$d_5$ = 0.1 ml pyridine-$d_5$ + 0.9 ml $CD_3CN$.

$^{c)}$ $\delta$ of protons *ortho* to the diazonio group measured from the strongest line of the *meta* and *para* protons of nitrobenzene.

Table 10. *Experimental data* (60 MHz) *for the stability constant of benzenediazonium tetrafluoroborate*[a]) *and pyridine*-$d_5$ *in* $CF_3CH_2OD$ *at 15 ± 5°*

| $CF_3CH_2OD$ ml | Py-$d_5$ ml | Py-$d_5$ M/l | $\sum_i m_i$ mmol | $\delta$[b]) Hz | $\Delta$ Hz |
|---|---|---|---|---|---|
| 0.40 | – | – | – | 61 | 0.0 |
| 0.30 | 0.10 | 2.496 | 6.734 | 70 | 9 |
| 0.25 | 0.15 | 3.744 | 6.681 | 73 | 12 |
| 0.20 | 0.20 | 4.992 | 6.627 | 79 | 18 |
| 0.15 | 0.25 | 6.240 | 6.573 | 82 | 21 |
| 0.10 | 0.30 | 7.489 | 6.519 | 86 | 25 |

[a]) Stock solution = 122 mg benzenediazonium tetrafluoroborate + 1.0 ml $CF_3CH_2OD$ + 1 drop of benzene.

[b]) $\delta$ of the strongest line in spectrum measured from benzene.

Table 11. *Experimental data* (60 MHz) *for the stability constant of* p-*chlorobenzenediazonium tetrafluoroborate*[a]) *and pyridine*-$d_5$ *in* $CF_3CH_2OD$ *at 15 ± 5°*

| TFE-OD ml | Py-$d_5$ ml | Py-$d_5$ M/l | $\sum_i m_i$ mmol | $\delta$[b]) Hz | $\Delta$ Hz |
|---|---|---|---|---|---|
| 0.40 | – | – | – | 68.1 | 0.0 |
| 0.35 | 0.05 | 1.248 | 6.784 | 75 | 7.9 |
| 0.30 | 0.10 | 2.496 | 6.730 | 79.3 | 11.2 |
| 0.25 | 0.15 | 3.744 | 6.676 | 84 | 15.9 |
| 0.20 | 0.20 | 4.992 | 6.622 | 89 | 20.9 |
| 0.15 | 0.25 | 6.241 | 6.569 | 94 | 25.9 |

[a]) Stock solution = 133 mg *p*-chlorobenzenediazonium tetrafluoroborate + 1.0 ml $CF_3CH_2OD$ + 1 drop of chlorobenzene.

[b]) $\delta$ of protons *ortho* to the diazonio group measured from the strongest line of chlorobenzene.

Table 12. *Linear regression* (eq. 5) *values of stability constants of arenediazonium ions with pyridine*-$d_5$ *in acetonitrile at 0°*

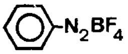
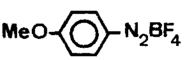
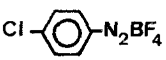
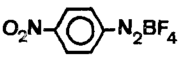
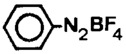
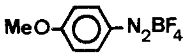
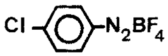
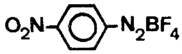
| Salt | All Data | | 'Best Fit' | | $K_X$ |
|---|---|---|---|---|---|
| | r | – slope | r | – slope | ±0.05 |
|  | 0.934 | 1.19 | 0.957 | 0.80 | 0.80 |
|  | 0.878 | 0.65 | 0.934 | 0.56 | 0.60 |
|  | 0.951 | 0.57 | 0.997 | 0.87 | 0.90 |
|  | 0.621 | 13.65 | 0.900 | 14.95 | 15.0 |

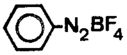
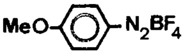
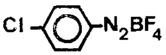
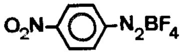
Table 13. *Confidence levels for the correlations of eq. 5* (Table 12)

| Salt | All Data | | | 'Best Fit' | | |
|---|---|---|---|---|---|---|
| | n[a] | t[b] | confidence level | n[a] | t[b] | confidence level |
|  | 5 | 4.528 | >95% | 4 | 4.665 | >95% |
|  | 5 | 3.177 | 90–95% | 4 | 3.697 | 90–95% |
|  | 5 | 5.327 | 95–98% | 3 | 1.288 | <90% |
|  | 8 | 1.940 | 90% | 6 | 4.129 | 98–99% |

a) n = number of points.

b) $t = r[(n-2)/(1-r^2)]^{1/2}$.

Table 14. *Errors in stability constants calculated to 90% and 95% confidence levels*

| Salt | $K_x$ | n[a] | STD[b] | 95% | | 90% | |
|---|---|---|---|---|---|---|---|
| | | | | t | error[c] | t[c] | error[c] |
|  | 0.802 | 4 | $7.91 \times 10^{-2}$ | 4.303 | 0.34 | 2.920 | 0.23 |
|  | 0.564 | 4 | $1.03 \times 10^{-1}$ | 4.303 | 0.44 | 2.920 | 0.30 |
|  | 0.865 | 3 | $2.18 \times 10^{-2}$ | 12.706 | 0.78 | 6.314 | 0.14 |
|  | 14.95 | 6 | 5.88 | 2.776 | 16.3 | 2.132 | 12.5 |

a) n = number of points.

b) STD = standard deviation of slope of the linear regression of eq. 5.

c) Error = t × STD.

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# 154. Cuprous Complexes and Dioxygen, VII1). Competition between One- and Two-Electron Reduction of $O_2$ in the Autoxidation of $\mathrm{Cu(1\text{-}Methyl\text{-}2\text{-}hydroxymethyl\text{-}imidazole)_2^+}$

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(22. X. 75)

*Summary.* The complexation of 1-methyl-2-hydroxymethyl-imidazole (L) with Cu(I) and Cu(II) has been studied in aqueous acetonitrile (AN). Cu(I) forms three complexes, $\mathrm{Cu(AN)L^+}$, $\mathrm{CuL_2^+}$, and $\mathrm{Cu(AN)H_{-1}L}$, with stability constants $\log K(\mathrm{Cu(AN)^+ + L \rightleftharpoons Cu(AN)L^+}) = 4.60 \pm 0.02$, $\log\beta_2 = 11.31 \pm 0.04$, and $\log K(\mathrm{Cu(AN)H_{-1}L + H^+ \rightleftharpoons Cu(AN)L^+}) = 10.43 \pm 0.08$ in 0.15 M AN. The main species for Cu(II) are $\mathrm{CuL^{2+}}$, $\mathrm{CuH_{-1}L^+}$, $\mathrm{CuH_{-1}L_2^+}$, and $\mathrm{CuH_{-2}L_2}$.

The autoxidation of $\mathrm{CuL_2^+}$ was followed with an oxygen sensor and spectrophotometrically. Competition between the formation of superoxide in a one-electron reduction of $O_2$ and a path leading to $H_2O_2$ *via* binuclear $\mathrm{(CuL_2)_2O_2^{2+}}$ was inferred from the rate law

$$-\mathrm{d[O_2]/dt} = [\mathrm{CuL_2^+}]^2[\mathrm{O_2}]\left(\frac{k_a}{1+k_b[\mathrm{CuL^+}]} + \frac{k_c[\mathrm{L}]+k_d+(k_f/[\mathrm{L}]+k_g+k_h[\mathrm{L}])/[\mathrm{H^+}]}{[\mathrm{CuL_2{}^+}]+k_e[\mathrm{Cu(II)}]_{tot}}\right)$$

with $k_a = (2.31 \pm 0.12) \cdot 10^4\,\mathrm{M^{-2}s^{-1}}$, $k_b = (1.0 \pm 0.2) \cdot 10^3\,\mathrm{M^{-1}}$, $k_c = (2.85 \pm 0.07) \cdot 10^2\,\mathrm{M^{-2}s^{-1}}$, $k_d = 3.89 \pm 0.14\,\mathrm{M^{-1}s^{-1}}$, $k_e = 0.112 \pm 0.004$, $k_f = (2.06 \pm 0.24) \cdot 10^{-10}\,\mathrm{M\,s^{-1}}$, $k_g = (1.35 \pm 0.07) \cdot 10^{-7}\,\mathrm{s^{-1}}$, and $k_h = (6.8 \pm 1.4) \cdot 10^{-7}\,\mathrm{M^{-1}\,s^{-1}}$.

The autoxidation of Cu(I) has been established to be an integral part of the reaction mechanism of several biological systems [2], including the copper-catalysed autoxidation of hemoglobin [3]. Low redox potential and easy formation of a 'cupric-like' tetracoordinate transitory dioxygen adduct have been inferred as prerequisites for rapid reaction [4] [5]. In several cases $H_2O_2$ was the metastable product of dioxygen reduction. Altough it has been uncertain whether this is achieved in aqueous solutions by one-electron steps with superoxide as an intermediate or *via* binuclear $\mathrm{Cu_2L_xO_2^{2+}}$, in the organic solvents DMSO [1], $\mathrm{CH_3COOH}$ [6], and $\mathrm{CH_3NO_2}$ [7] the latter mechanism has been found. *Pecht & Anbar* [8] postulated a dimeric transition

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1) Part VI, see [1].