

27. Magnetic-Field Effect in Aromatic Dediazonation¹⁾

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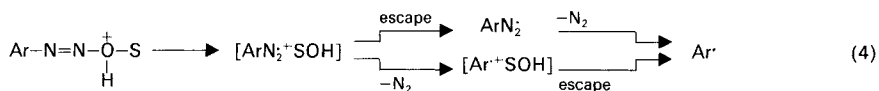
(17.IX.90)

Homolytic dediazonation of tribromo- and trichloro-benzenediazonium tetrafluoroborates in highly ionizing, low-nucleophilicity solvents (trifluoroethanol and trifluoromethanesulfonic acid (TfOH)) exhibits a strong magnetic-field dependency of dediazonation products; a more facile singlet-to-triplet intersystem crossing results in increased radical-escape products at higher magnetic fields.

Introduction. – Solvent nucleophilicity and the electron demand at N(β) provide two important channels for controlling the mechanism of aromatic dediazonation [1].

Heterolytic dediazonation (Ar^+ formation; *Eqn. 1*) is usually observed in low-nucleophilicity, highly ionizing solvents ($\text{CF}_3\text{CH}_2\text{OH}$, $(\text{CF}_3)_2\text{CHOH}$, and protic superacids) and when electron-donating substituents are present on the aryl ring [2] [3] (*Scheme 1*). Homolysis ($\text{Ar}^\cdot$ formation), on the other hand, becomes dominant in the more nucleophilic solvents (MeOH, DMSO, NO_2^- /buffer, and hexamethylphosphoric triamide) and in the presence of electron-withdrawing substituents, which increase the electron demand at the N-atom [4] [1].

Scheme 1. Heterolytic and Homolytic Dediazonation



Despite several multinuclear CIDNP studies (^1H , ^{13}C , and ^{15}N) [5–7] on homolytic dediazonation probing radical intermediates, to our knowledge, homolytic dediazonation has never been subjected to an extensive magnetic-field (MF) study. Homolytic chemistry in a magnetic field provides an opportunity to alter the course of a chemical reaction (rate and products) through entropic factors ($k = A e^{-E/RT}$). Intersystem crossing (ISC) may be promoted or hindered by an external magnetic field, depending on the mechanism of spin interactions. This in turn controls the relative efficiency of escape

¹⁾ Presented at the 21st ACS Central Regional Meeting, Cleveland, Ohio, June 1989.

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vs. cage products [8–13]. Four distinct classes of MF dependency of ISC are known [8]. In principle, for a singlet pair it is possible to observe more cage or more escape products. For a triplet pair, where ISC ($T \rightarrow S$) cannot compete with diffusion, a micellar environment (super cage) may be used to hinder diffusion and hence form a higher percentage of cage products. Pioneering work by *Turro et al.* [11] in this area has provided a number of examples including application in radical polymerization [14].

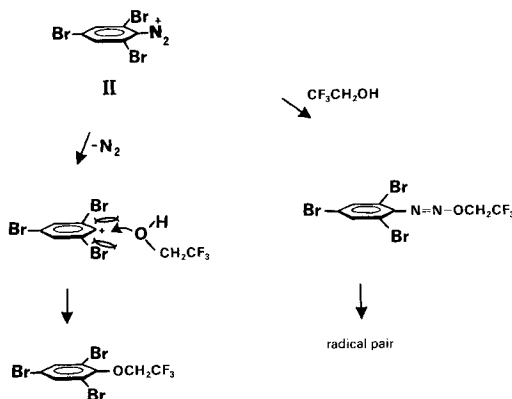
A direct homolysis of ArN_2^+ (Eqn. 2) requires the formation of the highly unstable N_2 radical cation and is energetically unfavorable. Based on a body of experimental evidence [1], it is believed that nucleophilic attack by solvent on $\text{N}(\beta)$ occurs first (Eqn. 3). Homolysis is then followed (an inner-sphere ET) to form a singlet radical pair $\text{ArN}_2^+ \text{SOH}$ in the solvent cage (diazenyl radical and the radical cation of the solvent; Eqn. 4). The diazenyl radical $[\text{ArN}_2^+ \text{SOH}]$ could undergo loss of N_2 within the cage to give $[\text{Ar}^+ \text{SOH}]$ as a second geminate pair or might dissociate only following escape, to give Ar^+ and N_2 (Scheme 1).

If the dissociation of ArN_2^+ to Ar^+ occurs only after diffusion escape, then the percentage of arene product should, in principle, not depend on the magnetic field (no radical pair). Similarly, the formation of ArN_2^+ from $\text{ArN}_2^+ \text{X}^-$ and its collapse to Ar^+ by any process other than a radical-pair mechanism should result in an MF-independent process.

Results and Discussion. – Product analysis of dediazonation in $\text{CF}_3\text{CH}_2\text{OH}$ shows *exclusive* heterolytic dediazonation for a variety of substituted benzenediazonium ions including $4\text{-ClC}_6\text{H}_4\text{N}_2^+$. Tribromo- and trichlorobenzenediazonium ions **I** and **II**, respectively, are, however, exceptional cases, for which product analysis of the dediazonation showed the presence of the corresponding arenes, indicative of homolysis and H^+ abstraction [2]. This change in the mechanism as a function of steric factors can be explained in terms of steric inhibition to solvolysis for a heterolytic pathway which renders attack on $\text{N}(\beta)$, homolysis, and subsequent H^+ abstraction energetically more favorable (Scheme 2).

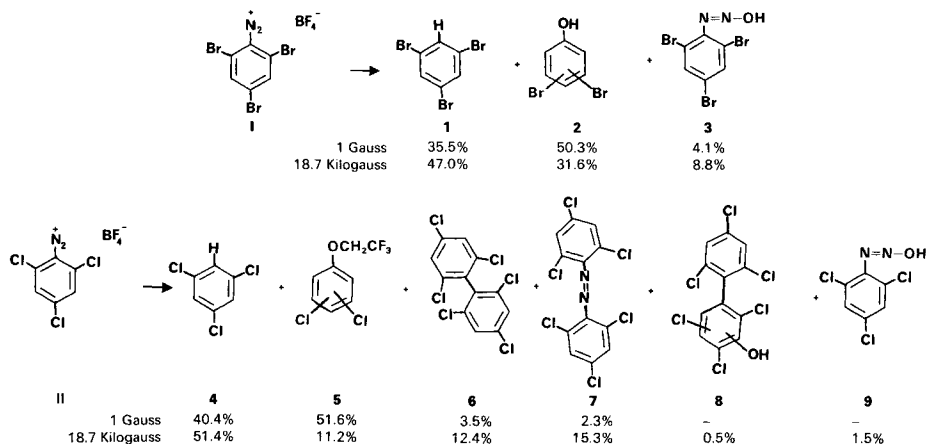
Using $\text{CF}_3\text{CH}_2\text{OH}$ and trifluoromethanesulfonic acid (TfOH) as solvents, we studied the ambient dediazonation of the purified tetrafluoroborate salts **I** and **II** at 1 G (earth's magnetic field) and at 18.7 KG (in the probe of an 80-MHz NMR instrument) under

Scheme 2. Steric Inhibition to Solvolysis in a Heterolytic Pathway



identical conditions of concentration, reaction times, and temperature under a dry N_2 atmosphere. The reaction mixtures were quenched after 24 h at 34° and subjected to capillary GC and GC/MS analysis. Noticeable differences in product distributions (GC %) were observed as a function of field. Dediazonation of **I** in CF_3CH_2OH at 1 G resulted in two major and one minor products, *i.e.* tribromobenzene **1**, dibromo-hydroxybenzene **2**, and tribromophenyl diazohydroxide **3**³). The same experiment conducted at 18.7 KG showed that products **1** and **3** increased, whereas **2** decreased (*Scheme 3*). With

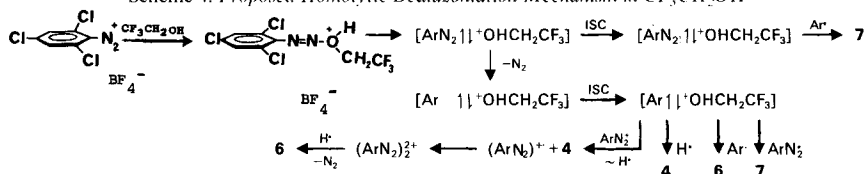
Scheme 3. Dediazonation of **I** and **II** in CF_3CH_2OH



II, two major and two minor products were formed at 1G, *i.e.* trichlorobenzene **4**, dichloro(trifluoroethoxy)benzene **5**, hexachlorobiphenyl **6**, and its corresponding diazo compound **7** (*Scheme 3*). The 18.7-KG experiment showed that, except for **5**, all other products increased at higher magnetic field. In addition, two new, very minor products were observed which were tentatively identified as hexachlorohydroxybiphenyl **8** and the diazohydroxide **9**.

Our proposed homolytic dediazonation mechanism is shown in *Scheme 4*. Nucleophilic attack on $N(\beta)$ by the solvent results in an oxonium ion. Upon homolysis, a singlet radical pair is generated. Loss of N_2 results in a second singlet pair. ISC ($S \rightarrow T$) is facilitated in the magnetic field and results in a more efficient escape of both the diazenyl

Scheme 4. Proposed Homolytic Dediazonation Mechanism in CF_3CH_2OH

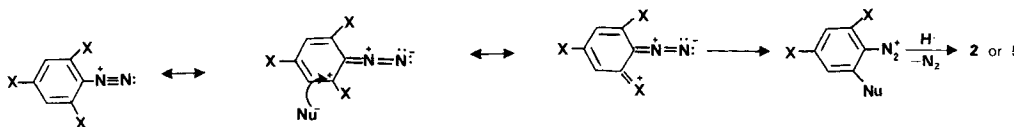


³) Our GC/MS assignment of this minor product should be considered tentative, as $RN=NOH$ is expected to have limited thermal stability.

radical and the aryl radical from the solvent cage. Upon diffusion, these radicals can react with each other, dimerize, or abstract H-atoms. $\text{CF}_3\text{CH}_2\text{OH}$ provides a convenient source of $\text{H}^\cdot$, and substantial amounts of the arene **4** are thus formed⁴⁾.

We propose that the formation of products **2** and **5** illustrates the ambident character of the diazonium ions [15] and provides new examples for substitution of a nucleofugal leaving group prior to homolytic dediazonation and $\text{H}^\cdot$ abstraction (*Scheme 5*)⁵⁾. Since at a higher magnetic field, a more favored ISC ($\text{S} \rightarrow \text{T}$) leads to a substantial increase in the escape products, in a relative sense, substitution of the nucleofugal leaving group becomes a minor pathway.

Scheme 5. Ambident Character of Diazonium Ion; Substitution of Nucleofugal Leaving Group



Dediazoniation of **I** in TfOH at 1 G resulted in two major products identified by GC/MS as tribromobenzene (25%) and a tetrabromobenzene isomer (41%). The magnetic-field experiment (18.7 KG) did not show a noticeable increase in the arene content! With **II**, however, the percentage of arene almost doubled (1 G, 6.8%; 18.7 KG, 13%). It should be noted that dediazoniation in TfOH is complicated by an apparent acid-catalyzed bromine disproportionation, following dediazoniation and arene formation. It is, nevertheless, clear that ISC ($\text{S} \rightarrow \text{T}$) is again facilitated.

Formation of arene requires an $\text{H}^\cdot$. Unlike $\text{CF}_3\text{CH}_2\text{OH}$, TfOH is not a suitable $\text{H}^\cdot$ donor. Moreover, the highly non-nucleophilic nature of the triflate anion [18] makes the attack on $\text{N}(\beta)$ unlikely. For the first step, a TfOH-catalyzed outer-sphere ET mechanism involving the gegenion (BF_4^-) may be considered. To test the validity of an 'anion-induced' ET process in homolytic dediazoniation of tribromobenzenediazonium cation, we prepared salts with different gegenions ($\text{X} = \text{Cl}^-$, CF_3COO^- , and TfO^-) having varied oxidation potentials. Dediazoniation was studied in TfOH in the probe of a 60-MHz NMR instrument (14 KG), under identical conditions (25°, 24 h). The amount (GC %) of tribromobenzene was found to be indeed gegenion-dependent; with the Cl^- salt, 34.3% of **I** was present, whereas with the CF_3COO^- and TfO^- salts, the amount of **I** was reduced to 20 and 4.4%, respectively.

In conclusion, our MF-dependency studies provide strong support for a radical-pair mechanism in homolytic dediazoniation of **I** and **II**. Our work is being extended to other diazonium ions and solvents and to dediazoniation at much higher magnetic fields, with particular interest in borderline mechanistic cases (involving both $\text{Ar}^\cdot$ and Ar^+), where dediazoniation in a magnetic field might alter the mechanistic course. We are also studying the effect of micelles and crown ethers on the $\text{S} \rightarrow \text{T}$ process, in the hope that a less favorable diffusion [19] may result in direct observation of the oxonium-ion intermediate.

⁴⁾ A minor pathway involving $\text{H}^\cdot$ transfer from ArN_2^+ could also lead to **4**. Dimerization of the resulting radical cation followed by dediazoniation and $\text{H}^\cdot$ abstraction could lead to **6** (*Scheme 4*).

⁵⁾ The ambident character of benzenediazonium ions was elegantly demonstrated by Olah and coworkers through ^{13}C -NMR studies [16] as well as by-product analysis after dediazoniation in pyridine/HF [17].

Experimental Part

General. The diazonium salts **I** and **II** were freshly prepared by conventional diazotization ($\text{NaNO}_2/\text{HBF}_4$) and precipitation from $\text{MeCN}/\text{Et}_2\text{O}$ (IR: 2360 and 2313 cm^{-1} ($\text{N}\equiv\text{N}$)). The Cl^- , CF_3COO^- , and TfO^- salts were similarly prepared by conventional diazotization with NaNO_2/HCl , $\text{NaNO}_2/\text{CF}_3\text{COOH}$, and $\text{NaNO}_2/\text{TfOH}$, resp., and by careful precipitation from $\text{MeCN}/\text{Et}_2\text{O}$. The characteristic $\bar{\nu}$ ($\text{N}\equiv\text{N}$) of the diazonium salts showed gegenion dependency: 2271 ($\text{Br}_3\text{C}_6\text{H}_2\text{N}_2^+\text{Cl}^-$), 2280 ($\text{Br}_3\text{C}_6\text{H}_2\text{N}_2^+\text{CF}_3\text{COO}^-$), 2281 ($\text{Br}_3\text{C}_6\text{H}_2\text{N}_2^+\text{TfO}^-$), 2280 ($\text{Cl}_3\text{C}_6\text{H}_2\text{N}_2^+\text{Cl}^-$), 2243 ($\text{Cl}_3\text{C}_6\text{H}_2\text{N}_2^+\text{CF}_3\text{COO}^-$), 2299 cm^{-1} ($\text{Cl}_3\text{C}_6\text{H}_2\text{N}_2^+\text{TfO}^-$). GC Analyses: *HP-5809 A* instrument, 25-m fused-silica (*OV101*) and 5-m *HP* methylsilicon gum capillary columns. GC/MS Analyses (m/z (%)): *Finnigan-Mat-4500* instrument.

I-G Experiments. The diazonium salt (0.015 g) was charged into 10-ml flask equipped with magnetic stirrer bar, a drying tube, and a N_2 inlet⁶). $\text{CF}_3\text{CH}_2\text{OH}$ (0.5 ml) or TfOH (ca. 0.5 ml) was slowly added to give a homogeneous soln. which was allowed to react for 24 h at 24° , prior to workup and GC analysis.

Magnetic-Field Experiments. The salt was charged into a pre-dried 5-mm NMR tube to which 0.5 ml of $\text{CF}_3\text{CH}_2\text{OH}$ or TfOH was slowly added *via* a pipet or a syringe under N_2 (vortex mixing). TfOH addition was always done with pre-cooling of both the diazonium salt and the superacid to avoid local overheating.

2,4,6-Tribromobenzenediazohydroxide (3): GC/MS: 357 (30, $[M + H]^+$), 359 (83), 361 (80), 363 (29), 327 (32, $[M + H - \text{NO}]^+$, ArNH_2^+), 329 (100), 331 (98), 333 (32), 311 (12, $\text{Br}_3\text{C}_6\text{H}_2^+$), 313 (30), 315 (29), 317 (9), 299 (17), 301 (45), 303 (45), 305 (13), 232 (30, $[311 - \text{Br}]^+$), 234 (60), 236 (31), 153 (45, $[232 - \text{Br}]^+$), 155 (47), 74 (86).

2,4,6-Trichlorobenzenediazohydroxide (9): GC/MS: 225 (35, $[M + H]^+$), 227 (35), 229 (9), 195 (62, $[M + H - \text{NO}]^+$, ArNH_2^+), 197 (58), 199 (20), 179 (15, $\text{Cl}_3\text{C}_6\text{H}_2^+$), 181 (13), 183 (4), 167 (27), 169 (22), 171 (8), 143 (22), 145 (14), 147 (6), 109 (32), 84 (75), 49 (100).

We thank Kent State University for a Graduate Teaching Assistantship (to H.G.) and for research support. We are grateful to Dr. Dave Hehemann of Cleveland State University for recording the GC/MS.

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⁶⁾ The I-G experiments were run in a thermostatic bath in the dark, in order to ascertain identical conditions as for the experiments carried out at higher fields in the NMR probe.