# Dediazoniation of Arenediazonium Ions in Homogeneous Solution. 10.[1] Solvent Effects on the Reactions of Benzene- and 2,4,6-Trimethylbenzenediazonium Ion. Evidence for Two Intermediates[2]

Ivanka Szele[3] and Heinrich Zollinger*

Contribution from the Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland. Received July 18, 1977

Abstract: The dediazoniation of benzene- (**1**) and 2,4,6-trimethylbenzenediazonium tetrafluoroborate (**2**) was investigated in solvents of low nucleophilicity (1,1,1,3,3,3-hexafluoro-2-propanol and fluorosulfonic acid) and was compared with the corresponding data in 2,2,2-trifluoroethanol. The reactions proceed heterolytically, and the solvent effects on the dediazoniation rate, the isotopic N_α-N_β rearrangement, and the exchange reaction of the diazonio group of β-^{15}N labeled diazonium salts with external nitrogen (300 atm) were studied. Diazonium salt **2** shows in HFIP by far the highest amount ever observed of isotopic rearrangement (36.97%) and exchange with external nitrogen (16.50%) at 70% dediazoniation. The corresponding values for diazonium salt **1** in HFIP are lower (10.47 and 6.26%, respectively). The results are interpreted in terms of (at least) two intermediates in the course of the dediazoniation, namely, a tight nitrogen aryl cation molecule–ion pair through which the rearrangement occurs, and a (solvated) aryl cation, free of or solvent separated from nitrogen. The results indicate that the exchange reaction proceeds through the second intermediate.

Dediazoniations of arenediazonium ions are generally considered to be the only examples of a nucleophilic aromatic substitution proceeding via an S_N1-like mechanism.[4,5] The evidence is well established and quite compelling.[6-12] Some years ago it was found that N_α-N_β rearrangement takes place to a small extent during the dediazoniation of substituted benzenediazonium salts in water.[13] A significantly higher percentage of rearrangement was later observed in the less nucleophilic solvent 2,2,2-trifluoroethanol[6] (TFE). In addition, evidence was presented for a reaction of nitrogen molecules with a purely organic reagent—the phenyl cation or a related species—in TFE solution during the solvolysis of benzenediazonium ions.[6,14] The reversibility of the dediazoniation reaction (1) thus being demonstrated, and the overall mechanism

$$\langle \bigcirc \rangle - \overset{+}{N} \equiv N \rightleftharpoons \text{intermediate(s)} + N_2 \longrightarrow \text{products} \quad (1)$$
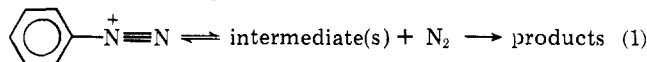
being roughly established, a detailed mechanistic picture remained to be elucidated. With this in mind, the work described in this and in the following paper[15] was undertaken. In the present paper we present the results obtained in the study of the dediazoniation of benzene- and 2,4,6-trimethylbenzenediazonium tetrafluoroborate in solvents of low nucleophilicity (1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and fluorosulfonic acid) and compare them with the corresponding data in TFE.[6,15] The results imply that not only one, but two reaction intermediates are involved in the mechanism of dediazoniation.

Experimental Section

Materials. Reagent grade (Fluka puriss.) 2,2,2-trifluoroethanol was used without further purification. 1,1,1,3,3,3-Hexafluoro-2-propanol (Fluka purum) was distilled (bp 53–54 °C) and the purity was checked by GLC (>99.9%). Fluorosulfonic acid (Fluka purum) was distilled[16] (bp 161–162 °C) under a continuous stream of dry nitrogen in an all-glass apparatus which had been flamed in a stream of nitrogen before use. It was kept under nitrogen. 2-Naphthol was recrystallized from ethanol (mp 121 °C). The disodium salt of 2-naphthol-3,6-disulfonic acid (R-salt) was recrystallized twice from water and charcoal. Aniline and 2,4,6-trimethylaniline were distilled under reduced pressure prior to use. Sodium nitrite and labeled sodium nitrite (Stohler Isotope Chemicals, 99.2% ^{15}N) were used without purification.

Benzenediazonium-β-^{15}N tetrafluoroborate was prepared according to the method of Starkey.[6,17] The filtrate obtained after removal of crystalline benzenediazonium-β-^{15}N tetrafluoroborate was used for the synthesis of the labeled azo compound. The filtrate was added immediately to a solution of 2-naphthol (0.288 g, 2 mmol) in 50 mL of 1 M sodium hydroxide at 0 °C. The azo compound formed was filtered, dried, and recrystallized from ethanol. Half of the 1-phenylazo-2-naphthol was reduced[6,18] to give anilinium hydrochloride. The azo compound and anilinium hydrochloride thus obtained were used as reference materials for mass spectral analyses. Unlabeled benzenediazonium tetrafluoroborate was prepared in the same way as the labeled salt.

2,4,6-Trimethylbenzenediazonium-β-^{15}N tetrafluoroborate and the corresponding unlabeled salt were prepared[15] in the same way as benzenediazonium tetrafluoroborate.

Fluoromesitylene (2-fluoro-1,3,5-trimethylbenzene) was prepared from 3,4,6-trimethylbenzenediazonium tetrafluoroborate by the general procedure of Balz and Schiemann.[19] The crude product was dried over MgSO₄ and distilled (bp 164–165 °C, lit.[2] 164.8–165.1 °C).

2,4,6-Trimethylphenyl 1′,1′,1′,3′,3′,3′-hexafluoro-2′-propyl ether was synthesized from 2,4,6-trimethylbenzenediazonium tetrafluoroborate in HFIP (2.34 g, 0.01 mol in 60 mL of HFIP at room temperature). After completion of the reaction ($t > 10t_{1/2}$) 50 mL of water was added and the solution was neutralized with NaHCO₃. Then the solution was extracted with ether and the ether layer was dried over MgSO₄. The solvent was removed by distillation through a Vigreux column (bp 30–75 °C[21]) and the residue was analyzed by GLC (Ucon, 150 °C). It consisted mainly of the desired aryl alkyl ether (ca. 94%) together with fluoromesitylene (ca. 5%, bp 165 °C) and mesitylene (ca. 1%, bp 164 °C). Attempted purification by distillation was unsuccessful, but an NMR spectrum of the mixture was in accordance with the proposed structure of the main reaction product. NMR (CDCl₃) δ 2.16 (s, 3 H), 2.20 (s, 6 H), 4.68 (h, 1 H, $J = 6$ Hz), 6.74 (s, 2 H). MS m/e (% of base peak) 286 (M⁺, 49), 135 (100), 91 (27).

Kinetic Measurements. All dediazoniations were followed for at least 2 half-lives. They obeyed first-order kinetics within the range studied. Correlation coefficients for trimethylbenzenediazonium salt in HFIP were better than 0.99, while those in FSO₃H were sometimes as bad as 0.92.

A. Dediazoniation of Benzene- and 2,4,6-Trimethylbenzenediazonium Tetrafluoroborate in Hexafluoro-2-propanol. The measurements were carried out in a jacketed three-neck reaction vessel thermostated at 25 ± 0.1 °C. Before addition of the salt HFIP was deoxygenated by bubbling dry nitrogen through it for about 30 min. The reaction vessel was equipped with a reflux condenser, which was fitted with an inlet for nitrogen and a balloon, and a rubber septum through which

samples were taken. The third opening was tightly stoppered. The flask was wrapped in aluminum foil to exclude light. About 100 mg of the diazonium salt was added to the deoxygenated HFIP (containing the necessary amount of $Bu_4N^+ClO_4^-$ if the salt effect was measured), and the solution was stirred rapidly. At definite time intervals 0.2-mL samples were extracted and then added to 20 mL of R-salt solution. The volume was adjusted to 250 mL with water and the optical density of the coupling product at λ_{max} was measured (490 nm for benzene- and 497 nm for 2,4,6-trimethylbenzenediazonium salt, respectively). The R-salt solution was prepared by dissolving 1.78 g of R-salt in 200 mL of water. Enough sodium bicarbonate and ca. 0.2 g of sodium hydroxide were then added, to give the solution at pH of approximately 9.5–10.0.

B. Dediazoniation of Benzene- and 2,4,6-Trimethylbenzenediazonium Tetrafluoroborate in Fluorosulfonic Acid. The measurements were carried out in the same apparatus as described above for HFIP except that the nitrogen balloon was replaced by a continuous stream of dry nitrogen. Before addition of the solvent, the reaction vessel was flushed with dry nitrogen for 30 min. About 100 mg of diazonium salt was added to 10 mL of FSO_3H, and the measurements were carried out in the same way as those in HFIP.

The R-salt solution was prepared by dissolving 1.78 g of R-salt in 200 mL of water containing ca. 1.5 g of sodium hydroxide, which was necessary to neutralize the strong acid and thus provide the needed basic medium for the coupling reaction. Aliquots from the reaction vessel were added to 20 mL of R-salt solution, and made up to 100 mL. The reproducibility of the measurements in fluorosulfonic acid was not as good as that in fluoro alcohols. This is probably due to the partial decomposition of the remaining diazonium salt during addition of the 0.2-mL aliquots to the strongly basic R-salt solution.
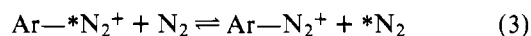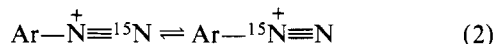
Analysis of Dediazoniation Products of 2,4,6-Trimethylbenzenediazonium Salt in HFIP. A solution of 200 mg of diazonium salt in 20 mL of HFIP was stirred overnight at 25 °C under nitrogen in the apparatus used for kinetic measurements. The separation and analysis of the products was carried out by GLC at 150 °C with a 2-m column (2-mm diameter) containing 10% Ucon LB 550 X on Chromosorb W (80/100), acid washed. The identity of the products was determined by comparison with authentic samples. No mesitylene was detected in the product mixture. Yields were approximated from the relative peak areas in the gas chromatogram and were found to be ca. 95% trimethylphenyl hexafluoroisopropyl ether and ca. 5% fluoromesitylene.

Dediazoniation of Labeled 2,4,6-Trimethylbenzene- and Benzenediazonium Tetrafluoroborate. The reactions in HFIP were performed in the same way as those in TFE described in the following paper[15] except that the rearrangement reaction was studied at atmospheric pressure under nitrogen at 25 °C in the apparatus used for kinetic measurements. The rearrangement reaction in fluorosulfonic acid was studied in the above apparatus under a continuous stream of dry nitrogen (150 mg of β-^{15}N diazonium salt in 5 mL of FSO_3H). After approximately 70% of dediazoniation the reaction was quenched by carefully pouring the solution into a vigorously stirred suspension of 2-naphthol (150 mg) in 150 mL of ice/water, all cooled in an ice bath behind a safety shield. As soon as the vigorous reaction subsided, 8 g of sodium hydroxide was added to the suspension (this amount was found to be sufficient to neutralize the acid and bring the solution to ca. pH 10), and stirring was continued until all the NaOH dissolved and the azo coupling was complete. The cold suspension was filtered and the azo dye was dried in vacuo (in the case of 1-phenylazo-2-naphthol the dye was extracted from the aqueous solution with benzene). The reduction of the azo dye was performed in the manner described in the following paper.[15] The steam distillate after reduction of 1-phenylazo-2-naphthol was acidified to pH 1 with 1 M HCl and extracted with ether in order to remove other organic solvolysis products, if present.

Measurement of Nitrogen Solubility in HFIP at 300 atm. The solubility of nitrogen in HFIP was determined in a simple bubbling-type apparatus.[23] The procedure was that employed for the measurement of gas solubility in TFE in the following paper.[15] Owing to the high volatility of HFIP, however, the buret system could not be maintained at the same temperature as the autoclave (25 °C), but had to be kept at 1.5 °C. Assuming that *the volume of HFIP does not change from 1.5 to 25 °C*, the volume of nitrogen at 25 °C was calculated from the ideal gas law. The average of ten measurements gave the solubility of nitrogen as (120.96 ± 2.21^a) mL/mL HFIP (a = 95% confidence limits), or 4.94 mol/L at 25 °C and 300 atm.

Results and Discussion

In the course of this work three processes were monitored during dediazoniation of arenediazonium salts in a given solvent: (1) dediazoniation rate, i.e., overall rate for the disappearance of diazonium ions; (2) N_α-N_β rearrangement (eq 2) of β-^{15}N labeled diazonium ions, and (3) exchange of the labeled diazonio group with external nitrogen at 300 atm (eq 3). The last two processes compete with the decomposition reaction.

$$Ar—\overset{+}{N}\equiv^{15}N \rightleftharpoons Ar—^{15}\overset{+}{N}\equiv N \qquad (2)$$

$$Ar—*N_2^+ + N_2 \rightleftharpoons Ar—N_2^+ + *N_2 \qquad (3)$$

These reactions have already been studied for some para-substituted benzenediazonium salts and it has been found that the substituent has very little effect on the extent of N_α-N_β rearrangement in water[13b,c] and in TFE.[6] The same applies to the amount of exchanged diazonio group in TFE under 300 atm of nitrogen. On the other hand, ortho substituents influence the reactions under study significantly (see following paper[15]). Indeed, the extent of rearrangement, as well as the extent of exchange for 2,4,6-trimethylbenzenediazonium ion in TFE, is about 2.6 times larger than the corresponding value for the unsubstituted compound.[6,15] This can be explained in terms of steric interference of the ortho methyl groups with the approach of solvent molecules. The much smaller nitrogen can reach the reactive site of the intermediate more easily, and as a consequence, more rearrangement and more exchange is observed relative to the normal solvolysis products.

We have tried to check this reasoning by investigating reaction systems where even more steric hindrance is expected. The final goal would be a system in which, for steric reasons, the reaction of the aryl cation and any nucleophile present would be slow enough to allow spectroscopic observation of the intermediate. One possible approach is to increase the size of the ortho substituents, for example, substitution of ethyl, isopropyl, and *tert*-butyl for methyl. However, the corresponding diazonium salts are not known—there are indications that, owing to steric crowding, the diazonio group is expelled soon after it is formed in a diazotization reaction.[24]

Since chloro and bromo substituents are larger than a methyl group we have studied the dediazoniation of 2,4,6-trichloro- and 2,4,6-tribromobenzenediazonium tetrafluoroborate. However, product analyses showed that 1,3,5-trichlorobenzene (ca. 35%) and 1,3,5-tribromobenzene (ca. 59%) were formed in these reactions. These products are typical for a radical mechanism. Therefore these diazonium salts are unsuitable for comparison with systems reacting heterolytically.

Thus, since attempts to increase steric crowding during dediazoniation by introducing larger ortho substituents have not proved successful, the other obvious approach was tried, that is, increasing the size of the reacting nucleophile, in our case the solvent. Hexafluoro-2-propanol was chosen because its other characteristics as a solvent are comparable to those of TFE. The nucleophilicity[27] of HFIP is somewhat lower and the ionizing power[27,28] somewhat higher than the corresponding values for TFE. For comparison, some measurements were also done in fluorosulfonic acid, which is known to be very nonnucleophilic,[27b] and an extremely good ionizing solvent.[29] The results, together with some pertinent data[6,15] obtained in TFE, are presented below.

Dediazoniation Rates. The first-order rate constants for the thermal decomposition of benzenediazonium tetrafluoroborate (**1**) and 2,4,6-trimethylbenzenediazonium tetrafluoroborate (**2**) are given in Table I.

The effect of the concentration of added tetra-*n*-butylammonium perchlorate in HFIP on the dediazoniation of salt **2** is shown in Table II. It is obvious that the dediazoniation rates

Table I. Dediazoniation of Diazonium Salts **1** and **2** at 1 atm N_2 in the Dark

Diazonium salt	Rxn conditions	$k_s \times 10^4$, s^{-1}
1	CF_3CH_2OH, 25 °C	0.807[a]
1	$(CF_3)_2CHOH$, 25 °C	0.792
1	FSO_3H, 25 °C	0.465
2	CF_3CH_2OH, 25 °C	1.65[b]
2	$(CF_3)_2CHOH$, 25 °C	1.93
2	$(CF_3)_2CHOH$, 15 °C	0.351
2	FSO_3H, 25 °C	2.37

[a] References 6 and 30. [b] References 15 and 30.

Table II. Dediazoniation of Diazonium Salt **2** in HFIP at 25 °C, 1 atm N_2, in the Dark in the Presence of $Bu_4N^+ClO_4^-$

$[Bu_4N^+ClO_4^-]$, mol/L	$k \times 10^4$ s^{-1}
0	1.93
0.1	1.88
0.3	1.81
0.5	1.76

vary very little in the solvents studied. For comparison, the solvolyses of alkyl halides or arenesulfonates are increased by a factor of $\sim 10^{16}$ by changing from TFE to FSO_3H. The low sensitivity of dediazoniation rates to changes in solvent has been known for a long time[6,7,31] and is probably due to the fact that both the ground state and the reaction transition state are ionic. The lack of covalent bonding of HFIP to carbon at the transition state for the dediazoniation of **2** can also be deduced from the large entropy of activation, $\Delta S^{\ddagger} = 18$ eu ($\Delta H^{\ddagger} = 117$ kJ mol^{-1} (28 kcal mol^{-1}), $\Delta G^{\ddagger} = 96$ kJ mol^{-1} (23 kcal mol^{-1})), which is comparable to the value for diazonium salt **1** in TFE[32] ($\Delta S^{\ddagger} = +16$ eu) and in water[33] ($\Delta S^{\ddagger} = +10.5$ eu).

As can be seen from Table II, no special salt effect was observed in the dediazoniation of salt **2** in HFIP; in fact, a slight linear decrease in the rate with increasing salt concentration occurs. This parallels the results obtained with potassium fluoride in TFE.[15] This does not necessarily exclude return from the reaction intermediate(s), since ion pair return was shown not to be a sufficient criterion for special salt effect.[34] The perchlorate ion does not seem to be a strong enough nucleophile to trap the cationic intermediate and thus prevent return to the starting diazonium ion.[35]

Dediazoniation Products. The products of the thermal dediazoniations of diazonium salt **2** in HFIP under nitrogen were analyzed and were found to consist of ca. 95% of 2,4,6-trimethylphenyl hexafluoroisopropyl ether and ca. 5% of fluoromesitylene. No mesitylene could be detected. This excludes the occurrence of aryl radicals in the dediazoniation and is in accordance with the assumption that the reaction proceeds heterolytically. It is interesting to compare the yield of fluoromesitylene in the dediazoniation of salt **2** in HFIP with the corresponding yields of fluorobenzene in the dediazoniation of salt **1** in TFE and in H_2O. Trifluoroethanolysis of salt **1** yields 34.5% fluorobenzene,[36] while its dediazoniation in 1 and 7 M H_2SO_4 only yields 1.2–1.4 and 0.8–1.0%, respectively.[7] These data support the assumption[10] that the Schiemann reaction product is formed from Ar^+/BF_4^- ion pairs. The yield of the fluorobenzene decreases in the sequence TFE–HFIP[37]– 1 M H_2SO_4–7 M H_2SO_4 and parallels the ion pairing tendency, which gets smaller as the ionizing power of the solvent rises.

Isotopic Rearrangement and Reaction with External N_2. The results of several experiments for the rearrangement (eq 2) and the exchange reaction with external nitrogen (eq 3) are given in Tables III and IV, respectively. Control experiments with

Table III. Extent of N_α-N_β Rearrangement of Diazonium Salts Accompanying 70% Dediazoiation at 25 °C, 1 atm N_2 in the Dark

Diazonium salt	Solvent	P, %[a]	k_r/k_s[b]	$10^5 k_r$, s^{-1} [c]
1	TFE[d]	7.96	0.072	0.581
1	HFIP	10.47	0.098	0.776
1	FSO_3H	3.66	0.032	0.149
2	TFE[d]	20.89	0.225	3.72
2	HFIP	36.97	0.559	10.8
2	FSO_3H	15.62	0.157	3.72

[a] Percent isotopic rearrangement adjusted to exactly 70% dediazoniation. [b] $k_r/k_s = \log (1 - 2p)/(2 \log A/A_0)$; $p = P/100$; A = absorbance of azo dye obtained after 70% dediazoniation; A_0 = original azo dye absorbance (ref 13b). [c] Calculated from the ratio k_r/k_s and the k_s values in Table I. [d] Data from ref 6, 15, and 30.

Table IV. Exchange of β-^{15}N Diazonium Ions with External Nitrogen (300 atm) at 25 °C in the Dark

Diazonium salt	Solvent	—N$\equiv$^{15}N— content of azo dye[a] (A)	% dediaz	—N$\equiv$^{15}N— content of azo dye[b] (B)
1	TFE[c]	99.20	70.00	96.74
1	HFIP	98.62	69.61	92.39
2	TFE[d]	98.62	70.00	92.29
2	HFIP	99.33	75.28	81.58

[a] Azo dye obtained before dediazoniation. [b] Azo dye obtained from the remaining diazonium salt after dediazoniation. [c] Reference 6. [d] Reference 15.

diazonium salt **2** in HFIP and FSO_3H have shown that no reaction with external nitrogen takes place at atmospheric pressure. Obviously the concentration of nitrogen in the solvent is too low to give observable amounts of products in this case. If a quantitative comparison between the amounts of exchange in different solvents is desired, the exact concentration of nitrogen in the solvents at the given pressure must be known. Therefore the solubility of nitrogen under 300 atm at 25 °C in HFIP was measured and was compared with the known[15] solubility in TFE. The values follow: HFIP, 4.94 mol N_2/L (120.96 mL/mL); TFE, 3.05 mol N_2/L (74.70 mL/mL).[15] It is interesting to compare the solubility of nitrogen in HFIP and TFE with that in water, which can be extrapolated to 300 atm from literature data[38] at 25 °C: H_2O, 0.16 mol N_2/L (3.95 mL/mL). The increase in solubility in going from water to fluorinated alcohols is striking. It is probably due to a large extent to much weaker TFE–TFE and HFIP–HFIP intermolecular interactions, compared to H_2O–H_2O. This, in turn, is due to significant intramolecular hydrogen bonding in the fluoro alcohols.[39] If the relative solubilities of other gases in H_2O and TFE parallel that of nitrogen, it is not surprising that no reaction with carbon monoxide was detected during dediazoniation in water,[13a] while 5.2% of the corresponding reaction product was found to be formed in the dediazoniation in TFE.[6] The CO concentration in water is too low for it to compete successfully with the even more nucleophilic water molecules for the reactive intermediate.

A summary of the solvent effects on the N_α-N_β rearrangement and on the exchange reaction with external nitrogen is given in Table V. The first interesting observation resulting from an inspection of Tables III–V is the fact that both diazonium salts in each solvent give significantly more rearranged product than product formed by exchange with external nitrogen. The concentration of external nitrogen in solution is several orders of magnitude higher than that of the labeled nitrogen formed in the dediazoniation, that is, roughly 3.3 M

Table V. Solvent Effects on the Rearrangement and the Exchange Reaction of Diazonium Salts

Solvent	Reaction[a]	Salt 2	Salt 1	2/1[b]
HFIP	Re	36.97	10.47	3.53
	Ex	16.50	6.26	2.64
	Re/Ex	2.24	1.67	
TFE	Re	20.89	7.96	2.62
	Ex	6.33	2.46	2.57
	Re/Ex	3.30	3.24	
FSO$_3$H	Re	15.62	3.33	4.69
HFIP[c]	Re	1.77	1.32	
TFE	Ex	1.61	1.57	

[a] Re = N_α-N_β rearrangement (*P* percent values from Table III). Ex = percent exchange with external nitrogen accompanying 70% dediazoniation, calculated from data in Table V: Ex = ((A − B)/(% dediaz)) × 70. [b] Ratio of corresponding values for diazonium salts **2** and **1**, respectively. [c] Ratio of the corresponding values in HFIP and TFE, respectively. The ratio for the exchange reaction was obtained by multiplying the observed ratio by 0.62 so that the difference in N$_2$ concentration in TFE and HFIP is compensated for.

in TFE and 5.4 M in HFIP as compared to 0.05 M starting concentration of labeled diazonium salt. The local concentration of external nitrogen around every diazonium salt molecule is thus at least as big as that of labeled nitrogen originating from the diazonium ion. The concentration of solvent molecules in TFE is 13.8 mol/L and that in HFIP is 9.6 mol/L. It follows that the ratios of solvent vs. nitrogen molecules in TFE and HFIP are 4.52 and 1.94, respectively. Assuming a statistical distribution of molecules, it is reasonable to conclude that in both TFE and HFIP the first solvation shell contains at least one external nitrogen molecule.[40] Therefore, if both the rearrangement and the exchange reaction were occurring through the same reaction intermediate, at least as much exchange would be expected as rearrangement. However, the amount of rearrangement is 1.67–3.30 times higher than the amount of exchange (Table V), implying that not only one, but two reaction intermediates are involved in the dediazoniation of salt **1** and **2** in TFE and HFIP. The intermediate for the rearrangement reaction must come earlier along the reaction coordinate than that for the exchange, i.e., during rearrangement the nitrogen is in relatively closer contact with the rest of the molecule. The rearrangement/exchange ratios are higher in TFE than in HFIP for two reasons: (1) the number of nitrogen molecules in the vicinity of each diazonium ion molecule is smaller in TFE than in HFIP and the N_α-N_β rearrangement can thus better compete with the exchange reaction in TFE than in HFIP, and (2) increasing ionizing power of the solvent (from TFE to HFIP) will decrease the number of tight molecule-ion pairs and disfavor the rearrangement reaction relative to exchange. The rearrangement/exchange ratio in HFIP for diazonium salt **2** (2.24) is higher than that for salt **1** (1.67). This is probably due to steric hindrance to solvation, which favors rearrangement.

The same applies to the ratio **2/1** (last column in Table V). Steric hindrance to solvation of 2,4,6-trimethylbenzenediazonium salt (**2**), as well as to the reaction with solvent molecules, makes the amount of isotopically rearranged and exchanged product by far the highest ever observed. This is especially true in HFIP, which has the bulkiest molecules among the solvents under study, and again more so for the rearrangement reaction than for the exchange. The fact that the rearrangement reaction is more favored by steric hindrance than the exchange reaction (compare **2/1** ratios in HFIP) also supports the conclusion that two intermediates are involved in the dediazoniation and that the intermediate for rearrangement has the N$_2$ part closer to the rest of the molecule. The increase in the amount of isotopic rearrangement ac-

companying dediazoniation from the first observed value[13b] for benzenediazonium ion in water (k_r/k_s = 0.014[13b] or 0.016[6,9]) to the highest observed value for salt **2** in HFIP (k_r/k_s = 0.559, Table III) is quite spectacular. The observation that steric hindrance to solvation, owing to bulky substituents and/or solvent molecules, increases the amount of rearranged and exchanged product, i.e., favors return from the reaction intermediates relative to their capture by the solvent, parallels results obtained in the solvolysis of vinyl halides where an increased selectivity was found with the increased bulk of β substituents.[42]

In addition to the steric effects caused by the bulkiness of salt and solvent, the ionizing power and the nucleophilicity of the solvent play a crucial role. Low nucleophilicity of the solvent greatly favors the reaction with nitrogen, e.g., the isotopic rearrangement of salt **1** is more than four times larger in TFE than in water.[6] High ionizing power should in principle favor rearrangement, too. However, if the rearrangement proceeds through tight molecule ion pairs, as can be assumed in our case, an increase in solvent ionizing power actually reduces the rearrangement observed. A good example is seen in the results obtained for salts **1** and **2** in fluorosulfonic acid (Tables III and V), where in spite of its extremely low nucleophilicity the reaction with nitrogen does not compete as well with the reaction with solvent molecules, as it does in TFE and HFIP. The effect is more pronounced with salt **1**, where there is no hindrance to solvation, and consequently the **2/1** ratio (Table V) is highest in fluorosulfonic acid from all the solvents studied. The ratios HFIP/TFE in Table V for salts **1** and **2** also reflect the complicated balance of the influence of solvent nucleophilicity and ionizing power on the rearrangement and exchange reactions. Owing to the lower nucleophilicity of HFIP the HFIP/TFE ratio is always larger than one. For salt **1** exchange is more accelerated than the rearrangement in going from TFE to HFIP, while for salt **2** the opposite occurs. The higher ionizing power of HFIP disfavors the formation of tight molecule-ion pairs and the rearrangement in salt **1** while, for steric reasons, this does not happen for salt **2**.

We emphasize that, in spite of the expected extreme reactivity of the aryl cation, it is still selective. Thus, steric effects can modify the generality of the reactivity-selectivity principle, as found also for vinylic systems by Rappoport.[42]

The dependence of the extent of isotopic rearrangement in dediazoniations on the solvent parallels earlier observations in solvolytic reactions; e.g., the oxygen-18 scrambling in the solvolysis of 2-octyl brosylate is seven times smaller in methanol than in acetic acid.[43] The observed results were also rationalized in terms of different solvent nucleophilicities.

All the results presented above support the view that at least two reaction intermediates occur in the dediazoniation of salts **1** and **2** in TFE and HFIP (eq 4).[44] One of them is probably a tight molecule-ion pair,[46] while the other is either a solvent-separated molecule-ion pair or the usually postulated "free" aryl cation.

$$\text{Ar}-\text{N}_2{}^+ \rightleftharpoons |\text{Ar}^+\text{N}_2| \rightleftharpoons \text{Ar}^+ + \text{N}_2 \rightarrow \text{products} \quad (4)$$

The intervention of ion pairs in solvolytic reactions was postulated and demonstrated a long time ago, first in rearrangements of allylic systems,[47] then in substrates that give rise to bridged cations,[48] and later in stable classical cations,[49] in unactivated RX systems,[43,50] in vinyl cations,[51] and recently even in primary RX systems.[52] Recently it was shown by CNDO/2 calculations of the system $CH_3F \cdot 11H_2O$ that intimate and solvent-separated ion pairs of fluoromethane in water exist as energy minima on the potential energy surface.[53] While it has already been suggested[6,14] that heterolytic dediazoniations may proceed through a molecule-ion pair of a phenyl cation and molecular nitrogen, this paper presents the first

evidence for such a claim. The large group of reactions known to involve ion pairs has been expanded to include those involving molecule–ion pairs in heterolytic dediazoniations.

As these conclusions are based essentially on solvent effects only, we wanted to verify them by a detailed evaluation of the kinetics of dediazoniations. In the following paper,[15] therefore, such evidence for the two intermediate mechanisms will be presented, and the nature of the intermediates will be discussed in more detail.

References and Notes

(1) Part 9: H. Loewenschuss, G. H. Wahl, Jr., and H. Zollinger, *Helv. Chim. Acta,* **59**, 1438 (1976).
(2) Presented in part at the 26th IUPAC Congress, Tokyo, Sept 4–10, 1977.
(3) On leave of absence from the Department of Chemistry, Faculty of Science, University of Zagreb, Zagreb, Yugoslavia.
(4) (a) H. G. Richey, Jr., and J. M. Richey, in "Carbonium Ions", Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1970, p 923; (b) J. Miller, "Aromatic Nucleophilic Substitution", Elsevier, Amsterdam, 1968, p 29 ff; (c) H. Zollinger, *Acc. Chem. Res.,* **6**, 335 (1973).
(5) A. Streitwieser, Jr., and A. Dafforn, *Tetrahedron Lett.,* 1435 (1976); L. R. Subramanian, M. Hanack, L. W. K. Chang, M. A. Imhoff, P. v. R. Schleyer, F. Effenberger, W. Kurtz, P. J. Stang, and T. E. Dueber, *J. Org. Chem.,* **41**, 4099 (1976); L. R. Subramanian and M. Hanack, *Chem. Ber.,* **105**, 1465 (1972).
(6) R. G. Bergstrom, R. G. M. Landells, G. H. Wahl, Jr., and H. Zollinger, *J. Am. Chem. Soc.,* **98**, 3301 (1976).
(7) C. G. Swain, J. E. Sheats, and K. G. Harbison, *J. Am. Chem. Soc.,* **97**, 783 (1975).
(8) C. G. Swain, J. E. Sheats, D. G. Gorenstein, and K. G. Harbison, *J. Am. Chem. Soc.,* **97**, 791 (1975).
(9) C. G. Swain, J. E. Sheats, and K. G. Harbison, *J. Am. Chem. Soc.,* **97**, 796 (1975).
(10) C. G. Swain and R. J. Rogers, *J. Am. Chem. Soc.,* **97**, 799 (1975).
(11) E. S. Lewis and J. E. Cooper, *J. Am. Chem. Soc.,* **84**, 3847 (1962).
(12) E. S. Lewis and J. M. Insole, *J. Am. Chem. Soc.,* **86**, 34 (1964).
(13) (a) E. S. Lewis and J. M. Insole, *J. Am. Chem. Soc.,* **86**, 32 (1964); (b) E. S. Lewis and R. E. Holliday, *ibid.,* **88**, 5043 (1966); (c) *ibid.,* **91**, 426 (1969).
(14) R. G. Bergstrom, G. H. Wahl, Jr., and H. Zollinger, *Tetrahedron Lett.,* 2975 (1974).
(15) Y. Hashida, R. G. M. Landells, G. E. Lewis, I. Szele, and H. Zollinger, *J. Am. Chem. Soc.,* following paper in this issue.
(16) J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.,* **3**, 1149 (1964).
(17) E. B. Starkey, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 225.
(18) G. A. Swan and P. Kelly, *J. Chem. Soc.,* 416 (1954).
(19) G. Balz and G. Schiemann, *Ber.,* **60**, 1186 (1927).
(20) G. Illuminati and G. Marino, *J. Am. Chem. Soc.,* **78**, 4975 (1956).
(21) HFIP and ether form a 1:1 complex distilling at 80–81 °C.[22]
(22) H.-J. Koetzsch, *Chem. Ber.,* **99**, 1143 (1966).
(23) R. Wiebe, V. L. Gaddy, and C. Heins, Jr., *Ind. Eng. Chem.,* **24**, 823 (1932).
(24) This conclusion was drawn from unsuccessful attempts[25] to diazotize *o*-ethyl- and *o*-isopropylaniline to give a stable product. The same pertains

for the *o-tert*-butyl compound.[26]
(25) Y. Hashida, private communication.
(26) J. Cortier, H. Gilon, and A. Halleux, *Bull. Soc. Chim. Belg.,* **64**, 667 (1955).
(27) (a) F. L. Schadt, P. v. R. Schleyer, and T. W. Bentley, *Tetrahedron Lett.,* 2335 (1974); (b) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *J. Am. Chem. Soc.,* **98**, 7667 (1976).
(28) D. E. Sunko and I. Szele, *Tetrahedron Lett.,* 3617 (1972).
(29) A. Diaz, I. Lazdins Reich, and S. Winstein, *J. Am. Chem. Soc.,* **91**, 5637 (1969).
(30) R. G. M. Landells, Ph.D. Thesis, University of Edinburgh, 1976.
(31) H. A. H. Pray, *J. Phys. Chem.,* **30**, 1477 (1926).
(32) Calculated from the data in ref 6.
(33) M. L. Crossley, R. H. Kienle, and C. H. Benbrook, *J. Am. Chem. Soc.,* **62**, 1400 (1940).
(34) D. J. Raber, J. M. Harris, and P. v. R. Schleyer in "Ions and Ion Pairs in Organic Reactions", Vol. 2, M. Szwarc, Ed., Wiley, New York, N.Y., 1974, p 247 ff.
(35) The much more nucleophilic thiocyanate ion causes a significant rate increase in the dediazoniation of salt **2** in TFE.[15]
(36) P. Burri, H. Loewenschuss, H. Zollinger, and G. K. Zwolinski, *Helv. Chim. Acta,* **57**, 395 (1974).
(37) The value for salt **2** in HFIP was compared with values for salt **1** in the other solvents. The corresponding yield of fluorobenzene in HFIP would be expected to be even smaller, because the reaction with the solvent for system **2** is probably sterically more hindered than that with BF₄⁻, which favors the formation of fluoromesitylene.
(38) W. C. Eichelberger, *Ind. Eng. Chem.,* **47**, 2223 (1955).
(39) K. F. Purcell and S. T. Wilson, *J. Mol. Spectrosc.,* **24**, 468 (1967); J. Murto and A. Kivinen, *Suom. Kemistil. B,* **40**, 14 (1967); K. F. Purcell, J. A. Stikeleather, and S. D. Brunk, *J. Mol. Spectrosc.,* **32**, 202 (1969).
(40) This conclusion is valid if there are at least six solvent + nitrogen molecules in the first solvation shell around the diazonium salt. This seems reasonable, judging from experimental data on solvation shells of other substrates.[41] We are aware of the fact that, owing to the large difference in polarity between N_2 and fluoro alcohols, the distribution of the solvent molecules in the first solvation shell around the ionic ground state and/or transition state may not be statistical and that specific solvation might occur.
(41) D. N. Glew and E. A. Moelwyn-Hughes, *Discuss. Faraday Soc.,* **15**, 150 (1953).
(42) Z. Rappoport, I. Schnabel, and P. Greenzaid, *J. Am. Chem. Soc.,* **98**, 7726 (1976); Z. Rappoport, *Acc. Chem. Res.,* **9**, 265 (1976).
(43) A. F. Diaz, I. Lazdins, and S. Winstein, *J. Am. Chem. Soc.,* **90**, 1904 (1968).
(44) A mechanism with two intermediates in the dediazoniation of *p*-toluenediazonium tetrafluoroborate in water was already proposed by Lewis et al.[12] but later rejected by the same author.[13c,45]
(45) E. S. Lewis, L. D. Hartung, and B. M. McKay, *J. Am. Chem. Soc.,* **91**, 419 (1969).
(46) In the whole discussion, the diazonium salt counterion BF₄⁻ has been neglected. It probably acts as the more or less solvated anionic counterpart of the diazonium ion, or of the aryl cation–nitrogen molecule ion pair. Since BF₄⁻ does not seem to be involved in the reactions discussed here, it was omitted in the discussion for the sake of simplicity.
(47) W. G. Young, S. Winstein, and H. L. Goering, *J. Am. Chem. Soc.,* **73**, 1958 (1951).
(48) S. Winstein and D. Trifan, *J. Am. Chem. Soc.,* **74**, 1154 (1952); S. Winstein and K. C. Schreiber, *ibid.,* **74**, 2165 (1952); S. Winstein and G. C. Robinson, *ibid.,* **80**, 169 (1958); E. F. Jenny and S. Winstein, *Helv. Chim. Acta,* **41**, 807 (1958).
(49) S. Winstein, R. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.,* No. **19**, 109 (1965), and references cited therein.
(50) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *J. Am. Chem. Soc.,* **87**, 3682 (1965); R. A. Sneen and J. W. Larsen, *ibid.,* **88**, 2593 (1966).
(51) Z. Rappoport and Y. Apeloig, *J. Am. Chem. Soc.,* **97**, 821 (1975); 836 (1975).
(52) A. Pross and H. Aronovitch, *J. Chem. Soc., Chem. Commun.,* 817 (1976).
(53) P. Cremaschi, A. Gamba, and M. Simonetta, *J. Chem. Soc., Perkin Trans. 2,* 162 (1977).