276. Dediazoniation of Arenediazonium Ions. Part XIX. Effect of Thiocyanate Ion in the Reactions of 2,4,6-Trimethylbenzenediazonium Tetrafluoroborate in 2,2,2-Trifluoroethanol[1][2]

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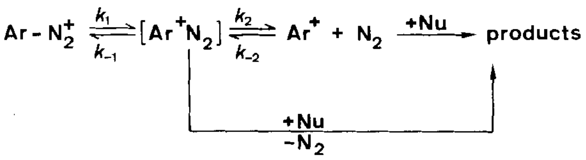
Summary

The dediazoniation of 2,4,6-trimethylbenzenediazonium tetrafluoroborate (**1**) in 2,2,2-trifluoroethanol (TFE) was studied in the presence of potassium thiocyanate. The effect of added salt on the dediazoniation rate, the N_α-N_β rearrangement *(Eqn. 2)*, the exchange of the ^{15}N-labelled diazo group with molecular nitrogen *(Eqn. 3)*, and the reaction products was determined. With 0.3 M KSCN a dediazoniation-rate increase of 16.5% was achieved, and the amounts of rearranged and exchanged product were reduced to 88% and 70%, respectively, of the values found in pure TFE. The dediazoniation products formed are ArF (**3**), $ArOCH_2CF_3$ (**4**), ArSCN (**5**), ArNCS (**6**) and traces of 5,7-dimethylindazole (**7**). All the data are in agreement with, and support the previously proposed mechanism *(Equ. 1)* of heterolytic dediazoniation of arenediazonium salts.

Introduction. - The dediazoniation of 2,4,6-trimethylbenzenediazonium tetrafluoroborate (**1**) in 2,2,2-trifluoroethanol (TFE) was shown to proceed *via* two intermediates, a tight aryl-cation/N_2-molecule pair and a free aryl cation *(Eqn. 1)* [2-4].



$$\begin{tikzcd} Ar{-}N_2^+ \arrow[r, shift left, "k_1"] & {[Ar^+N_2]} \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_2"] \arrow[rr, bend right, "{+Nu \; -N_2}"'] & Ar^+ + N_2 \arrow[l, shift left, "k_{-2}"] \arrow[r, "+Nu"] & \text{products} \end{tikzcd} \qquad (1)$$

Two reactions accompanying the dediazoniation, namely the N_α-N_β rearrangement of the two N-atoms in the diazo group *(Eqn. 2)*, and the exchange of the ^{15}N-labelled diazo group with external N_2-molecules *(Eqn. 3)*, were found to occur from the first and the second intermediate, respectively [2] [3]. This conclusion is

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also supported by a recent CNDO/2 calculation of the system benzenediazonium cation/water [5].

$$\mathrm{Ar}-\overset{+}{\mathrm{N}}\equiv{}^{15}\mathrm{N} \longrightarrow \mathrm{Ar}-\overset{15+}{\mathrm{N}}\equiv\mathrm{N} \qquad (2)$$

$$\mathrm{Ar}-\overset{+}{\mathrm{N}}\equiv{}^{15}\mathrm{N} + \mathrm{N}\equiv\mathrm{N} \longrightarrow \mathrm{Ar}-\overset{+}{\mathrm{N}}\equiv\mathrm{N} + {}^{15}\mathrm{N}\equiv\mathrm{N} \qquad (3)$$

We now report that all of these reactions are affected by added potassium thiocyanate. A product analysis after the dediazoniation of **1** in TFE in the absence and presence of KSCN is reported, and the implications of the observed salt effects on the reaction mechanism are discussed.

Results and discussion. - *Dediazoniation kinetics.* It is generally assumed that nucleophiles are not involved in the rate-determining step during the decomposition of arenediazonium salts. However, dediazoniation reactions are known in which the reaction rate is increased by added salts [3] [6] [7]. The dediazoniation rates[3]) of **1** in TFE as a function of the concentration of added KSCN are shown in *Table 1* and in the *Figure.* The rate is increased by up to 20% in the presence of 0.365 M KSCN in TFE. This rate increase is relatively small and is about the same as that observed [3] under 300 atm N_2 or Ar. From the rate equation [3] [4] for *reaction 1* it follows that, at high concentrations of added nucleophile, the observed rate, k_s, approaches the ionization rate, k_1, of the arenediazonium salt to the aryl-cation/N_2-molecule pair. Owing to the low solubility of KSCN in TFE, the concentration cannot be increased beyond 0.365 M KSCN. The addition of an equimolar quantity of 18-crown-6 to 0.3 M KSCN in TFE does not influence the dediazoniation rate, probably because the stabilization of the diazonium salt by the crown ether [8], abrogates rate enhancement by SCN^-.

The dediazoniation rate increase resulting from added SCN^- is most likely due to capture of one, or both intermediates, which reduces the back reaction. In a previous paper [3] the capture of both intermediates by SCN^- was postulated. If this is so, the addition of KSCN should decrease the amount of N_α-N_β *rearrangement 2* and exchange with external N_2 *(Eqn. 3)* in the dediazoniation of ^{15}N-labelled arenediazonium salts since both the rearranged and the exchanged products result from the back reaction.

Table 1. *Dediazoniation rate constants for 2,4,6-trimethylbenzenediazonium ion in the presence of KSCN and/or 18-crown-6 (TFE, 25°, 1 atm N_2)*

Added substance	$k_s \times 10^4$ [s^{-1}]	Added substance	$k_s \times 10^4$ [s^{-1}]
-	1.76 ± 0.05[a])	0.365 M KSCN	2.11 ± 0.02
0.1 M KSCN	1.95 ± 0.06	0.3 M 18-crown-6	1.62 ± 0.02
0.2 M KSCN	2.01[b])	0.3 M (KSCN + 18-crown-6)	2.05 ± 0.01
0.3 M KSCN	2.05 ± 0.02		

[a]) Standard deviation. [b]) Based on one measurement.

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[3]) Good first-order kinetics are observed for more than three half-lives.

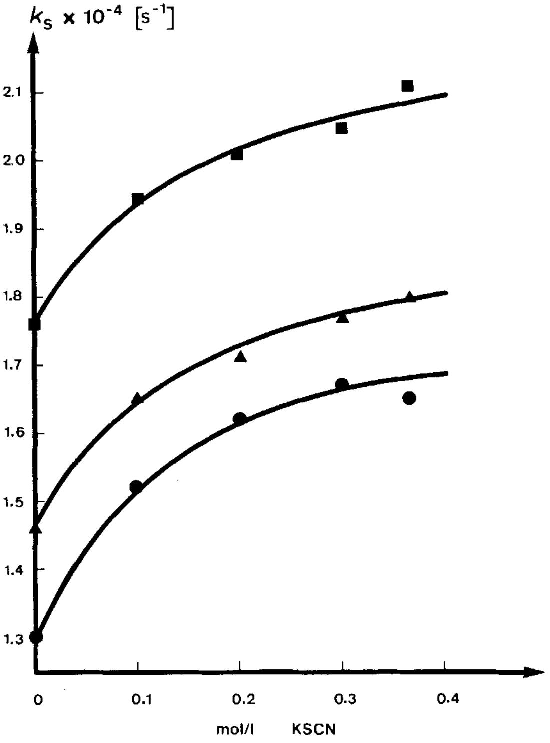

Figure. *Dediazoniation rate constants for 2,4,6-trimethylbenzenediazonium ion in TFE at 25° as a function of [KSCN]*
■ 1 atm N_2; ▲ 300 atm Ar [3]; ● 300 atm N_2 [3].

N_α-N_β Rearrangement and exchange of the diazo group with external N_2. The amount of N_α-N_β rearrangement and that of exchange with external N_2 for β-^{15}N labelled 2,4,6-trimethylbenzenediazonium salt in TFE at 70% dediazoniation *(Table 2)* was determined as described previously [2] [3].

As would be predicted on the basis of the proposed mechanism, the addition of KSCN to TFE leeds to a decrease in the yields of exchanged and rearranged product. Addition of 0.3 M KSCN reduces the amounts of the exchanged and rearranged product to 70% and 88%, respectively, of the values found in pure TFE. The effect is somewhat larger when an equimolar amount of 18-crown-6 is added to the KSCN-solution. The question can be asked why such a strong nucleophile as the SCN^- does not trap the intermediates more effectively, and does not completely prevent the formation of exchanged and rearranged products through the back reaction. The most plausible answer seems to be the extremely high reactivity and low selectivity⁴) of the aryl cation-like intermediates. This is also indicated by the fact that up to now aryl cations are the only reactive intermediates known to give products with molecular nitrogen in solution [2] [3] [10], without the intervention of organometallic or enzymatic catalysts.

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4) For the selectivity of phenyl cation in arylations see [9].

Table 2. *Extent of* N_α-N_β *rearrangement and of exchange with external* N_2 *at 70% dediazoniation for 2,4,6-trimethylbenzenediazonium-β-*N^{15} *ion (TFE, 25°, 300 atm* N_2*)*

Added substance	% Exchange	% Rearrangement
–	6.33 ± 0.60[a])[b])	19.36 ± 1.04[a])[b])
0.3 M KSCN	4.41 ± 0.37	17.03 ± 0.90
0.3 M (KSCN + 18-crown-6)	4.12 ± 1.07	15.81 ± 0.40

a) From [3]. b) Standard deviation.

It is interesting to compare the extent of N_α-N_β rearrangement and exchange with external N_2 of diazonium salt **1** in the presence of thiocyanate ion with the effect of chloride ions on the *cis, trans*-isomerization of 1,2-dianisyl-2-phenylvinyl halides and mesylates during solvolysis [11]. The solvolysis in acetic acid proceeds *via* ion pairs, through which the *cis, trans*-isomerization takes place, and free ions. While the isomerization is practically unaffected by added Cl^-, more than 90% of the free ions are captured by Cl^-. Thus vinyl cations in solution are obviously much more selective than phenyl cations, although their stabilities in the gas phase are reported to be comparable [12].

The N_α-N_β rearrangement of isotopically labelled diazonium salts in aqueous solution has been studied by *Lewis & Holliday* [13]. The extent of rearrangement in water was much smaller, ranging from 2-3%, and not suppressed by 3 M NaBr [13]. Considering the small absolute values for the rearrangement in H_2O relative to that in TFE, the smaller difference in nucleophilicity between water and Br^- than between TFE and SCN^-, and the obviously small selectivity of the phenyl cation intermediate, it is not surprising that no repression of the rearrangement could be observed even with 3 M NaBr in water [13].

There is no indication that the dediazoniation mechanism changes with the addition of KSCN to TFE. The thiocyanate anion does not form covalent arylazo compounds with arenediazonium salts [6], and the UV. spectrum of 2,4,6-trimethylbenzenediazonium tetrafluoroborate in TFE[5]) does not change on addition of KSCN, as opposed to the behaviour of *e.g.* the cyanide ion, where the formation of diazocyanides can be observed spectrophotometrically [14]. Also as shown in *Table 3*, the secondary deuterium isotope effect in the dediazoniation of [2,4,6-$^2H_3$]-

Table 3. *Solvolysis rate constants and secondary deuterium isotope effects in the dediazoniation of [2,4,6-*$^2H_3$*]-benzenediazonium tetrafluoroborate ([*$^2H_3$*]-**2**) in TFE and in 0.3 M KSCN in TFE* (25°, 1 atm N_2)

Reaction medium	Compound	$k_s \times 10^5$ [s^{-1}]	k_H/k_{D_3}[a])
TFE[b])	**2**	7.95 ± 0.14[c])	
	[$^2H_3$]-**2**	5.46 ± 0.05	1.47 ± 0.09
0.3 M KSCN	**2**	10.14 ± 0.43	
	[$^2H_3$]-**2**	6.88 ± 0.33	1.46 ± 0.03

a) The isotope effects are uncorrected. The deuterium content was found to be 97% D_3.
b) Data from [15].
c) Standard deviation.

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[5]) $\lambda_{max} = 285$ nm, shoulder at 325 nm.

benzenediazonium tetrafluoroborate ([$^2H_3$]-**2**) in 0.3 M KSCN in TFE is within experimental error the same as that in pure TFE. Secondary deuterium isotope effects of this magnitude have been interpreted as a further indication for the intermediacy of phenyl cations in dediazoniations of benzenediazonium salts [15] [16].

The reduction in the amount of exchanged product observed in 0.3 M KSCN in TFE relative to that in pure TFE could perhaps also be due to reduced solubility of molecular nitrogen in the KSCN-solution. The yield of the exchanged product is directly proportional to the concentration of N_2 in the reaction medium *(Eqn. 3), i.e.* the exchange reaction is first-order with respect to N_2. In order to check this possibility, the solubility of molecular nitrogen in 0.3 M KSCN in TFE was measured at 300 atm and 25°, and found to be (3.098 ± 0.127 mol/l)[6]), *i.e.* the same as that determined in pure TFE [3]. Therefore, the repression of the exchange reaction in 0.3 M KSCN must indeed be caused by the capture of the aryl cation intermediate by SCN^-.

The fact that the exchange reaction is affected by KSCN more strongly than the rearrangement reaction is in agreement with the former occurring later along the reaction coordinate than the latter, and is a further indication for the existence of two intermediates in the reaction under study.

Reaction products. The dediazoniation of **1** in TFE and in KSCN-solutions in TFE *(Table 4)* yields the products shown in the *Scheme*.

The products in pure TFE, **3** and **4**, are those expected for heterolytic dediazoniation and result from a reaction of the reactive intermediate(s) with the

Scheme

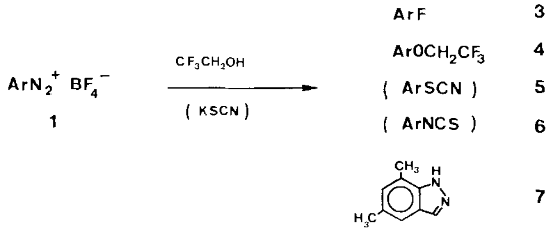

Table 4. *Reaction products after the dediazoniation of 2,4,6-trimethylbenzenediazonium tetrafluoroborate* (**1**) *in TFE, and in KSCN and (KSCN + 18-crown-6) solutions in TFE* (25°, 1 atm N_2)

Product[a])	Reaction medium			
	TFE	+ 0.1 M KSCN	+ 0.3 M KSCN	$+0.3\,\text{M}\left\{\begin{array}{l}\text{KSCN}\\ \text{18-crown-6}\end{array}\right.$
ArF (**3**)	30.92	22.07	17.86	16.83
$ArOCH_2CF_3$ (**4**)	69.08	64.14	58.09	57.75
ArSCN (**5**)	-	11.51	20.37	20.23
ArNCS (**6**)	-	2.28	3.68	5.19

[a]) Identified by comparison with authentic samples. Average of two runs in mol% (obtained from the relative peak areas, corrected by the response factors determined from mixtures of authentic samples of known composition). Standard deviations ≤ 0.60 (≤ 1.2 for the runs with crown ether).

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[6]) Confidence limits: 95%.

counter-ion and the solvent, respectively. Their ratio is comparable to that observed in the dediazoniation of benzenediazonium tetrafluoroborate (**2**) in TFE (34.5% C_6H_5F, 62.3% $C_6H_5OCH_2CF_3$) [17] indicating that in this case the product composition depends more on the reaction medium than on the structure of the substrate[7]).

When KSCN is added to TFE thiocyanate ions compete with the solvent molecules, resulting in lower yields of the solvolysis product and the reaction product with the counter-ion. With increasing concentration of KSCN the yield of ArF (**3**) is more strongly affected, than that of $ArOCH_2CF_3$ (**4**), and it may follow the tendency of ion pair formation in a given medium. Parallel to this, as expected, the yield of the thiocyanate and isothiocyanate products **5** and **6** increases, their relative ratio being about 5:1. The combined yield of **5** and **6** is in reasonably good agreement with the increase in the dediazoniation rates at the respective KSCN concentrations. 5,7-Dimethylindazole (**7**) which was found in trace amounts in the solvolysis products is obviously formed by intramolecular cyclization of the diazonium ion[8]). The dediazoniation of benzenediazonium tetrafluoroborate has previously been investigated in aqueous KSCN-solutions by *Lewis & Cooper* [6]. Much higher concentrations of KSCN (4-10 mol/l) were needed in water than in TFE to yield the same amount of thiocyanate and isothiocyanate products, and also to achieve the maximum dediazoniation rate increase of about 20% at highest concentration of KSCN. The relative reactivities of a common intermediate towards formation of a bond to sulfur, to nitrogen and to water were found to be about 6:2.8:1 [6], although the yields were not satisfactorily reproducible.

The fact that in dediazoniations the ratio of thiocyanate to isothiocyanate product is so low (*ca.* 5 in TFE, *ca.* 2 in H_2O) is additional support for a mechanism involving aryl cations. The reactivity of the ambident nucleophile SCN^- depends on the mechanism of substitution. In S_N2 reactions it is primarily the more polarizable, 'softer' [21] S-atom that attacks the electrophilic centre, and k_S/k_N values of 100-1000 are observed [22], while in S_N1-type reactions the more electronegative, 'harder' [21] N-atom successfully competes for the carbenium ion intermediate, and the k_S/k_N ratio is about 5 [23].

Conclusion. - In addition to the available evidence [2-4] for the mechanism of heterolytic dediazoniation shown in *Eqn. 1*, the new data, *i.e.* the effect of added KSCN salt on the dediazoniation kinetics, the *rearrangement 2* and the *exchange reaction 3*, respectively, and the reaction products, lend further support for the proposed mechanism.

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[7]) In less nucleophilic solvents of higher ionizing power such as 1,1,1,3,3,3-hexafluoro-2-propanol and sulfuric acid, the yield of fluoroarene is reduced sharply [2] [18], supporting the proposed [19] mechanism of its formation from $ArN_2^+BF_4^-$ ion pairs.

[8]) In $CHCl_3$ with an excess of $(CH_3)_4N^+AcO^-$ this is a convenient preparative method for the synthesis of indazoles [20]. See *Experimental Part*.

Experimental Part

Materials. - Solvents and starting materials were purified, and the 2,4,6-trimethylbenzenediazonium tetrafluoroborate (**1**), β-^{15}N-labelled **1** and 2-fluoro-1,3,5-trimethylbenzene (**3**) were synthesized as described [2] [3].

2,4,6-Trimethylphenyl 2,2,2-trifluoroethyl ether (**4**) was prepared by dediazoniation of **1** in TFE. The reaction mixture was distilled, and the product was isolated on a Kieselgel 60 (70-230 mesh) column with petroleum ether. - NMR. ($CDCl_3$): 2.25 (*s*, 9 H); 4.15 (*qa*, 2 H, J = 8 Hz); 6,80 (*s*, 2 H).

2,4,6-Trimethylphenylthiocyanate (**5**) was prepared by the procedure of *Bacon & Guy* [24], m.p. 72.5° ([24]: 71-72°).

2,4,6-Trimethylphenylisothiocyanate (**6**) was prepared by the procedure of *Eisenberg* [25], m.p. 60.9° ([25]: 64°).

5,7-Dimethylindazole (**7**) was prepared by the general procedure of *Huisgen & Nakaten* [20], m.p. 132-133° ([26]: 133-134°).

Benzenediazonium tetrafluoroborate (**2**) and [$^2H_3$]-**2** were prepared as described in [2] and [16] respectively. The deuterium content of [$^2H_3$]-**2** was found to be 97% $^2H_3$.

Product analysis. - A solution of 200 mg of **1** in 20 ml TFE was stirred overnight at 25° under N_2 in the apparatus used for kinetic measurements. The separation and analysis of the products was carried out by GC. at 60-230° with a 3 m column (2 mm diameter) containing 10% FFAP on chromosorb T. The identity of the products was determined by comparison with authentic samples. The yields were obtained from the relative peak areas, corrected by the response factors determined from mixtures of authentic samples of known composition.

The kinetic measurements, the dediazoniation of β-^{15}N-labelled **1** in an autoclave, the determination of the extent of rearrangement and exchange, and the measurement of gas solubility were carried out as before [2] [3].

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