

- [19] K. Rüfenacht, *Helv.* **55**, 1979 (1972).  
[20] B. Holmberg, *J. prakt. Chem.* [2] **84**, 634 (1911).  
[21] J. Wangel, *Arkiv Kemi* **7**, 431 (1951) [*Chem. Abstr.* **44**, 6818d (1950)].  
[22] M. Busch & M. Starke, *J. prakt. Chem.* [2] **93**, 49 (1916).  
[23] W. Massot, *Ber. deutsch. chem. Ges.* **27**, 1226 (1894).  
[24] H. J. Backer & W. Meyer, *Rec. Trav. chim. Pays-Bas* **45**, 82 (1926).  
[25] G. Opitz & M. Kleemann, *Liebigs Ann. Chem.* **665**, 114 (1963).  
[26] A. N. Nesmeyanov, N. K. Kochetkov & M. I. Rybinskaya, *Chem. Abstr.* **45**, 1585b (1951).  
[27] J. C. Martin, K. R. Barton, P. H. Gott & R. H. Meen, *J. org. Chemistry* **37**, 943 (1966).  
[28] G. T. Morgan & I. Ackerman, *J. chem. Soc.* **123**, 1308 (1923).  
[29] R. H. Wiley & P. E. Hexner, *Org. Synthesis, Coll. Vol. IV*, 315 (1963).  
[30] K. von Auwers & K. Bähr, *J. prakt. Chem.* [2] **116**, 65 (1927).  
[31] K. von Auwers & F. Niemeyer, *J. prakt. Chem.* [2] **110**, 153 (1925).  
[32] A. Michaelis & A. Lachwitz, *Ber. deutsch. Chem. Ges.* **43**, 2106 (1910).  
[33] E. Buchner & M. Fritsch, *Liebigs Ann. Chem.* **273**, 256, 265 (1893).  
[34] L. Knorr, *Liebigs Ann. Chem.* **279**, 188, 228 (1894).  
[35] Tsukasa Kuwaishi, *Pharm. Bull.* **4**, 497 (1956) [*Chem. Abstr.* **51**, 13853f (1957)].  
[36] D. T. Mowry, *J. Amer. chem. Soc.* **75**, 1909 (1953).  
[37] Ch. Grundmann, *Chem. Ber.* **81**, 1 (1948).  
[38] W. G. Overend & L. F. Wiggins, *J. chem. Soc.* **1947**, 239.  
[39] S. Gabriel & J. Colman, *Ber. deutsch. chem. Ges.* **32**, 395 (1899).  
[40] R. H. Mizsoni & P. Spoerri, *J. Amer. chem. Soc.* **73**, 1873 (1951).  
[41] J. Druey, Kd. Meier & K. Eichenberger, *Helv.* **37**, 121 (1954).  
[42] R. H. Mizsoni & P. Spoerri, *J. Amer. chem. Soc.* **76**, 2201 (1954).  
[43] J. C. Howard, G. Gever & P. H. L. Wei, *J. org. Chemistry* **28**, 868 (1963).

### 233. Dediazoniations of Arene Diazonium Ions in Homogeneous Solution. Part III: Heterolytic Arylations in 2,2,2-Trifluoroethanol – an $S_N1$ - or an $S_N2$ -Reaction?<sup>1)</sup>

by Peter Burri and Heinrich Zollinger

Technisch-Chemisches Laboratorium  
Eidgenössische Technische Hochschule, Zürich

(28. V. 73)

*Summary.* Benzenediazonium tetrafluoroborate in 2,2,2-trifluoroethanol decomposes to give fluorobenzene and phenyl 2,2,2-trifluoroethyl ether. In the presence of benzene, toluene, trifluoromethyl-benzene or anisole, the respective biphenyl derivatives are formed in addition to fluorobenzene and the ether. The distribution of the isomeric substituted biphenyls is consistent with an electrophilic substitution. No homolytic products (diazo tars, benzene) are formed. The reaction kinetics clearly show that ether formation and aryl-dediazoniations are of second-order type, *i.e.* that trifluoroethanol and the benzene derivatives mentioned above are rate-determining factors. It is shown that these results exclude the  $S_N1$ -mechanism which is usually assumed for heterolytic dediazoniations; free aryl cations are therefore not involved in these reactions. An  $S_N2$ -like mechanism seems to be the most likely, but one involving an encounter complex containing the dissociated benzenediazonium ion is also consistent with the experimental data.

<sup>1)</sup> Part II: See [1]. We have changed the general title of this series slightly by using the word 'dediazoniation'<sup>2)</sup> instead of 'decomposition'.

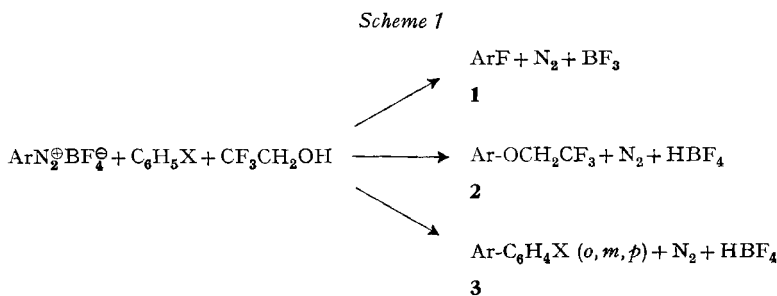
**1. Introduction.** - Dediazoniations<sup>2)</sup> of arene diazonium ions may be either homolytic or heterolytic. The classical *Gomberg-Bachmann* arylation is an example of a homolytic mechanism (see [3]); the formation of phenols in hot aqueous solution (hydroxy-dediazonation) is a heterolytic reaction. Since 1968, however, investigations by several research groups have revealed that small changes in solvent, additives, or substituents on the aryl nucleus may bring about a change from a hetero to a homolytic mechanism, or *vice versa*. In a recent paper [4] we discussed the factors fundamentally responsible for these changes.

We found that 2,2,2-trifluoroethanol (TFE) is a relatively good solvent for arene diazonium salts and that in TFE products resulting from a heterolytic decomposition of the diazonium salt are found exclusively. We decided therefore to investigate the mechanism of *heterolytic* arylations of benzene derivatives with arene diazonium ions in more detail. Since 1968, three research groups [1] [5-6] have found independently that under certain conditions aryl-dediazoniations do not follow the (homolytic) *Gomberg-Bachmann* pathway, but unexpected isomers of bi-phenyl derivatives are formed. This could be explained by a mechanism involving substitution of the arene substrate by means of an electrophilic reagent.

On the basis of the generally accepted view that heterolytic hydroxy-dediazonation is an  $S_N1$ -type substitution, it would be expected that the electrophilic reagent in these aryl-dediazoniations is an aryl cation. However, *Lewis et al.* [7] have presented evidence indicating that in reactions competing with hydroxy-dediazoniations the additional nucleophile may participate in the rate-determining step of the reaction.

As 2,2,2-trifluoroethanol is a much weaker nucleophile than water [8] and as arene diazonium salts and monosubstituted benzenes are soluble in TFE, we decided to investigate the kinetics of aryl-dediazoniations in this solvent.

**2. Reaction Products of Aryl-Dediazoniations in 2, 2, 2-Trifluoroethanol.** - Decomposition of benzenediazonium tetrafluoroborate in mixtures of benzene or monosubstituted benzenes ( $C_6H_5X$ ) in TFE yields three types of products (scheme 1),



<sup>2)</sup> We use the general nomenclature suggested by *Bunnett* [2] for substitution reactions of all types, giving first the name of the group (or atom) introduced, followed by de- and the name of the leaving group; *e.g.* the hydrolysis of methyl chloride is a hydroxy-dechlorination; and the nitration of benzene a nitro-deprotonation; nucleophilic and homolytic decompositions of arene diazonium ions are therefore dediazoniations, provided that  $N_2$  is released in one of the reaction steps.

namely fluorobenzene (**1**), phenyl 2,2,2-trifluoroethyl ether (**2**) and biphenyl or the biphenyl derivatives, substituted in the 2-, 3- or 4-position (**3**).

Reaction products were estimated by gas-liquid chromatography (GLC.). Reaction conditions and yields using anisole, toluene, benzene, trifluoromethyl-benzene or nitrobenzene are summarized in Tab. 1. As we are interested primarily in the formation of the biphenyl derivatives, the yields of fluorobenzene (**1**) and of phenyl 2,2,2-trifluoroethyl ether (**2**) were not determined in every case. Where all three types of product were evaluated the total yields were close to 100%<sup>3)</sup>; practically no by-products, in particular no diazo tars, were found.

The results in Tab. 1 demonstrate that the yield of the respective biphenyl derivatives (**3**) increases with the nucleophilicity of the aromatic substrate. Taking into account the fact that in some cases different amounts of aromatic substrates were present (*e.g.* for the comparison of C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> with C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>), one obtains the

Table 1. Reaction conditions and yields of aryl-dediazoniations of benzenediazonium tetrafluoroborate in 2,2,2-trifluoroethanol (TFE) in the presence of different aromatic substrates

C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> BF <sub>4</sub> mol	TFE ml	C <sub>6</sub> H <sub>5</sub> X		Temp. °C	Ar-F %	Ar-OCH <sub>2</sub> CF <sub>3</sub> %	Ar-C <sub>6</sub> H <sub>4</sub> X ( <i>o, m, p</i> ) %	Total yield %
		X	ml					
0.01	30	CH <sub>3</sub> O	30	50	–	–	33.2	–
0.01	20	CH <sub>3</sub> O	20	50	–	–	33.2	–
0.01	20	CH <sub>3</sub>	20	50	–	–	39.1	–
0.01	30	CH <sub>3</sub>	20	70	–	38.8	28.6	–
0.01 <sup>a)</sup>	30	CH <sub>3</sub>	20	74	–	–	28.6	–
0.005	40	CH <sub>3</sub>	10	30	24.8	52.2	27.6	(105)
0.01 <sup>b)</sup>	30	H	30	70	42.3 ± 0.7	27.0 ± 0.6	29.6 ± 0.1	100
0.01	20	CF <sub>3</sub>	20	50	–	–	5.0	–
0.01	30	CF <sub>3</sub>	20	74	–	35.0	6.4	–
0.005	40	CF <sub>3</sub>	11.5	30	34.2	62.0	6.2	(102)
0.01 <sup>b)</sup>	10	NO <sub>2</sub>	38	50	–	–	7.0 ± 1.0	–

<sup>a)</sup> In air (all other runs under N<sub>2</sub>).

<sup>b)</sup> Average of two runs.

Table 2. Distribution of isomeric biphenyl derivatives (**3**) formed in aryl-dediazoniations

C <sub>6</sub> H <sub>5</sub> X	Temp.	Yield of <b>3</b> (%)	<i>ortho</i> (%)	<i>meta</i> (%)	<i>para</i> (%)
OCH <sub>3</sub>	50°	33.2	50.3	20.5	29.2
CH <sub>3</sub>	30°	27.9	54.5	22.7	22.8
CF <sub>3</sub>	30°	6.2	29.2	65.6	5.2
NO <sub>2</sub>	50°	6.0	12.8	53.0	34.2

following sequence of reactivity: C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> < C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> < C<sub>6</sub>H<sub>6</sub> < C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub><sup>4)</sup>. If one assumes that the three reactions of scheme 1 are competitive, this is the sequence expected for an electrophilic arylation. In addition, the electrophilic character of

<sup>3)</sup> The fact that the sum of the yields, in two cases, is higher than 100%, is due to the difficult separation of the parent hydrocarbon from the fluorobenzene formed.

<sup>4)</sup> The apparent anomaly of anisole (C<sub>6</sub>H<sub>5</sub>OCH<sub>3</sub>) will be discussed later in this paper.

the arylation becomes obvious from the isomer ratios (Tab. 2), which indicate that a highly unselective electrophile must be involved<sup>5</sup>). The fact that the yield of the biphenyl product is not influenced by the presence of air or nitrogen, is compatible with a heterolytic process; this observation does not completely exclude a homolytic reaction, which is unlikely however. Finally, it should be mentioned that a thorough search was made to detect any benzene, *i.e.* the (typical homolytic) reaction product that might have been formed, but no trace of it was found.

We conclude therefore that all reactions shown in scheme 1 are heterolytic.

**3. Kinetics of Competitive Dediazoniations in Trifluoroethanol.** – The three competitive reactions of scheme 1, namely the fluoro-, the trifluoroethoxy- and the aryl-dediazoniatio of benzenediazonium tetrafluoroborate were studied in TFE at  $30.00 \pm 0.05^\circ$ . The decrease in diazonium ion concentration was followed by allowing aliquot samples of the reaction mixture to react with 2-naphthol-3,6-disulfonic acid; the concentration of the resulting dye was measured spectrophotometrically. All kinetic runs were carried out using 0.005 mol benzenediazonium tetrafluoroborate in a system which contained either a total of 0.65 moles of TFE + benzene derivatives, or, in the experiments without aromatic substrate, 0.65 moles of TFE.

Owing to the differences in densities of TFE and the benzene derivatives used, the composition of the reaction systems is given in mass units (mol) and not in concentration units ( $\text{mol l}^{-1}$ ). The mass units are proportional to mol fractions, as all systems contained a total of 0.655 mol. For the calculation of first-order and pseudo first-order rate constants, mass units or mol fractions can of course be used instead of concentrations; second-order rate constants, however, were calculated from pseudo first-order constants using the concentration of aromatic substrate, and therefore have the usual units.

For each run the products were determined by GLC. after completion of the reaction. The percentages of **1**, **2** and **3**, and the isomer ratios of the biphenyl derivatives are given in the Ex-

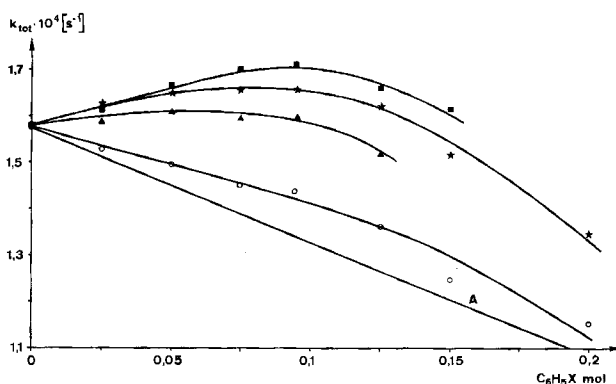


Fig. 1. Pseudo first-order rate constants of dediazoniations as a function of the aromatic substrate present in the system

● without aromatic substrate; ■  $C_6H_6$ ; ★  $C_6H_5CH_3$ ; ▲  $C_6H_5OCH_3$ ; ○  $C_6H_5CF_3$ ; A see text.

<sup>5</sup>) See the comparisons of the  $(o+p)/m$ -, the  $o/p$ - and  $m/p$ -ratios with those in nitrations and homolytic arylations, given in [9a]. The low yields with  $X = CF_3$  and  $NO_2$  (Table 2) do not allow any definite conclusions to be drawn.

perimental Part (Tab. 5-10). The total (overall) pseudo first-order rate constants  $k_{\text{tot}}$  for all systems are given in Fig. 1. For runs which were carried out in the presence of less than 0.1 mol of the aromatic substrate most of the constants are average values of two to four runs (see Experimental). The rate constants were calculated from 8 to 10 measurements made in each run by linear regression, correlation coefficients were always  $r > 0.999$ .

Fig. 1 also contains the straight line A; this represents the pseudo first-order rate constant of the heterolysis in TFE with an inert additive in place of the aromatic substrate<sup>6)</sup>.

The total pseudo first-order rate constants  $k_{\text{tot}}$  can be evaluated for the formation of the biphenyl derivatives only if, in all runs, the two other competitive reactions which yield fluorobenzene (**1**) and phenyl 2,2,2-trifluoroethyl ether (**2**) follow the same kinetic law. Therefore we compared statistically the ratio of yields **2:1** in all series of experiments [10]. Tab. 3 shows the mean values and standard deviations obtained.

An F-test demonstrated that there are no significant differences in the standard deviations ( $P = 0.95$ ). Therefore, a T-test was made in order to compare the mean values obtained with and without the various additives. For  $P = 0.90$  no significant

Table 3. *Ratio of yields of phenyl 2,2,2 trifluoroethyl ether (2) and fluorobenzene (1) in dediazoniations of benzenediazonium tetrafluoroborate in the presence of benzene derivatives*

Added benzene derivative	Ratio <b>2:1</b>		
	Number of experiments	Mean value	Standard deviation
No addition	3	1.72	0.14
C <sub>6</sub> H <sub>6</sub>	10	1.80	0.17
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	14	1.77	0.20
C <sub>6</sub> H <sub>5</sub> CF <sub>3</sub>	11	1.92	0.30
C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	6	2.08	0.17

difference was found between the series of experiments without additive and those with benzene, toluene and trifluoromethyl-benzene. The experiments with anisole, however, show a marked difference for the ratio **2:1** is significantly higher; the case of anisole is therefore excluded from the following discussion and will be commented upon at the end of this communication.

The isomer distributions of the kinetic runs carried out in the presence of toluene, trifluoromethyl-benzene and anisole were determined as described for the preparative experiments in section 2 of this communication. They do not differ significantly (Tab. 10, Experimental).

**4. Discussion of the Kinetic Results.** – In all cases the total rate of disappearance of diazonium salt was strictly first-order. The ratio of fluorobenzene (**1**) to phenyl trifluoroethyl ether (**2**) formed was, with the exception of reactions carried out in the presence of anisole, independent of the nature and amount of aromatic substrate added, and much the same as that found in the absence of an additive. Up to a ratio of 0.10 mol aromatic substrate to 0.55 mol TFE the rate was linearly dependent on the mol fraction of aromatic substrate.

<sup>6)</sup> Therefore this straight line reaches a rate constant  $k_{\text{tot}}$  of zero at 0.65 mol.

These results are consistent with a competition between three parallel reactions, namely:

a) a *Schiemann* type fluoro-dediazoni-ation of the benzenediazonium tetrafluoroborate ion pair, i.e. a first-order decomposition, the mechanistic details of which we have not investigated, but which follows the overall stoichiometry given in scheme 1.

b) a trifluoroethoxy-dediazoni-ation which exhibits pseudo first-order kinetics, but is overall *second-order*, namely first-order in diazonium salt and first-order in TFE (in excess). The sum of the pseudo first-order rate constants of this and of the *Schiemann* reaction is given graphically by the straight line A in Fig. 1.

c) analogous to b); an aryl-dediazoni-ation exhibiting pseudo first-order kinetics, i.e. overall second-order, namely first-order with respect to both the diazonium salt and the aromatic substrate  $C_6H_5X$  (in excess) for molar ratios of the substrate to TFE smaller than 0.1:0.55.

The first-order rate constant measured in the absence of an aromatic substrate  $k_{tot} = 1.587 \pm 0.13 \text{ s}^{-1}$  is the sum of the rates of the fluoro- and trifluoroethoxy-dediazoni-ation. With the help of the product ratio (Tab. 3) the *Schiemann* reaction rate constant,  $k_s = 0.583 \cdot 10^{-4} \text{ s}^{-1}$ , and the pseudo first-order rate constant for phenyl-trifluoroethyl ether formation  $k'_{TFE} = 1.004 \cdot 10^{-4} \text{ s}^{-1}$  are obtained. Using the value  $13.9 \text{ mol} \cdot \text{l}^{-1}$  for the concentration of TFE in pure TFE, the second-order rate constant  $k_{TFE} = 0.722 \cdot 10^{-5} \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  for the trifluoroethoxy-dediazoni-ation is obtained.

The pseudo first-order rate constant of the aryl-dediazoni-ation reaction ( $k'_x$ ) corresponds to the difference between the constant  $k_{tot}$  and the respective value  $k_A$  in Fig. 1. The rate constants  $k'_x$  are given in Fig. 2 and the respective second-order constants  $k_x = k'_x/[C_6H_5X]$  in Table 4.

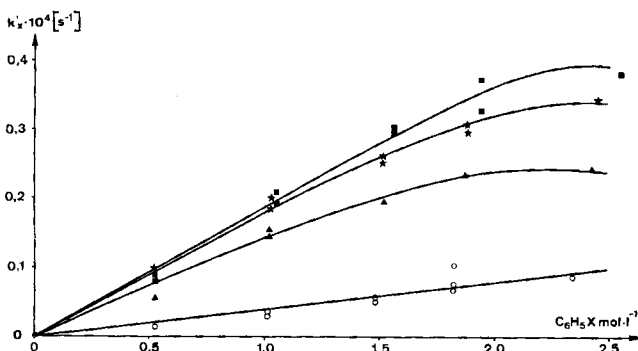


Fig. 2. Pseudo first-order rate constants  $k'_x$  of the aryl-dediazoni-ation of benzenediazonium tetrafluoroborate in  $C_6H_5X/TFE$  mixtures ( $C_6H_5X + TFE = 0.65 \text{ mol}$ )

Fig. 2 and the kinetic data for aryl-dediazoni-ations shown in Tab. 4 demonstrate that up to a concentration of 2M aromatic substrate  $C_6H_5X$ , the reaction is first-order with respect to  $C_6H_5X$  and, therefore, overall second-order.

The relatively large deviations from constancy of the second-order rate constants  $k_x$  for the reaction with trifluoromethyl-benzene are due to the fact that the aryl-dediazoni-ation accounts for only 2.6 to 7.4% of the total reaction at trifluoromethyl-

Table 4. Second-order rate constants  $k_x$  of the aryl-dediazoniations shown in Fig. 2

$C_6H_5X$		$k_x \cdot 10^{-4}$		$C_6H_5X$		$k_x \cdot 10^{-4}$
X	$mol \cdot l^{-1}$	$l \cdot mol^{-1}s^{-1}$		X	$mol \cdot l^{-1}$	$l \cdot mol^{-1}s^{-1}$
H	0.529	0.160	mean: 0.182	CF <sub>3</sub>	0.520	0.0230
	1.050	0.189			1.013	0.0315
	1.561	0.190			1.482	0.0361
	1.944	0.190			1.823	0.0457
	2.556	0.148			2.342	0.0371
	3.041	0.134			2.756	0.0417
CH <sub>3</sub>	0.525	0.188	mean: 0.177	OCH <sub>3</sub>	0.524	0.109
	1.031	0.188			1.028	0.144
	1.518	0.170			1.514	0.127
	1.880	0.162			1.872	0.125
	2.446	0.142			2.433	0.099
	2.885	0.103				
3.729	0.067					

benzene concentrations below 2M, the other reactions being formation of fluorobenzene (1) and phenyl trifluoroethyl ether (2).

The decrease in the rate constants at higher concentrations of aromatic substrates is, in our opinion, due to a solvent effect: 2M solutions of the aromatic substrates correspond to mol fractions of 0.15 or 15 (and more)-weight percentages of the system. TFE is a good solvent for diazonium salts; on the other hand, aromatic compounds such as those used in this investigation are extremely poor solvents for diazonium salts. It is therefore reasonable to assume that in solutions of these aromatic substrates in TFE, containing relatively large proportions of the aromatic compounds, the solvation sphere around the diazonium ion pairs contains less aromatic substrate than expected for a homogenous mixture of these compounds with TFE.

The kinetic data show clearly that the aromatic substrate enters into the rate-determining part of the aryl-dediazoniation. In addition, the rate constant  $k_{CF_3}$  is significantly smaller than  $k_H$  and  $k_{CH_3}$ , as expected for the deactivating trifluoromethyl substituent.

The constant  $k_{CH_3}$  is not larger than  $k_H$ . Here, owing to the fact that there are six potential sites of substitution in benzene, but only five in toluene, the rate constant of benzene has to be reduced by 1/6 (or that of the monosubstituted benzene derivatives has to be increased by 1/5) for comparison of relative reactivities. The expected sequence of reactivities  $C_6H_5CH_3 > C_6H_6 > C_6H_5CF_3$  is obtained.

However, the constant for the reaction with anisole, which one would expect to be significantly higher than in the case of toluene, is lower. This apparent anomaly can be explained by complex formation between anisole and the boron trifluoride formed in these reactions and/or a nucleophilic substitution of one fluoride ion of the tetrafluoroborate ion by anisole. The latter possibility is supported by the statistically significant difference in the product ratio of phenyl trifluoroethyl ether (2) to fluorobenzene (1) in the presence of anisole (Tab. 3): Tetrafluoroborate anions are removed from the ion pair by anisole and therefore the concentration of ion pairs

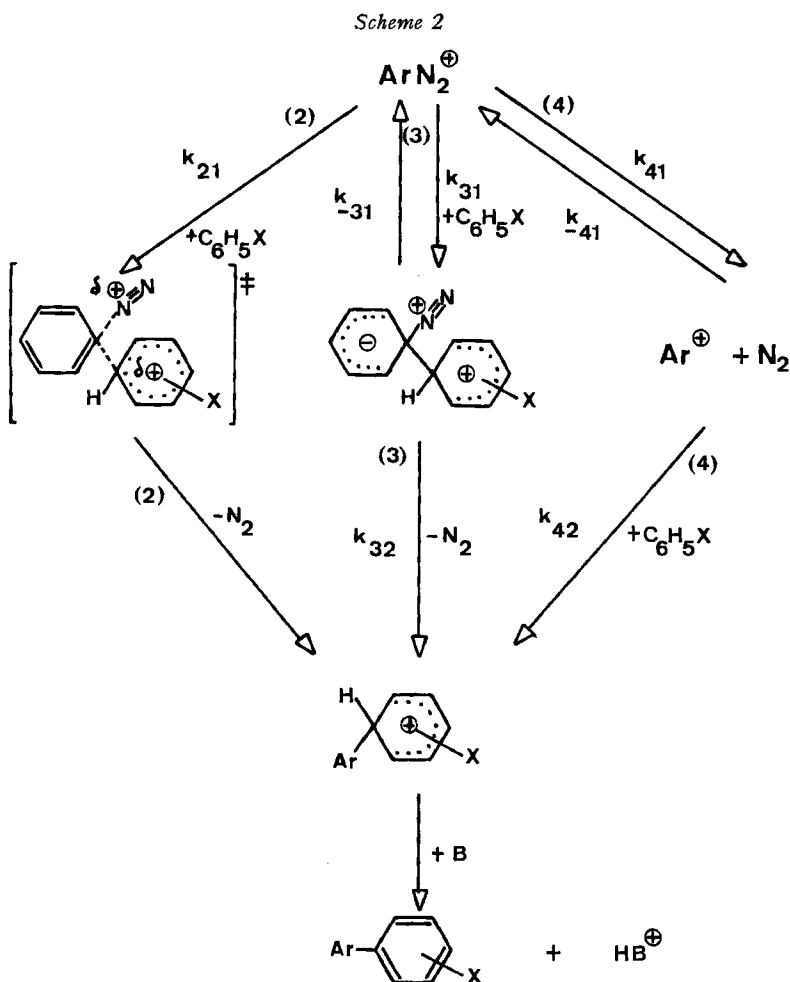
available for the *Schiemann* reaction is decreased due to the complex formation with anisole. The complex of anisole with boron trifluoride is known to be stable [11].

Our kinetic results are consistent with three mechanisms of dediazonation, namely with an  $S_N2$ -type mechanism (2), with the  $S_NAr$ - or addition-elimination mechanism (3) and with the  $S_N1$ -mechanism (4) (scheme 2).

$$\text{rate (2)} = k_{21} [\text{ArN}_2^\oplus] [\text{C}_6\text{H}_5\text{X}] \quad (1)^7$$

$$\text{rate (3)} = [\text{ArN}_2^\oplus] [\text{C}_6\text{H}_5\text{X}] \frac{k_{31} k_{32}}{k_{-31} + k_{32}} \quad (2)$$

$$\text{rate (4)} = [\text{ArN}_2^\oplus] \frac{k_{41} k_{42} [\text{C}_6\text{H}_5\text{X}]}{k_{-41} [\text{N}_2] + k_{42} [\text{C}_6\text{H}_5\text{X}]} \quad (3)$$



<sup>7)</sup>  $(\text{C}_6\text{H}_5\text{X})$  in  $\text{mol} \cdot \text{l}^{-1}$ . Equations (1)–(3) do not take into account the possibility that these three reactions are competitive processes with a common steady-state intermediate.



The last of these is usually assumed to apply to heterolytic dediazoniations. In our case, however, it is only compatible with the experimental data, if the aryl cation is a steady state intermediate and if, in the kinetic equation (3) for that mechanism, the inequality  $k_{-41} [N_2] \gg k_{42} [C_6H_5X]$  holds. This means that the aryl cations would react much faster with a nitrogen molecule than with the aromatic substrate. Such a result is, however, in contradiction to all previous experience regarding the reactivity of nitrogen molecules.

The  $S_N1$ -mechanism (4) is, therefore, in our opinion, extremely unlikely if the first step leads to the formation of a *free* nitrogen molecule. An alternative, however, is an  $S_N1$ -like mechanism in which the first step of the reaction pathway leads to an encounter complex between a phenyl cation and an 'activated' nitrogen molecule<sup>8)</sup>.

The  $S_N$ -Ar-mechanism (3) can be excluded with certainty as this reaction does not show the substituent effects typical for  $S_N$ -Ar-substitutions: -I, -M-substituents in the *p*-position of the benzenediazonium ion (e.g. *p*-NO<sub>2</sub>) do not increase either the yield or rate of this aryl-dediazoniatio[n] [9b] or of hydroxy-dediazoniatio[n]s in water [12].

Mechanism (2) corresponds almost exactly to the  $S_N2$ -mechanism occurring at  $sp^3$  carbon atoms. The transition state, given in square brackets, shows, however, that it differs from the  $S_N2$  transition state at an  $sp^3$  carbon, which has a trigonal bipyramid symmetry ('pentacoordinated' carbon); in our case there are only four ligands at the  $sp^2$ -carbon atom where substitution occurs. It seems appropriate therefore to call this mechanism  $S_N2$ -like. Until now such a mechanism has not been revealed in aromatic substitutions; nevertheless, in addition to the fact that it is not in conflict with any of the experimental evidence, we see no fundamental theoretical reasons against it. Arguments which seemed to support a rate-limiting dissociation of the carbon-nitrogen bond in substituted benzenediazonium ions apply, as discussed elsewhere [4], also to the  $S_N2$ -like mechanism (2): here also, a partial dissociation of that bond takes place.

We therefore come to the conclusion that aryl-dediazoniatio[n]s in TFE take place either by an  $S_N2$ -like mechanism, or by a mechanism involving a steady-state complex (probably an encounter complex) consisting of a dissociated benzenediazonium ion, *i.e.* an aryl cation and an N<sub>2</sub> particle which has to be in a more reactive form than that of ordinary nitrogen molecules. The present results definitely cannot be explained by the  $S_N1$ -mechanism with a rate-limiting dissociation of the carbon-nitrogen bond to form aryl cations and free nitrogen molecules, which is usually assumed for the reaction in water.

*Acknowledgments.* This investigation is part of a research project supported by the *Schweizerische Nationalfonds zur Förderung der Wissenschaftlichen Forschung* (projects No. 2.245.69 and 2.722.72). In addition we thank *Ciba-Geigy AG* and *Sandoz AG* for financial support.

<sup>8)</sup> Usually the term 'encounter complex' is used for a bimolecular reaction, e.g.  $A + B \rightarrow (A, B) \rightarrow A - B$ , where (A, B) symbolizes the encounter complex. On the basis of the concept of microscopic reversibility, the same complex is formed in the reverse reaction too. The term 'encounter complex' can be used therefore for a dissociation of a molecule or ion into two particles.

## 5. Experimental Part

5.1. *Instrumental Analysis*. UV.-VIS. spectra: *Beckman* Acta II and *Unicam* SP 800 A. IR. spectra *Beckman* IR 33 and IR 5. NMR. spectra: *Varian* A 60 and TL 60, reference TMS (tetramethylsilane). Mass spectra: *Hitachi-Perkin Elmer* RMU-2. GLC.: *Varian* Aerograph 1520 and 1420-1.

5.2. *Preparation of Materials*. Benzene (*purissimum*, thiophene-free) and toluene were obtained from *Merck*; fluorobenzene, trifluoromethyl-benzene and 2,2,2-trifluoroethanol from *Fluka*. The purity of these substances was checked by GLC., and they were used without further purification. Anisole was washed with 20% aqueous NaOH and water, dried ( $\text{CaCl}_2$ ) and distilled (153°). Biphenyl, and *p*-methylbiphenyl were recrystallized twice from aqueous ethanol. *o*-, *m*- and *p*-Trifluoromethylbiphenyl and *o*-methylbiphenyl were synthesized according to *Pettit & Tallow* [13], and *m*-methylbiphenyl was prepared by *Gomberg & Pernert's* method [14]. Methoxybiphenyls were obtained from the respective hydroxybiphenyls by the standard method [15] using dimethyl sulfate.

*Phenyl 2,2,2-trifluoroethyl ether (2)*. This was isolated from the aryl-dediazotiation; see below. B.p. 130–135°. NMR. ( $\text{CDCl}_3$ ): 4.35 (*g*, 2H,  $\text{CH}_2$ ,  $J = 8.5$  Hz); 6.75–7.55 (*m*, 5H). MS. (*m/e*, (% of base peak)): 176( $M^+ 100$ ), 107(55), 93(20), 77(67), 65(56), 51(26), 39(33).

*Benzenediazonium tetrafluoroborate*. A sample, prepared by *Roe's* method [16], was washed several times with cold fluoroboric acid, water, ethanol and ether. It was vacuum dried at room temperature and kept in a refrigerator in the dark.

5.3. *GLC. determinations*. For the reactions described in Section 2, a 4.8 meter column (2 mm diameter) with 10% silicon SE 30 on Aeropak 30 (70/80) was used at 200–220° with 30 ml/min He. The separation and analysis of the products of the kinetic experiments (Section 3) was carried out with aid of a 5 m column (2 mm diameter) containing 10% Apiezon L on Chromosorb W (80/100) at 150–200° with 30 ml/min He. For determination of yields the following internal standards were used: Benzene and toluene for fluorobenzene; toluene and resorcinol dimethyl ether for phenyl 2,2,2-trifluoroethyl ether, *p*-nitrobiphenyl, 2-naphthol and biphenyl; and resorcinol dimethyl ether for the derivatives of biphenyl. Yields were calculated by copying the peaks of the gas-chromatogram onto heavy paper and cutting out and weighing. Reproducibility was >2%. All yields in the Tables refer to percentages relative to the amount of diazonium salt used in the experiment.

5.4. *Experimental procedure for aryl-dediazotiations*. The diazonium salt was added to TFE or TFE/aromatic substrate mixtures with vigorous magnetic stirring in a three-neck vessel equipped with a reflux condenser (fitted with a  $\text{CaCl}_2$  tube). For amounts of diazonium salt and other materials see Tab. 1. Before addition of the salt, the liquid was degassed with dry nitrogen; during the reaction the system was kept under nitrogen. The vessel equipped with a thermostat, was kept in the dark (aluminium film). The end of the reaction was controlled by means of 2-naphthol. For GLC. analysis, first 20 ml ice-cold water were added, followed by some ether, and the ether fraction was then washed with 10% aqueous  $\text{Na}_2\text{CO}_3$  and dried with  $\text{Na}_2\text{SO}_4$ . Before addition of the standard, the ether fraction was evaporated down to one half of its initial volume. The aqueous layer was neutralized with HCl and re-extracted with ether.

5.5. *Kinetic Measurements* were carried out in a three-necked vessel (60 ml) normally used for polarographic measurements (*Metrohm AG*, Herisau). It was equipped with a reflux condenser, which was fitted with an inlet for nitrogen and a balloon, and the middle opening of the vessel was closed with a rubber septum, through which a syringe was inserted for taking samples. The required amount of liquid (TFE or TFE/aromatic substrate mixture, but always a total of 0.65 mol) was first added and degassed with nitrogen; afterwards the diazonium salt (0.005 mol) was added through the third opening of the vessel which was then tightly stoppered. The decrease in concentration of the diazonium salt was determined by the method of *Lewis* [17] by a diazo coupling reaction with 2-naphthol-3,6-disulfonic acid: At certain intervals, samples were taken with the syringe and an exact volume (micropipette) was added to a tenfold stoichiometric excess of the coupling component dissolved in aqueous  $\text{Na}_2\text{CO}_3$ -sol. The solution of the resulting azo compound was so diluted that the optimum range of sensitivity of the spectrophotometer could be used: Measurements were made at 490 nm,  $\epsilon = 2.2 \times 10^4$ . Pseudo first-order rate constants  $k_{\text{tot}}$  were calculated with a linear regression programme on a *Hewlett-Packard* 9100 A computer

GLC. product-ratio determinations of the kinetic runs were made without neutralisation etc. (see 5.4), so that columns had to be regenerated fairly often.

### 5.6. Kinetic Results.

Table 5. Reaction of 0.005 mol benzenediazonium tetrafluoroborate with 0.65 mol TFE (without aromatic substrate) at  $30.00 \pm 0.05^\circ$

Products (%)		$10^4 \cdot k_{\text{tot}}$ (s <sup>-1</sup> )	
1	2		
36.0	64.0	1.574	
39.1	60.9	1.604	mean: 1.587
35.5	64.5	1.582	

Table 6. Reaction of 0.005 mol benzenediazonium tetrafluoroborate in TFE/benzene mixtures  
T =  $30.00 \pm 0.05^\circ$ ; TFE + benzene = 0.65 mol

Benzene		Products (%)			$10^4 \cdot k_{\text{tot}}$ s <sup>-1</sup>	$10^4 \cdot k_{\text{A}}$ s <sup>-1</sup>	$10^4 \cdot k_{\text{x}}$ 1 · mol <sup>-1</sup> s <sup>-1</sup>
mol	mol · l <sup>-1</sup>	1	2	3			
0.025	0.529	35.0	54.7	10.3	1.607	1.525	0.155
0.025	0.529	31.5	57.3	11.2	1.612	1.525	0.164
0.050	1.050	30.0	52.2	17.8	1.655	1.464	0.182
0.050	1.050	28.6	52.4	19.0	1.670	1.464	0.196
0.075	1.561	24.2	51.2	24.6	1.701	1.403	0.191
0.075	1.561	24.7	50.3	25.0	1.700	1.403	0.190
0.094	1.944	26.5	45.5	28.0	1.735	1.357	0.194
0.094	1.944	26.4	46.0	27.6	1.680	1.357	0.186
0.125	2.556	23.2	43.5	33.3	1.660	1.281	0.148
0.150	3.041	26.4	43.0	30.6	1.627	1.220	0.134

Table 7. Reaction of 0.005 mol benzenediazonium tetrafluoroborate in TFE/toluene mixture  
T =  $30.00 \pm 0.05^\circ$ ; TFE + toluene = 0.65 mol

Toluene		Products (%)			$10^4 \cdot k_{\text{tot}}$ s <sup>-1</sup>	$10^4 \cdot k_{\text{A}}$ s <sup>-1</sup>	$10^4 \cdot k_{\text{x}}$ 1 · mol <sup>-1</sup> · s <sup>-1</sup>
mol	mol · l <sup>-1</sup>	1	2	3			
0.025	0.525	33.3	57.0	9.7	1.622	1.525	0.185
0.025	0.525	31.5	56.0	12.5	1.626	1.525	0.192
0.050	1.031	30.4	50.3	19.3	1.668	1.464	0.198
0.050	1.031	27.0	54.2	18.8	1.648	1.464	0.178
0.075	1.518	27.1	47.5	25.4	1.666	1.403	0.173
0.075	1.518	29.2	46.2	24.6	1.658	1.403	0.168
0.094	1.880	28.0	44.5	27.5	1.667	1.357	0.165
0.094	1.880	23.7	49.7	26.6	1.653	1.357	0.157
0.094	1.880	24.1	48.9	27.0	1.661	1.357	0.162
0.094	1.880	27.5	44.9	27.6	1.664	1.357	0.163
0.125	2.446	24.2	41.7	34.1	1.628	1.281	0.142
0.150	2.885	21.8	45.4	32.8	1.516	1.220	0.103
0.200	3.729	26.3	39.1	34.6	1.343	1.098	0.066
0.200	3.729	24.1	38.7	37.2	1.351	1.098	0.068

Table 8. Reaction of 0.005 mol benzenediazonium tetrafluoroborate in TFE/trifluoromethyl-benzene mixtures.  $T = 30.00 \pm 0.05^\circ$ ; TFE + trifluoromethyl-benzene = 0.65 mol

Trifluoromethyl-benzene		Products (%)			$10^4 \cdot k_{tot}$	$10^4 \cdot k_A$	$10^4 \cdot k_x$
mol	$\text{mol} \cdot \text{l}^{-1}$	1	2	3	$\text{s}^{-1}$	$\text{s}^{-1}$	$1 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$
0.025	0.520	37.1	60.2	2.7	1.523	1.525	(0)
0.025	0.520	32.2	65.3	2.5	1.537	1.525	0.0230
0.050	1.013	30.8	64.0	5.2	1.493	1.464	0.0286
0.050	1.013	29.6	64.4	6.0	1.499	1.464	0.0345
0.075	1.482	28.9	63.9	7.2	1.458	1.403	0.0371
0.075	1.482	33.2	59.3	7.5	1.455	1.403	0.0351
0.094	1.823	33.3	60.5	6.2	1.425	1.357	0.0373
0.094	1.823	31.8	62.2	6.0	1.462	1.357	0.0576
0.094	1.823	–	–	–	1.433	1.357	0.0422
0.125	2.342	–	–	–	1.368	1.281	0.071
0.150	2.756	34.0	57.8	8.2	1.172	1.220	(0)
0.150	2.756	26.2	63.7	10.1	1.335	1.220	0.0417
0.200	3.510	38.2	52.0	9.8	1.156	1.098	0.0165

Table 9. Reaction of 0.005 mol benzenediazonium tetrafluoroborate in TFE/anisole mixtures.  $T = 30.00 \pm 0.05^\circ$ ; TFE + anisole = 0.65 mol

Anisole		Products (%)			$10^4 \cdot k_{tot}$	$10^4 \cdot k_A$	$10^4 \cdot k_x$
mol	$\text{mol} \cdot \text{l}^{-1}$	1	2	3	$\text{s}^{-1}$	$\text{s}^{-1}$	$1 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$
0.025	0.524	29.8	60.4	9.8	1.582	1.525	0.109
0.050	1.028	30.3	54.0	15.7	1.618	1.464	0.150
0.050	1.028	25.3	57.7	17.0	1.607	1.464	0.139
0.075	1.514	24.6	54.0	21.4	1.595	1.403	0.127
0.094	1.872	23.7	50.9	25.4	1.592	1.357	0.125
0.125	2.433	22.2	45.7	32.1	1.523	1.281	0.099

Table 10. Distribution of isomeric biphenyl derivatives in kinetic runs (Tab. 7 to 9) of aryl-dediazoniations with toluene, trifluoromethyl-benzene, and anisole

Substrate	<i>ortho</i> (%)	<i>meta</i> (%)	<i>para</i> (%)
toluene	$51.2 \pm 3.3$	$23.5 \pm 1.5$	$25.3 \pm 2.0$
trifluoromethyl-benzene	$27.7 \pm 2.5$	$65.6 \pm 3.2$	$6.7 \pm 1.4$
anisole	$58.5 \pm 3.6$	$14.8 \pm 2.4$	$26.7 \pm 1.6$

## REFERENCES

- [1] B. Gloor, B. L. Kaul & H. Zollinger, *Helv.* 55, 1596 (1972).
- [2] J. F. Bunnett, *J. chem. Soc.* 1954, 4717.
- [3] C. Rüchardt, B. Freudenberg & E. Merz, *Chem. Soc. Special Publ.* 19, 154 (1965).
- [4] H. Zollinger, *Accounts chem. Res.* 6, in print (1973).
- [5] R. A. Abramovitch & F. F. Gadallah, *J. chem. Soc. B* 1968, 497; M. Kobayashi, H. Minato, E. Yamada & N. Kobori, *Bull. chem. Soc. Japan* 43, 215 (1970).

- [6] *B. L. Kaul & H. Zollinger*, *Helv.* **51**, 2132 (1968).
- [7] *E. S. Lewis & W. H. Hinds*, *J. Amer. chem. Soc.* **74**, 304 (1952); *E. S. Lewis & M. D. Johnson*, *ibid.* **82**, 5408 (1960); *E. S. Lewis, L. D. Hartung & B. M. Kay*, *ibid.* **91**, 419 (1969).
- [8] *L. M. Mukherjee & E. Grunwald*, *J. phys. Chemistry* **62**, 1311 (1958); *F. L. Scott*, *Chem. & Ind.* **1959**, 224; *N. S. Trahanovsky & M. P. Doyle*, *Tetrahedron Letters* **1968**, 2155; *V. J. Shiner, W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky & M. W. Rapp*, *J. Amer. chem. Soc.* **91**, 4838 (1969); *D. F. Evans, J. A. Nadas & M. A. Matesich*, *J. phys. Chemistry* **75**, 1708 (1971).
- [9] *P. Burri*, *Ph. D. Thesis* ETH Zürich 1973, a) Table 6; b) Chapter 4.2.
- [10] *A. Linder*, 'Statistische Methoden', Birkhäuser Basel 1960, p. 465; *K. Doerffel*, 'Statistik in der analytischen Chemie', VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1966, S. 123, 129.
- [11] *H. Boulus & J. A. Nieuwland*, *J. Amer. chem. Soc.* **53**, 3835 (1931); *A. V. Topchiev, S. V. Zavgorodnii & Y. M. Panshkin*, 'Boron Fluoride and its Compounds as Catalysts in Organic Chemistry', Pergamon London 1959, p. 71.
- [12] *D. Schulte-Frohlinde & H. Blume*, *Z. physikal. Chem.* **59**, 299 (1968).
- [13] *M. R. Pettit & J. C. Tallow*, *J. chem. Soc.* **1954**, 1072.
- [14] *M. Gomberg & J. C. Pernert*, *J. Amer. chem. Soc.* **48**, 1379 (1926).
- [15] 'Organikum, Organisch-chemisches Grundpraktikum', VEB Deutscher Verlag der Wissenschaften, Berlin 1968, p. 186.
- [16] *A. Roe*, *Organic Reactions*, Wiley New York 1952, vol. 5, p. 193.
- [17] *E. S. Lewis, J. L. Kinsey & R. R. Johnson*, *J. Amer. chem. Soc.* **78**, 4295 (1956).

## 234. Reduction of Tosylamino Acids and Related Compounds with Sodium in Liquid Ammonia; Stoichiometry and Products<sup>1)</sup>

by **Josef Rudinger** and **Helena Maassen van den Brink-Zimmermannová**

Institute of Molecular Biology and Biophysics, Swiss Federal Institute of Technology,  
CH-8049 Zürich

This paper is dedicated to Professor *František Šorm*, in respect and gratitude,  
on the occasion of his 60th birthday.

(29. V. 73)

**Summary.** Using an extraction procedure which permits determination of end-points, the reduction of a number of tosylamino acids, their derivatives, and model compounds with sodium in liquid ammonia has been investigated. When the molecule contains a single acidic group in addition to the tosylamino group (as in the case of the simple mono-tosylamino monocarboxylic acids) reduction proceeds with the consumption of 2 g-at. Na per tosyl group and the formation of toluene-4-sulphinic acid. If the number of acidic groups in the products is insufficient to accommodate the number of electrons consumed in the reduction, the reduction of ionisable tosylamino groups is incomplete unless an acid is added. If the number of acidic groups is higher, or excess acid is added, the sulphur-containing products include thiocresol and sulphite. This last reaction course is also observed whenever calcium is used in place of sodium. A partial interpretation of the results is offered.

<sup>1)</sup> Much of the work described in this paper was carried out at the Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Science, Prague, in 1962–1966 and formed part of a thesis submitted by the second author (*cf.* [1]). Some of the results were presented at the XIXth International Congress of Pure and Applied Chemistry, London 1963, and at the 6th European Peptide Symposium, Athens 1963 (*cf.* [2–3]).