three free radical species. The primary phenoxyl radical can be further oxidized $(1e,1H^+)$ to a very reactive quinone imine, which is attacked by water to give 4,5-dihydroxytryptamine. This is then further oxidized $(2e,2H^+)$ to tryptamine-4,5-dione. Since a peak corresponding to the reduction of radicals **2**, **3**, or **5** or to reduction of quinone imine **6** (Figure 6) cannot be observed in CVs of **1** at sweep rates as high as 5 V s^{-1}, the lifetimes of these intermediates must be significantly less than 10 ms. In a recent report[36] it was concluded that at low pH a minor route for the electrochemical oxidation of **1** proceeds via 5,7-DHT to **10** (Figure 7) and finally to **11**. We arrived at this conclusion because **11** was isolated as a minor product of oxidation of **1** and major product of oxidation of 5,7-DHT. However, this conclusion is clearly incorrect and the first dihydroxytryptamine to appear in the oxidation of **1** is 4,5-dihydroxytryptamine. The earlier study employed much higher concentrations of **1** than in this report and the appearance of **11** as a minor product is now thought to be due to chemical decomposition of one or possibly more oligomeric products.[48]

This study provides the first unequivocal evidence that 4,5-dihydroxytryptamine (**7**) and its oxidized form B are major oxidation products of **1**. In addition, evidence is presented for the formation of trihydroxytryptamines (**10** and **11**, Figure 7) along with several hydroxylated dimers (A, F/**9**, Figure 6, and E, Figure 7). While this study has been restricted to the oxidation of very low concentrations of **1** at low pH the information obtained might be of relevance to the role of this chemistry in mental illnesses. This is so because it has been known for some time that 5,6- and 5,7-DHT[15–21] and 4,5-DHT (**7**)[49,50] are powerful neurotoxins. An even more powerful neurotoxin is 5-hydroxytryptamine-4,7-dione (**11**).[36] Thus oxidation of **1** in very dilute solution at low potentials leads to formation of at least two neurotoxins, **7** and **11**. It seems very possible that other products identified in this study might also have neurotoxic properties. Thus, the suggestion that a faulty mechanism in the oxidative metabolism of **1** might lead to diseases such as schizophrenia and depression[7–10] seems to have significant justification based upon the oxidation chemistry of this neurotransmitter.

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Dediazoniation of Arenediazonium Ions. 24. Dual and Triple Substituent Parameter Evaluation of Competitive Heterolytic and Homolytic Dediazoniations of Diazonium Ions Complexed with 18-Crown-6 Ether[1]

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The dediazoniation of eight para-substituted benzenediazonium ions in 1,2-dichloroethane is a heterolytic reaction. The corresponding 18-crown-6 ether complexes of these diazonium ions, however, react also homolytically. The rate constants for heterolytic dediazoniation of the free diazonium ions (k_1), the rate constants for competitive heterolytic and homolytic dediazoniation of the crown ether complexed diazonium ions (k_3 and k_4, respectively), and the equilibrium constants for formation of the diazonium ion–crown ether complexes (K) were correlated with dual substituent parameter (DSP) treatments. A comparison has been made with the following substituent constants: Taft's original DSP substituent constants, Taft's triple substituent parameter constants (TSP) based on gas-phase reactions (1987), Charton's modified DSP constants, and the original (1968) and revised (1983) constants proposed by Swain. The reaction constants with the best (smallest) standard deviations and confidence limits and the highest regression coefficients are obtained with the substituent constants of Taft (both the original and the new gas-phase constants) and those of Charton. The heterolytic dediazoniation is characterized by clearly opposing signs of the field and resonance reaction constants (ρ_F and ρ_R), in contrast to the homolytic dediazoniations. The DSP treatments currently available do not provide meaningful results with homolytic dediazoniation.

The dediazoniation of meta- and para-substituted benzenediazonium ions is probably the best known example of the failure of the classical Hammett equation, i.e., of a single-parameter approach. Dickson and Eaborn[2] first pointed out that the rates of these dediazoniations could be described by a dual substituent parameter equation (DSP). This suggestion was taken up in 1973 by Taft and co-workers[3] and 2 years later by Swain et al.[4] Their treatment of experimental results demonstrates that dediazoniation is characterized by inverse signs of the resulting two reaction parameters for inductive (field) and

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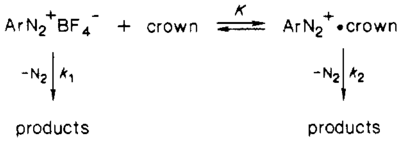
0022-3263/87/1952-2825$01.50/0

Scheme I



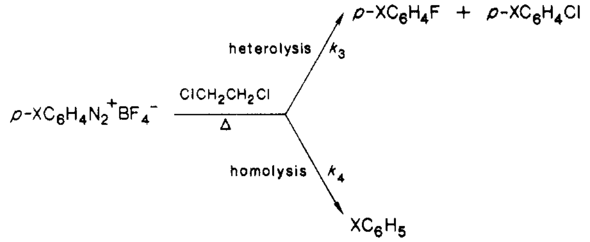
resonance effects, i.e., negative values of $\lambda \equiv \rho_R/\rho_F$ in Taft's nomenclature.

In the context of the recent discussion on the optimization of DSPs,[5,6] we think that a more detailed examination of dediazoniation might have some significance for DSP treatments in general because of the negative value of λ and because of the possibility of testing the application of DSPs for a system involving competitive reactions. This is the case for dediazoniation in the presence of crown ethers. In this study we have also included a triple substituent parameter (TSP) treatment (see below).

Bartsch and co-workers[7] observed the markedly enhanced thermal stability of solutions of *p*-*tert*-butylbenzenediazonium tetrafluoroborate complexed with 18-crown-6 ether relative to solutions of the uncomplexed diazonium ion. On the basis of Scheme I the complex equilibrium constant K and the rate constants k_1 and k_2 for dediazoniation of the free and the complexed diazonium ion, respectively, were determined by Kuokkanen and Virtanen.[8] The rate constant k_1 was found to be about 100 times larger than k_2.

We have previously investigated[9] in greater detail the rates of decomposition of diazonium ions complexed with three different crown ethers in 1,2-dichloroethane. For five out of seven meta- and para-substituted benzenediazonium ions a linear relationship was found between log k_1 and log k_2 with slopes close to unity (e.g. with 18-crown-6 ether: 0.92). We concluded that the thermal dediazoniation of complexed diazonium ions must therefore proceed by essentially the same heterolytic mechanism as that of the free diazonium ion. Two of the diazonium ions studied (*p*-Cl, *m*-CN), however, deviated markedly from the straight lines obtained for log k_1/log k_2 with the other compounds. With these strongly electronegative diazonium salts, the faster than expected rates k_2 indicate a change in mechanism caused by the addition of crown ether. That an additional *homolytic* mechanism of dediazoniation operates in the case of the *p*-chloro- and the *m*-cyanobenzenediazonium ion is clearly shown by the reaction products obtained: With all substituted benzenediazonium ions, the respective fluoroarenes XC_6H_4F (reaction of the aryl cations with the BF_4^- counter ion) and chloroarenes XC_6H_4Cl (as products of the reaction of aryl cations with the solvent 1,2-dichloroethane) were detected in large amounts and only 2% to 4% of the compounds in which the *diazonio* group was substituted by hydrogen, C_6H_5X (protodediazoniation, Scheme II). In the case of the *p*-chloro and *m*-cyano derivatives the protodediazoniation product was the major product (66.8% and 87.6%, respectively). Substitution of the diazonio group by hydrogen is a typical homolytic reaction (see ref 10).

Scheme II



In this paper we report the complex equilibrium constants K, the rate constants k_1 and k_2, and the yield of products C_6H_5X for eight para-substituted benzenediazonium ions at 50 °C in 1,2-dichloroethane in the presence of 18-crown-6. From the yields and k_2, the rate constants k_3 and k_4 for the competitive heterolytic and homolytic dediazoniation, respectively, were calculated under the assumption that they are competitive pseudo-first-order or first-order reactions (Scheme II).

We correlated the constants K, k_1, k_2, k_3, and k_4 by the classical Hammett $\rho\sigma$ relationship where applicable (equilibrium constants K) and all constants by the original DSP equation developed by Taft (1),[3,11] using Taft's substituent constants[3,12] and Charton's modified constants.[13] In some cases, comparisons were made with the corresponding equation of Swain and co-workers in its original[4] and revised[5] versions.

Furthermore, we have included a triple substituent parameter (TSP) treatment (2) that is based on the more recent investigations of Taft et al.[15,16] on substituent effects in gas-phase reactions. Taft has shown that there are two further kinds of primary substituent effects, namely, the electronegativity and the polarizability, in addition to the well-known field (or inductive) and resonance (mesomeric) effects. Following the evaluation by Taft et al.,[15,16] this extended treatment can also be used for reactions in solution. The electronegativity effect can be neglected in the type of reactions that we report here (for details see Taft and Topsom[16]). We therefore applied eq 2 to our data. The index α refers to the polarizability. As discussed by Taft and Topsom,[16] the resonance effect for substituted cations (as is the case for our reactions) is zero for +R substituents.

$$\log (k_{\mathrm{X}}/k_{\mathrm{H}})_{\mathrm{p}} = \sigma_{\mathrm{F}}\rho_{\mathrm{F}} + \sigma_{\mathrm{R}}^{+}\rho_{\mathrm{R}} + i \qquad (1)$$[17]

$$\log (k_{\mathrm{X}}/k_{\mathrm{H}})_{\mathrm{p}} = \sigma_{\alpha}\rho_{\alpha} + \sigma_{\mathrm{F}}\rho_{\mathrm{F}} + \sigma_{\mathrm{R}}\rho_{\mathrm{R}} + i \qquad (2)$$

In addition to specific mechanistic interests in diazonium ion chemistry, our investigation offers possibilities of more general interest, namely, (a) to compare correlation of various forms of multiparameter treatments for reactions in which the reaction constants are of opposite sign and (b) to study the applicability of DSP and TSP to a ho-

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(17) We add in eq 1 and 2 i, sometimes called "intercept" constant.[13] It is numerically equivalent to the difference between the calculated and experimental values for log k of the unsubstituted benzene derivative (X = H).

Table I. Thermal Dediazoniation Products[a] of Para-Substituted Benzenediazonium Tetrafluoroborates in 1,2-Dichloroethene at 50 °C with and without Added 18-Crown-6

substit	crown ether	FC_6H_4X	ClC_6H_4X	C_6H_5X
H[b]		48.6	51.4	
	18-C-6	30.4	65.0	4.6
$COCH_3$		58.4 (± 2.1)	41.6 (± 2.1)	
	18-C-6	40.3 (± 1.1)	26.0 (± 0.7)	33.7 (± 0.4)
CN		89.2 (± 0.3)	10.8 (± 0.3)	
	18-C-6	13.3 (± 0.3)	19.2 (± 0.9)	67.5 (± 1.2)
CH_3		33.8 (± 1.2)	64.7 (± 1.15)	1.5 (± 0.05)
	18-C-6	33.3 (± 0.4)	56.2 (± 0.8)	10.5 (± 0.4)
Cl[b]		44.1	49.2	6.7
	18-C-6	2.1	4.3	93.6
Br		43.4 (± 0.4)	56.6 (± 0.4)	
	18-C-6	6.6 (± 0.3)	11.1 (± 0.5)	82.3 (± 0.8)
I		41.4 (± 0.5)	58.6 (± 0.5)	
	18-C-6	32.5 (± 0.1)	36.6 (± 0.2)	30.9 (± 0.3)
t-Bu		30.4 (± 0.9)	69.4 (± 0.9)	
	18-C-6	35.8 (± 0.6)	55.3 (± 0.4)	8.9 (± 0.2)

[a] Products analyzed after 3 to 5 reaction half-lives. Product composition shown in the table was obtained by extrapolation to 100% reaction. Average and experimental error from two reactions are given. [b] The product composition was obtained by extrapolation to 100% reaction from ref 9.

molytic reaction that is competitive with a heterolytic reaction for the same series of substituted benzene derivatives.

Experimental Section

The analysis of products in the thermolysis of arenediazonium salts were performed on a Shimadzu GC-4CPF gas chromatograph using a capillary column (25 m × 0.25 mm) of methyl silicone (FS-WCOT Silicone OV-1). The concentrations used were 0.004 or 0.01 M of arenediazonium tetrafluoroborates and 0.03 M of 18-crown-6. Results are given in Table I.

Kinetic measurements were performed in 1,2-dichloroethane at 50 °C in the same manner as before,[9] i.e., in ratios of [18-crown-6]/[arenediazonium ion] of ca. 2.0, 3.0, and 6.0. Rates were measured in two independent experiments, resulting in values of k_{obs} that differed from one another by <4%. From k_{obs} and k_1 the rate constants k_2 and the equilibrium constants K were determined graphically by using eq 3.[8]

$$\frac{1}{k_k - k_{obs}} = \frac{1}{(k_1 - k_2)K} \frac{1}{[\text{18-crown-6}]} + \frac{1}{k_1 - k_2} \qquad (3)$$

The yield ratio of $[C_6H_5X]$/[total yield] corresponds, at least roughly, to the percentage of homolysis of the total reaction. Values of k_4 were calculated by using eq 4. If heterolysis and

$$k_4 = k_2[C_6H_5X]\% \times \frac{1}{100} \qquad (4)$$

homolysis are both first-order reactions, values of k_3 correspond to $k_3 = k_2 - k_4$. Error limits for k_3 and k_4 were estimated on the basis of the error limits of $[C_6H_5X]\%$.

Results

The equilibrium constants for complex formation and the rate constants k_1, k_2, k_3, and k_4 (see Schemes I and II) are summarized in Table II.

Our results for the influence of substituents on the complex equilibrium constant K and the rate constant k_1 are in agreement with values obtained previously for the complexation of arenediazonium ions with 18-crown-6.[8,9,18]

Application of the Hammett equation to the constants K using σ values as reported by Ritchie and Sager[19] gave for para-substituted derivatives (including X = H) $\rho = 1.02$ ($\pm$ 0.12), $n = 8$, $r^2 = 0.929$. If we include meta-substituted compounds from ref 9 (m-CH_3, m_2-CH_3O, m-$COCH_3$, m-CN), the result is $\rho = 1.06$ ($\pm$ 0.08), $n = 12$, $r^2 = 0.945$.

The equilibrium constants K and all four rate constants were first correlated by Taft's DSP equation (1) by using σ_F and σ_R^+ values reported by Ehrenson, Brownlee, and Taft[3,12] (EBT) and by Charton[13] (Ch). The results are summarized in Table III. The constants k_1 were also correlated with Swain's substituent constants in the original (1968)[14] and in the revised (1983)[5] versions, as well as by Taft's TSP substituent constants used for gas-phase reactions (1987).[16] These results will be considered in the Discussion section of this paper.

Discussion

The Hammett ρ values obtained from the complexation equilibrium constant with or without meta-substituted compounds are not significantly different. This result is in agreement with those of previous investigations.[8,9,18] A relatively small reaction constant is expected for this type of weak noncovalent interaction as present in complexes of diazonium ions with crown ethers. The ρ value is comparable in magnitude to the reaction constant found for complexation equilibria of 18-crown-6 with substituted phenols[20] ($\rho = 1.30$).

The ρ value is much lower, however, than those obtained for reactions of various nucleophiles forming a covalent bond to the β-N atom of arenediazonium ions.[21,22] Equilibrium data are available in the literature[22] for the addition of hydroxyl, cyanide, and azide ions. They give ρ constants of 6.58 (2 OH^-), 3.53 (CN^-) and 4.7 (N_3^-), respectively.

The DSP treatment of the equilibrium of arenediazonium ions with hydroxyl ions gives $\rho_F = 6.57$ and $\rho_R = 5.34$.[3] As this is actually an "overall-equilibrium" of two consecutive equilibria,[23] the two reaction constants ρ_R and ρ_R need to be divided by 2. Even so they are significantly larger than those for complex formation with 18-crown-6. Therefore they allow the conclusion that field *and* resonance effects are less effective in these crown ether complexes. Their relative weights ($\lambda = 0.55$), however, are smaller than those of covalent bond formation with hydroxyl ions ($\lambda = 0.81$). The difference of these two λ values cannot in our opinion be interpreted as the two equilibrium systems were measured in very different solvents (1,2-dichloroethane and water, respectively).

Before discussing ρ_F and ρ_R of the rate constants listed in Table III we will compare the standard deviations (parentheses), 95% confidence limits (brackets), and regression coefficients using substituent constants as originally suggested by Taft's group and as modified by Charton (EBT and Ch columns, respectively, in Table III). The results with Swain's old and new substituent constants for the rate constants k_1 are given in Table IV together with the corresponding evaluation of Kuokkanen and Virtanen.[8]

The comparison of standard deviations, confidence limits, intercept constants i, and correlation coefficients r^2 obtained with the EBT and Ch sets of substituent constants (Table III) shows (a) that the intercept constants

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Table II. Equilibrium and Rate Constants of Para-Substituted Tetrafluoroborates and Complex Formation Constants (*K*) in 1,2-Dichloroethane at 50 °C

substit	10^4K, L mol^{-1}	10^4k_1, s^{-1}	10^6k_2, s^{-1}	10^5k_3, s^{-1}	10^7k_4, s^{-1}
H	4.69[a]	13.1 (± 0.2)[a]	18.0[a]	1.72	8.28
$COCH_3$	11.2[b]	1.98[b]	3.0[b]	0.199 (± 0.001)	10.1 (± 0.1)
CN	16.3	0.119 (± 0.002)	0.80	0.026 (± 0.001)	5.40 (± 0.1)
CH_3	2.47[a]	1.44 (± 0.04)[a]	2.2[a]	0.197 (± 0.0009)	2.31 (± 0.09)
Cl	7.72[a]	0.0235 (± 0.0005)[a]	0.23[a]	0.0015	2.15
Br	8.80	0.0492 (± 0.0003)	0.13	0.0023 (± 0.0001)	1.07 (± 0.01)
I	7.66	0.210 (± 0.002)	0.75	0.0518 (± 0.0004)	2.32 (± 0.04)
t-Bu	1.92[b]	2.28[b]	3.0[b]	0.273 (± 0.0006)	2.67 (± 0.06)

[a] From ref 9. [b] From ref 8.

Table III. Dual Substituent Parameter Evaluation of Equilibrium and Rate Constants of Dediazoniations of Para-Substituted Benzenediazonium Ions in the Presence of 18-Crown-6 Ether[a]

	ρ_F		ρ_R		$\lambda = \rho_R/\rho_F$		i		r^2	
	EBT	Ch	EBT	Ch	EBT	Ch	EBT	Ch	EBT	Ch
K	1.18 (± 0.16) [± 0.42]	1.13 (± 0.15) [± 0.38]	0.65 (± 0.20) [± 0.48]	1.10 (± 0.31) [± 0.79]	0.55	0.97	−0.110	−0.094	0.929	0.937
k_1	−3.52 (± 0.36) [± 0.92]	−3.39 (± 0.39) [± 1.01]	2.26 (± 0.42) [± 1.07]	3.88 (± 0.82) [± 2.11]	−0.64	−1.14	−0.204	−0.171	0.961	0.949
k_2	−2.31 (± 0.40) [± 1.04]	−2.24 (± 0.35) [± 0.90]	1.88 (± 0.47) [± 1.20]	3.34 (± 0.73) [± 1.88]	−0.81	−1.49	−0.289	−0.244	0.905	0.923
k_3	−3.62 (± 0.64) [± 1.64]	−3.52 (± 0.60) [± 1.54]	2.75 (± 0.74) [± 1.90]	4.77 (± 1.30) [± 3.23]	−0.76	−1.36	−0.162	−0.107	0.900	0.904
k_4	−0.32 (± 0.25) [± 0.64]	−0.33 (± 0.23) [± 0.60]	1.48 (± 0.29) [±0.74]	2.57 (± 0.49) [± 1.25]	−4.63	−7.79	−0.114	−0.078	0.848	0.854

[a] Solvent: 1,2-dichloroethane. Standard deviations are in parentheses, 95% confidence limits in brackets. *n* = 8. Origin of substituent constants used: EBT = ref 3, 12; Ch = ref 13.

Table IV. Dual Substituent Parameter Evaluation of the Dediazoniation Rate (k_1) of Para-Substituted Benzenediazonium Ions by the Original (1968)[14] and Revised (1983)[5] Equations of Swain et al.[a]

origin of rate data	substit constants[b]	f	r_s[c]	i	r^2	n
Kuokkanen[8]	1968	−2.72 (± 0.23) [± 0.65]	4.38 (± 0.37) [± 1.04]	−0.278	0.982	7
this paper	1968	−2.15 (± 0.42) [± 1.09]	2.68 (± 1.03) [± 2.64]	−0.410	0.850	8
this paper	1983	−2.52 (± 0.34) [± 0.88]	1.06 (± 0.28) [± 0.72]	−0.429	0.916	8

[a] Solvent: 1,2-dichloroethane, 50 °C, no crown ether. Standard deviations are in parentheses, 95% confidence limits in brackets. [b] 1968 = ref 14, 1983 = ref 5. [c] We write r_s in order to differentiate Swain's resonance reaction constant from the correlation coefficient *r*.

are in all cases smaller than the standard deviations, (b) that the Ch intercept constants *i* are smaller than the corresponding EBT values, (c) that neither the EBT nor the Ch set gives consistently higher r^2 values, (d) that standard deviations of ρ_F are very similar, (e) that standard deviations of ρ_R are significantly better (smaller) with EBT values, (f) that confidence levels show similar characteristics as standard deviations, and (g) that the absolute value of λ is always almost twice as large for the Ch set. As a general conclusion we think that for these reactions there is no preferred set of substituent constants.

For the comparison of the EBT and the Ch results (Table III) with the two Swain treatments (Table IV), we give numerical data for k_1 because of the inclusion of data published by Kuokkanen and Virtanen[8] who applied the original (1968) Swain substituent constants. Their results, which are given on the first line of Table IV, are significantly different from our experimental data. Although both rate constants for five diazonium ions are comparable in size, Kuokkanen et al. included *p*-OCH_3 whereas we included *p*-Br and *p*-I. If we take our rate constants for those substituted benzenediazonium ions that were used also by Kuokkanen et al., we obtain practically identical results: $f = -2.76$, $r_s = 4.36$, $i = -0.30$, $r^2 = 0.980$.

This clearly demonstrates that a set of seven or eight substituted benzene derivatives is hardly sufficient if one requires accurate numerical results. This is, of course, well-known and has been emphasized both by Taft's group[3] and by others. A comparison of the two Swain sets (second and third line of Table IV) shows clearly that the 1983 set is better. It is, however, not as good as the EBT and the Ch results for k_1 in Table III. Although we also correlated the other rate constants with the two Swain sets, we do not publish them because they are also less precise than those in Table III.

Table V. Triple Substituent Parameter Evaluation[16,17] of Equilibrium and Rate Constants of Dediazoniation of Para-Substituted Benzenediazonium Ions in the Presence of 18-Crown-6[a,b]

	ρ_α	ρ_F	ρ_R	i	r^2
K	0.26 (± 0.27) [± 0.86]	1.33 (± 0.24) [± 0.76]	1.56 (± 0.88) [± 2.8]	−0.011	0.9101
k_1	0.19 (± 0.37) [± 1.18]	−2.84 (± 0.33) [± 1.05]	7.32 (± 1.20) [± 3.82]	−0.105	0.9814
k_2	0.52 (± 0.33) [± 1.05]	−1.68 (± 0.30) [± 0.95]	5.91 (± 1.10) [± 3.5]	−0.070	0.970
k_3	0.18 (± 0.12) [± 0.38]	−2.86 (± 0.11) [± 0.35]	9.72 (± 0.38) [± 1.21]	−0.039	0.998
k_4	0.19 (± 0.40) [± 1.27]	0.09 (± 0.35) [± 1.11]	4.21 (± 1.3) [± 4.14]	−0.014	0.814

[a] Solvent: 1,2-dichloroethane. Parentheses and brackets, see Table III; *n* = 7. [b] The Taft–Topsom equation substituent constants for X = *p*-I are not available.[16,17]

The reaction constants using Taft's TSP evaluation (2) for gas-phase reactions[15,16] are given in Table V. Mechanistically, the results again show opposing signs for reaction constants ρ_F and ρ_R and, in general, a small contribution of the polarizability effect (ρ_α). These results explain, in addition to data published in Taft and Topsom's review,[16] that for reactions in solution the polarizability contributes little to the overall influence of substituents. Standard deviations and 95% confidence limits are in part better, in part worse, than those of the EBT and the Ch evaluations (Table III), but better than those with the two sets of Swain substituent parameters (Table IV). Except for the rates of homolytic dediazoniations (k_4), the regression coefficients r^2 are better with the TSP treatment. This result is however not surprising if one compares a TSP with a DSP treatment.

As mentioned in the introduction, dediazoniation of substituted benzenediazonium ions is mechanistically an interesting case for DSP and TSP treatments because of the opposing signs of the reaction constants ρ_F and ρ_R, i.e., negative values for λ. Very few reactions of this type are described in the literature.[24]

It was mechanistically conceivable to obtain opposing field and resonance effects for this reaction after independent evidence was given[4,26] that in the rate-limiting part of dediazoniation the C–N bond is cleaved heterolytically and does not involve the nucleophile. First, a π-electron donor in the para position stabilizes the reactant by resonance (mesomeric structure with C=N double bond) and vice versa for π-electron acceptors, whereas substituents that donoate (withdraw) electrons *inductively* will stabilize (destabilize) the electron-deficient transition state more strongly than the reactant. A more detailed discussion of the mechanistic implications of the opposing field and resonance effects of this and other reactions is given elsewhere.[27]

Taft and co-workers[3] expect opposing signs for ρ_F and ρ_R if, on going from the reactant to the transition state, positive charge is moved closer to the substituent (therefore negative values of ρ_F are expected). Loss of reactant state *p*-quinoidal resonance stabilization during reactions will give positive ρ_R values.

Our reaction constants ρ_F and ρ_R for dediazoniations in 1,2-dichloroethane (k_1, Table III) correspond, in principle, to those of Taft's group[3] which are based on rates measured in water at 29 °C: $\rho_F = -4.09$ ($\pm$ 0.20), $\rho_R = 2.72$ ($\pm$ 0.20), $r^2 = 0.990$, $n = 5$. A more detailed comparative discussion of the reaction constants is not meaningful, as the solvent and temperature are different and because of the limits of accuracy of DSP treatments as mentioned above in the context of the data in Table IV.

The field reaction constants for the heterolytic dediazoniation of complexed diazonium ions (k_3) are similar to those of the free diazonium ion (k_1). The resonance reaction constants for k_3 are larger, but the difference with those for k_1 is not statistically significant. We do not, therefore, discuss that difference mechanistically.

Reaction constants for k_2 are mechanistically not meaningful as they are a composite of heterolytic and homolytic dediazoniations.

The evaluation of the DSP constants for homolysis (k_4), however, gives ρ values that are clearly different from the others (Tables III and V). This is particularly true for the field reaction constants ρ_F that are numerically more than ten times smaller than those for k_3, but still negative. Within the confidence limits obtained, however, a ρ_F value of zero is indicated. This result is also obtained in the TSP treatment (Table V). Here the mean value of ρ_F is even slightly positive, but including clearly a zero field effect. These results for ρ_F indicate that in the rate-limiting transition state for homolysis the C–N$_\alpha$ bond may be weakened (therefore ρ_F may be negative), but on the other hand, there are many mechanistic data indicating that the rate-limiting step of homolytic dediazoniation involves either an electron transfer to the β-N atom or a steady-state intermediate by formation of a covalent bond between N$_\beta$ and a nucleophilic particle (see ref 10, Sect. D, for summary). For such a reaction a positive value of ρ_F is expected.

The ρ_F values found for homolytic dediazoniation are therefore likely to be caused by one of the following two possibilities: (a) by a reaction step in which one or more oxygens of the crown ether approach the β-N and at the same time a concerted weakening of the C–N bond takes place, thus resulting in an approximate compensation of a positive and a negative field effect, or (b) by a reaction that shows practically no field influence. The resonance reaction constant ρ_R is smaller than that found for dediazoniation of the free diazonium ion, but still positive. The absolute values of all standard deviations and 95% confidence limits of reaction constants ρ_F and ρ_R are smaller for k_4 than for the other three rate constants k_1, k_2, and k_3. As the absolute values of ρ_F and ρ_R are also smaller, the size of the standard deviations and confidence limits for the evaluations of k_4 does *not* imply a better fit of the DSP treatments for k_4. The fit is actually significantly worse as seen from the smaller values of r^2 for k_4.

From other reactions of arenediazonium ions in which the C–N bond is broken homolytically, little quantitative information on the influence of substituents is available. Most cases of which we know refer to overall kinetics of chain reactions. Such data have very limited or no value as the influence of a specific substituent as reflected in an overall rate constant may be a complex mixture of rate constants for individual steps with reaction parameters ρ, ρ_F, ρ_R (etc.) of different magnitude and sign. This is, in our opinion, a major reason for the fact that Hammett and DSP correlations could not be applied to the majority of homolytic reactions. This is likely to be the case also for our homolytic rate constants k_4.

Nevertheless we have evaluated two sets of literature data of homolytic dediazoniation reactions with Taft's dual substituent parameter treatment, which are likely to be one-step reactions, namely Elofson and Gadallah's measurements of the polarographic half-wave potential of the most positive wave in sulfolane as solvent[28] (5) and Packer et al.'s investigation on free-radical hydrodediazoniations (6) in aqueous solutions using benzyl alcohol radicals

$$\mathrm{ArN_2^+ + e^- \rightarrow ArN_2^{\bullet} \rightarrow Ar^{\bullet} + N_2} \qquad (5)$$

$$\mathrm{ArN_2^+ + RH^{\bullet} \rightarrow Ar^{\bullet} + N_2 + R + H^+} \qquad (6)$$

(RH$^\bullet$).[29] Although reaction 6 is part of a chain reaction, the authors were able to design the experimental procedure in such a way that the intrinsic rate constant of the step

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[24] Two other reactions of this type are mentioned by Taft's group:[3] Decomposition of ArCON$_3$ and acid-catalyzed esterification of ArCOOH. Later, Moss[25] found an additional case in his investigations of relative reactivities of a series of singlet carbenes with alkenes.

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given here could be determined for five substituted benzenediazonium ions.

Our treatment of these reactions was made with $\sigma_{R(BA)}$ and σ_R^+ substituent constants of the EBT set and with the three σ constants of the Taft–Topsom equation. For the polarographic reduction (5), half-wave potentials for the benzenediazonium ion and five para-substituted derivatives (X = CN, Me, Cl, Br, I) were available from the literature.[28] For the hydrodediazoniation with benzyl alcohol radicals (6), rate constants for five para-substituted, but not for the unsubstituted, benzenediazonium ions are reported by Packer et al.[29] (X = MeO, Me, Cl, CN, NO_2).

Using ρ_F and $\rho_{R(BA)}$ constants,[3] we obtained

for (5)

$$\rho_F = 0.26\ (\pm\ 0.04)\ [\pm\ 0.13];\ \rho_R = 0.12\ (\pm\ 0.08)\ [\pm\ 0.24];\ r^2 = 0.927$$

for (6)

$$\rho_F = 0.64\ (\pm\ 0.16)\ [\pm\ 0.70];\ \rho_R = 0.91\ (\pm\ 0.14)\ [\pm\ 0.58];\ r^2 = 0.982$$

With ρ_F and $\rho_{R(BA)}{}^+$ constants, the results are

for (5)

$$\rho_F = 0.25\ (\pm\ 0.04)\ [\pm\ 0.12];\ \rho_R = 0.10\ (\pm\ 0.05)\ [\pm\ 0.15];\ r^2 = 0.941$$

for (6)

$$\rho_F = 0.62\ (\pm\ 0.20)\ [\pm\ 0.82];\ \rho_R = 0.60\ (\pm\ 0.11)\ [\pm\ 0.46];\ r^2 = 0.976$$

The TSP treatment of Taft and Topsom[16] gives the following results

for (5)

$$\rho_\alpha = -0.03\ (\pm\ 0.10)\ [\pm\ 0.28];\ \rho_F = 0.26\ (\pm\ 0.08)\ [\pm\ 0.22];\ \rho_R = 0.61\ (\pm\ 0.08)\ [\pm\ 0.22];\ r^2 = 0.970$$

for (6)

$$\rho_A = 0.73\ (\pm\ 0.19)\ [\pm\ 2.41];\ \rho_F = 0.77\ (\pm\ 0.07)\ [\pm\ 0.89];\ \rho_R = 1.76\ (\pm\ 0.14)\ [\pm\ 1.78];\ r^2 = 0.998$$

As in Tables III and IV standard deviations are given in parentheses, 95% confidence limits in brackets.

In comparison to heterolytic reactions of arenediazonium ions, the reaction constants ρ_F and ρ_R are closer to zero, i.e., the influence of substituents is relatively small. Both reactions are related to the heterolytic additions of nucleophiles mentioned above and, indeed, ρ_F and ρ_R are positive.

The reaction parameters for the homolytic dediazoniation of crown ether complexed diazonium ions that we determined (k_4, Table III) are clearly different from those of reactions 5 and 6. This is probably due, first, to the general uncertainty in the applicability of DSP treatments to homolytic reactions and, second, to the fact that we are not able to claim that our rate constants k_4 are intrinsically constant (i.e., rate constants of single steps) or complex constants of chain processes.

Summarizing the results of this investigation, we think that the interpretation of substituent effects in heterolytic dediazoniation is probably the best case of the usefulness of DSP or TSP treatments of reactions with opposing field and resonance effects, but we also have to emphasize that DSP and TSP evaluations do not help much in the mechanistic understanding of homolytic reactions of arenediazonium ions.

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Registry No. 18-C-6, 17455-13-9; p-$XC_6H_4N_2{}^+BF_4{}^-$ (X = H), 369-57-3; p-$XC_6H_4N_2{}^+BF_4{}^-$ (X = $COCH_3$), 350-47-0; p-$XC_6H_4N_2{}^+BF_4{}^-$ (X = CN), 2252-32-6; p-$XC_6H_4N_2{}^+BF_4{}^-$ (X = CH_3), 459-44-9; p-$XC_6H_4N_2{}^+BF_4{}^-$ (X = Cl), 673-41-6; p-$XC_6H_4N_2{}^+BF_4{}^-$ (X = Br), 673-40-5; p-$XC_6H_4N_2{}^+BF_4{}^-$ (X = I), 1514-50-7; p-$XC_6H_4N_2{}^+BF_4{}^-$ (X = t-Bu), 52436-75-6.