

58. Dediazoniations of Arenediazonium Ions

Part 26¹⁾2)

Influence of Substituents on the Formation of Benzoic Acids in Reactions of Aryl-Cation-Type Intermediates with CO

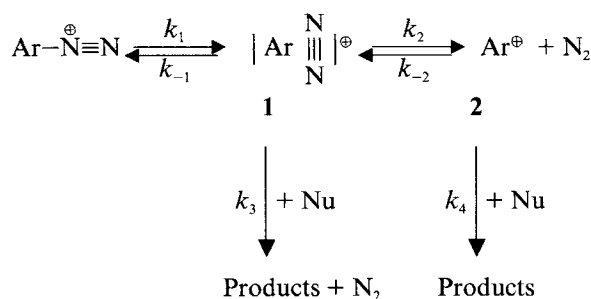
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The N₂-molecule-aryl-cation pair formed as the first intermediate in dediazoniations of arenediazonium ions can be trapped with CO in H₂O with formation of the corresponding arenecarboxylic acids. This reaction is considered as a model for the reverse of dediazonation, since CO is isoelectronic with N₂. The evaluation of the yields of arenecarboxylic acids formed from substituted benzenediazonium ions using *Taft*'s dual substituent parameter treatment demonstrates that the field reaction constant ρ_F and the resonance reaction constant ρ_R are positive and negative, respectively, as expected for a reaction which corresponds electronically to the addition of N₂ to aryl cations.

1. Introduction. – In previous papers of this series (for references, see [1]), we demonstrated that the dediazonation of substituted benzenediazonium ions in solvents of low nucleophilicity, *e.g.* 2,2,2-trifluoroethanol (TFE), follows the mechanism shown in the *Scheme*. However, H₂O as a solvent of relatively high nucleophilicity reacts with the first intermediate, the tight ion-molecule pair **1**, so efficiently that the route *via* the free (solvated) aryl cation **2** is almost completely suppressed [2].



Nu = nucleophile

The kinetic equation for the complete system of the *Scheme* [3] cannot be evaluated numerically, but semiquantitative evidence for the reverse of the first and the second steps

¹⁾ Part 25: see [1].

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of the *Scheme* can be given by ^{15}N -labelling of either the $\text{N}(\alpha)$ or the $\text{N}(\beta)$ atom of the diazonium ion: the kinetics of the $\text{N}(\alpha),\text{N}(\beta)$ -rearrangement can be followed easily. In addition, by running dediazoniations of labelled diazonium ions in the presence of a large excess of unlabelled N_2 , the exchange of the originally labelled diazonio group for an unlabelled diazonio group can be measured quantitatively.

The rate constants for solvolysis and for rearrangement (k_s and k_r , respectively) of substituted benzenediazonium ions follow dual substituent-parameter treatments and yield *negative* field (ρ_F) and *positive* resonance (ρ_R) reaction constants [1]. Dediazonation, therefore, belongs to the small group of reactions with *opposing* inductive (field) and resonance reaction constants.

For the reverse of dediazonation, *i.e.* the addition of N_2 to an aryl cation **2** and/or the recombination of the ion-molecule pair **1**, one expects, therefore, by the principle of microscopic reversibility, opposite signs of ρ_F and ρ_R relative to those of dediazonation. Unfortunately, however, for the two reverse steps in the *Scheme*, the intrinsic rate constants k_{-1} and k_{-2} cannot be calculated from experimentally determined overall kinetic data. The results of exchange of the diazonio group of ^{15}N -labelled diazonium ions with unlabelled molecular N_2 in large excess yields values for ρ_F and ρ_R which are close to zero [1] because they are based on a complex mixture of rates of forward and backward steps.

As mentioned above, the reaction system is less complex in H_2O , which traps the ion-molecule pair **1** almost completely. A better nucleophile than N_2 may be competitive with H_2O and may allow the determination of relative rate constants of the ion-molecule pair.

A suitable compound for this purpose is CO , which is particularly interesting in this context, because it is isoelectronic with N_2 . The primary substitution of N_2 in the molecule-ion pair **1** by CO yields first a benzoyl cation which then rapidly forms benzoic acid in an aqueous medium.

In the new nomenclature for organic reactions recommended by IUPAC [4], the substitution of a diazonio group ($-\text{N}_2^+$) by a carbonyl group ($-\text{CO}^+$) with CO as a reagent is called a carbonylo-dediazonation. *Lewis* and *Insole* [5] attempted to perform this reaction with the benzenediazonium ion in H_2O under a pressure of 47.6 bar, but they were unsuccessful. Later, we were able to obtain the 2,2,2-trifluoroethyl ester of benzoic acid in TFE under a pressure of 320 bar in 5.2% yield [6]. More recently, *Speranza* and coworkers [7] demonstrated the formation of benzoyl cations by the decay technique, which utilises the spontaneous β decay of covalently bound tritium atoms as a source of phenyl cations: in presence of CO , benzoyl cations were obtained from tritiated benzene in the gas phase.

In this communication, we report the yields of formation of *p*-substituted benzoic acids from the corresponding benzenediazonium ions in H_2O in the presence of a larger concentration of CO (930 to 1070 bar CO) than that used by *Lewis* and *Insole* [5], and on the evaluation of the relative yields by the *Taft* dual substituent-parameter treatment [8].

2. Results. – The results are based on dediazoniations of 0.1M aq. solutions of 11 *p*-substituted benzenediazonium tetrafluoroborates in the presence of 930 to 1070 bar CO . With 9 diazonium salts, dediazoniations were carried out at $50 \pm 1^\circ$; with 2 others, higher temperatures were required because their rate at 50° were too slow (see *Table 1*). For those at higher temperatures, 2–3 runs were conducted at a minimum of 3 different

Table 1. Yields of Substituted Benzoic Acids in Dediazoniations of Aqueous Solutions of *p*-Substituted (X) Benzene-diazonium Tetrafluoroborates (Extrapolated to 90% Dediazonation) in the Presence of CO (1000 ± 70 bar^a)

Substituent X	Temp. [°]	Number of experiments	Yield [%] of substituted benzoic acid (90% dediazonation)	
			found	extrapolated to 50°
MeO	65	3	56.9	} 59 ± 5
	75	3	53.5	
	85	3	41.6	
Me ₂ N	65	1	–	} 1.24 ± 0.35 ^b
	75	2	–	
	85	2	–	
	100	2	–	
F	50	3	7.3	
Cl	50	3	33	
Br	50	3	42	
NO ₂	50	3	46	
COMe	50	3	17	
Me	50	2	≤ 0.1	
Et	50	2	≤ 0.1	
Me ₃	50	3	1.4	
COOEt	50	1	1.0	

^a) Accurate pressures for each experiment given in Table 2.

^b) As the scatter between values obtained for the same temperature was greater than the scatter between the mean values at different temperatures, each value was extrapolated linearly to 90% dediazonation. The value given here is the mean value of all these extrapolations (with standard deviation).

temperatures. After stopping the reaction at appropriate times and quantitative determination of substituted phenols and benzoic acids by ¹H-NMR, the results were extrapolated linearly to 90% dediazonation. From runs at higher temperatures, product yields at 50° and 90% dediazonation were calculated with the help of the *Arrhenius* equation.

Among various methods for the determination of the substituted phenols and benzoic acids formed in these dediazoniations, the ¹H-NMR analysis in (D₆)acetone/D₂O 5:2 of evaporated product solutions was the most reliable although its accuracy, particularly in cases with low yields (see *Exper. Part*), was not excellent. With 2 diazonium salts (X = Me, Et), only traces (< 0.1%) of the corresponding benzoic acids could be detected. These 2 diazonium salts are, however, those for which low yields (< 0.1%) of *p*-alkylbenzoic acids are expected on the basis of the dual substituent-parameter treatment which is, as shown in *Discussion*, applicable to the addition of CO to aryl cations and/or N₂-molecule-aryl-cation pairs. For the same reason, we did not include the unsubstituted benzenediazonium salt in this investigation. The results, extrapolated to 90% dediazonation, are given in Table 1.

3. Discussion. – Yields of a certain product in reactions forming several competitive products from the same reagent can be used for linear free-energy relationships, *e.g.* for the evaluation of reactions of benzene derivatives with simple *Hammett* or more complex substituent relationships.

Based on the arguments given in *Introduction*, we tested the applicability of *Taft's* dual substituent-parameter treatment on the yields of substituted benzoic acid as one of the reaction products formed by trapping the N₂-molecule-aryl-cation pair with CO in the

dediazonation of substituted benzenediazonium tetrafluoroborates in aqueous solution. For mechanistic reasons discussed in the preceding two papers of this series [1] [2] and taking into account the experimental difficulties in analyzing the complex mixture of products, we hoped to check at least our hypothesis that the reaction of the N_2 -molecule-aryl-cation pair with CO is closely related to the reverse reaction of the molecule-ion pair (reforming the diazonium ion). As the forward reaction, *i.e.* the formation of the molecule-ion pair from the diazonium ion has a negative field reaction constant ρ_F and a positive resonance reaction constant ρ_R , we anticipated reversed signs of these constants for the reaction with CO. The corresponding calculations are based on the yields in % of benzoic acids (*Table 1*). They do indeed give the expected result:

$$\log (\% \text{XC}_6\text{H}_4\text{COOH}) = \log (\% \text{C}_6\text{H}_5\text{COOH}) + 4.13 (\pm 1.3) \sigma_F - 0.66 (\pm 0.46) \sigma_R$$

$$r = 0.617, n = 9$$

We write the *Taft* equation in a slightly different form as the yield of the carbonylation reaction of the unsubstituted aryl cation ($\% \text{C}_6\text{H}_5\text{COOH}$) is too low to be determined. Indeed, if one applies the dual substituent constants ρ_F and ρ_R of the above equation to $X = \text{H}$, one gets a calculated yield of benzoic acid of 0.6%, *i.e.* a yield which is at the limits of sensitivity of the applied ^1H -NMR technique. It is now clear why *Lewis et al.* [5] were unable to detect benzoic acid in their experiments. In an analogous manner, we can show that only traces of *p*-methyl- and *p*-ethylbenzoic acid in the reaction mixtures of the corresponding *p*-alkylated benzenediazonium ions are to be expected.

The low regression coefficient which we obtained for this evaluation is due to a mechanistic factor and to analytical reasons: the yields are not exclusively determined by the intrinsic reaction step of CO, namely its addition to the molecule-ion pair **1**, but include also a partial contribution of the first step of the forward reaction of dediazonation. The analytical reasons are related to the accuracy of quantitative analysis of substituted benzoic acids in mixtures of products. For example, it is not impossible that in some of these reactions, the formed substituted benzoic-acid molecules are further attacked by other molecule-ion pairs, forming the corresponding substituted diphenylbenzoic acids. Furthermore, our method of (linear) extrapolation of yields to that expected for 90% dediazonation is, of course, fairly accurate if one extrapolates from, say, 85%, but less so from, say, 65%. By a very large number of experiments this uncertainty could be eliminated by the number of experiments, but there is still the open question, whether our analytical technique gives correct results for all 11 reaction systems studied.

If we eliminate the results for those substituted diazonium ions which showed either the largest deviations in the 2 or 3 experiments made and in which the linearity of the extrapolation to 90% dediazonation was not reliable, or for which only 1 experiment was made ($X = \text{F}, \text{NMe}_2, \text{NO}_2, \text{COOEt}$), we get a significantly better correlation for the other substituted derivatives ($X = \text{Br}, \text{Cl}, \text{COMe}, \text{Me}_3\text{C}, \text{MeO}$):

$$\log (\% \text{XC}_6\text{H}_4\text{COOH}) = \log (\% \text{C}_6\text{H}_5\text{COOH}) + 2.77 (\pm 0.83) \sigma_F - 0.59 (\pm 0.36) \sigma_R$$

$$r = 0.943, n = 5$$

We emphasize that, because of the experimental uncertainties mentioned, the actual calculated values of ρ_F and ρ_R are not highly significant; however, the result that the 2 reaction constants do have opposing signs, *i.e.* $\rho_F/\rho_R < 0$, is statistically significant.

We will, however, not discuss the absolute magnitude of the reaction constants, ρ_F and ρ_R found. This will be done later in a comparative study of a series of 5 reactions which are characterized by opposite signs of reaction constants in dual substituent parameter treatments (see preliminary communication [9]).

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Experimental Part

1. *Syntheses* of substituted benzenediazonium tetrafluoroborates were carried out following *Starkey's* method [10]. The salts were recrystallized from MeOH (X = Cl), MeOH/H₂O (X = Me, F), MeOH/HBF₄ (X = COOEt), MeOH/Et₂O (X = NO₂), MeOH/Et₂O 9:1 (X = COMe), EtOH (X = MeO), EtOH/Et₂O (X = NMe₂, Me, Et), acetone (X = Br), and CH₂Cl₂/pentane (X = Me₃C) and characterized by m.p., UV, and IR (comparison with [11]).

2. *Deidiazoniations in Presence of CO*. Appropriate reaction times for deidiazoniations were calculated from *Arrhenius* parameters given in the literature for aq. soln. [11] or 2,2,2-trifluoroethanol [12]. Experiments were conducted with 0.002 mol of diazonium salt in 50 ml of H₂O in a steel autoclave with a glass insert as described previously [13], but in the presence of CO instead of N₂. The pressure could not be kept at exactly 1000 bar, but varied a little as shown in *Tables 1* and 2. These pressure differences do influence the concentration of CO in the soln., but we consider these differences to be negligible.

Table 2. *Percentages of Deidiazoniations and Yields of Substituted Benzoic Acid* (as measured)

Substituent X	CO [bar]	Temp. [°]	Reaction time [h]	Deidiazonation [%]	Substituted benzoic acid [%]
MeO	1000	65	66	82.6	57.3
	1000		66	83.5	55.7
	1000		90	96.0	57.4
	1050	75	25	83.6	41.1
	1040		26.5	92.0	55.4
	1070		26.5	90.3	55.2
	1030	85	7	77.1	37.5
	1066		7.5	91.6	41.8
	1040		8	89.9	42.0
Me ₂ N	990	65	96	51.5	1.38
	1000	75	48	96.1	1.04
	1050		45	77.9	1.56
	1000	85	21	88.6	0.58
	1040		24	90.5	1.38
	1060	100	2.5	87.2	4.63
	1070		2.5	94.3	1.98
F	1000	50	46	95.5	8.2
	1000		46	92.8	13.2
	980		48	94.2	10.4
Cl	1000	50	66	64.4	16.5
	1000		118	80.2	26.6
	970		118	97.5	37.8
Br	1000	50	62.5	95.9	44.0
	1000		62	95.5	44.3
	1000		62.5	96.9	49.4
NO ₂	930	50	48	100	60.7
	1000		48	91.7	48.7
	990		48	98.0	60.3

Table 2 (cont.)

Substi- tuent X	CO [bar]	Temp. [°]	Reaction time [h]	Dediazo- nation [%]	Substituted benzoic acid [%]
COMe	1000	50	2.5	76.9	6.73
	1030		2.8	80.2	9.55
	1020		3	82.5	11.59
Me	950	50	4.5	82.9	≤ 0.1
	1030		4.5	88.0	≤ 0.1
	1050		4	79.0	≤ 0.1
Et	1020	50	2.8	69.2	≤ 0.1
	1000		4	86.4	≤ 0.1
	1000		4	87.4	≤ 0.1
Me ₃ C	1040	50	1.8	63.2	0.68
	1000		2.5	77.6	0.93
	1030		2.5	65.4	0.53
COOEt	1000	50	3	71.2	0.80

3. *Determination of Products.* Experiments to determine the yields of the substituted benzoic acids by acidimetric titrations failed since hydrotetrafluoroboric acid and its hydrolysis products are also formed. We finally found a suitable and satisfactory (although not perfect) soln. to the anal. problems: after the chosen reaction time and after dissolving separated products with acetone and simultaneously compensating the H₂O loss during depressurising the autoclave, 20 of 50 ml of the soln. were evaporated, and the residue was dried (P₂O₅). The remaining soln. (30 ml) was used for determining the amount of residual diazonium salt by spectrophotometric determination of the azo dye formed with 3-hydroxynaphthalene-2,7-disulfonic acid [13] [14].

To the residue of the 20 ml of product soln., ca. 20 wt.-% of 1,3,5-trinitrobenzene (weighed exactly) were added as an internal ¹H-NMR standard. This mixture was dissolved in 0.5–1.0 ml of (D₆)acetone/D₂O 5:2. The substituted benzoic acids formed were identified in the ¹H-NMR (300 MHz; Bruker AM 300-WB spectrometer) with reference spectra of authentic samples in the same solvent mixture. The phenols were identified with the help of shift increments given in [15]. ¹H-NMR: 1,3,5-trinitrobenzene, ca. 9.36 ppm (s); 4-substituted benzoic acids and phenols, AA'BB' or AA'XX' pattern; the rel. scatter of the analyses of integrals was in the range of ±2 to ±50% (50% for compounds obtained in yields below 1.0%).

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