

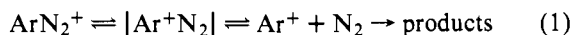
# Dediazoniation of Arenediazonium Ions in Homogeneous Solution. 11.<sup>1</sup> Evidence for Two Intermediates in the Reaction of the 2,4,6-Trimethylbenzenediazonium Ion in 2,2,2-Trifluoroethanol<sup>2</sup>

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**Abstract:** A detailed investigation of the dediazoniation of 2,4,6-trimethylbenzenediazonium tetrafluoroborate in 2,2,2-trifluoroethanol is presented. The dediazoniation rate, the isotopic  $N_\alpha$ - $N_\beta$  rearrangement, and the exchange reaction of the diazonio group with external nitrogen in  $\beta$ -<sup>15</sup>N labeled diazonium salts were monitored under a constant pressure of 300 atm mixed nitrogen/argon gas, as a function of the partial pressure of nitrogen. The results obtained provide evidence additional to that presented in the preceding paper for the presence of two reaction intermediates during the course of the dediazoniation. A statistical treatment of the kinetic data excludes the possibility that one reaction intermediate can account for all the phenomena observed. The reaction mechanism of eq 7 is proposed. Rearrangement occurs at the first intermediate, a tight molecule-ion pair, while the exchange with external nitrogen takes place via the second, free aryl cation, intermediate.

The results concerning solvent effects on the decomposition of benzene- and 2,4,6-trimethylbenzenediazonium ion described in the preceding paper<sup>1</sup> support the existence of two reaction intermediates during the course of the dediazoniation:



This paper deals with a detailed kinetic investigation of the dediazoniation of a convenient system, 2,4,6-trimethylbenzenediazonium tetrafluoroborate in 2,2,2-trifluoroethanol (TFE) under a constant pressure (300 atm) of mixed nitrogen/argon gas, but different partial pressures of nitrogen. The results provide evidence, additional to that already presented,<sup>1</sup> for the validity of the proposed two-intermediate mechanism. A statistical treatment of the kinetic data excludes the possibility that one reaction intermediate can account for all the phenomena observed.

## Experimental Section

**Materials.** In the study of the rearrangement and exchange reaction reagent grade (Fluka puriss.) TFE was used without further purification. The solvent which was used for kinetic and solubility measurements was recovered and was used repeatedly after purification by the following method.<sup>4</sup> TFE was dried over potassium carbonate and distilled. Phosphorus pentoxide was then added to the distillate, and the solvent was distilled again (bp 73–74 °C). The GLC analysis of the recovered solvent showed no impurities. 2-Naphthol was recrystallized from ethanol (mp 121 °C). The disodium salt of 2-naphthol-3,6-disulfonic acid (R-salt) was recrystallized twice from water and charcoal. 2,4,6-Trimethylaniline was distilled under reduced pressure (bp 120 °C, 20 mmHg), and the GLC of the distillate showed no impurities. Reagent grade potassium thiocyanate, potassium fluoride, and sodium nitrite were used without purification.

**2,4,6-Trimethylbenzenediazonium- $\beta$ -<sup>15</sup>N Tetrafluoroborate.** Fluoroboric acid (2 mL, 50% aqueous solution) and water (2.5 mL) were added to 0.489 g (3.62 mmol) of 2,4,6-trimethylaniline. The solution was cooled in an ice-salt bath and 0.250 g (3.57 mmol) of Na<sup>15</sup>NO<sub>2</sub> (99.2% nitrogen-15, Stohler Isotope Chemicals) in 0.5 mL of water was added slowly with stirring. The precipitate was collected by filtration and washed twice with ice-cold water. The diazonium salt was dried in a vacuum desiccator over phosphorus pentoxide at room temperature for 3–5 h. It was reprecipitated from acetonitrile/ether. The salt was dissolved in the minimum amount of acetonitrile and filtered. Ether was added to the filtrate and the resulting precipitate filtered and dried in a vacuum desiccator over phosphorus pentoxide for 3–5 h. The diazonium salt thus obtained was stored at –30 °C in

the dark: yield 0.6039 g (72.6%); mp 88–89 °C dec; IR 2220 cm<sup>-1</sup> (position of the diazonio absorption in Nujol).

The filtrate obtained after diazotization was used for the synthesis of the labeled azo compound. The filtrate was added immediately to an alkaline solution of 2-naphthol (0.144 g, 1 mmol) in 50 mL of water at 0 °C. The azo compound formed was filtered, dried, and recrystallized (0.1110 g, 0.383 mmol). Half of the azo compound was reduced to give 2,4,6-trimethylaniline hydrochloride. The azo compound and amine hydrochloride thus obtained were used for mass spectral analyses as reference materials. Unlabeled trimethylbenzenediazonium tetrafluoroborate was prepared in the same way as the labeled salt using approximately 2.20 g (0.0163 mol) of amine: yield 2.56 g (67.5%); mp 88–89 °C dec; IR 2260 cm<sup>-1</sup> (position of the diazonio absorption in Nujol).

**Measurement of the Dediazoniation Rate.** The rate measurements under high pressure were performed in a stainless steel autoclave (Autoclave Engineers, Inc., Erie, Pa., Model MM 2T) equipped with a sampling tube, a cooling coil, and a stirrer. The temperature of the cooling water was controlled to within 25 ± 0.03 °C. A typical kinetic measurement was carried out as follows.

Trimethylbenzenediazonium salt (0.420 g, 1.80 mmol) was added to TFE (150 mL) thermostated at 25 °C in the autoclave. The autoclave was then sealed and pressurized to the desired value. Samples of the reaction solution were withdrawn via the sampling valve and an aliquot (1 mL) of this sample solution was then added to an R-salt solution (20 mL) to quench the remaining diazonium salt. After diazo coupling the solution was diluted to 250 mL, and its optical density was measured at the maximum wavelength of absorbance of the dye formed (497 nm). For each kinetic run, nine samples of the reaction solution were withdrawn at definite time intervals.

The kinetic measurements at 1 atm were performed in a similar manner using the same stainless steel autoclave. Samples were taken by applying a pressure of approximately 1–2 atm to the sealed autoclave, then opening the sampling valve.

The R-salt solution was prepared as follows. R-Salt (1.78 g) was dissolved in water (200 mL) with stirring. Enough sodium bicarbonate and ca. 0.2 g of sodium hydroxide were then added to give the solution a pH of approximately 9.5–10.0.

**Dediazoniation of Labeled 2,4,6-Trimethylbenzenediazonium Salt in an Autoclave.** TFE (10 mL) was added to the labeled diazonium tetrafluoroborate (0.120 g, 0.513 mmol) in a specially designed glass vessel. The vessel was placed in a stainless steel autoclave and pressurized to 300–310 atm. During dediazoniation the autoclave was shaken in an oil bath at 24–26 °C, the glass vessel preventing any contact of the reaction solution with the metal surface. Aliquots were extracted and quenched in R-salt before pressurization, and after approximately 70% reaction in order to determine the exact extent of reaction. The time lag between initiation of dediazoniation and

**Table I.** Isotopic  $N_{\alpha}$ - $N_{\beta}$  Rearrangement of Substituted Benzenediazonium- $\beta$ - $^{15}N$  Tetrafluoroborate during Dediazoniation in TFE in the Dark (1 atm  $N_2$ )

Substituent	$T$ , °C	$P$ , % <sup>a</sup>	$k_r/k_s$ <sup>b</sup>	$10^4 k_s$ , s <sup>-1</sup>	$10^5 k_r$ , s <sup>-1</sup>	Ref
H	30	7.96	0.072	1.59	1.14	5
2,4,6-CH <sub>3</sub>	25	20.89	0.225	1.65	3.72	This work

<sup>a</sup> Percent isotopic rearrangement adjusted exactly to 70% dediazoniation. <sup>b</sup>  $k_r/k_s = \log(1 - 2p)/2 \log(A/A_0)$ ;  $p = P/100$ ;  $A$  = absorbance of azo dye obtained after 70% dediazoniation;  $A_0$  = original azo dye absorbance (ref 8). <sup>c</sup> Assumed equal to the rate of disappearance of diazonium salt.

**Table II.** Exchange of Substituted  $\beta$ - $^{15}N$  Diazonium Ions with External  $N_2$  (300 atm) in TFE at 25 °C

Substituent	% exchange <sup>a</sup>	Ref
H	2.46 ± 0.40	5
2,4,6-CH <sub>3</sub>	6.33 ± 0.59 <sup>b</sup>	This work

<sup>a</sup> Corresponds to the percent of external  $N_2$  incorporated into the unreacted  $\beta$ - $^{15}N$  labeled diazonium salt adjusted exactly to 70% dediazoniation. <sup>b</sup> Average of 20 separate mass spectrometric determinations from four independent experiments; see below.

attainment of the final working pressure in the autoclave was about 10 min. The residual reaction solution was treated with 2-naphthol (0.05 g) dissolved in 20 mL of 0.3 M sodium hydroxide. The resulting precipitate was filtered, washed with water, and dried. Recrystallization from benzene/methanol (1:5 v/v) gave pure 1-(2',4',6'-trimethylphenylazo)-2-naphthol: yield 0.0355 g, 0.122 mmol; mp 134.5–135 °C. Anal. (C<sub>19</sub>H<sub>18</sub>N=NO) C, H, N.

The  $^{15}N$  content of the azo dye (the extent of the exchange reaction) was determined mass spectrometrically<sup>5</sup> by comparing the intensity ratio of peaks for  $m/e$  290/291 with that of the fully labeled azo reference compound which was prepared whenever labeled diazonium salt was synthesized.

The extent of  $N_{\alpha}$ - $N_{\beta}$  rearrangement of the diazonio group in trimethylbenzenediazonium salt was determined mass spectrometrically<sup>5</sup> using the reduction product of the azo dye. A typical reduction was carried out as follows.<sup>6</sup> Approximately 0.0125 g (0.0431 mmol) of 1-(2',4',6'-trimethylphenylazo)-2-naphthol was refluxed with 0.050 g of sodium dithionite in a mixture of 5 mL of water, 10 mL of methanol, and ca. 0.1 g of sodium hydroxide, until the color disappeared. The pH of the reaction mixture was adjusted to ca. 8.5 with 1 M sodium hydroxide, the solution was steam distilled, and the distillate containing trimethylaniline (~100 mL) was acidified with HCl and evaporated to dryness. The crude product was sublimed under reduced pressure (140–150 °C, ~50 mmHg), dissolved in a small amount of methanol, and reprecipitated with ether. The filtered amine hydrochloride was washed with ether and dried: yield 0.0041 g, 0.0239 mmol, 55.4%. Anal. (C<sub>9</sub>H<sub>14</sub>NCl) C, H, N. The purity of 2,4,6-trimethylanilinium hydrochloride was usually checked by TLC (silica gel, *n*-hexane/acetone (10:1 v/v),  $R_f$  ~0.54), since its melting point is very high (>280 °C).

**Measurement of Gas Solubility in TFE.** The solubilities of gases in TFE were determined in a simple bubbling type apparatus.<sup>7</sup> The autoclave employed was the same as that for kinetic measurements under high pressure. The experimental procedure was as follows.

The solvent was introduced into the autoclave and was thermostated at 25 °C. Gas at a pressure of 2–10% higher than that finally required was then passed into the autoclave. The solution was stirred for 1–2 h and the pressure was then adjusted to the desired value. Solvent samples were withdrawn at suitable intervals to ensure saturation. Saturation was confirmed by measuring the ratio of solute to solvent. Normally 0.5–1.5 h was sufficient to attain equilibrium conditions. After equilibrium had been established, samples were withdrawn, and the volumes of liquid and gas released from the samples were measured in burets. The buret system was also maintained at 25 °C.

Because of the nature of the apparatus, we could not measure the absolute solubility of gas at 1 atm. However, gas solubility at 1 atm is generally so small that it can be neglected when the solubilities at high pressure are compared with each other.

**Table III.** Solubilities of Nitrogen and Argon in TFE at Various Pressures (25 °C)

Gas	Pressure, atm	Solubility	
$N_2$	45	12.27 <sup>a</sup> ± 0.74 <sup>b</sup>	(0.5014 ± 0.0303) <sup>c</sup>
$N_2$	90	24.11 ± 0.80	(0.9853 ± 0.0327)
$N_2$	135	34.95 ± 0.72	(1.428 ± 0.029)
$N_2$	165	42.16 ± 1.97	(1.723 ± 0.081)
$N_2$	210	51.35 ± 1.36	(2.098 ± 0.056)
$N_2$	255	61.99 ± 1.15	(2.533 ± 0.047)
$N_2$	300	74.70 ± 1.68	(3.053 ± 0.069)
Ar	45	15.99 ± 0.88	(0.6534 ± 0.0360)
Ar	90	31.02 ± 2.00	(1.268 ± 0.082)
Ar	135	49.27 ± 2.24	(2.013 ± 0.092)
Ar	165	58.65 ± 2.13	(2.397 ± 0.087)
Ar	210	74.74 ± 1.28	(3.054 ± 0.052)
Ar	255	90.46 ± 2.40	(3.697 ± 0.098)
Ar	300	104.5 ± 0.8	(4.270 ± 0.032)

<sup>a</sup> mL of gas at 1 atm per mL of TFE. <sup>b</sup> 95% confidence limits. <sup>c</sup> Solubility in units of mol/L.

**Table IV.** Solubilities of Mixed  $N_2$ /Ar Gas in TFE at 300 atm (25 °C)

Gas	Solubility	
85% $N_2$ + 15% Ar	76.61 <sup>a</sup> ± 0.85 <sup>b</sup>	(3.131 ± 0.035) <sup>c</sup>
70% $N_2$ + 30% Ar	81.09 ± 1.42	(3.314 ± 0.058)
55% $N_2$ + 45% Ar	88.32 ± 1.21	(3.609 ± 0.049)
45% $N_2$ + 55% Ar	89.10 ± 0.51	(3.643 ± 0.021)
30% $N_2$ + 70% Ar	94.99 ± 0.74	(3.882 ± 0.030)
15% $N_2$ + 85% Ar	101.4 ± 1.1	(4.143 ± 0.044)

<sup>a</sup> mL of gas at 1 atm per mL of TFE. <sup>b</sup> 95% confidence limits. <sup>c</sup> Solubility in units of mol/L.

## Results

**Comparison of Unsubstituted with Substituted Benzenediazonium Ions.** Some representative data which allow a comparison of benzenediazonium salt with the 2,4,6-trimethylbenzenediazonium salt are given in Tables I and II.

It can be seen that both the amount of isotopic rearrangement and the percentage of incorporated external nitrogen are significantly higher for the 2,4,6-trimethyl substituted compound. Since this investigation involved the repetitive measurement of these quantities under gradually changing conditions (i.e., different concentration of nitrogen in the mixed nitrogen/argon gas), the system with larger absolute values will provide a better opportunity for accurate determination of small relative differences. Therefore, 2,4,6-trimethylbenzenediazonium tetrafluoroborate was chosen as a suitable model.

**Solubility of Gas in TFE.** As stated above, all experiments in this work were performed under a constant pressure of 300 atm of mixed  $N_2$ /Ar gas, but with a variable partial pressure of nitrogen. In order to know the exact concentration of  $N_2$  in the solvent, the solubility in TFE of  $N_2$ , Ar, and the mixed gas was measured under different pressures. Representative data are given in Tables III and IV and in Figure 1. It can be seen from Table III and Figure 1 that the solubilities of  $N_2$  and Ar obey Henry's law within the whole pressure range studied. A linear least-squares fit of the measured solubilities gives the equations

$$S_{N_2} = (9.939 \pm 0.387) \times 10^{-3} \times p + 0.0493 \quad (2)$$

$$S_{Ar} = (1.436 \pm 0.035) \times 10^{-2} \times p + 0.0144 \quad (3)$$

$S$ : solubility in mol/L

$p$ : pressure in atm

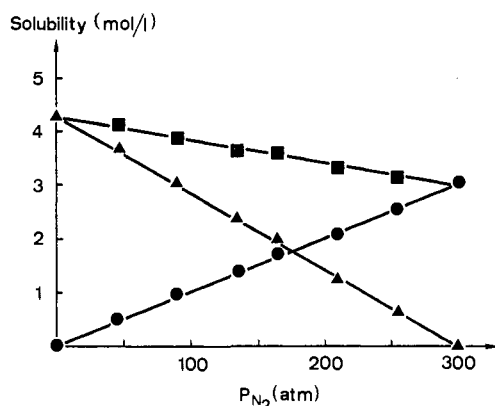


Figure 1. Solubility of nitrogen and argon in TFE: ●, N<sub>2</sub> solubility; ▲, Ar solubility ( $p_{Ar} = 300 - p_{N_2}$ ); ■, solubility of mixed N<sub>2</sub>/Ar gas at various partial pressures of N<sub>2</sub> and a total pressure of 300 atm. The line for the solubility of mixed gas is calculated from eq 4.

Table V. Dediazonation Rate of 2,4,6-Trimethylbenzenediazonium Ion under Various Pressures in TFE at 25 °C

Atmosphere	Pressure, atm	$k_s \times 10^4, s^{-1}$
Ar	1	$1.67 \pm 0.05^a$
Ar	50	$1.62 \pm 0.03$
Ar	100	$1.60 \pm 0.06$
Ar	200	$1.51 \pm 0.04$
Ar	300	$1.46 \pm 0.01$
N <sub>2</sub>	100	$1.51^b$
N <sub>2</sub>	200	$1.38^b$
N <sub>2</sub>	300	$1.30 \pm 0.02$

<sup>a</sup> 95% confidence limits. <sup>b</sup> Based on one experiment only.

for N<sub>2</sub> and Ar, respectively, with correlation coefficients better than 0.999. Table IV shows the solubilities of different N<sub>2</sub>/Ar gas mixtures in TFE under a total pressure of 300 atm. It is generally accepted that the solubility of each component in a gas mixture can be estimated with reasonable accuracy using Henry's law. It is assumed that the pressure of a second gas does not affect the solubility of another component gas, although exceptions are known.<sup>9</sup> Use of this assumption enables the solubility of the mixed gas to be calculated as a sum of the individual components' solubilities:

$$(S_{\text{mixed gas}})_p = (S_{N_2})p_{N_2} + (S_{Ar})p_{Ar} \quad (4)$$

$$p = p_{N_2} + p_{Ar} = 300 \text{ atm}$$

Figure 1 demonstrates that the above assumption is valid in our experiments since the calculated line for the solubility of mixed gas coincides almost exactly with the experimentally determined values (represented as squares). Therefore it can be assumed that in our experiments the nitrogen concentration in TFE is proportional to the N<sub>2</sub> content in the atmosphere at constant total pressure.

**Effect of Pressure on the Dediazonation Rate.** In all experiments the dediazonation rate was followed by coupling aliquots of the reaction solution with R-salt (disodium salt of 2-naphthol-3,6-disulfonic acid) and measuring the concentration of the resulting azo dye spectrophotometrically. Dediazonation rates were measured under different pressures of argon as well as nitrogen. The results are summarized in Table V.

Figure 2 shows the dependence of the rate on pressure, plotted as  $\ln k$  against  $p$ .

It can be seen that the rate is reduced more under nitrogen than under a corresponding argon pressure indicating that nitrogen exerts not only a pressure effect, but also a chemical

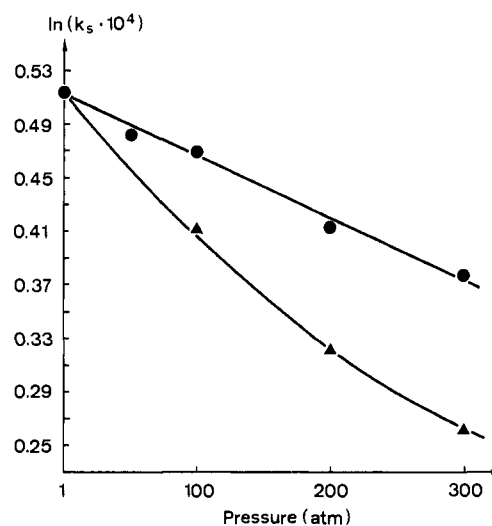


Figure 2. Effect of pressure on the dediazonation rate ( $k_s$ ) for 2,4,6-trimethylbenzenediazonium ion in TFE at 25 °C: ▲, under N<sub>2</sub>; ●, under Ar.

Table VI. Dediazonation Rate of 2,4,6-Trimethylbenzenediazonium Ion in TFE under Mixed N<sub>2</sub>/Ar Gas at 300 atm (25 °C)

Atmosphere	N <sub>2</sub> concn, <sup>a</sup> mol/L	$k_s \times 10^4, s^{-1}$
100% Ar	0.0	$1.46 \pm 0.01^b$
85% Ar + 15% N <sub>2</sub>	0.4966	$1.43 \pm 0.04$
70% Ar + 30% N <sub>2</sub>	0.9438	$1.38 \pm 0.02$
55% Ar + 45% N <sub>2</sub>	1.391	$1.36 \pm 0.02$
45% Ar + 55% N <sub>2</sub>	1.689	$1.35 \pm 0.08$
30% Ar + 70% N <sub>2</sub>	2.136	$1.33 \pm 0.03$
15% Ar + 85% N <sub>2</sub>	2.583	$1.32 \pm 0.03$
100% N <sub>2</sub>	3.031	$1.30 \pm 0.02$

<sup>a</sup> Based on the equation of Henry's law. <sup>b</sup> 95% confidence limits.

influence. From the slope of the line for Ar in Figure 2, the volume of activation  $\Delta V^\ddagger = 11.06 \pm 2.7 \text{ cm}^3/\text{mol}$  was calculated. This value is in good agreement with those previously determined for various substituted benzenediazonium salts in water ( $\Delta V^\ddagger = 9.0\text{--}11.4 \text{ cm}^3/\text{mol}$ ).<sup>10</sup> This suggests that the rate-limiting transition state in TFE is not significantly different from that in H<sub>2</sub>O.

**Effect of Atmospheric Composition on Dediazonation Rate.** Rate measurements were performed under a constant total pressure of 300 atm, but with varying partial pressures of nitrogen in the argon/nitrogen gas mixture. Thus, the pressure effect being compensated for, only the chemical influence of nitrogen is monitored. The results are summarized in Table VI. The N<sub>2</sub> concentration in TFE was calculated using eq 2. As expected for a reaction where an intermediate and nitrogen are formed reversibly (eq 1), the overall decomposition rate decreases with an increase in N<sub>2</sub> concentration. In Figure 3 the dediazonation rate is plotted against the N<sub>2</sub> concentration in TFE; it is noticeable that the relationship does not appear to be linear.

**Effect of Potassium Thiocyanate on Dediazonation Rate.** It is generally assumed that nucleophiles are not involved in the rate-determining step during the decomposition of arenediazonium ions.<sup>11</sup> However, dediazonation reactions are known which are less consistent with an S<sub>N</sub>1 mechanism, and which may have a bimolecular rate-determining step.<sup>11-14</sup> We investigated the dependence of the dediazonation rate on the concentration of KSCN in TFE under 300 atm of Ar and N<sub>2</sub>, respectively. The results, together with those for solutions of KF in TFE under argon, are summarized in Table VII and are

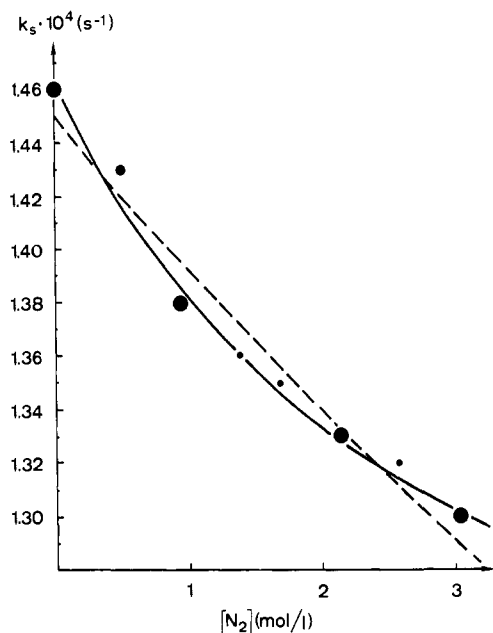


Figure 3. Experimental values and calculated curves for the dependence of the dediazonation rate ( $k_s$ ) for 2,4,6-trimethylbenzenediazonium tetrafluoroborate on nitrogen concentration (TFE, 300 atm, 25 °C): ---, model 1; —, model 2 (see Discussion). The experimental points are average values of seven (●), four (●), and three (●) measurements, respectively.

Table VII. Dediazonation Rate of 2,4,6-Trimethylbenzenediazonium Ion in the Presence of KSCN or KF at 300 atm (TFE, 25 °C)

Atmosphere	Salt (mol/L)	$k_s \times 10^4, s^{-1}$
N <sub>2</sub>		1.30 ± 0.02 <sup>a</sup>
N <sub>2</sub>	KSCN (0.100)	1.52
N <sub>2</sub>	KSCN (0.200)	1.62
N <sub>2</sub>	KSCN (0.300)	1.67
N <sub>2</sub>	KSCN (0.365)	1.65
Ar		1.46 ± 0.01 <sup>a</sup>
Ar	KSCN (0.100)	1.65
Ar	KSCN (0.200)	1.71
Ar	KSCN (0.300)	1.77
Ar	KSCN (0.365)	1.80
Ar	KF (0.100)	1.51
Ar	KF (0.200)	1.46
Ar	KF (0.400)	1.50
Ar	KF (0.500)	1.49

<sup>a</sup> Cited from Table V. The other values are based on one kinetic measurement only.

represented in Figure 4. It can be seen that the dediazonation of 2,4,6-trimethylbenzenediazonium salt in TFE is accelerated by added thiocyanate ions, and that the rate under argon increases by a similar amount as does that under nitrogen. On the other hand, the addition of an equivalent amount of fluoride ion, which is a much weaker nucleophile, does not increase the dediazonation rate substantially.

**Effect of Atmospheric Composition on the Exchange Reaction of the Diazonio Group with External Nitrogen.** The amount of exchange with external nitrogen was determined by solvolysing  $\beta$ -<sup>15</sup>N labeled 2,4,6-trimethylbenzenediazonium tetrafluoroborate to 70% completion of the reaction under an atmosphere containing nitrogen of normal isotopic abundance (~0.4% <sup>15</sup>N). The remaining diazonium salt was then coupled with 2-naphthol and the resulting azo dye was analyzed for the <sup>15</sup>N content mass spectrometrically. The fact that the exchange reaction

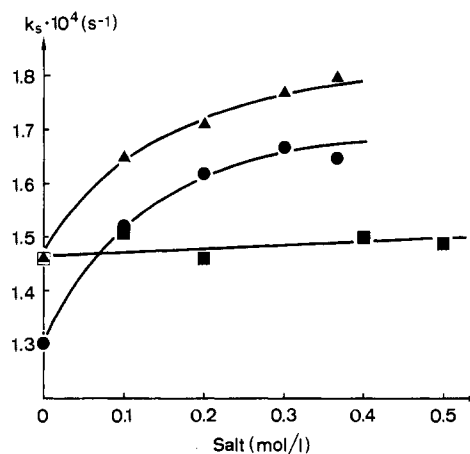
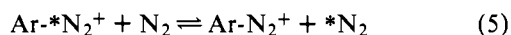


Figure 4. Dediazonation rate of 2,4,6-trimethylbenzenediazonium ion in TFE (300 atm, 25 °C) with added KSCN or KF: ●, KSCN under N<sub>2</sub>; ▲, KSCN under Ar; ■, KF under Ar.

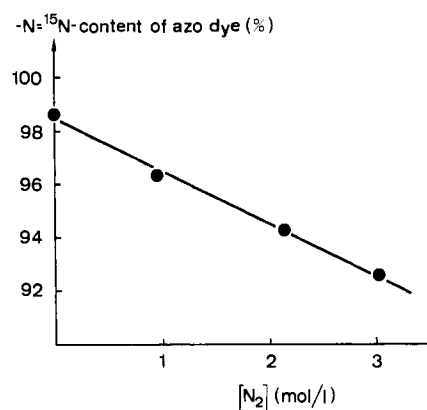


Figure 5. Exchange with external N<sub>2</sub> accompanying 70% dediazonation of the diazonio group in 2,4,6-trimethylbenzenediazonium- $\beta$ -<sup>15</sup>N tetrafluoroborate as a function of N<sub>2</sub> concentration in TFE (25 °C, 300 atm). The point at [N<sub>2</sub>] = 0 is based on the -N=<sup>15</sup>N- content before dediazonation (see Table VIII).

with external N<sub>2</sub> molecules does take place<sup>5,15</sup> during the course of the dediazonation demonstrates the reversibility of the formation of the reaction intermediate(s). It is expected that the amount of exchange will depend on the N<sub>2</sub> concentration in TFE, i.e., on the partial pressure of N<sub>2</sub> in the mixed gas. The results obtained under a total pressure of 300 atm are given in Table VIII.

It can be seen that with increasing nitrogen content in the atmosphere increasing amounts of labeled diazonio groups are lost in the remaining diazonium ion. This is also shown in Figure 5 where the -N=<sup>15</sup>N content of the azo dye derived from the diazonium ion after 70% dediazonation is plotted against N<sub>2</sub> concentration in TFE calculated from eq 2. Within the range studied, a linear relationship seems to exist between the extent of exchange and the N<sub>2</sub> concentration in TFE ( $r = 0.998$ ).

**Effect of Atmospheric Composition on the Rearrangement Reaction of the Diazonio Group.** The N<sub>α</sub>-N<sub>β</sub> rearrangement reaction was investigated in a manner similar to that described above for the exchange reaction. The extent of rearrangement was determined according to Scheme I. Under Ar the recovered diazonium ion after approximately 70% dediazonation consists only of the starting diazonium ion (A) and the rearranged ion (B). Thus, the extent of rearrangement B/(A + B) can be easily determined by mass spectral analysis of the reduced compound (A' + B') derived from the azo dye (A' + B'). In dediazonations under N<sub>2</sub>-containing atmospheres, however, the recovered diazonium ion consists also of the ex-

**Table VIII.** Exchange Reaction of 2,4,6-Trimethylbenzenediazonium- $\beta$ - $^{15}\text{N}$  Tetrafluoroborate with External  $\text{N}_2$  in TFE under Mixed  $\text{N}_2/\text{Ar}$  Gas at 300 atm (25 °C)

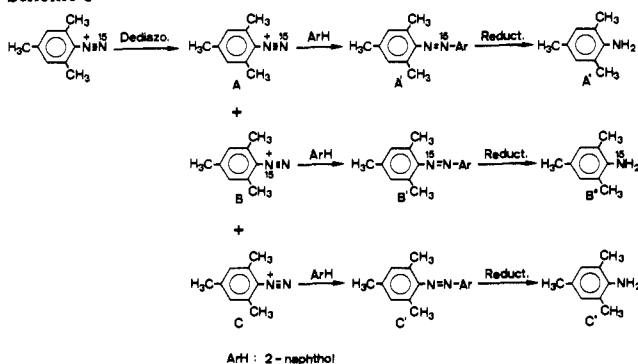
Atmosphere	-N= $^{15}\text{N}$ - content of azo dye, % <sup>a</sup>	[ $\text{N}_2$ ] in TFE, mol/L	% dediazonation	-N= $^{15}\text{N}$ - content azo dye, % <sup>b</sup>	% exchange
100% $\text{N}_2$	99.01 $\pm$ 0.49	3.031	61.28	93.32 $\pm$ 0.38 (92.51) <sup>c</sup>	6.33
	98.90 $\pm$ 0.16		79.24	90.36 $\pm$ 0.15 (91.36)	
	98.65 $\pm$ 0.82		70.09	92.42 $\pm$ 0.27 (92.43)	
	99.22 $\pm$ 0.14		71.46	92.72 $\pm$ 0.05 (92.85)	
				Av (92.29 $\pm$ 0.57)	
70% $\text{N}_2$ + 30% Ar	98.24 $\pm$ 0.25	2.136	73.32	94.41 $\pm$ 0.15 (94.53)	4.36
	98.06 $\pm$ 0.11		72.11	94.26 $\pm$ 0.63 (94.37)	
	99.00 $\pm$ 0.25		71.83	93.82 $\pm$ 0.19 (93.95)	
	98.56 $\pm$ 0.31		68.77	94.54 $\pm$ 0.06 (94.47)	
	98.22 $\pm$ 0.34		65.83	94.22 $\pm$ 0.33 (93.96)	
				Av (94.26 $\pm$ 0.37)	
30% $\text{N}_2$ + 70% Ar	98.32 $\pm$ 0.44	0.9438	67.66	96.13 $\pm$ 0.36 (96.05)	2.30
	98.51 $\pm$ 0.37		71.39	96.20 $\pm$ 0.24 (96.24)	
	98.65 $\pm$ 0.23		63.37	96.80 $\pm$ 0.38 (96.67)	
				Av (96.32 $\pm$ 0.79)	

<sup>a</sup> Azo dye obtained before dediazonation. <sup>b</sup> Azo dye obtained after dediazonation. <sup>c</sup> -N= $^{15}\text{N}$ - content of azo dye adjusted to exactly 70% dediazonation (it was assumed that the extent of exchange is proportional to the percentage dediazonation).

**Table IX.** Isotopic Rearrangement of 2,4,6-Trimethylbenzenediazonium- $\beta$ - $^{15}\text{N}$  Tetrafluoroborate in TFE under Mixed  $\text{N}_2/\text{Ar}$  Gas at 300 atm (25 °C)

Atmosphere	% dediazonation	$P'$ , % <sup>a</sup>	$P'$ , % cor <sup>b</sup>	$P$ , % cor <sup>c</sup>	$k_r/k_s$ <sup>d</sup>	$k_r \times 10^5, \text{s}^{-1}$ <sup>e</sup>
100% Ar	56.00	14.83 $\pm$ 0.67	20.16	20.16	0.2031	2.97
	78.17	22.53 $\pm$ 1.10	18.87	18.87		
	83.65	25.20 $\pm$ 0.84	18.63	18.63		
	65.48	17.32 $\pm$ 0.56	19.11	19.11		
	72.46	20.98 $\pm$ 0.98	19.92	19.92		
				Av 19.34		
70% Ar + 30% $\text{N}_2$	63.37	18.23 $\pm$ 0.70	20.92	21.64	0.2194	3.03
	71.39	19.54 $\pm$ 0.11	18.96	19.70		
	67.66	18.49 $\pm$ 0.76	19.44	20.24		
				Av 20.53		
30% Ar + 70% $\text{N}_2$	68.77	17.60 $\pm$ 0.48	18.08	19.14	0.2101	2.79
	71.83	18.32 $\pm$ 0.08	17.55	18.67		
	65.83	18.71 $\pm$ 0.21	20.44	21.75		
				Av 19.85		
100% $\text{N}_2$	79.24	22.04 $\pm$ 0.45	17.96	19.66	0.2033	2.64
	70.09	16.85 $\pm$ 0.96	16.82	18.20		
	71.46	19.37 $\pm$ 0.59	18.77	20.22		
				Av 19.36		

<sup>a</sup> Apparent extent of isotopic rearrangement. <sup>b</sup> Apparent isotopic rearrangement adjusted to exactly 70% dediazonation (the following equation was employed for the calculation:  $k_r/k_s = \log(1 - 2p)/2 \log x$ , where  $p = P'/100$ ,  $x$  = the fraction of remaining diazonium salt; see ref 8). <sup>c</sup> Real extent of isotopic rearrangement (see Appendix). <sup>d</sup> See equation in footnote b. <sup>e</sup> Calculated from  $k_r/k_s$  and  $k_s$  values in Table VI.

**Scheme I**

changed product (C) in addition to the labeled compound (A + B). In order to deduce the real extent of rearrangement in those cases, the apparent results must be corrected for the competitively occurring exchange reaction. This was done as

follows. From the mass spectral analysis of the azo dye ( $A' + B' + C'$ ) the ratio  $C/(A + B + C)$  was obtained (see Table VIII). Mass spectral analysis of the reduction product ( $A'' + B'' + C''$ ) derived from the same azo dye gave the ratio  $B/(A + B + C)$ , that is, the apparent extent of rearrangement ( $P'$  in Table IX). Using these two values, the real extent of rearrangement, i.e., the ratio  $B/(A + B)$ , was calculated (see Appendix). The results are summarized in Table IX.

It is obvious that the dependence of the rearrangement rate ( $k_r$ ) on atmospheric composition, if any, is very slight.

## Discussion

Comparison of our results with those obtained earlier for the benzenediazonium ion<sup>5</sup> shows that the 2,4,6-trimethylbenzenediazonium ion gives about three times more rearranged and exchanged product. As reported previously,<sup>5</sup> substituents in the para position of the benzene nucleus have practically no effect on the amount of isotopic rearrangement and exchange. It was pointed out in the preceding paper that our results can be explained by the steric effect of the methyl groups at posi-

tions 2 and 6. The addition of a bulky solvent molecule to the reaction intermediate is sterically hindered and hence the probability of attack by a small nitrogen molecule increases, resulting in a higher amount of exchanged and rearranged product.

The effect of pressure on the overall dediazonation rate can best be seen in Figure 2. The volume of activation for the dediazonation of 2,4,6-trimethylbenzenediazonium salt in TFE ( $\Delta V^\ddagger = +11.06 \text{ cm}^3/\text{mol}$ ) is in close agreement with that found for benzenediazonium salt in the same solvent ( $\Delta V^\ddagger = 11.4 \text{ cm}^3/\text{mol}$ ).<sup>5,16</sup> Both values are in good agreement with a transition state where the carbon-nitrogen bond is considerably stretched, assuming that changes in the charge distribution, and consequently solvent electrostriction, in going from the ground state to the dediazonation transition state are small. Since at any one pressure argon reduces the rate to a smaller extent than nitrogen, it can be concluded that in addition to a simple pressure effect, nitrogen also influences the reaction chemically. This could have been expected on the basis of the observed exchange of labeled diazonio groups with external nitrogen. It has been already pointed out in the Results section that the pressure effect on all reactions under study has been compensated for by working under a constant total pressure of 300 atm, and only varying the partial pressure of nitrogen. Therefore, the effect of nitrogen concentration independent of pressure will be discussed in the following paragraphs.

As can be seen from Figure 5, the label remaining in the diazonium ion after 70% dediazonation drops linearly with increasing concentration of nitrogen in TFE. This means that the amount of exchange rises proportionally with the nitrogen concentration. This is in agreement with the assumption that the exchanged product is formed in a reaction of an intermediate with molecular nitrogen. The observed behavior provides further support for the mechanism proposed in the preceding paper<sup>1</sup> requiring that the  $N_\alpha-N_\beta$  rearrangement and the exchange reaction proceed through different intermediates. The same conclusion can be drawn from the fact that the amount of rearranged product in all cases is several times higher than the amount of exchanged product although the concentration of <sup>15</sup>N labeled nitrogen in solution is orders of magnitude smaller than that of the nitrogen added to the solution. This

$$k_s = \frac{(k_{DX}k_{XP}k_{YX}[\text{Nu}][\text{N}_2] + k_{DX}(k_{XY}k_{YP}[\text{Nu}] + k_{XP}k_{YP}[\text{Nu}]^2))}{(k_{XD}k_{YX} + k_{XP}k_{YX}[\text{Nu}][\text{N}_2] + k_{XD}k_{YP}[\text{Nu}] + k_{XY}k_{YP}[\text{Nu}] + k_{XP}k_{YP}[\text{Nu}]^2)}$$

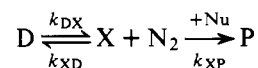
observation and its consequence have been discussed in detail in the preceding paper.<sup>1</sup>

While there is no doubt about the effect of  $\text{N}_2$  concentration on the exchange reaction, it is much harder to discern a definite trend in the case of the rearrangement reaction. It can be seen from Table IX that, although the apparent percentage of isotopically rearranged compound gets smaller with increasing  $\text{N}_2$  concentration, the "real rearrangement" (corrected for the parallel occurring exchange) does not change within experimental error in the region of nitrogen concentrations studied. The same applies to the  $k_r/k_s$  ratios. Consequently, the rate constants for the rearrangement reaction, calculated from the  $k_r/k_s$  ratios and the dediazonation rates,  $k_s$ , which decrease with increasing  $\text{N}_2$  concentration (Table VI), also decrease as the concentration of nitrogen in TFE rises. The effect, however, is very small and could well be within experimental error.<sup>17</sup> It is hard to predict what the expected influence of concentration of nitrogen in TFE would be. Assuming that the isotopic rearrangement occurs through a tight molecule-ion pair,<sup>1</sup> only a change in the reaction medium (i.e., solvent + other molecules dissolved in it) would influence the  $k_r$  value. Since a change in nitrogen concentration, that is, in the partial pressure of nitrogen in the  $\text{N}_2/\text{Ar}$  gas mixture, would hardly change the

reaction medium significantly, the effect, if any, of  $\text{N}_2$  concentration on the rearrangement reaction would be expected to be minute.

The most conclusive evidence for the proposed dediazonation mechanism is provided by the effect of changing nitrogen concentration in TFE on the overall dediazonation rate,  $k_s$ . The decrease in the dediazonation rate with increasing nitrogen concentration is shown in Figure 3. The mere fact that this decrease occurs is already evidence of the existence of a "free" (i.e., where  $\text{N}_2$  is fully dissociated) phenyl cation along the dediazonation pathway, which is formed reversibly (possibly, but not necessarily, through another intermediate) from the diazonium salt. This is in accordance with all the evidence available to date.<sup>1,5,11,12,18-21</sup> However, as mentioned above, some results presented in this and in the preceding<sup>1</sup> paper indicate that at least two reaction intermediates must be involved in heterolytic dediazonations. Computer curve-fitting of the  $k_s$  vs.  $[\text{N}_2]$  data on the basis of a "one-intermediate" and a "two-intermediate" model, and consequent statistical treatment of the values obtained, provide additional evidence for the two-intermediate mechanism.

Model 1<sup>22</sup>

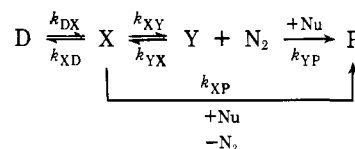


Overall rate constant

$$\text{rate} = k_s[\text{D}]$$

$$k_s = \frac{k_{DX}k_{XP}[\text{Nu}]}{k_{XD}[\text{N}_2] + k_{XP}[\text{Nu}]}$$

Model 2<sup>22</sup>



Application of the steady state assumption to both X and Y yields the equation for the total rate and consequently the overall rate constant  $k_s$ .

If only the dependence of  $k_s$  vs.  $[\text{N}_2]$  is monitored, the rate equations for models 1 and 2 can be written as follows:

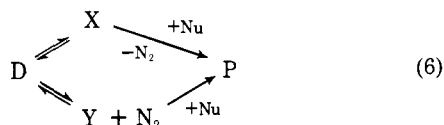
$$\text{Model 1} \quad k_s = \frac{a}{b[\text{N}_2] + c} \quad \text{Model 2} \quad k_s = \frac{a'[\text{N}_2] + b'}{c'[\text{N}_2] + d'}$$

These two equations were used with a nonlinear least-squares program (NLWOOD) to fit the experimental data.<sup>23</sup> The best fits for both models together with the experimental values are represented in Figure 3.

Setting "a" and "b" equal to 1, the other coefficients were determined by computer. If  $a'$  were negligibly small compared with  $b'$ ,  $c'$ , and  $d'$ , model 2 would become model 1, and it could be concluded that no improvement is achieved by introducing an additional coefficient. However,  $a'$  is comparable in size with the other values, and its 95% confidence limits are well above zero, implying that the best fit for model 2 is significantly different from that for model 1. An F-test of model 2 against model 1 shows at the 99% confidence level that there is an improvement in the fit in going from model 1 to model 2.<sup>23</sup> This can also be seen just by looking at Figure 3. There is obviously a trend in the deviations of the experimental values from those calculated with model 1, while the deviations are random with model 2. On the basis of all the arguments presented above,

model 1 can be rejected. This means that not even the dependence of the dediazonation rate on nitrogen concentration can be accounted for with just one reaction intermediate. An important difference between the two models is the fact that in model 1 the rate at  $[N_2] = \infty$  approaches zero, while in model 2 a limiting value, greater than zero, is approached,  $(k_s)_{[N_2]=\infty} = 1.15 \times 10^{-4} \text{ s}^{-1}$ , as calculated from the ratio of  $a'/c'$ . This is due to the fact that in model 2 an additional product-forming pathway from the first intermediate is possible, which does not involve free nitrogen. Obviously this pathway in the mechanism is necessary in order to account for all the experimental results.

In addition to the two-intermediate mechanism in model 2, there is another mechanism with two competitively formed intermediates which could mathematically also fulfill all the requirements, i.e., give an equation with the general form  $k_s = (a'[N_2] + b')/(c'[N_2] + d')$ . This mechanism is represented in eq 6.

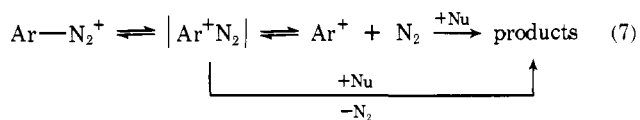


However, when the nature of the intermediates, discussed in this and the preceding paper,<sup>1</sup> is taken into account, i.e., the fact that Y is a "free" aryl cation and X a nitrogen-aryl cation molecule-ion pair, it follows logically that X should lie on the path from D to Y as assumed in the mechanism in model 2.

Inspection of the data concerning the effect of potassium thiocyanate on the dediazonation rate (Table VII and Figure 4) shows that the rate increases significantly in going from 0 to 0.365 M KSCN in TFE, and that the amount of rate increase under 300 atm Ar parallels that obtained under 300 atm  $N_2$ . Owing to the low solubility of KSCN in TFE higher concentrations could not be tested, but in the concentration range investigated the rate increases by about 20%. It is interesting to compare this rate increase with the decrease caused by raising the nitrogen concentration from 0 to ca. 3 M ( $\sim 11\%$ , Table VI) with the amount of rearrangement at 70% reaction ( $\sim 20\%$ , Table IX) and with the amount of exchange at 70% reaction ( $\sim 6.3\%$ , Table VIII). The rate increase resulting from added thiocyanate ion is most likely due to capture of one or both reaction intermediates, which prevents the back reaction. This only happens with the strong nucleophile  $SCN^-$ , while the effects of KF and  $Bu_4N^+ClO_4^-$  are negligible. Since the return reaction is responsible for all the phenomena mentioned above, some conclusions can be drawn from the comparison of the respective values. The percent of exchange is smaller than the reduction of the rate with 3 M  $N_2$ . Although both reactions proceed through the same intermediate, the observed difference is expected since (1) exchange is monitored only at 70% dediazonation, and (2) some of the exchange remains undetected if already exchanged (unlabeled) diazonium salt molecules are involved. While only 11% rate retardation is observed with 3 M  $N_2$  present, the rate acceleration with added  $SCN^-$  is at least 20%. This means that some of the acceleration is due to the trapping of the first intermediate formed, the nitrogen aryl cation molecule-ion pair. However, as can be judged from the amount of rearrangement observed, not all of this intermediate is trapped by  $SCN^-$ , since if this were the case the acceleration by  $SCN^-$  should be higher than the amount of rearrangement.<sup>24</sup>

To summarize the conclusions drawn from the results presented in this and the preceding paper:<sup>1</sup> Dediazoniations of benzene- and 2,4,6-trimethylbenzenediazonium salts in TFE and HFIP proceed heterolytically through two consecutively and reversibly formed reaction intermediates. The first intermediate is a tight nitrogen aryl cation molecule-ion pair, and it is responsible for the observed rearrangement reaction.

The exchange reaction occurs at the second intermediate which is the free (no nitrogen) aryl cation.<sup>25</sup> Dediazonation products can be formed by nucleophilic attack on both intermediates.



The evidence given in this and the preceding paper for the existence of (at least) two aryl cation-like species in the dediazonation of arenediazonium salts must be viewed in the context of recent theoretical investigations<sup>26,27</sup> on the existence and stability of aryl cations and of the unsuccessful attempts of five research groups<sup>28</sup> to form aryl cations from aryl triflates and similar compounds in analogy to the formation of vinyl cations. Heterolytic dediazonation seems to be still the only reaction known to yield aryl cation-like intermediates.

We emphasize here that the second intermediate which we postulate is called "free" because it is free of the nitrogen molecule. We put "free" in quotation marks in order to indicate that this aryl cation may still be solvated by solvent molecules in a specific way.

In TFE (and in hexafluoro-2-propanol) the energy of the second intermediate is only slightly higher than that of the first intermediate  $[\text{Ar}^+\text{N}_2]$ . Therefore a significant part of the reaction goes through the second intermediate as demonstrated by our results on exchange with external nitrogen and on the reaction with CO.<sup>5</sup> In water, however, the first intermediate reacts so easily with the more nucleophilic solvent that the  $N_\alpha$ - $N_\beta$  rearrangement, i.e., the back reaction of the first step, is observable to a small extent, but not the reactions of the second intermediate with external  $N_2$  or CO. This is partly also due to the low solubility of gases in water relative to that in fluorinated alcohols. In other words, the activation energy of the direct solvolysis of the first intermediate is much smaller in water than the activation energy of the transformation of the first into the second intermediate.

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## Appendix

Let  $X$  be the fraction of the diazonium ion that has undergone exchange with external  $N_2$  up to 70% reaction, and let  $Y$  be the corresponding apparent fraction having undergone rearrangement.

$$X = \frac{C}{A + B + C} \quad (8)$$

$$Y = \frac{B}{A + B + C} \quad (9)$$

Elimination of  $C$  in eq 8 and 9 yields

$$(A + B) \frac{X}{1 - X} = \frac{B}{Y} - B - A \quad (10)$$

Rearrangement of eq 10 provides eq 11, which was used to calculate the real fraction of the diazonium ion having undergone rearrangement.

$$\frac{B}{A + B} = \frac{Y}{1 - X} \quad (11)$$

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- (2) Presented in part at the 26th IUPAC Congress, Tokyo, Sept 4–10, 1977.
- (3) (a) Department of Chemistry, Gunma University, Kiryu, Gunma, Japan. (b) Research and Development Division, B. P. Chemicals Ltd., Grangemouth, U.K. (c) Department of Organic Chemistry, University of Adelaide, Adelaide, South Australia. (d) On leave of absence from the Department of Chemistry, Faculty of Science, University of Zagreb, Zagreb, Yugoslavia.
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- (22) D = diazonium ion; X and Y = reaction intermediates; P = reaction products; Nu = any nucleophile present in solution (i.e., solvent,  $N_2$ ,  $BF_4^-$ , etc.).
- (23) In the computer fitting of the experimental data as well as in the F-test of one model against the other, individual measurements and not the mean values were used. This way, the relatively large errors in the rate measurements (Table VI) are taken into account, and it is shown that they do not interfere with the differentiation of the two models by the F-test.
- (24) The actual rate of return from the first intermediate to the diazonium ion should be twice the rate of isotopic rearrangement, since, assuming two equivalent nitrogens, only half of the returns result in rearrangement. This implies that at high concentrations of  $SCN^-$ , provided that all the intermediate is trapped, rate increases of more than 40% are expected.
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## Intramolecular Proton-Transfer Mechanism in the Uracil Monoanions and Derivatives. A Temperature-Jump Study

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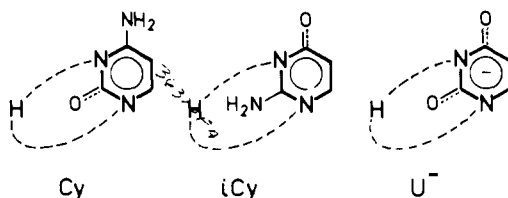
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*Received May 23, 1977*

**Abstract:** The tautomeric interconversion of the monoanions of uracil and of 5-fluorouracil are shown by laser and joule-heated temperature-jump spectroscopy to proceed via a two-step mechanism involving the protonated or the deprotonated forms common to both tautomers. No contribution from a bifunctional nondissociative proton transfer mechanism involving water molecules is detected in the interconversion kinetics.

### Introduction

Interconversion between the N(1)H and the N(3)H tautomers of the neutral pyrimidines, cytosine<sup>2</sup> (Cy) and isocytosine<sup>3</sup> (iCy), has been shown from temperature-jump relaxation experiments to proceed, in aqueous solutions, through intermediate protonation or deprotonation leading to a species common to both tautomers. This last species is then deprotonated or protonated yielding one of the tautomers ("D mechanism," dissociative).<sup>4</sup> In contrast, in the structurally closely related case of the uracil monoanion ( $U^-$ )<sup>5</sup> for which the D



mechanism is expected, it has been reported<sup>6a</sup> from dynamic NMR data that a concerted nondissociative proton transfer

involving water molecules ("ND mechanism" nondissociative) would greatly contribute to the tautomeric interconversion rate.

Contribution of the ND mechanism to tautomeric interconversion has been shown by us<sup>3</sup> to be strongly related to the geometry of the tautomeric systems. It therefore seems that either the presence of a negative charge favors the ND mechanism, or the dynamic NMR technique gives information different from that obtained by relaxation spectrometry on aqueous solutions containing tautomeric molecules. Among the various systems studied<sup>6</sup> by the dynamic NMR technique, only the uracil monoanions absorb in the near UV, thus providing a unique opportunity to compare both methods.

### Methods

**Laser Temperature-Jump Experiments.** Quantitative measurements on fast relaxation spectra (relaxation time smaller than 5  $\mu$ s) were performed with the previously described laser temperature-jump apparatus.<sup>7</sup> For these measurements the detection bandwidth was limited to 5 MHz, in order to reduce