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SOLVOLYTIC BEHAVIOR OF p-DIMETHYLAMINO-α-BROMOSTYRENE IN WATER SOLUTIONS

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Abstract - Nmr and UV studies show that p-dimethylamino-α-bromostyrene, I, undergoes S_N1 reaction in H_2O and $HClO_4$ ($k_{S_N1} = 6 \times 10^{-1} sec.^{-1}$ at 25°). The vinyl cation has an extraordinary selectivity for capture by aromatic amines relative to H_2O, including I itself to give the dimer II.

On the basis of studies on p-dimethylamino-α-bromostyrene reported herein we wish to state that the report by Schubert and Barfknecht that p-amino-α-bromostyrene undergoes acid-catalyzed hydration-elimination is in error.[1] The conclusion of Grob and coworkers that a solvolysis mechanism pertains is correct,[2,3] though we found the behavior of both bromostyrenes to be far from simple and very difficult to unravel. We were unable to pin-point the source of Barfknecht's error, though we did establish that he was not following hydration of p-aminophenyl acetylene. However, the hydrobromide salt that Barfknecht used as his substrate, prepared by a method of Grob,[2a] may have been of questionable identity. In later work Grob reported that this method of preparing the hydrobromide salt of p-amino-α-bromostyrene frequently yielded substantial by-products.[2b]

In the work described herein, the main complication encountered was essentially instant dimerization, I → II, when UV solutions in H_2O, pH > 3, were prepared by methods A or B, Table I. However, when monomer I was introduced into $HClO_4$, 0.01 to 0.5 M., dimer formation was averted by instantaneous and extensive N-protonation, and a clean first order spectral change from that of monomer I to that of the acetophenone VI was observed. The k_{obsd} values, Table II, are inversely dependent on $[H_3O^+]$, indicating an S_N1 mechanism. The nmr spectrum in 20% $DClO_4$-D_2O, perfectly consistent with N-deuterated I, changed slowly to that of VI without prior exchange of vinyl protons. This indicates direct solvolysis of I rather than of a reversibly formed hydrate. Based on extrapolated UV spectra in $HClO_4$ solutions at 5°, $K_{SH^+} = 1.5 \times 10^{-4}$. Using this value in the equation $k_{S_N1} = k_{obsd} (K_{SH^+} + [H_3O^+])/K_{SH^+}$ one obtains $k_{S_N1} = 6 \times 10^{-1}$ $sec.^{-1}$ at 25°. The eight-fold decrease in k_{obsd} brought about in 0.01 M. $HClO_4$ by added sodium bromide, 0.1 M., is indicative of appreciable return reaction from solvent separated vinyl cation back to vinyl bromide when $[Br^-]$ is sufficiently high.

Table I: Substrate Introduction Methods[a]

Method	Volume Dioxane	Volume H_2O	Substrate Concentration
A	0.4 ml.	4 ml.	$3\text{-}5 \times 10^{-5}$ M.[b]
B	0.4 ml.	30 ml.	$3\text{-}5 \times 10^{-6}$ M.[c]
C	4 ml.	30 ml.	$3\text{-}5 \times 10^{-6}$ M.[c]

[a] 1 μ of an ether extract of I was introduced into the dioxane and the solution flooded immediately with the H_2O solution. [b] 1 cm. cell [c] 10 cm. cell.

Table II: Observed First Order Rate Constants in Aqueous $HClO_4$ at 25°

M $HClO_4$	Monomer (I)	Dimer (II)[a]
0.0051	b	1.7×10^{-3}
0.0103	8.45×10^{-3}	
0.0514	1.62×10^{-3}	1.1×10^{-4}[c]
0.103	7.59×10^{-4}	
0.514	1.06×10^{-4}	3.6×10^{-6}
0.0103, 0.1M.NaBr	1.10×10^{-3}	

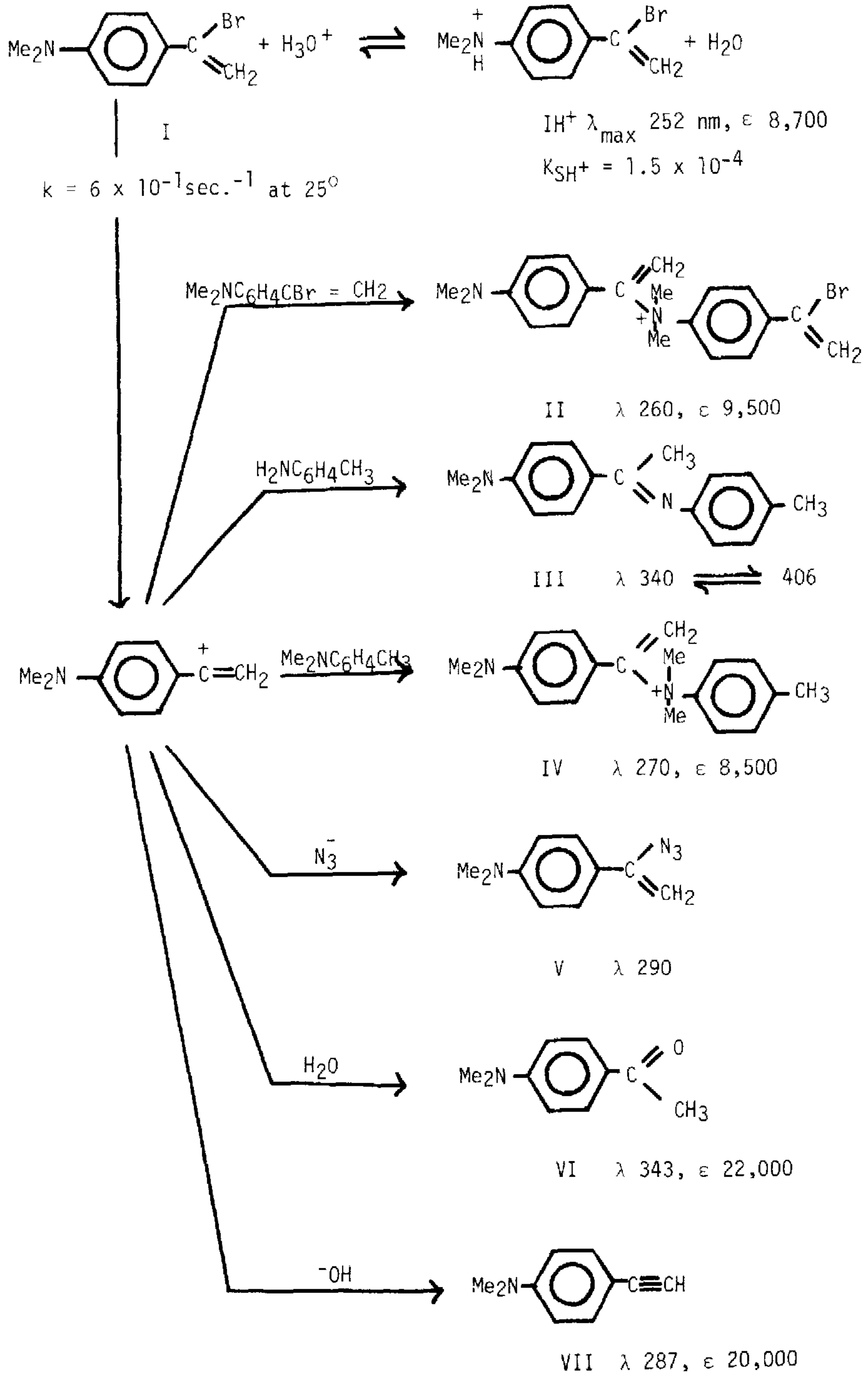
[a] Solutions prepared by method A into H_2O followed by aqueous $HClO_4$; [b] Curved rate plot.
[c] Unchanged in the presence of 0.1M. NaBr.

In H_2O, pH > 3, only solvolysis products were observed at the first UV scan, within 10 sec. after mixing. This is an agreement with the large k_{S_N1} value derived from the data on I in $HClO_4$.

When sample introduction methods A or B were employed to introduce I into water, the initial UV spectrum was that of the dimer II, which in turn solvolyzed rapidly. The identity of the dimer was established by its solvolytic behavior, its analogy to other nucleophile capture products of I, and its reversion back to I in 91% dioxane (discussed in the adjoining paper[4]). The dimerization, I → II, occurred locally, i.e., while I was being dispersed into solution. This was shown by the following experiments: a solution in 0.1M $HClO_4$, known to contain monomer, was quickly diluted to 3×10^{-6}M. substrate by immediately mixing it with an equal volume of 0.1M sodium acetate. An immediate spectral scan revealed no II, but nearly fully formed acetophenone, VI. Later, local formation of dimer also was averted by the use of method C to introduce I (3×10^{-6}M.) into water. The initial and constant spectrum at the first quick scan was that of VI. When method C was used to introduce I into 0.5M NaOH, the initial spectrum was that of the acetylene VII, > 90%, along with a little VI, < 10%.

Not only was it observed that dimerization can occur locally (method A or B) but also in very dilute solution. That is, when the solution in 0.1M $HClO_4$ of known I was diluted to a substrate concentration of 3×10^{-5}M. (in a 1 cm. cell) by the addition of aqueous sodium acetate, the initial spectrum and subsequent changes were those of dimer II. However, as mentioned above, dimerization was largely averted, i.e., the initial spectrum was that of VI, when similar dilution of I was carried to 3×10^{-6}M. (10 cm cell) instead of 3×10^{-5}M.

Behavior of Dimer II - Between pH 3 and 6 the spectrum of the dimer II changed rapidly to that of VI, whereas at pH 8 some acetylene VII (30%) also was formed. The first order rate constant was pH independent over this range ($k_{obsd} = 6 \times 10^{-3}$sec.$^{-1}$ at 21°C). In $HClO_4$ solutions, the first order process II → VI showed an inverse acidity dependence (Table II). Addition of Br^- had no rate-depressing effect as was observed for monomer, consistent with the solvolysis of II proceeding by initial C-N heterolysis.



IH$^+$ λ_{max} 252 nm, ε 8,700

$K_{SH^+} = 1.5 \times 10^{-4}$

$k = 6 \times 10^{-1}$ sec.$^{-1}$ at 25°

II λ 260, ε 9,500

III λ 340 ⇌ 406

IV λ 270, ε 8,500

V λ 290

VI λ 343, ε 22,000

VII λ 287, ε 20,000

Nucleophile Capture - The ready dimerization I → II indicated that the intermediate vinyl cation was very prone to capture by nucleophiles other than H_2O. Indeed, it was shown to be readily captured by low concentrations of nucleophiles ranging from Cl^- and N_3^- to amines. Method C was used to introduce I into aqueous nucleophile solutions. When I was thus introduced into a buffer of p-N,N-dimethyltoluidine (4.3×10^{-5}M.) and its perchloric acid salt (1.2×10^{-4}M.) the initial spectrum,[5] that of IV, resembled that of II. As is to be expected, the solvolysis IV → VI proceeded at a slower rate ($k = 1.1 \times 10^{-4} sec^{-1}$ at 21°) than II → VI, and also with different isoabsorptive points. In similar experiments, monomer I (3×10^{-6}M) was captured by a buffer of p-toluidine (3.7×10^{-5}M.) and p-toluidinium perchlorate (8.3×10^{-5}M.) to yield the anil III, partly in its N-protonated form (λ_{max} 406).[6] The anil hydrolyzed to VI with $k = 3.8 \times 10^{-4}$ sec^{-1}. It is estimated that at most 15% of the acetophenone VI was initially formed from I along with amine captured product. The selectivity of the vinyl cation for aromatic amines relative to H_2O is extraordinarily high. The lower limit value of $k_{p\text{-toluidine}}/k_{H_2O}$ is 8×10^6! Compare this with $k_{\phi NH_2}/k_{H_2O} = 2.5 \times 10^4$ in the hydrolysis of p-nitrophenyl acetate[7] and 5.8×10^3 in the reaction with the oxonium ion from syn-2-(4-methoxyphenyl)-4,5-trimethylene-1,3-dioxolane.[8]

References and Notes

1. W. M. Schubert and G. Barfknecht, J. Amer. Chem. Soc., **92**, 207 (1970).
2. (a) C. A. Grob and G. Czeh, Helv. Chim. Acta, **47**, 194 (1964); (b) C. A. Grob and H. R. Pfaendler, ibid., **54** 2060 (1970).
3. For a thorough review of S_N1 reactions of vinyl derivatives, see P. J. Stang, Z. Rappoport, M. Hanack and L. R. Subramanian "Vinyl Cations", Academic Press, 1979.
4. W. M. Schubert and D. C. Green, Tetrahedron Lett.,   (1980).
5. The blank 10 cm. cell contained the buffer solution.
6. A dimeric protonated anil, λ_{max} 380, was obtained within 3 seconds when method A was used to introduce p-amino-α-bromostyrene into mildly acidic H_2O. This anil in turn hydrolyzed to p-aminoacetophenone by an acid-catalyzed mechanism.
7. W. P. Jencks and J. Carriuolo, J. Amer. Chem. Soc., **82**, 1778 (1960).
8. J. D. Kruger, Ph.D. Thesis, University of Washington, 1972.

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