Unimolecular Heterolysis of a Nitrogen–Nitrogen Bond

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Summary Alkyl-aryl-triazenes, R–N=N–NHAr, can, when Ar contains electron-withdrawing groups, decompose in aqueous solution by simple unimolecular heterolysis, $\text{R–N=N–NHAr} \rightarrow \text{R–N}\overset{+}{\equiv}\text{N} + \overline{\text{N}}\text{HAr}$.

ALKYL-ARYL-TRIAZENES exist as a tautomeric mixture of forms (**1**) and (**2**).[1] Proton-donation to the arene-bound

$$\underset{(\mathbf{1})}{\text{R–NH–N=N–Ar}} \rightleftharpoons \underset{(\mathbf{2})}{\text{R–N=N–NHAr}}$$

nitrogen results in decomposition to give $ArNH_2$, N_2, and products typical of deamination-reactions from the R fragment.[2] The kinetics of this process have been thoroughly examined in non-aqueous solvents, and it has been established that a proton is 'in flight' at the rate-determining transition state.[3]

We now report that in aqueous solution (1M-KCl at 25 °C) unimolecular departure of $NHAr^-$ from the RN_2^+ fragment also takes place. In addition to acid-catalysed processes analogous to those studied in non-aqueous solvents,[4] a pH-independent hydrolysis of propyl-, benzyl-, and β-D-galactopyranosylmethyl-(*p*-nitrophenyl)triazenes, with rate constants of $2{\cdot}3_4 \times 10^{-3}$, $9{\cdot}_5 \times 10^{-5}$, and $3{\cdot}5 \times 10^{-5}$ s^{-1}, respectively, has been observed. The sole chromophoric product from the nitrophenyl unit is *p*-nitroaniline, and the examination of the products from decomposition of β-D-galactopyranosyl-[^{14}C]methyl-(*p*-nitrophenyl)triazene[5] reveals two main radioactive components, in accordance with the observation of hydride-shift products when β-D-galactopyranosylmethylamine is deaminated by nitrous acid.[6] A normal deamination-pathway is being followed.

This normal deamination-pathway, catalysed by a variety of acidic species, must involve the alkane-diazonium ion as a free, solvent-equilibrated intermediate, for the following reasons. (i) The rates of H_3O^+-catalysed decomposition of various triazenes R–NH–N=N–Ph correlate excellently with the acid dissociation constant of $R\text{–}NH_3^+$, irrespective of the ease of generation of R^+ (Figure). (ii) No *N*-alkylated anilines are formed in this process. (iii) The H_3O^+-catalysed reaction of $Ph\text{–}CD_2NH\text{–}N{=}N\text{–}Ph$ shows an isotope effect (k_H/k_D) of 1·1 ± 0·2; *i.e.* the C–H bond is not broken in the rate-determining step. (iv) Replacing 1M-KCl as 'inert' electrolyte with 1M-NaN_3 in the hydrolysis of benzyl-(*p*-methoxyphenyl)-, benzyl-(*p*-methylphenyl)-, benzyl-(phenyl)-, propyl(phenyl)-, propyl-(*p*-methoxyphenyl)-, and propyl-(*p*-chlorophenyl)-triazenes in 0·1M-ethanolamine–HCl at pH 9 produces an average rate decrease of 17 ± 19%.

Nothing is therefore happening at the crypto-cationic centre in the rate-determining transition state of the acid-catalysed process. That the same is also true of the pH-independent process is further demonstrated by the negligible change in the rate for propyl-(*p*-nitrophenyl)triazene when the electrolyte is changed to 1M-NaN_3 (k $2{\cdot}5_1 \times 10^{-3}$ s^{-1}).

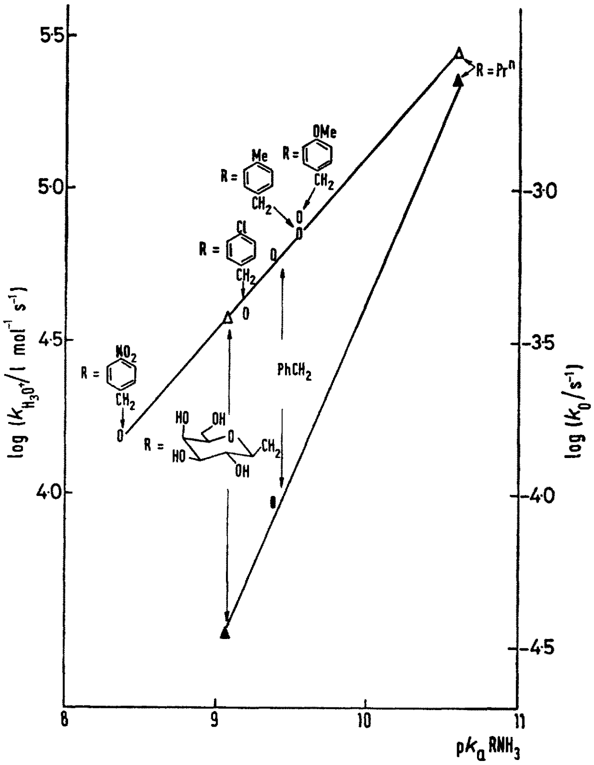

FIGURE. ○ rates of H_3O^+-catalysed hydrolysis of the triazenes R–N=N–NHPh; ● rates of uncatalysed hydrolysis of R–N=N–NH–$C_6H_4NO_2$-*p* as a function of the p*K*a of RNH_3^+.

Despite the pK_a of *p*-$NO_2C_6H_4NH_2$ being 18·9,[7] well above the p*K*$_a$ of water, we are constrained by the following facts to propose that *p*-$O_2NC_6H_4NH^-$ departs from the alkane-diazonium ion without significant proton donation from, and consequent immobilisation of, a solvent molecule. (i) The pD-independent rate of hydrolysis of propyl-(*p*-nitrophenyl)triazene in D_2O is $2{\cdot}1_7 \times 10^{-3}$ s^{-1}, giving a solvent deuterium isotope effect of $1{\cdot}0_8$. The $H_2PO_4^-$-catalysed hydrolysis of the same compound exhibits an isotope effect of 3·0. (ii) $\Delta S^\ddagger$ for the pH-independent hydrolysis of benzyl-(*p*-nitrophenyl)triazene is near zero (+ 2 ± 3 cal mol^{-1} K^{-1}). (iii) The pH-independent hydrolysis of propyl-(3,5-dichlorophenyl)triazene has been detected (k 9×10^{-5} s^{-1}). This datum, combined with that for the *p*-nitro-compound, gives a β_{lg} value, uncorrected for substituent effects on the (**1**) ⇌ (**2**) equilibrium, of −1·0.† In the acid-catalysed processes, β_{lg} changes only slightly (from + 0·61 to + 0·44 ± 0·05) as the pK_a of the catalysing acid changes by 8·3 units (from −1·74 for H_3O^+ to 6·55 for $H_2PO_4^-$). A drastic reversal of the sign of β_{lg} as the pK_a of the catalysing acid is increased a further 9·2 units to that of water is therefore unlikely.

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† This estimate used p*K*$_a$ values of $ArNH_3^+$. If p*K*$_a$ values of $ArNH_2$ are used, the β_{lg} value becomes −0·3.

The rates we have measured for the pH-independent hydrolyses of alkyl-aryl-triazenes, after correction for the fraction of reactive tautomer, are thus the rates of the unimolecular reaction (1).

$$\mathrm{R{-}N{=}N{-}NHAr} \rightarrow \mathrm{R{-}\overset{+}{N}{\equiv}N} + \mathrm{\overset{-}{N}HAr} \qquad (1)$$

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