Bimolecular Displacement of Nitrogen (S_N2) in an Alkanediazonium Ion

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Summary Kinetic studies on the bis(trifluoromethyl)-methanediazonium ion in FSO_3H show loss of N_2 through an S_N2 pathway.

THERE has been controversy over the loss of molecular nitrogen from diazonium ions during the past two decades.[1] Deamination of aliphatic amines and acid-catalysed solvolysis of diazo-compounds have been most often interpreted as proceeding through carbonium ion or ion-pair intermediates in the product-forming step. Loss of N_2 from alkanediazonium ions through bimolecular substitution at carbon has also been proposed.[2] However, direct investigation of alkanediazonium ions has not been possible owing to their instability. Isolation and characterization of the bis-(trifluoromethyl)methanediazonium ion (II) in FSO_3H solutions has allowed a direct kinetic study. We report here an overall second-order rate law, $-d[RN_2^+]/dt = k_2[RN_2^+][OSO_2F^-]$.

Bis(trifluoromethyl)diazomethane (I) was synthesized by reaction of nitrous acid with bis(trifluoromethyl)methylamine[3] in water at pH 3. Slow addition of (I) in $CDCl_3$ to FSO_3H at −70° with good stirring gave a solution of the diazonium ion (II) in the lower acid layer. Both ^1H and ^{19}F n.m.r. spectra indicate the presence of (II). The results are consistent with our earlier investigation of the 2,2,2-trifluoroethanediazonium ion.[4] The fluorosulphate ester (III), formed by loss of N_2, was characterized by elemental and spectroscopic analyses.

$$\underset{\text{(I)}}{(CF_3)_2CN_2} + FSO_3H \xrightarrow[-70^\circ]{} \underset{\text{(II)}}{(CF_3)_2CHN_2^+} + OSO_2F^- \xrightarrow{k_2} \underset{\text{(III)}}{(CF_3)_2CHOSO_2F} + N_2$$

Kinetic measurements were made with a JEOL C-60HL n.m.r. spectrometer over a temperature range of −5 to +5°, using a methanol sample for temperature calibration.[5] Rates were calculated from integrated ^1H peak areas of (II) (septet, −7·5 p.p.m., J_{HF} 3·9 Hz) and (III) (septet, −5·9 p.p.m., J_{HF} 5·1 Hz). Me_4NBF_4 was used as a primary internal standard for obtaining accurate concentration data. Diazonium ion concentrations of 0·15—0·4M were commonly used for the kinetic measurements.

Protonation of (I) with FSO_3H was rapid and complete. The ^{19}F n.m.r. spectrum showed no remaining unprotonated diazo-compound; thus, equal concentrations of diazonium cation and FSO_3^- formed initially. Excess of FSO_3K (99%)[6] was added to determine the kinetic order of FSO_3^-. Apparent first-order (k_1) and second-order (k_2) overall rate constants were calculated using linear least-squares analyses.

Consistent second-order rate constants were obtained over a three-fold range of FSO_3^- concentration. Whereas values of k_2 are relatively constant over this range at constant temperature, apparent values of k_1 show large and systematic variation. k_2 at +0·5° is $1{\cdot}0 \times 10^{-3}$ l mol^{-1} s^{-1}. Addition of a large excess of Me_4NBF_4 to the mixture had virtually no effect on the rate. The E_a for N_2 loss was 19 ± 4 kcal mol^{-1}. Again, a reasonable plot of $\ln k$ *vs.* $1/T$ was obtained only for k_2. Use of apparent k_1 values showed no systematic temperature variation.

Since the bis(trifluoromethyl)methyl cation would be strongly destabilized by inductive electron withdrawal, one might expect that bimolecular attack on the diazonium ion could be more likely than S_N1 fragmentation. However, molecular nitrogen is an excellent leaving group, so much so that often only S_N1 reactions of diazonium ions are considered. In addition, the FSO_3^- must be an extremely weak nucleophile.

Our results are consistent with a dominant bimolecular rate-limiting component in the nucleophilic substitution of alkanediazonium ions when a reasonably stable carbonium ion cannot form; *e.g.*, primary or strongly destabilized secondary systems. In these cases cleavage of the carbon–nitrogen bond can have an appreciable E_a.

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