

## Bimolecular Displacement of Nitrogen ( $S_N2$ ) in an Alkanediazonium Ion

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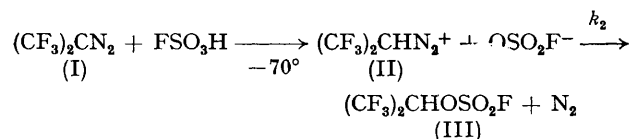
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**Summary** Kinetic studies on the bis(trifluoromethyl)methanediazonium ion in  $\text{FSO}_3\text{H}$  show loss of  $\text{N}_2$  through an  $S_N2$  pathway.

THERE has been controversy over the loss of molecular nitrogen from diazonium ions during the past two decades.<sup>1</sup> 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  $\text{N}_2$  from alkanediazonium ions through bimolecular substitution at carbon has also been proposed.<sup>2</sup> 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  $\text{FSO}_3\text{H}$  solutions has allowed a direct kinetic study. We report here an overall second-order rate law,  $-\text{d}[\text{RN}_2^+]/\text{d}t = k_2[\text{RN}_2^+][\text{OSO}_2\text{F}^-]$ .

Bis(trifluoromethyl)diazomethane (I) was synthesized by reaction of nitrous acid with bis(trifluoromethyl)methylamine<sup>3</sup> in water at pH 3. Slow addition of (I) in CDCl<sub>3</sub> to FSO<sub>3</sub>H at -70° with good stirring gave a solution of the diazonium ion (II) in the lower acid layer. Both <sup>1</sup>H and <sup>19</sup>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.<sup>4</sup> The fluorosulphate ester (III), formed by loss of N<sub>2</sub>, was characterized by elemental and spectroscopic analyses.



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.<sup>5</sup> Rates were calculated from integrated <sup>1</sup>H peak areas of (II) (septet, -7.5 p.p.m., *J*<sub>HF</sub> 3.9 Hz) and (III) (septet, -5.9 p.p.m., *J*<sub>HF</sub> 5.1 Hz). Me<sub>4</sub>NBF<sub>4</sub> 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<sub>3</sub>H was rapid and complete. The <sup>19</sup>F n.m.r. spectrum showed no remaining unprotonated diazo-compound; thus, equal concentrations of diazonium cation and FSO<sub>3</sub><sup>-</sup> formed initially. Excess of FSO<sub>3</sub>K (99%)<sup>6</sup> was added to determine the kinetic order of FSO<sub>3</sub><sup>-</sup>. Apparent first-order (*k*<sub>1</sub>) and second-order (*k*<sub>2</sub>) overall rate

constants were calculated using linear least-squares analyses.

Consistent second-order rate constants were obtained over a three-fold range of FSO<sub>3</sub><sup>-</sup> concentration. Whereas values of *k*<sub>2</sub> are relatively constant over this range at constant temperature, apparent values of *k*<sub>1</sub> show large and systematic variation. *k*<sub>2</sub> at +0.5° is 1.0 × 10<sup>-3</sup> l mol<sup>-1</sup> s<sup>-1</sup>. Addition of a large excess of Me<sub>4</sub>NBF<sub>4</sub> to the mixture had virtually no effect on the rate. The *E*<sub>a</sub> for N<sub>2</sub> loss was 19 ± 4 kcal mol<sup>-1</sup>. Again, a reasonable plot of ln *k* vs. 1/*T* was obtained only for *k*<sub>2</sub>. Use of apparent *k*<sub>1</sub> 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<sub>N</sub>1 fragmentation. However, molecular nitrogen is an excellent leaving group, so much so that often only S<sub>N</sub>1 reactions of diazonium ions are considered. In addition, the FSO<sub>3</sub><sup>-</sup> 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*<sub>a</sub>.

We thank the National Science Foundation (U.R.P. Program) and the Research Corporation for their support of this work.

(Received, 19th June 1974; Com. 721.)

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