## **Supporting Information**

## The Rapid Formation and Slow Collapse of a Carbocation-Anion Pair to a Neutral Molecule.

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Table S1. Time ratios  $(t_{0.50}/t_{0.05})$  for the Reactions of TMT<sup>+</sup> and sodium acetate in Acetic ....S2 Acid at 298 K.

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[TMT <sup>+</sup> ] <sup>a</sup>	[NaOAc] <sup>a</sup>	$t_{0.50}/t_{0.05}$
0.20	500	20.0
0.20	250	17.8
0.20	125	19.5
0.20	10.0	18.8
0.20	2.50	23.2
0.010	0.10	16.4
0.010	0.020	19.7
Single-step		13.5
	<b>[TMT<sup>+</sup>]<sup>a</sup></b> 0.20 0.20 0.20 0.20 0.20 0.010 0.010	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

**Table S1.** Time ratios  $(t_{0.50}/t_{0.05})$  for the Reactions of TMT<sup>+</sup> and sodium acetate in Acetic Acid at 298 K.

## <sup>a</sup>concentrations in mM

The time ratio  $(t_{0.50}/t_{0.05})$  is a very effect probe to test for (a) complex mechanism behavior and (b) whether or not the data are wavelength dependent. In the latter case, if the ratio is wavelength dependent, this is strong evidence that an intermediate absorbs over the same wavelength that the absorbance is monitored. Otherwise, in the absence of interference from an intermediate the ratio is expected to be independent of wavelength.

*Figure S1.* Sliding 51 point IRC analysis over the first half-life of the reaction of  $TMT^+$  (0.1 mM) with NaOAc (0.5 M) at 298 K and 520 nm.



*Figure S2.* IRC analysis of the first 3% of the extent of reaction – time profile for the concentration jump experiment on the reaction of  $TMT^+$  (0.22 mM) with NaOAc (0.5 M) carried out at 298 K and 520 nm.



In order to insure that the more rapid initial reaction is not due to a small amount of reactive impurity in the acetate solution, the latter was treated with a sufficient quantity of  $TMT^+$  to result in an equilibrium concentration of 0.02 mM for the combined  $TMT^+$  / TMT-OAc species. This solution was then used in the second reactant syringe during a stopped-flow experiment at 520 nm and 298 K in which  $[TMT^+]$  was jumped from 0.02 to 0.22 mM.

Reference for Instantaneous Rate Constant Analysis: (33) Parker, V.D. J. Phys. Org. Chem. **2006**, *19*, 714.

Figure S3. Eyring plot of data for the reaction of TMT<sup>+</sup> with NaOAc (0.5 M) in HOAc/AN (1/1)



Figure S4. van't Hoff type plot of data for the reaction of  $TMT^+$  with NaOAc (0.5 M) in HOAc/AN (1/1)







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Figure S6. <sup>1</sup>HNMR spectra of Equilibrium Reaction Mixture

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