

Supplemental Table 1. $[\text{N}_2\text{H}_5^+]_{\text{T}}$ Dependence on the Rate of the $\text{N}_2\text{H}_5^+/\text{Br}_2$ Reaction on APPSF^a

$10^4[\text{N}_2\text{H}_5^+]_{\text{T}}, \text{M}$	$k_{\text{obsd}}, \text{s}^{-1}$	$k_{\text{corr}}, \text{s}^{-1}$
0.216	31.7	31.9
0.324	49.6	50.1
0.432	62.6	63.5
0.540	74.2	75.4
0.756	105	107
0.972	159	165
1.080	173	180
1.296	194	203
1.512	228	240
1.620	241	254
1.836	267	283
2.160	311	333

^a Conditions: $[\text{Br}^-] = 0.7716 \text{ M}$, $[\text{H}^+] = 0.246 \text{ M}$, $[\text{Br}_2]_{\text{T}} = (0.37 \text{ to } 1.9) \times 10^{-5} \text{ M}$, $\mu = 1.0 \text{ M}$, $\lambda = 266 \text{ nm}$, 25.0°C .

Supplemental Table 2. $[\text{Br}^-]^a$ and $[\text{H}^+]^b$ Dependences on the Rate of the $\text{N}_2\text{H}_5^+/\text{Br}_2$ Reaction on APPSF

$[\text{Br}^-], \text{M}$	$k_{\text{obsd}}, \text{s}^{-1}$	$k_{\text{corr}}, \text{s}^{-1}$	$[\text{H}^+], \text{M}$	$k_{\text{obsd}}, \text{s}^{-1}$	$k_{\text{corr}}, \text{s}^{-1}$
0.1157	519	585 ± 18	0.0995	216	227
0.1929	365	396 ± 6	0.199	203	212
0.2701	276	294 ± 2	0.299	190	198
0.3858	210	220 ± 1	0.398	180	187
0.5015	170	176 ± 2	0.498	173	180
0.5787	150	155 ± 2	0.597	162	168
0.6559	133	137 ± 1			
0.7716	118	121 ± 2			
0.8873	104	106 ± 1			

^a Conditions: $[\text{N}_2\text{H}_5^+]_{\text{T}} = 7.63 \times 10^{-5} \text{ M}$, $[\text{H}^+] = 0.125 \text{ M}$, $[\text{Br}_2]_{\text{T}} = 1.14 \times 10^{-5} \text{ M}$, $\mu = 1.0 \text{ M}$, $\lambda = 266 \text{ nm}$, 25.0°C . ^b Conditions: $[\text{N}_2\text{H}_5^+]_{\text{T}} = 7.63 \times 10^{-5} \text{ M}$, $[\text{Br}^-] = 0.3858 \text{ M}$, $[\text{Br}_2]_{\text{T}} = 1.20 \times 10^{-5} \text{ M}$, $\mu = 1.0 \text{ M}$, $\lambda = 266 \text{ nm}$, 25.0°C .

Supplemental Table 3. Pseudo-First-Order Reactions of Cl_2 and N_2H_5^+ on PAF^a

$10^3[\text{N}_2\text{H}_5^+]_{\text{T}}$ M	$10^4[\text{Cl}_2]_{\text{T}}$ M	$[\text{N}_2\text{H}_5^+]_{\text{T}}/[\text{Cl}_2]_{\text{T}}$	$t_{1/2}$ μs	second-order method	$10^{-7}k_{\text{obsd}}$ s^{-1}
0.648	0.510	12.7	20	M-plot	3.5 ± 0.6
1.037	0.858	12.9	10	M-plot	6.8 ± 0.4
1.297	1.130	11.5	8	M-plot	8.6 ± 0.9
1.945	1.738	11.2	6	expanded M-plot	12 ± 2
2.593	3.300	7.9	4	expanded M-plot	16.3 ± 0.4

^a Conditions: $[\text{HCl}] = 1.00 \text{ M}$ ("Br⁻-free"), 25.0°C , $\lambda = 230 \text{ nm}$.

Supplemental Table 4. $[\text{N}_2\text{H}_5^+]_{\text{T}}$ Dependence for the Reactions of BrCl and N_2H_5^+ on PAF^a

$10^4[\text{N}_2\text{H}_5^+]_{\text{T}}, \text{M}$	$10^5[\text{BrCl}]_{\text{T}}, \text{M}$	first-order method	$10^{-4}k_{\text{obsd}}, \text{s}^{-1}$
0.476	0.469	double-reciprocal	0.23 ± 0.01
0.952	0.938	M-plot	0.77 ± 0.02
1.430	1.406	M-plot	1.17 ± 0.02
1.910	1.875	M-plot	1.65 ± 0.04
2.380	2.344	M-plot	2.15 ± 0.05

^a Conditions: $[\text{HCl}] = 1.00 \text{ M}$ ("Br⁻-free"), 25.0°C , $\lambda = 232 \text{ nm}$.

Supplemental Table 5. $[\text{H}^+]$ ^a and $[\text{Cl}^-]$ ^b Dependences for the Reactions of BrCl and N_2H_5^+ on PAF

$[\text{H}^+]$, M	$10^{-4}k_{\text{obsd}}$, s^{-1}	$[\text{Cl}^-]$, M	$10^{-4}k_{\text{obsd}}$, s^{-1}
0.423	3.21 ± 0.03	0.462	2.69 ± 0.01
0.529	3.13 ± 0.03	0.578	2.20 ± 0.01
0.634	3.08 ± 0.04	0.811	1.71 ± 0.01
0.739	3.00 ± 0.05	0.928	1.56 ± 0.01
0.844	2.90 ± 0.03		

^a Conditions: $[\text{N}_2\text{H}_5^+]_{\text{T}} = 1.43 \times 10^{-4}$ M, $[\text{BrCl}]_{\text{T}} = 1.41 \times 10^{-5}$ M, $[\text{Cl}^-] = 0.318$ M, $\mu = 1.0$ M, 25.0°C , $\lambda = 232$ nm. ^b Conditions: $[\text{N}_2\text{H}_5^+]_{\text{T}} = 1.40 \times 10^{-4}$ M, $[\text{BrCl}]_{\text{T}} = 1.405 \times 10^{-5}$ M, $[\text{H}^+] = 0.462$ M, $\mu = 1.0$ M, 25.0°C , $\lambda = 232$ nm.