Supporting Information

Routes of Spontaneous Disintegration of DNA and the Rate Enhancements Produced by DNA Glycosylases and Deaminases

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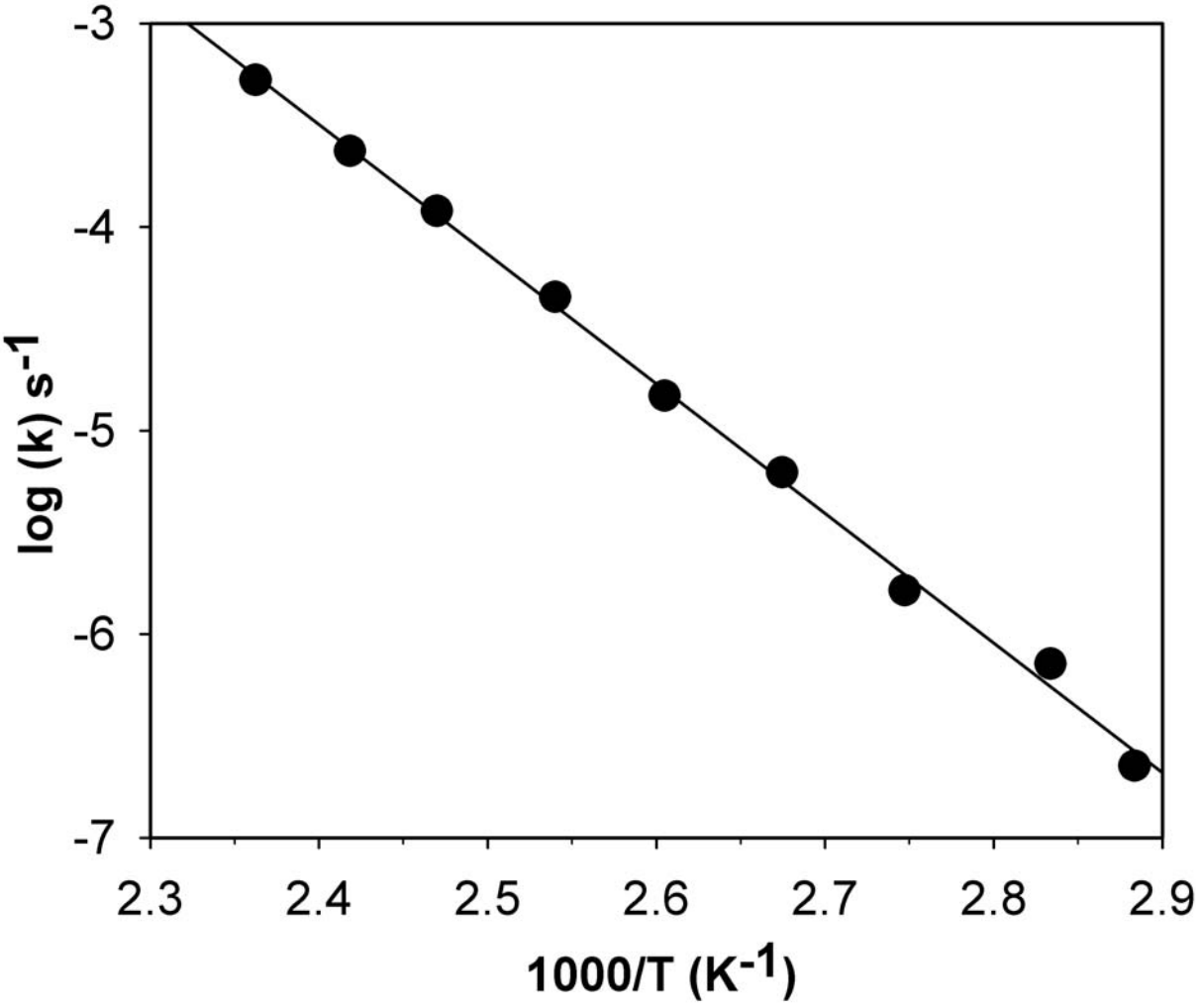
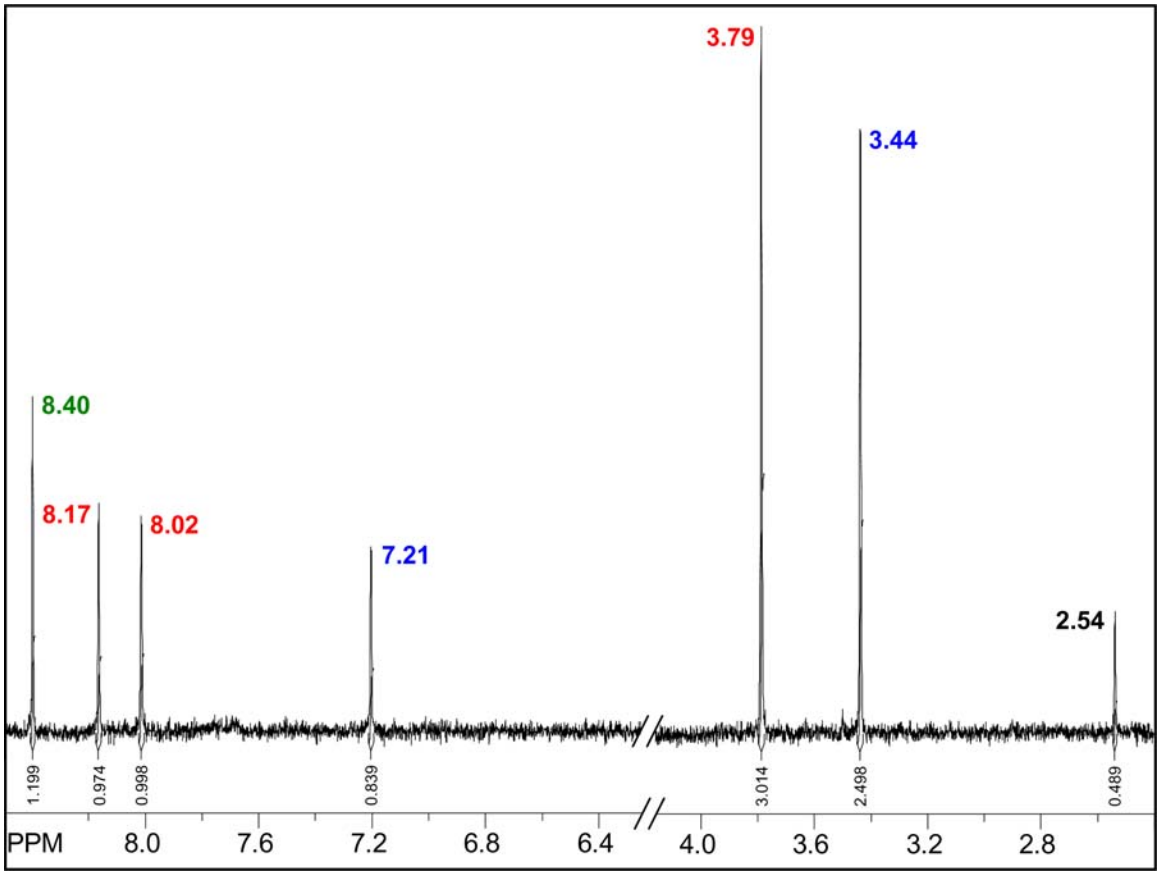
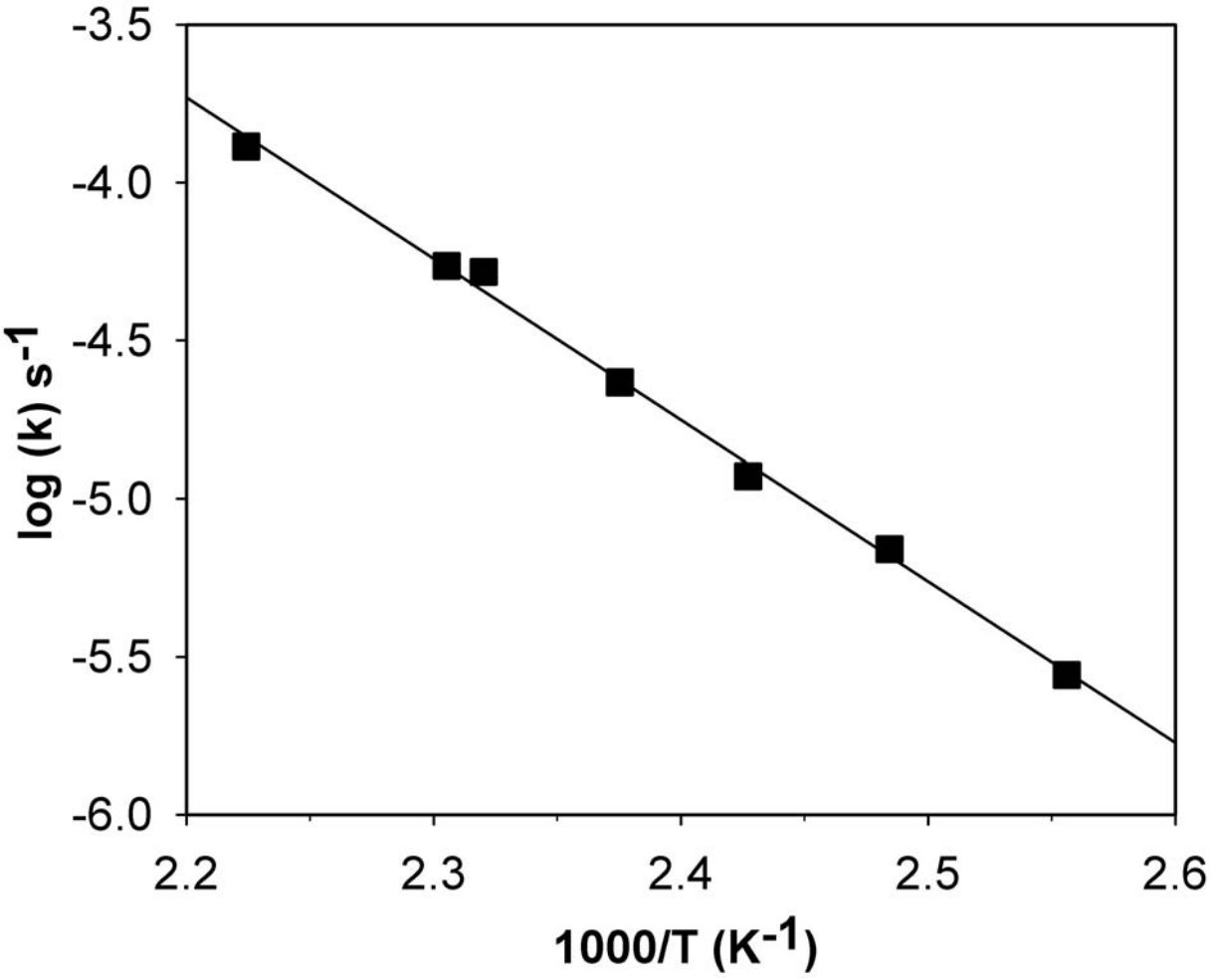
Supporting Information Figure 1. Arrhenius plot of the rate constants for the glycoside cleavage of 2'-deoxyuridine (●) at pH 6.8.



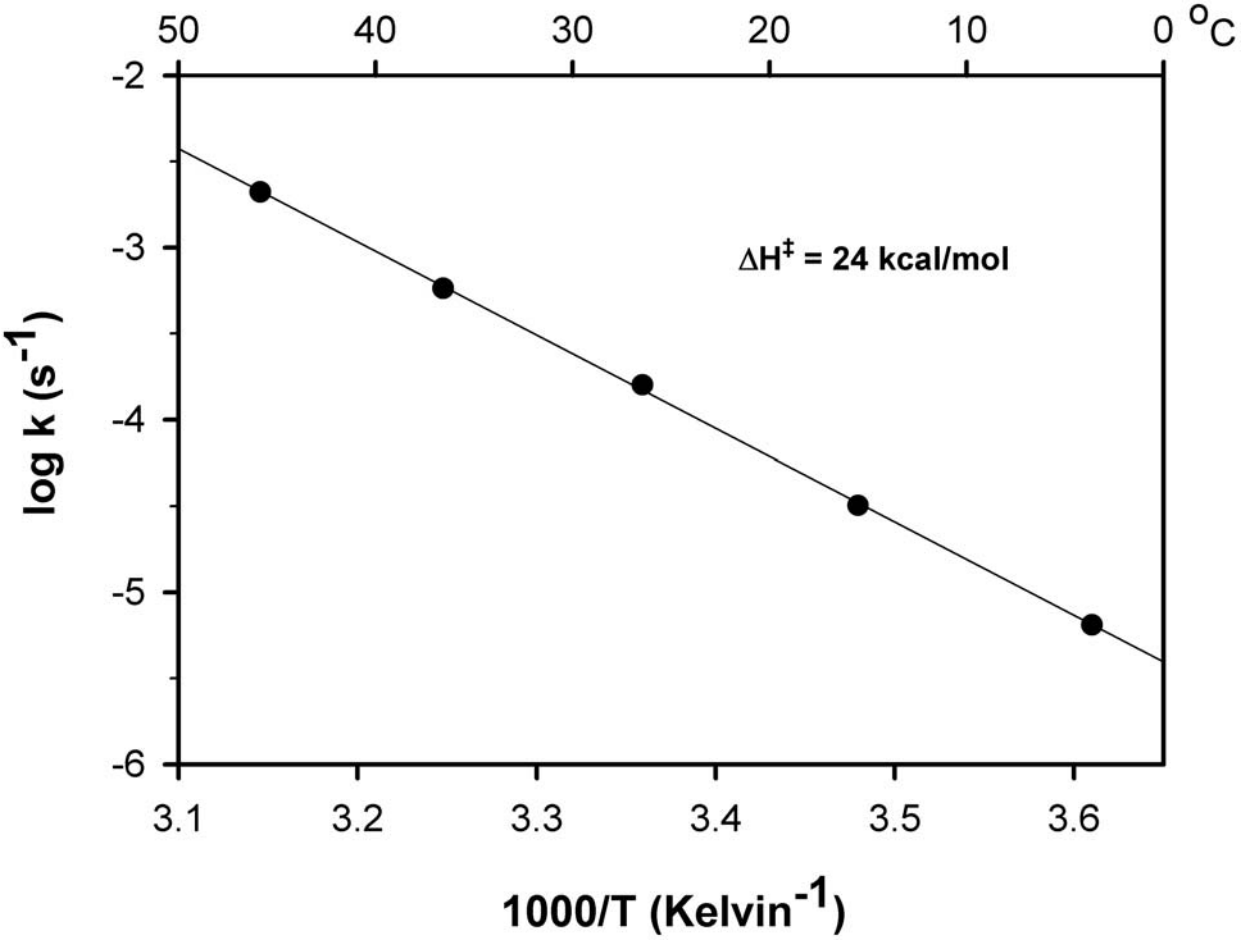
Supporting Information Figure 2. 500 MHz proton NMR spectrum (in D_2O) of a sample of 9-methylhypoxanthine incubated at 170 ^{o}C for 5.5 hours. Peak labels correspond to 9-methylhypoxanthine (red), compound **I** (blue), compound **II** (black) and formate (green) as indicated in Scheme 2.



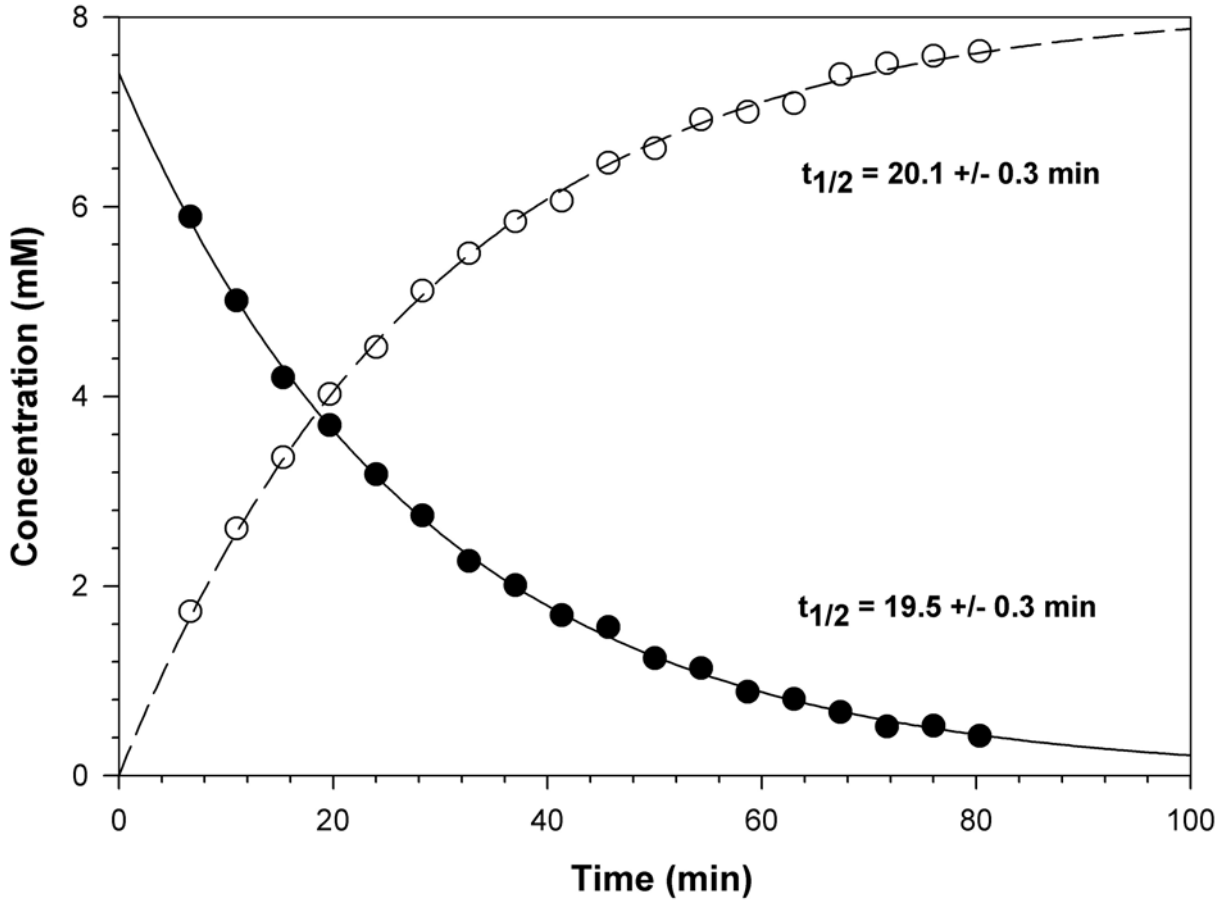
Supporting Information Figure 3. Arrhenius plot of the rate constants for the deamination of cytosine (■) at pH 6.8.



Supporting Information Figure 4. Arrhenius plot of the apparent first order rate constants for the glycoside cleavage of 2'-deoxyadenosine (●) at pH 1 ([HCl] = 0.185 M). The data fit a linear regression satisfactorily ($R^2 > 0.99$). The enthalpy of activation in acid (24 kcal/mol) was lower than the enthalpy of activation at neutral pH (27 kcal/mol).



Supporting Information Figure 5. Time course for the glycoside cleavage of 2'-deoxyadenosine (●) to adenine (○) at pH 1 and 35 °C. The solid line is a fit of the integrated ^{1}H NMR data to an exponential decay curve ($R^2 > 0.99$) and the dashed line is a fit of the integrated ^{1}H NMR data to an exponential rise to maximum ($R^2 > 0.99$). Rate constants determined by non-linear regression analysis were identical within experimental error, consistent with a direct cleavage event.



Supporting Information Figure 6. 500 MHz proton NMR spectrum (in DMSO-d_6) of a sample of 9-methylhypoxanthine incubated at 170 °C for 5.5 hours. Peak labels correspond to 9-methylhypoxanthine (red) and compound **I** (blue) as indicated in the included structures. The resonance shift values reported in the literature for authentic 5-amino-1-methyl-imidazole-4-carboxamide (*26*) are included in parenthesis. The large peak at ~3.33 ppm corresponds to residual water.