Table 1. Energetics of Different Enzymatic Reactions and the Corresponding Reference Reactions[a]

system[b]	$\Delta g^{\ddagger}_{w,w}$	$\Delta g^{\ddagger}_{p,w}$	$\Delta g^{\ddagger}_{cat}$	source[c]	$\Delta g^{\ddagger}_{p,w\rightarrow p,p}$ [d]
KI	27.0	22.1	11.2	224, 225	10.9 (15.8)
AR	22.5	22.5	14.8	226	5.7 (5.7)
CA	23.8	23.8	11.0	114	13.4 (13.4)
CM	24.5	24.5	15.4	90	9.0 (9.0)
trypsin	32.0	26.0	18.0	25, 28, 38	8.0 (14.0)
DhlA	27.0	27.0	15.3	95, 96	11.7 (11.7)
AP	27.5	27.5	15.2	109	12.0
Ras/G	27.5	27.5	16.1	112	11.4 (11.4)
TIM	26.4	28.4	14.0	227	14.4
Ach	36.0	29.5	13.5	13, 228	16.0 (22.5)
lysozyme	33.6	31.5	18.0	32	13.5 (15.6)
Rb (MI)	32.0	32.0	15.0	229	17.0 (17.0)
Rb (DI)	47.0	36.0	15.0	229	21.0 (32.0)
ATPase	37.0	37.0	14.8	126	22.2 (22.2)
Pol T7	32.0	38.2	15.0	113	23.2 (17.0)
ODCase	38.8	40.0	15.4	36, 203	24.6 (23.4)
Kf	36.0	46.4	19.0	230	27.4 (17.0)
SNase	36.0	51.5	14.9	39, 109, 111	33.9 (21.1)

[a] The table gives the activation barrier (in kcal/mol) for $[Rxn]_{w,w}$, $[Rxn]_{p,w}$, and the actual enzymatic reaction. [b] The following notation is used here: KI = ketosteroid isomerase; AR = aldose reductase; CA = carbonic anhydrase; CM = chorismate mutase; DhlA = haloalkane delahogenase; ATPase = F_1-ATPase; AP = alkaline phosphatase; Ras/G = Ras/GAP; TIM = triose phosphate isomerase; Ach = acetylcholine esterase; Rb(MI) = ribonuclease (monoionic intermediate); Rb (DI) = ribonuclease (diionic intermediate); Pol T7 = DNA polymerase T7; ODCase = orotidine 5′-monophosphate decarboxylase; Kf = the exonuclease activity of the Klenow fragment or DNA polymerase I; SNase = staphylococcal nuclease. [c] The indicated source includes a discussion and analysis of the reference reaction and the enzyme reaction. Note that, in several of the cases (e.g. TIM, SNase, and KI), we convert the reported $\Delta g^{\ddagger}_{cage}$ to $\Delta g^{\ddagger}_{w}$ by adding 2.5 kcal/mol (see ref 25 for discussion). For the reaction of ribonuclease, we consider both the diionic and monoionic mechanisms since it is not clear yet as to which mechanism is operational in the enzyme. The $[Rxn]_{p,w}$ reference reaction for Pol-T7 is taken with Asp as a base. The reference reaction for ATPase does not include the Mg^{2+} ion. For the lysozyme reaction, we consider the reaction with a carbonium ion intermediate. If the actual enzymatic reaction involves a nucleophilic attack by Asp 52, then the reference reaction still involves a major carbonium character and the activation barrier is similar to that estimated for the carbonium mechanism. [d] The catalytic effects relative to $[Rxn]_{p,w}$ and $[Rxn]_{w,w}$ are given with and without parentheses, respectively.