

Corrections

Rapid Reduction of Hg(II) by Mercuric Ion Reductase Does Not Require the Conserved C-Terminal Cysteine Pair Using HgBr_2 as the Substrate, by Stefan Engst* and Susan M. Miller*, Volume 37, Number 33, August 18, 1998, pages 11496–11507.

In the single turnover study illustrated in Figure 4, the monophasic conversion of species C to species G was attributed to the reduction of bound Hg(II), and the observed rate constant for the conversion $k_{\text{obs}}^{\text{slow}}$ was incorrectly equated with the rate constant for reduction, k_9 in Scheme 4. The process ($\text{C} \rightarrow \text{G}$) does indeed involve reduction of bound Hg(II); however, as described, species C is not a single species but rather an equilibrium mixture of species II* and III in Scheme 4. The kinetic data indicate that the equilibrium is established very rapidly, but the spectra indicate that it favors species II* ($K_{\text{eq}} = k_7/k_8 = 0.25$). Since species III is directly responsible for reduction of Hg(II), and K_{eq} is established rapidly, the correct expression should be $k_{\text{obs}}^{\text{slow}} \approx K_{\text{eq}} \times k_9$. Thus, $k_{\text{obs}}^{\text{slow}} \approx 23.5 \text{ s}^{-1} \approx 0.25 \times k_9$, and $k_9 \approx 94 \text{ s}^{-1}$. This equation for $k_{\text{obs}}^{\text{slow}}$ is also more consistent with the data of Figure 6C, which shows that the magnitude of $k_{\text{obs}}^{\text{slow}}$ decreases at high concentrations of HgBr_2 . Under these conditions K_{eq} also decreases, effectively going to zero at $[\text{HgBr}_2] \geq 600 \mu\text{M}$, as illustrated in Figure 3. Simulations of the data using the model in Scheme 4 with the value for k_9 of 94 s^{-1} give excellent fits to both the decrease in A_{340} shown in Figure 1 and the changes at 530 nm shown in the inset to Figure 2B. Inclusion of the equilibrium step also slightly alters the steady-state expression for k_{cat} to $k_{\text{cat}} = K_{\text{eq}}k_9k_{13}/[K_{\text{eq}}k_9 + k_{13}(1 + K_{\text{eq}})]$, which yields a value of 15 s^{-1} using the estimates for k_9 of 94 s^{-1} and for k_{13} of 70 s^{-1} , still comparable to the measured value of 18 s^{-1} . This corrected analysis of the data does not alter the conclusions of the paper significantly. The actual rate constant for transfer of electrons from the reduced flavin in species III to the bound Hg(II) is ca. 4-fold higher than previously stated and now comparable to the rate constant estimated for dissociation of NADP^+ . However, the transition state for the electron transfer is still envisioned as the overall highest barrier ($k_{\text{obs}}^{\text{slow}}$) as it is augmented by the thermodynamically uphill transfer of electrons from NADPH to FAD (species II* to III).

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Anionic Binding Site and 2,3-DPG Effect in Bovine Hemoglobin, by M. Marta, M. Patamia, A. Colella, S. Sacchi, M. Pomponi, K. M. Kovacs, C. Lydersen, and B. Giardina*, Volume 37, Number 40, October 6, 1998, pages 14024–14029.

Page 14024. The affiliations for K. M. Kovacs and C. Lydersen are incorrect. Their addresses should appear as follows: Department of Biology, UNIS, 9170 Longyearbyen, Svalbard, Norway (for K.M.K), and Norwegian Polar Institute, 9005 Tromsø, Norway (for C.L.).

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The Imine–Pyridine Torsion of the Pyridoxal 5'-Phosphate Schiff Base of Aspartate Aminotransferase Lowers Its pK_a in the Unliganded Enzyme and Is Crucial for the Successive Increase in the pK_a during Catalysis, by Hideyuki Hayashi, Hiroyuki Mizuguchi, and Hiroyuki Kagamiyama*, Volume 37, Number 43, pages 15076–15085.

Page 15085. In the legend of Figure 9, the value of $k_{cat}^{half}/K_m^{half}$ for aspartate has been incorrectly cited as $1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (3). This should have been $1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (3). The free energy profile of this figure had been drawn using the correct value. Therefore, the correction does not affect at all the discussion and the content of this article.

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