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Erratum

Perspective on Diabatic Models of Chemical Reactivity as Illustrated by the Gas-Phase S_N2 Reaction of Acetate Ion with 1,2-Dichloroethane.

[*J. Chem. Theory Comput.* 5, 1–22 (2009)]. By Rosendo Valero, Lingchun Song, Jiali Gao,* and Donald G. Truhlar*.

Pages 1–22. Our article¹ compared five quantum mechanical methods for computing diabatic states for the gas-phase haloalkane dehalogenase (DhlA) model reaction between an acetate ion and dichloroethane to one another and to the molecular mechanical diabatic states of EVB theory. The most recent application of EVB to DhlA is the work of Rosta et al.² This paper says that the EVB parameters are a small modification of those used in Olsson et al.³ The Olsson et al. paper says that the EVB parameters they used are a modification of those reported by Shurki et al.⁴ Neither paper reports the modified parameters. Reference 4 states that the EVB parameters used for reaction in water and in the protein are given in the Supporting Information, and we therefore chose that paper as one where we would have a full set of parameters. The parameters we used—including corrections of typographical errors and a correction of a factor of 2 to the exponential parameters of the nonbonded van der Waals interactions that was kindly provided by the first author of ref 4—are included in our paper.¹ (Note the following typos in our Supporting Information: all θ_0 values except that for O–C–O were set equal to 109.5 deg, as in ref 4). We did not include any terms whose parameters are not given in ref 4.

The parameters in ref 4 include a single gas-phase shift parameter α without explicitly specifying to which diagonal element it should be added. In our calculation,¹ we added this to the first EVB diabatic state because this yielded an

energy difference (–7 kcal/mol) between the product and reactant states in reasonable accord with the most accurate values reported in ref 1 (–11 kcal/mol from G3SX and M06-2X calculations). Files recently posted on the Warshel group Web site⁵ (the files are dated Feb. 23, 2009) indicate that they shifted the second diabatic state. Shifting the second diabatic state in our calculations yielded a very endothermic reaction, which is unreasonable. We conclude that additional terms—not included in our calculations—whose parameters were not published are needed to reproduce the potential underlying the published EVB calculations of refs 2–4. We therefore retract all quantitative results presented in our paper for the EVB potential of ref 4.

The removal of the molecular mechanical EVB calculations has no effect on the larger portion of the paper that is devoted to the quantum mechanical diabatic surfaces obtained by the 4-fold way and MOVb.

References

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- (4) Shurki, A.; Strajbl, M.; Villa, A.; Warshel, A. *J. Am. Chem. Soc.* **2002**, 124, 4097–4107.
- (5) <http://futura.usc.edu/wgroup/evb.html> (accessed Mar. 9, 2009). CT9002459

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