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ADDITION/CORRECTION

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Correction to "Direct-Dynamics VTST Study of the [1,7] Hydrogen Shift in 7-Methylocta-1,3-(Z),5(Z)-triene. A Model System for the Hydrogen Transfer Reaction in Previtamin D_3"

[*The Journal of Physical Chemistry A* **2007**, *111*, 719–725. DOI: 10.1021/jp0665269]. S. Hosein Mousavipour, Antonio Fernández-Ramos,* Rubén Meana-Pañeda, Emilio Martínez-Nuñez, Saulo A. Vázquez, and Miguel A. Ríos*

We have found two important errors in our article related to the number of conformers of 7-methylocta-1,3(Z),5(Z)-triene and to the optical isomers of most of those conformers. The errors are (1) the number of conformers of 7-methylocta-1,3-(Z),5(Z)-triene is thirteen, instead of seven, and (2) the transition state **TS7** has one enantiomer, and therefore all the thermal rate constants should be multiplied by a factor of 2. As a result of these changes, the calculated thermal rate constant are now in much better agreement with experiment. The errors affect Tables 1−3 and 5, and Figures 1 and 3. In this document, we include the corrected version of Tables 1−3 and 5 and of Figures 1 and 3.

Table 1. Relative Classical Potential Energies (kcal/mol) and Main Distances (Å) and Angles (Degrees) of the Stationary Points Involved in the [1,7] Hydrogen Shift in 7-Methylocta-1,3(Z),5(Z)-triene Calculated at the MPWB1K/6-31+G(d,p) Level (Numbering as for Structure R1 in Figure 1)

structure	energy (gas)	ϕ_1[a]	ϕ_2[a]	ϕ_3[a]	α_1[a]	α_2[a]	α_3[a]	$d(C_7-H_{17})$	$d(C_1-C_7)$	$d(C_1-H_{17})$
R1	0.00	180.0	180.0	0.0	109.7	117.1	110.5	1.089	6.745	6.400
R2	2.78	−175.3	55.6	−8.0	109.1	117.1	110.2	1.088	4.302	3.519
R3	3.18	−39.9	171.3	0.0	109.6	117.3	110.5	1.089	5.612	5.530
R4	3.30	180.0	180.0	180.0	105.9	117.1	111.6	1.090	6.793	7.727
R5	6.41	−39.8	170.2	−173.3	106.0	117.3	111.6	1.090	5.616	6.374
R6	7.44	179.3	97.7	164.1	106.3	117.1	110.8	1.091	5.431	6.424
R7	7.70	36.9	58.8	−8.5	108.6	117.4	110.4	1.088	3.685	3.265
R8	11.58	29.9	74.0	128.0	105.1	117.3	110.8	1.094	4.017	5.089
R9	6.79	−176.5	67.7	126.6	104.2	117.0	110.9	1.094	4.805	5.891
R10	3.80	−179.9	−179.3	126.5	105.1	117.1	110.3	1.094	6.888	7.533
R11	6.79	−37.6	166.4	−124.5	105.0	117.3	110.5	1.094	5.586	5.912
R12	6.85	−37.8	166.5	127.4	105.7	117.3	110.2	1.094	5.588	6.393
R13	11.28	−24.5	82.9	−111.4	106.5	117.1	110.4	1.096	3.717	3.382
TS1−2	4.82	179.8	98.5	5.1	108.2	117.0	110.7	1.090	5.376	4.940
TS1−3	6.08	−98.1	−178.7	−0.2	109.7	117.3	110.5	1.089	6.191	6.019
TS1−10	4.55	179.7	177.6	89.1	107.3	117.1	109.5	1.095	6.857	7.211
TS2−7	10.37	104.2	59.6	−3.7	108.7	117.2	110.3	1.089	4.493	4.023
TS2−10	7.77	−179.1	96.8	−122.2	105.9	117.1	110.6	1.094	5.510	5.540
TS3−7	8.81	18.7	93.5	6.2	108.2	117.1	110.8	1.090	4.350	4.260
TS3−11	7.82	−38.9	167.1	−81.6	107.2	117.3	109.5	1.094	5.614	5.651
TS3−12	7.35	−36.7	166.5	94.7	107.3	117.3	109.6	1.095	5.557	6.247
TS4−5	9.36	−98.2	−179.0	179.7	106.0	177.3	111.6	1.090	6.219	7.063
TS4−9	7.64	−179.6	97.9	133.2	105.6	117.0	110.8	1.094	5.503	6.585
TS4−10	4.19	−179.7	−177.5	153.9	105.1	117.1	110.8	1.091	6.830	7.666
TS5−11	7.09	−37.1	166.9	−149.0	105.2	117.3	110.9	1.092	5.563	6.120
TS5−12	7.47	−39.2	168.2	160.5	105.4	117.3	110.6	1.091	5.618	6.435
TS6−10	7.47	179.2	105.4	164.9	106.5	117.1	110.7	1.091	5.605	6.602
TS7−8	11.65	9.0	83.6	125.1	105.6	117.4	110.6	1.094	4.011	5.088
TS8−9	11.65	7.2	88.9	122.2	105.8	117.3	110.4	1.094	4.115	5.186
TS8−12	11.65	8.2	91.8	125.8	105.8	117.2	110.4	1.094	4.199	5.262
TS10−12	9.76	−97.5	−178.0	125.2	105.3	117.3	110.3	1.094	6.283	6.992
TS11−13	11.36	−27.0	95.9	−119.3	105.9	117.3	110.7	1.096	3.976	3.812
TS7	26.68	10.3	22.0	−64.5	100.0	114.8	114.0	1.330	2.641	1.368
TS2	45.38	−127.1	27.7	−80.8	103.0	114.8	114.3	1.434	2.756	1.382
P1	0.60	−0.1	4.1	−96.7	76.7	109.1	115.1	3.016	3.514	1.091
P2	0.67	176.8	4.7	−65.1	101.0	108.2	115.5	4.524	4.598	1.090

[a] $\phi_1 = \phi(C_1-C_2-C_3-C_4)$, $\phi_2 = \phi(C_3-C_4-C_5-C_6)$, $\phi_3 = \phi(C_5-C_6-C_7-C_{17})$, $\alpha_1 = \alpha(C_6-C_7-H_{17})$, $\alpha_2 = \alpha(H_{10}-C_1-H_{11})$, $\alpha_3 = \alpha(C_8-C_7-C_9)$.

Line 4 of the Abstract, "seven conformers" should be "thirteen conformers."

Table 2. Calculated (Columns 2, 3 and 4) and Experimental (Column 5) Thermal Rate Constants (s^{-1}) for the [1,7] Hydrogen (and Deuterium) Shift in 7-Methylocta-1,3(Z),5(Z)-triene

T (K)	TST	CVT	CVT/μOMT	exp[a]
		k_H		
298.2	1.48×10^{-7}	1.45×10^{-7}	1.09×10^{-6}	
333.2	1.02×10^{-5}	1.00×10^{-5}	4.80×10^{-5}	5.6×10^{-5}
348.2	4.82×10^{-5}	4.72×10^{-5}	1.96×10^{-4}	2.14×10^{-4}
368.2	3.12×10^{-4}	3.06×10^{-4}	1.08×10^{-3}	1.16×10^{-3}
388.2	1.67×10^{-3}	1.63×10^{-3}	5.03×10^{-3}	5.51×10^{-2}
400.0	4.13×10^{-3}	4.05×10^{-3}	1.16×10^{-2}	
		k_D		
298.2	3.23×10^{-8}	3.20×10^{-8}	1.55×10^{-7}	
333.2	2.60×10^{-6}	2.60×10^{-6}	8.72×10^{-6}	8.0×10^{-6}
348.2	1.30×10^{-5}	1.29×10^{-5}	3.84×10^{-5}	3.3×10^{-5}
368.2	9.03×10^{-5}	8.94×10^{-5}	2.33×10^{-4}	2.21×10^{-4}
388.2	5.13×10^{-4}	5.08×10^{-4}	1.19×10^{-3}	1.21×10^{-3}
400.0	1.31×10^{-3}	1.30×10^{-3}	2.89×10^{-3}	

[a] From ref 8.

Table 3. Arrhenius Parameters (Activation Energy, E_a, kcal·mol^{-1}, and Logarithm of the Preexponential Factor, log(A/s^{-1})), for [1,7] Sigmatropic Hydrogen (and Deuterium) Shift Reactions[a]

	[1,7] H shift		[1,7] D shift	
	E_a	log A	E_a	log A
CVT	23.81	10.62	24.65	10.58
CVT/ZCT	22.70	10.27	23.60	10.24
CVT/μOMT	21.74	9.94	22.97	10.00
Baldwin and Reddy[8]	21.5	9.8	23.5	10.3

[a] The fit to the calculated values included only temperatures in the interval 333.2−388.2 K to get a more reliable comparison with the experimental data.

The first paragraph of section 3 that describes the conformers should be replaced by the following paragraph: "Figure 1 shows the thirteen possible conformers of 7-methylocta-1,3(Z),5(Z)-triene. According to the MPWB1K/DIDZ calculations, all the conformers can be characterized by specifying the value of the three dihedral angles, ϕ_1, ϕ_2, and ϕ_3, which are defined as the torsions about the C_2-C_3, C_4-C_5, and C_6-C_7 atoms, respectively (Figure 1 and Table 1). **R1** is the most stable conformer with ϕ_1 and ϕ_2 in s-trans,s-trans configuration. According to the value of these two dihedral angles, all equilibrium structures can be divided in four groups, and in each of them the rotation about ϕ_3 leads to the different conformers. The first group includes all the s-trans,s-trans configurations, i.e., **R1**, **R4**, and **R10**. The second group involves the s-cis,s-trans structures, **R3**, **R5**, **R11**, and **R12**. The third group of conformers arises when ϕ_1 is kept in s-trans configuration and ϕ_2 takes values between 55° and 98° (conformers **R2**, **R6**, and **R9**). The fourth group includes the **R8**, **R13**, and **R7** conformations. They are obtained by rotation of both ϕ_1 and ϕ_2 with respect to the s-trans,s-trans configuration. With the exception of **R1** and **R4**, which are achiral (both of them have a plane of symmetry), all the other conformers are chiral and have enantiomers. Some of the key distances and angles of the thirteen conformers, together with some of the transition states involved in the interconversion between the conformers are listed in Table 1."

Table 5. Factors in the KIEs[a]

T (K)	η_{var}	η_{int}	η_{cl}	η_{tun}^{ZCT}	$\eta_{tun}^{\mu OMT}$	η_{calc}	η_{exp}
298.2	0.99	4.59	4.54	1.09	1.55	7.0	
333.2	0.98	3.92	3.84	1.08	1.43	5.5	$7.0^{+1.3}_{-0.8}$
348.2	0.99	3.70	3.67	1.08	1.40	5.1	$6.5^{+0.7}_{-1.1}$
368.2	0.99	3.46	3.42	1.07	1.35	4.6	$5.2^{+0.9}_{-0.6}$
388.2	0.99	3.25	3.22	1.07	1.32	4.2	4.6 ± 0.6
400.0	0.99	3.14	3.11	1.06	1.29	4.0	

[a] The classical, η_{cl}, and total, η_{calc}, KIEs are given by eqs 11 and 9, respectively. The experimental KIEs, η_{exp}, are taken from Baldwin and Reddy[8] considering a deviation of $E_a^D - E_a^H$) 0.1 kcal·mol^{-1}. The factors η_{tun}^{ZCT} and $\eta_{tun}^{\mu OMT}$ are also listed for comparison.

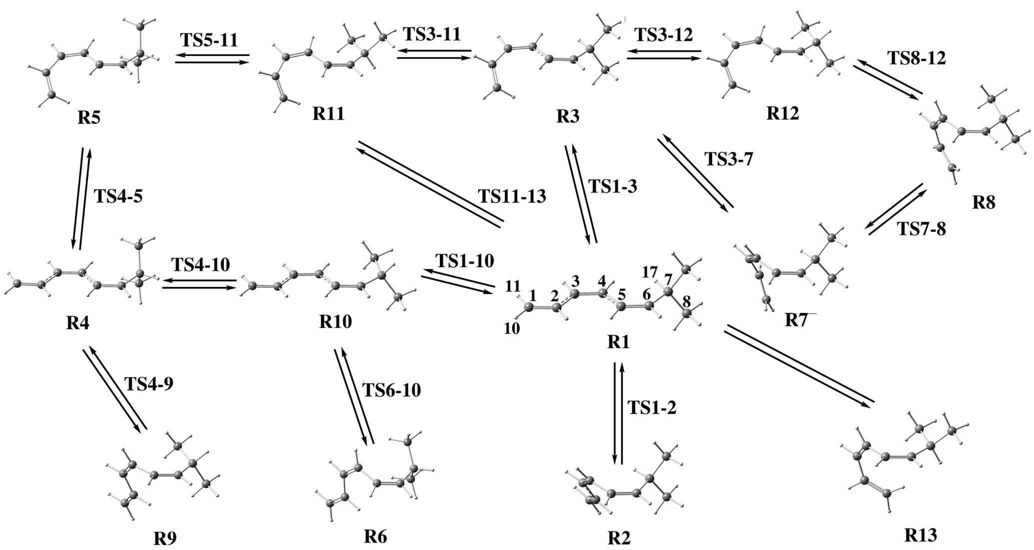

Figure 1. Thirteen conformers of the 7-Methylocta-1,3(Z),5(Z)-triene. The arrows between two structures indicate that there is a transition state connecting them (not all of them are shown). Details about the geometries and relative energies of the conformers and the transition states are given in Table 1.

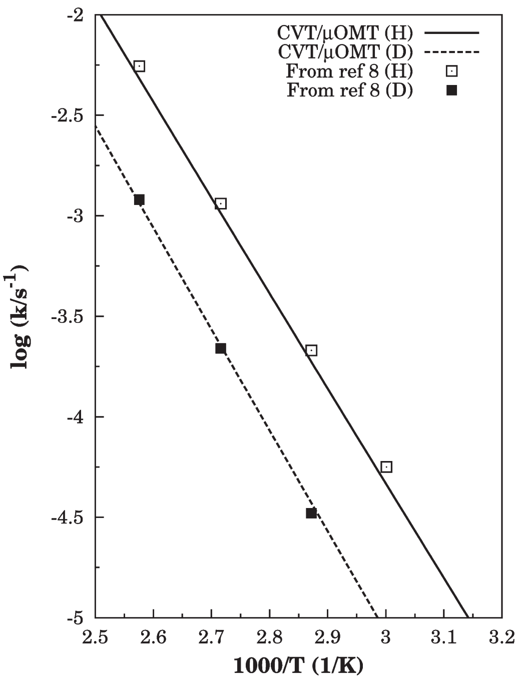

Figure 3. Thermal rate constants calculated in this work by the CVT/μOMT method for the hydrogen (solid line) and deuterium (dashed line) shift reactions of 7-methylocta-1,3(Z),5(Z)-triene. The experimental values (squares) are also plotted for comparison.

Equation 14 should be replaced by

$$k^{\mathrm{CVT}}(T) = \frac{2}{\beta h} \frac{Q^{\mathrm{GT}}(T, s_*{}^{\mathrm{CVT}})}{\sum_{i=1}^{13} (n^{\mathbf{R}_i}/\sigma^{\mathbf{R}_i}) Q^{\mathbf{R}_i}(T)\, \mathrm{e}^{-\beta \Delta E_{\mathbf{R}_i}}} \exp[-\beta V_{\mathrm{MEP}}(s_*^{\mathrm{CVT}})] \tag{14}$$

The first sentence after eq 14 should be replaced by "where the sum runs over the thirteen conformers ($i = 1, ..., 13$), with $Q^{\mathbf{R}_i}(T)$ and $\Delta E_{\mathbf{R}_i}$ being the partition function of conformer $\mathbf{R}_i$ and the relative energy of conformer $\mathbf{R}_i$ regarding the most stable conformer, respectively. The number two in the numerator takes into account that **TS7** has one enantiomer. The enantiomers of $\mathbf{R}_i$ are specified in $n^{\mathbf{R}_i}$, thus $n^{\mathbf{R}_i} = 2$ for all conformers except for $i = 1, 4$."

On page 722, the sentence "The CVT/μOMT values ... " should be replaced by "The CVT/μOMT values are in good agreement with the experimetal ones for both the hydrogen and deuterium transfer."

On page 723, the numerical values in the sentence "When the contribution of the ZCT ... " are slightly different: 0.06 should replace 0.04, 0.39 should replace 0.41, and 1.23 should replace 1.29.

On page 724 (third line of the second parapraph), 3.84 should replace 3.73 .

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