THE JOURNAL OF PHYSICAL CHEMISTRY A
J. Phys. Chem. A, 1998, 102(45), 8932-8940, DOI:10.1021/jp982923a

IS. Tri-exponential kinetics of relaxation to equilibrium in two simultaneous reactions

Let us consider a reactive system (species X, Y, and Z) consisting of the following reactions (first-order rate coefficients for direct and reverse reactions are given in parentheses):

$X \rightarrow$ wall	(γ)
$X \rightleftarrows Y$	(α_1,β_1)
$X \rightleftarrows Z$	(α_2,β_2)
$Y \rightarrow$ wall	(δ_1)
$Z \rightarrow$ wall	(δ_2)

The temporal evolution of concentrations X, Y, and Z is described by the system of differential equations:

$$\dot{X} = -(\alpha_1 + \alpha_2 + \gamma)X + \beta_1 Y + \beta_2 Z$$
$$\dot{Y} = \alpha_1 X - (\beta_1 + \delta_1)Y$$
$$\dot{Z} = \alpha_2 X - (\beta_2 + \delta_2)Z$$

which results in the determinant equation

$$\begin{vmatrix} -\alpha_1 - \alpha_2 - \gamma + \lambda & \beta_1 & \beta_2 \\ \alpha_1 & -\beta_1 - \delta_1 + \lambda & 0 \\ \alpha_2 & 0 & -\beta_2 - \delta_2 + \lambda \end{vmatrix} = 0$$

which is equivalent to

$$\lambda^3 + \xi\lambda^2 + \sigma\lambda + \omega = 0 \qquad \text{(S-I)}$$

Here,

$$\xi = \alpha_1 + \beta_1 + \delta_1 + \alpha_2 + \beta_2 + \delta_2 + \gamma$$

$$\sigma = (\alpha_1 + \gamma)(\beta_2 + \delta_2) + (\alpha_2 + \gamma)(\beta_1 + \delta_1) + \alpha_1\delta_1 + \alpha_2\delta_2$$

$$\omega = \alpha_1\delta_1(\beta_2 + \delta_2) + \alpha_2\delta_2(\beta_1 + \delta_1) + \gamma(\beta_1 + \delta_1)(\beta_2 + \delta_2)$$

Equation S-I has three roots (λ_1, λ_2, and λ_3) and can be solved via standard formulas (e.g., CRC handbook of mathematical sciences, CRC Press: West Palm Beach, Fla., 1987). Setting boundary conditions $X(t=0) = X_0$, $Y(t=0)=Z(t=0)=0$, and $X(t=\infty) = Y(t=\infty)=Z(t=\infty)=0$ we obtain a tri-exponential equation for the concentration of species X:

$$X(t) = X_1 \exp(-\lambda_1 t) + X_2 \exp(-\lambda_2 t) + X_3 \exp(-\lambda_3 t)$$

where coefficients X_i are given by

$$X_1 = X_0\left[\frac{\lambda_1 - \lambda_3}{\beta_1 + \delta_1 + \lambda_1} + \xi\frac{\lambda_2 - \lambda_3}{\beta_1 + \delta_1 + \lambda_2}\right]^{-1}$$

$$X_2 = \xi X_1$$

$$X_3 = X_0 - X_1 - X_2$$

Table 1S. Interatomic Distances, Angles, and Energies of the Conformations of the $CH_3CHCHCH_2$ Radical

Parameter	Conformation number				
	1 (*trans*)	2	3 (*cis*)	4	5
C2C1	1.3907	1.3877	1.3905	1.3879	1.3892
C3C1	1.3904	1.3943	1.3936	1.3959	1.3949
C4C3	1.5001	1.505	1.5012	1.5047	1.5028
H11C1	1.0796	1.0802	1.0787	1.0785	1.0786
H21C2	1.0744	1.0745	1.0745	1.0746	1.0746
H22C2	1.076	1.0761	1.0741	1.0749	1.0744
H31C3	1.079	1.0777	1.0777	1.0763	1.0771
H41C4	1.0849	1.0876	1.0824	1.0875	1.084
H42C4	1.0879	1.0838	1.0877	1.0837	1.0852
H43C4	1.0879	1.0877	1.0877	1.0875	1.0889
C3C1C2	124.7196	124.7268	127.3058	125.7853	126.6598
C4C3C1	124.3031	123.2608	126.5895	124.3586	125.5761

Table 1S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the $CH_3CHCHCH_2$ Radical

H11C1C2	117.6281	117.6486	116.6137	117.3514	116.9314
H21C2C1	121.2766	121.3417	120.4205	120.8806	120.6207
H22C2C1	121.2374	121.2028	122.6008	121.9902	122.33
H31C3C1	118.4749	118.4661	117.3118	117.8907	117.5303
H41C4C3	111.4826	111.5219	112.7434	111.5909	112.1909
H42C4C3	111.2581	111.2102	110.726	110.9202	110.6382
H43C4C3	111.2581	111.515	110.7382	111.5911	111.3344
H11C1C2C3	180.	179.9998	179.986	179.9995	180.1701
H21C2C1C3	180.	180.	180.0051	180.0001	180.2487
H22C2C1H21	180.	180.	180.0013	180.	180.1681
H31C3C1C4	180.	180.0005	180.013	179.9986	182.4336
H41C4C3C1	0.	59.8975	0.	60. fixed	30. fixed
H42C4C3H41	120.4627	120.0929	120.7673	120.0118	120.2875
H43C4C3H41	-120.4627	-119.8273	-120.7997	-119.9759	-120.6243

Table 1S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the $CH_3CHCHCH_2$ Radical

C4C3C1C2	180.	179.9992	0.	0.	-0.423
E(UHF/6-31G**) / h	-155.5186242	-155.5170151	-155.5168104	-155.5168057	-155.5168044
E(MP2/6-31G**) / h	-156.0362608	-156.0342444	-156.0346695	-156.0346817	-156.0347082
ZPVE [a] / J mol^{-1}	260157.6	259903.6	261106.8	260796.3	261029.7
ν_{tor} [b] / cm^{-1}	136.5	-154.7571	5.8235	-	-

[a] unscaled, torsions excluded.

[b] torsional frequency.

Table 2S. Interatomic Distances, Angles, and Energies of the Conformations of the *trans*-$CH_3CHCHCH_2O_2$ Radical

Parameter	Configuration number									
	1	2	3	4	5	6	7	8	9	10
C2C1	1.5023	1.5116	1.5023	1.5015	1.5016	1.5013	1.5023	1.501	1.5016	1.5014
C3C2	1.3186	1.3186	1.318	1.3194	1.3194	1.3195	1.3179	1.3198	1.3195	1.3196
C4C3	1.4991	1.4993	1.5022	1.496	1.4972	1.4956	1.5058	1.5053	1.4977	1.4966
H11C1	1.0844	1.0835	1.0843	1.0838	1.0839	1.0838	1.084	1.084	1.0839	1.0839
H12C1	1.0866	1.0855	1.0866	1.0867	1.0867	1.0864	1.0866	1.0865	1.0865	1.0864
H13C1	1.0866	1.0855	1.0867	1.0864	1.0864	1.0866	1.0866	1.0866	1.0867	1.0867
H21C2	1.0762	1.0752	1.0769	1.0795	1.0796	1.0795	1.0807	1.079	1.0797	1.0795
H31C3	1.0789	1.0797	1.0794	1.0762	1.0781	1.078	1.0771	1.0772	1.0779	1.0785
H41C4	1.0841	1.0841	1.0828	1.0813	1.0791	1.0828	1.0826	1.0814	1.0824	1.0827

Table 2S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the *trans*-$CH_3CHCHCH_2O_2$ Radical

H42C4	1.0841	1.0841	1.0835	1.0835	1.0838	1.082	1.0826	1.0822	1.0808	1.0814
O1C4	1.4205	1.4207	1.4195	1.4396	1.4335	1.429	1.4248	1.4299	1.429	1.4281
O2O1	1.3	1.3	1.3029	1.2945	1.2967	1.3003	1.2993	1.3005	1.3002	1.3018
C4C3C2	126.2835	126.2955	126.0913	122.9089	123.6928	123.6991	124.1179	123.5667	123.681	123.7215
C3C2C1	124.4265	124.0078	124.6647	125.1152	125.1694	125.1706	124.9417	125.0133	125.1895	125.2323
H11C1C2	111.7133	111.0248	111.6958	111.5436	111.5348	111.5473	111.3931	111.5697	111.5284	111.5514
H12C1C2	110.766	111.3902	110.764	110.8413	110.838	110.6451	110.886	110.6852	110.6821	110.6454
H13C1C2	110.766	111.3902	110.7727	110.6399	110.6724	110.8108	110.886	110.7537	110.8333	110.8315
H21C2C3	119.3218	119.028	119.249	119.0491	118.9769	118.9479	119.2695	118.9541	118.9939	118.8809
H31C3C2	120.015	120.093	120.0118	120.2784	120.31	120.4203	120.5676	119.9657	120.386	120.4309
H41C4C3	111.0179	111.0483	111.217	111.142	112.1303	111.7974	112.2768	111.3109	111.8592	111.517

Table 2S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the *trans*-$CH_3CHCHCH_2O_2$ Radical

H42C4C3	111.0178	111.0483	110.7823	111.0949	111.3588	111.8615	112.2766	112.2911	111.5635	111.9306
O1C4C3	109.7306	109.7414	113.5141	115.0713	109.5279	107.69	106.8434	108.6489	112.088	112.0502
O2O1C4	110.9205	110.9068	111.4858	114.6863	112.4797	111.0236	111.1445	110.8051	111.2216	111.3773
H12C1C2H11	120.7068	119.8972	120.6892	120.7472	120.7051	120.6296	120.5839	120.6325	120.6214	120.6208
H13C1C2H11	-120.7068	-119.8972	-120.7043	-120.5783	-120.6147	-120.7206	-120.5838	-120.7662	-120.6982	-120.7189
H41C4C3O1	119.8443	119.8223	122.3662	119.9781	119.787	117.9326	118.4941	118.9983	120.7146	115.1576
H42C4C3O1	-119.8443	-119.8223	-117.1045	-119.1913	-117.3388	-119.404	-118.494	-119.0084	-116.5803	-122.2296
C4C3C2C1	180.	180.	179.7201	183.1362	181.3466	178.4638	180.0004	180.9842	178.7325	178.8051
H21C2C3C1	180.	180.	179.9487	180.0216	179.8481	180.116	179.9998	179.051	180.1339	179.9502
H31C3C2H21	180.	180.	180.143	180.4945	180.3299	179.4514	180.0002	179.3145	179.808	179.3524
H11C1C2C3	0.	180.	-0.2233	-0.5259	-0.719	0.6797	-0.001	-1.2941	0.625	0.4329

Table 2S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the *trans*-$CH_3CHCHCH_2O_2$ Radical

O1C4C3C2	-0.0006	0.	2.8234	-120.7659	-123.9714	121.1595	180.	55.0324	119.8013	122.7813
O2O1C4C3	179.9996	180.0001	81.8453	-1.9347	128.2717	171.8108	180.0076	183.4069	73.8339	-72.8294
E(UHF) [a]	-305.1322925	-305.1289615	-305.1325564	-305.1282417	-305.1314285	-305.1338204	-305.1302037	-305.1301262	-305.1336283	-305.1341142
E(MP2) [b]	-306.0115432	-306.0083741	-306.0123055	-306.0099632	-306.0121654	-306.0135119	-306.0092554	-306.0103326	-306.0141035	-306.0135265
ZPVE [c]	294015.5798	294094.3497	294306.9154	294355.3261	294284.3915	294048.0143	293475.8295	293597.9548	294424.8179	294227.7214
ν_{tor} [d] / cm^{-1}	69.2894	68.946	102.4535	-157.0563	-93.8815	71.7157	76.5786	89.5152	109.8615	114.4661
ν_{tor} [e] / cm^{-1}	113.6248	121.1485	113.1574	96.5683	90.2008	102.888	-134.2398	-115.8256	76.7416	78.5024
ν_{tor} [f] / cm^{-1}	210.7697	-211.9287	214.4626	224.183	213.0356	216.7506	201.8249	205.8029	215.5004	215.3536

[a] E(UHF/6-31G**) / hartree.

[b] E(MP2/6-31G**) / hartree.

[c] Zero-point vibrational energy (unscaled, torsions excluded) / J mol^{-1}.

[d] C-OO Torsional frequency.

[e] C-CH_2OO Torsional frequency.

[f] C-CH_3 Torsional frequency.

Table 3S. Interatomic Distances, Angles, and Energies of the Conformations of the *cis*-$CH_3CHCHCH_2O_2$ Radical

Parameter	Configuration number								
	1	2	3	4	5	6	7	8	9
C2C1	1.5035	1.5122	1.5038	1.5035	1.5037	1.5038	1.5037	1.5039	1.5041
C3C2	1.3217	1.3213	1.3216	1.322	1.3216	1.3215	1.3219	1.3194	1.3218
C4C3	1.4974	1.4974	1.4995	1.4983	1.4985	1.4991	1.4976	1.5056	1.5012
H11C1	1.0818	1.086	1.082	1.0816	1.0818	1.082	1.0817	1.0838	1.0772
H12C1	1.0867	1.0851	1.0867	1.0868	1.0868	1.0867	1.0868	1.0866	1.0871
H13C1	1.0861	1.0831	1.0862	1.0861	1.0861	1.0862	1.0861	1.0866	1.0871
H21C2	1.0783	1.077	1.0784	1.0785	1.0783	1.0783	1.0784	1.0776	1.0789
H31C3	1.0771	1.0768	1.077	1.0777	1.0775	1.0773	1.0754	1.0759	1.079

Table 3S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the *cis*-$CH_3CHCHCH_2O_2$ Radical

H41C4	1.0832	1.0834	1.0826	1.0827	1.0809	1.084	1.0835	1.0827	1.0841
H42C4	1.0792	1.0804	1.0782	1.0786	1.0793	1.0767	1.0785	1.0827	1.0841
O1C4	1.429	1.4285	1.4291	1.4282	1.4327	1.4332	1.44	1.4249	1.4202
O2O1	1.3002	1.3002	1.3002	1.3019	1.2976	1.2966	1.2945	1.2992	1.3006
C4C3C2	127.1938	125.655	127.1552	127.2583	127.2976	127.1308	126.4038	125.6639	132.5396
C3C2C1	128.8057	126.8436	128.7887	128.7359	128.7681	128.638	129.0981	126.7925	131.0254
H11C1C2	113.3917	111.3761	113.4406	113.3696	113.4233	113.3565	113.5145	112.714	113.3974
H12C1C2	110.2912	112.0679	110.2958	110.3581	110.2974	110.31	110.375	110.5885	109.6449
H13C1C2	110.0265	110.5454	110.0895	109.9492	110.0494	110.1296	109.8679	110.5885	109.6444
H21C2C3	116.8016	117.2047	116.8622	116.872	116.8579	116.8937	116.6779	117.7191	115.2072

Table 3S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the *cis*-$CH_3CHCHCH_2O_2$ Radical

H31C3C2	118.5568	119.3329	118.5119	118.5173	118.557	118.5492	118.3014	119.5953	116.9065
H41C4C3	111.1799	111.4947	111.364	110.8847	111.5642	110.9033	110.3167	112.4984	109.9776
H42C4C3	113.4594	112.7914	113.0535	113.5171	112.9581	113.6531	112.6571	112.4984	109.9773
O1C4C3	107.0722	107.2258	111.4988	111.4088	109.2128	108.8078	114.804	106.5706	112.6311
O2O1C4	110.9838	111.0099	111.3391	111.2474	112.5754	112.4895	114.831	111.125	110.5259
H12C1C2H11	121.1736	120.8088	121.1276	121.3543	121.1469	121.075	121.4436	120.8051	121.554
H13C1C2H11	-121.026	-119.3888	-121.0366	-120.8187	-121.0366	-121.0449	-120.8156	-120.8052	-121.5522
H41C4C3O1	117.292	117.6276	120.0555	114.4821	118.0805	116.6761	118.5135	118.366	120.6361
H42C4C3O1	-119.6058	-119.3985	-116.8013	-122.5684	-118.5814	-119.9314	-120.5167	-118.366	-120.6352
C4C3C2C1	-1.0993	-1.0739	-0.7346	-1.0093	-0.8869	-0.7215	-3.3687	-0.0002	0.0062

Table 3S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the *cis*-$CH_3CHCHCH_2O_2$ Radical

H21C2C3C1	179.6563	179.9671	179.6339	179.9439	179.7052	179.5621	180.0587	180.0002	179.994
H31C3C2H21	-0.4616	-0.308	-0.0617	-0.5412	-0.4801	-0.2119	-0.5896	0.0001	-0.0021
H11C1C2C3	-4.01	-64.01	-3.4668	-4.3153	-4.2538	-3.7673	-4.4846	0.0001	-0.0261
O1C4C3C2	125.8995	127.3062	124.7766	124.5776	125.0935	131.1762	120.4875	180.	0.
O2O1C4C3	172.4838	173.0194	73.6974	-73.6516	119.1593	-128.4543	1.1162	180.0001	180.0051
E(UHF) [a]	-305.1306112	-305.1289315	-305.1304192	-305.130896	-305.1291107	-305.1283921	-305.1247432	-305.1293608	-305.1248675
E(MP2) [b]	-306.0104232	-306.0087647	-306.011063	-306.0104736	-306.0099974	-306.0092173	-306.0065959	-306.0086968	-306.0045037
ZPVE [c]	295382.6529	294797.4552	295699.1624	295530.3948	295656.115	295576.9782	295787.0652	294430.0014	295302.1488
ν_{tor} [d] / cm^{-1}	86.8447	87.0912	109.6892	117.3712	-78.4769	-94.9952	-163.5836	87.8544	83.6737
ν_{tor} [e] / cm^{-1}	53.7446	53.2657	44.9218	36.7232	53.2769	47.6348	56.2974	-62.6745	-35.5779

Table 3S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the *cis*-$CH_3CHCHCH_2O_2$ Radical

ν_{tor} [f] / cm^{-1}	135.8041	-131.4193	137.6464	136.6195	138.4618	137.4562	135.3326	133.4778	132.9862

[a] E(UHF/6-31G**) / hartree.

[b] E(MP2/6-31G**) / hartree.

[c] Zero-point vibrational energy (unscaled, torsions excluded) / J mol^{-1}.

[d] C-OO Torsional frequency.

[e] C-CH_2OO Torsional frequency.

[f] C-CH_3 Torsional frequency.

Table 4S. Interatomic Distances, Angles, and Energies of the Conformations of the $CH_3CH(OO)CHCH_2$ Radical

Parameter	Configuration number					
	1	2	3	4	5	6
C2C1	1.3173	1.3169	1.3200	1.3194	1.3169	1.3169
C3C1	1.5049	1.5012	1.5113	1.512	1.5099	1.5035
C4C3	1.5175	1.5214	1.5184	1.5206	1.521	1.523
H11C1	1.0778	1.0784	1.0775	1.0771	1.077	1.0786
H21C2	1.0753	1.0753	1.0754	1.0754	1.075	1.0754
H22C2	1.0751	1.0769	1.0765	1.0759	1.077	1.0739
H31C3	1.0852	1.0829	1.0833	1.0825	1.0838	1.0851

Table 4S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the $CH_3CH(OO)CHCH_2$ Radical

H41C4	1.083	1.0833	1.0827	1.0834	1.0835	1.0834
H42C4	1.0839	1.085	1.0851	1.0836	1.0839	1.0842
H43C4	1.0843	1.0844	1.0854	1.0844	1.0839	1.0851
C3C1C2	126.3027	123.9959	123.7285	124.6199	125.0216	126.4654
C4C3C1	116.3967	112.8011	112.971	114.7581	114.3485	112.4225
H11C1C2	119.637	120.3482	119.7886	119.315	120.0083	119.7531
H21C2C1	120.7391	121.4541	121.3121	121.044	120.9609	120.5579
H22C2C1	122.8378	121.8971	121.843	122.447	122.5994	122.2215
H31C3C1	109.015	110.4199	110.3859	109.4674	110.4034	109.5094

Table 4S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the $CH_3CH(OO)CHCH_2$ Radical

H41C4C3	109.6622	110.581	110.672	110.1913	110.2949	110.4437
H42C4C3	110.7787	110.5064	110.4355	111.0282	110.3195	110.2274
H43C4C3	110.5202	109.8139	109.9443	109.9217	110.2117	110.1749
H11C1C2C3	178.7006	181.4381	179.5742	181.9003	179.0424	179.7638
H21C2C1C3	181.7	178.0741	180.618	178.3213	180.7829	180.2349
H22C2C1H21	179.8005	180.1139	179.0803	180.9745	179.626	180.0046
H31C3C1C4	125.025	124.3835	123.8975	123.7771	125.1186	122.403
H41C4C3C1	183.4361	183.0683	181.3689	180.5525	182.4571	179.7231
H42C4C3H41	120.0555	120.3671	120.4927	120.3394	120.5872	120.5632

Table 4S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the $CH_3CH(OO)CHCH_2$ Radical

H43C4C3H41	-119.0463	-119.8881	-119.7076	-119.6368	-119.585	-119.5899
C4C3C1C2	-10.6426	-115.6697	179.6955	52.0482	-57.6728	122.1304
O1C3	1.4379	1.4369	1.4386	1.4398	1.4353	1.4292
O2O1	1.2998	1.2997	1.3002	1.3002	1.2988	1.2996
O1C3C1	104.7684	105.506	106.6473	106.2406	104.8866	107.9302
O2O1C3	111.6099	111.5975	111.3202	111.3668	111.7066	111.4823
O1C3C1C4	-121.6242	-119.9844	-120.9862	-121.7138	-120.3767	-121.4937
O2O1C3C1	-160.0807	-168.5206	-164.9431	-164.1331	-164.2554	-162.82
E(UHF) [a]	-305.1322243	-305.1333687	-305.1298065	-305.1287373	-305.130562	-305.1326027

Table 4S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the $CH_3CH(OO)CHCH_2$ Radical

E(MP2) [b]	-306.0146513	-306.0156843	-306.0107416	-306.0110295	-306.0127952	-306.0146688
ZPVE [c]	291834.0127	291373.2801	289344.8447	290147.2129	291228.3186	291800.8442
ν_{tor} [d] / cm^{-1}	121.4794	117.7288	116.4391	120.8013	110.7753	119.7925
ν_{tor} [e] / cm^{-1}	94.3013	87.3363	-105.05	-95.6197	-97.8442	86.6781
ν_{tor} [f] / cm^{-1}	273.8268	255.6755	273.7064	268.5972	264.5455	261.2475

Table 4S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the $CH_3CH(OO)CHCH_2$ Radical

Parameter	Configuration number					
	7	8	9	10	11	12
C2C1	1.3173	1.3174	1.3166	1.3169	1.3169	1.3167
C3C1	1.5015	1.5031	1.5026	1.5009	1.502	1.5012
C4C3	1.5205	1.5215	1.5201	1.522	1.5214	1.538
H11C1	1.0789	1.0775	1.0788	1.0764	1.0786	1.0786
H21C2	1.0754	1.0754	1.0753	1.0754	1.0754	1.0753
H22C2	1.0769	1.0772	1.0771	1.0769	1.0771	1.0769
H31C3	1.0831	1.0824	1.0837	1.0832	1.0807	1.082

Table 4S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the $CH_3CH(OO)CHCH_2$ Radical

H41C4	1.0839	1.0845	1.0822	1.0841	1.0843	1.0833
H42C4	1.0847	1.0834	1.083	1.085	1.0848	1.0827
H43C4	1.0838	1.0843	1.0842	1.0844	1.0844	1.0838
C3C1C2	124.0643	123.7342	124.0732	123.0901	124.0071	124.0026
C4C3C1	112.9212	113.3384	112.6549	112.7376	112.9708	113.2218
H11C1C2	120.395	120.3077	120.4326	120.2236	120.3039	120.3961
H21C2C1	121.5576	121.4765	121.5585	121.4279	121.5007	121.4543
H22C2C1	121.7891	121.9468	121.7958	121.9613	121.8715	121.8793
H31C3C1	110.3092	109.7489	109.5475	109.4976	110.528	109.9325

Table 4S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the $CH_3CH(OO)CHCH_2$ Radical

H41C4C3	110.4469	110.292	111.5273	110.3525	110.3172	111.0969
H42C4C3	110.6409	111.0108	111.6189	110.5318	110.6209	110.3134
H43C4C3	109.7897	109.623	107.8407	110.0768	110.0729	111.2801
H11C1C2C3	181.1144	181.3512	180.8162	183.1524	181.0693	181.4203
H21C2C1C3	178.3481	178.402	178.5118	176.5125	178.4727	178.1906
H22C2C1H21	179.8848	180.0897	179.9753	179.9276	180.0749	180.1554
H31C3C1C4	124.4687	123.526	122.4113	122.6922	124.9443	124.5112
H41C4C3C1	182.0936	181.9649	180.9851	182.369	181.7431	122.9293
H42C4C3H41	120.0938	120.5084	121.4496	119.8672	119.943	119.6847

Table 4S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the $CH_3CH(OO)CHCH_2$ Radical

H43C4C3H41	-120.1672	-119.7343	-119.3954	-120.0573	-120.1876	-120.2709
C4C3C1C2	-118.4487	-116.207	-115.8796	-118.2978	-115.2798	-117.1859
O1C3	1.4349	1.4382	1.4462	1.4462	1.4401	1.437
O2O1	1.3014	1.3	1.2947	1.2947	1.2968	1.2998
O1C3C1	110.1796	110.708	106.6113	113.3004	107.731	105.1637
O2O1C3	111.7682	112.2153	115.2235	115.0473	112.6498	111.4011
O1C3C1C4	-117.1162	-124.4852	-124.8427	-121.1188	-118.8001	-120.9935
O2O1C3C1	-71.2097	63.3488	122.9328	4.3579	-123.6296	-171.178
E(UHF) [a]	-305.1341211	-305.1326311	-305.1286924	-305.1282637	-305.131682	-305.1274673

Table 4S (continued). Interatomic Distances, Angles, and Energies of the Conformations of the $CH_3CH(OO)CHCH_2$ Radical

E(MP2) [b]	-306.0151177	-306.0154438	-306.0126762	-306.0119922	-306.0143233	-306.0095699
ZPVE [c]	291074.0256	291448.878	291867.1106	291798.9757	291631.3744	291911.1422
ν_{tor} [d] / cm^{-1}	118.1388	139.2298	-109.2426	-128.4434	-92.0833	124.5189
ν_{tor} [e] / cm^{-1}	87.7506	87.4725	98.9008	110.0604	94.4081	93.3291
ν_{tor} [f] / cm^{-1}	243.7427	250.0547	300.0609	261.3388	253.4855	-250.3792

[a] E(UHF/6-31G**) / hartree.

[b] E(MP2/6-31G**) / hartree.

[c] Zero-point vibrational energy (unscaled, torsions excluded) / J mol^{-1}.

[d] C-OO Torsional frequency.

[e] C-C_2H_3 Torsional frequency.

[f] C-CH_3 Torsional frequency.