Effects of alkyl substitution on the energetics of enolates anions and radicals

Supporting Information

Leah S. Alconcel, Hans-Jürgen Deyerl, Robert E. Continetti

Department of Chemistry and Biochemistry, 0314
University of California, San Diego
9500 Gilman Drive, La Jolla, CA 92093-0314

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The supporting information is provided in the following tables. The CASSCF and CASSCF-MP2 absolute energies, in Hartrees, of (E,Z)-n-propionaldehyde, (E)-n-butyraldehyde and i-butyraldehyde enolate anions and radicals corrected by zero point energies are displayed in Table 1. In Tables 2-5, the scaled frequencies of the normal vibrational modes,[1] in cm^{-1}, of the $X(^1A')$ state of the anion and the $X(^2A'')$ and $A(^2A')$ states of the neutral radical are provided in the first three columns. The symmetry of the vibrational modes is provided in the fourth column and the vibrational mode types are provided in the fifth column. Since the electronic states of (E)-n-C_4H_7O optimized to structures far from C_s symmetry, the fourth column of Table 4 is blank. The portion of the molecule in which the predominant displacement occurs is used to qualitatively describe the vibrational mode type. These frequencies were used in the Franck-Condon factor (FCF) calculations for (E)-n-$C_3H_5O^-$, (Z)-n-$C_3H_5O^-$, (E)-n-$C_4H_7O^-$ and i-$C_4H_7O^-$ and the tables are presented in this order.

Supporting Information for Franck-Condon Factor (FCF) Calculations

Table 1: Absolute CASSCF and CASSCF-MP2 energies

		CASSCF	CASSCF-MP2
(E)-n-C_3H_5O	X(^{1}A')	-191.3382452	-192.0209397
	X(^{2}A")	-191.3420168	-191.9663169
	A(^{2}A')	-191.3041134	-191.9227518
(Z)-n-C_3H_5O	X(^{1}A')	-191.3407684	-192.0239499
	X(^{2}A")	-191.3426178	-191.9673729
	A(^{2}A')	-191.3027503	-191.9217219
(E)-n-C_4H_7O	X(^{1}A')	-230.3546178	-231.2133876
	X(^{2}A")	-230.3553014	-231.1475169
	A(^{2}A')	-230.3166885	-231.1055707
i-C_4H_7O	X(^{1}A')	-230.3556316	-231.2102534
	X(^{2}A")	-230.3614199	-231.1590595
	A(^{2}A')	-230.3185338	-231.1084029

Table 2: (E)-n-C_3H_5O

X(^{1}A')	X(^{2}A")	A(^{2}A')	symmetry	type
104	57	272	a"	methyl rotor
236	179	389	a"	torsion
592	602	915	a"	CH wag
923	882	652	a"	CH wag
1016	981	1228	a"	methyl rock
1442	1451	1456	a"	methyl wag
2772	2914	2923	a"	methyl asym CH stretch
316	298	282	a'	CCC bend
557	528	498	a'	CCO bend
886	870	894	a'	methyl rock
1063	1093	1083	a'	C_2C_3 stretch
1198	1134	1633	a'	C_1C_2 stretch
1278	1315	1266	a'	HCCH sym wag
1327	1410	1274	a'	HCCH asym wag
1380	1400	1404	a'	methyl umbrella
1474	1468	1471	a'	methyl wag
1580	1518	1076	a'	CO stretch
2634	2877	3017	a'	CH stretch
2778	2870	2877	a'	methyl sym CH stretch
2866	2939	2937	a'	CH stretch
2940	3030	3005	a'	CH stretch

Table 3: (Z)-n-C_3H_5O

$X(^1A')$	$X(^2A'')$	$A(^2A')$	symmetry	type
60	27	111	a"	methyl rotor
248	493	771	a"	CH wag
566	231	495	a"	torsion
893	890	979	a"	CH wag
1021	983	1458	a"	methyl rock
1459	1458	1850	a"	methyl wag
2782	2911	2922	a"	methyl asym CH stretch
247	259	230	a'	CCC bend
692	672	618	a'	CCO bend
869	1127	877	a'	C_2C_3 stretch
1036	1036	1083	a'	methyl rock
1127	831	1618	a'	C_1C_2 stretch
1286	1363	1366	a'	HCCH sym wag
1355	1392	1414	a'	methyl umbrella
1421	1400	1208	a'	HCCH asym wag
1464	1463	1466	a'	methyl wag
1561	1533	1002	a'	CO stretch
2666	2889	3016	a'	CH stretch
2784	2873	2879	a'	methyl sym CH stretch
2921	2975	2950	a'	CH stretch
2946	3023	3035	a'	CH stretch

Table 4: (E)-n-C_4H_7O

$X(^1A')$	$X(^2A'')$	$A(^2A')$	symmetry	type
75	25	46		ethyl rotor
186	146	187		torsion
219	207	269		methyl rotor
336	296	453		CCC bend
389	368	484		CCC bend
551	518	301		CCO bend
632	620	900		CH wag
748	751	772		methyl wag
864	885	871		methyl rock
952	891	682		CH wag
973	967	979		CC stretch
1047	1039	1057		methyl rock
1099	1109	1109		CC stretch
1196	1250	1256		CH wag
1247	1296	1295		CH_2 wag
1311	1417	1353		CH_2 rock
1341	1365	1236		CH wag
1364	1396	1397		methyl umbrella
1371	1140	1531		CC stretch
1445	1459	1454		CH_2 scissors
1453	1469	1467		methyl wag
1466	1476	1471		methyl wag
1587	1517	1866		CO stretch
2653	2866	2871		CH stretch
2745	2875	2876		CH stretch
2812	2878	2900		CH stretch
2844	2903	2929		CH stretch
2875	2937	2935		CH stretch
2906	2938	2996		CH stretch
2937	3021	3228		CH stretch

Table 5: i-C_4H_7O

$X(^1A')$	$X(^2A'')$	$A(^2A')$	symmetry	type
70	315	2189	a"	CCC oop bend
174	94	125	a"	methyl rotor
232	112	187	a"	methyl rotor
362	199	287	a"	torsion
880	884	623	a"	CH wag
996	1022	945	a"	methyl asynchr rock
1032	951	990	a"	methyl synchr rock
1439	1448	1447	a"	methyl wag
1458	1464	1462	a"	methyl wag
2762	2901	2910	a"	methyl asynchr CH stretch
2769	2905	2915	a"	methyl synchr CH stretch
259	272	240	a'	CCO bend
342	345	346	a'	CCC bend
596	571	543	a'	CCC bend
784	771	774	a'	breathe
941	950	956	a'	methyl asynchr rock
1006	986	1016	a'	methyl synchr rock
1192	1227	1187	a'	CCC asym stretch
1286	1524	1107	a'	CO stretch
1346	1400	1316	a'	CH wag
1377	1390	1402	a'	asynchr methyl umbrella
1383	1405	1411	a'	synchr methyl umbrella
1455	1452	1462	a'	methyl wag
1472	1474	1470	a'	methyl wag
1583	1307	1643	a'	CC stretch
2669	2878	3022	a'	CH stretch
2765	2863	2868	a'	methyl asynchr CH stretch
2776	2866	2874	a'	methyl synchr CH stretch
2880	2940	2939	a'	CH stretch
2937	2979	2952	a'	CH stretch

(1) Scott, A. P.; Radom, L. *J Phys Chem* **1996**, *100*, 16502-16513.