

Explaining the antioxidant activity of some common non-phenolic components of essential oils

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APPENDIX A

(supplementary material)

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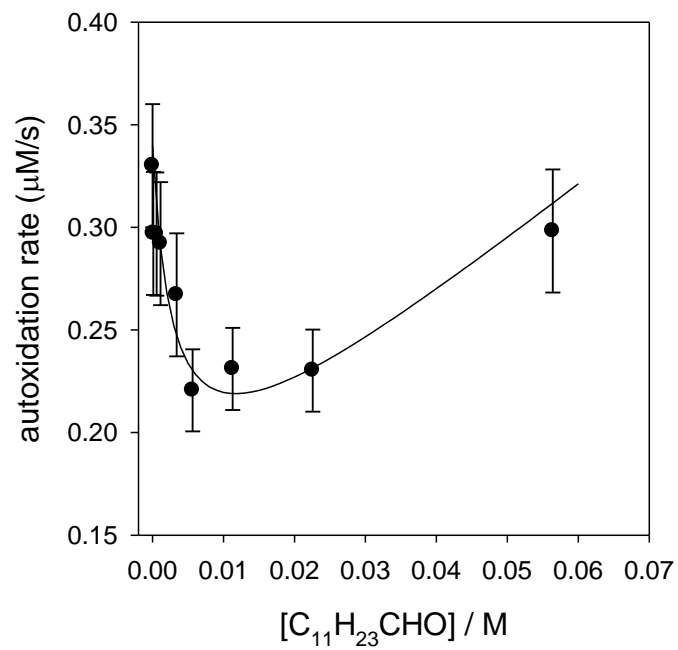


Figure 1S. Rate of O₂ uptake during the autoxidation of cumene (3.5 M) in chlorobenzene initiated by AIBN (0.05 M) at 30 °C, as function of the concentration of dodecanal (range 0.11-56 mM) range.

Experimental procedure for calculations

The activation enthalpy of the H-atom transfer from the aldehyde or allylic portion of citral to methylperoxyl radical were computed in the gas phase at the M05/6-311+g(2df,2p) level of theory [1,2], using Gaussian 09 [3]. The hydrocarbon portion of citral was simplified to 2-methyl-2-pentene and the aldehydic portion to 3-methyl-2-butenal [4]. Stationary points were confirmed by checking the absence of imaginary frequencies. Transition states had one imaginary frequency corresponding to the transfer of a H-atom. Bond orders for reactants and transition states were computed by using the built-in NBO Gaussian functionality. Orbitals were plotted by using GaussView software (see Figure 2S).

For the sake of comparison, calculations were repeated at the M06-2X/6-311++G(d,p) level of theory[5,6]. The results, summarized in Figure 3S, qualitatively confirm those calculated at the M05/6-311+g(2df,2p) level.

The bond dissociation enthalpies of the involved species were also computed at the CBS-QB3 level, and were used to calculate the exothermicity of the reaction [7], since this level had previously been shown to afford the most reliable results with similar reactions [8,9].

References

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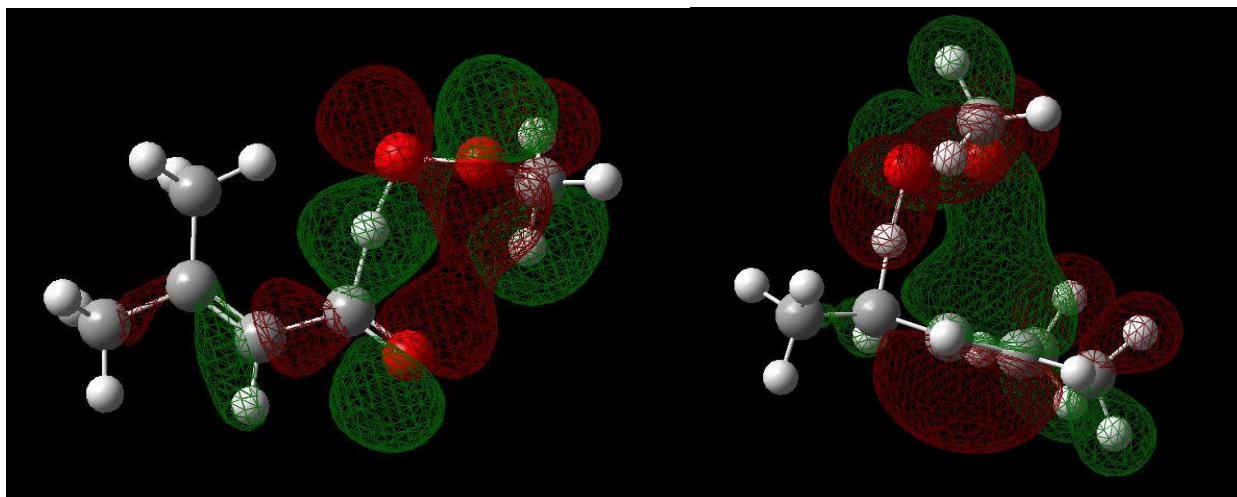


Figure 2S. Plot of SOMO-1 orbitals of the transition states for the reaction at the aldehyde (left) and allylic (right) CH bond, showing the through-space electron connection between the reactants.

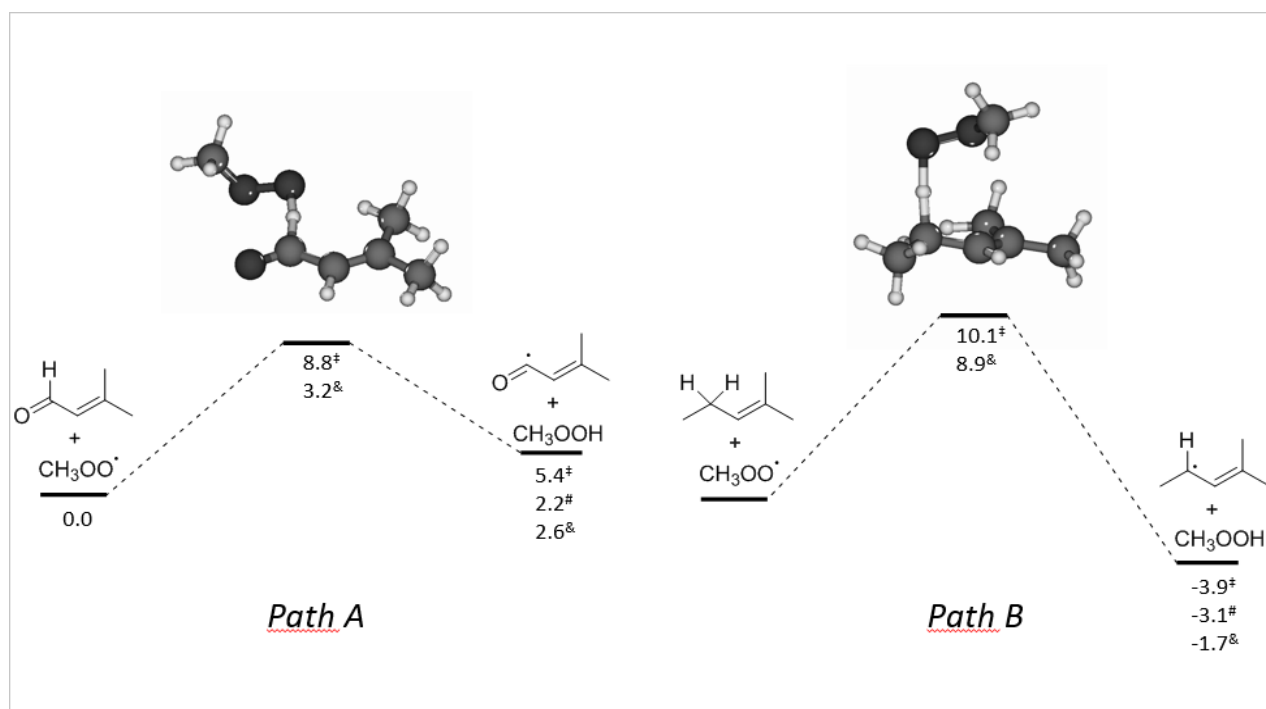

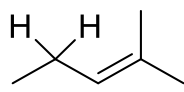
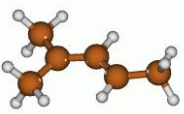
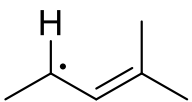
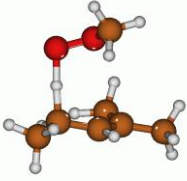
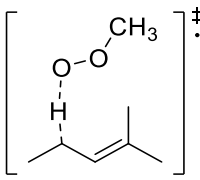
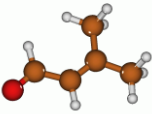
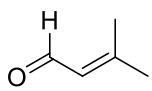
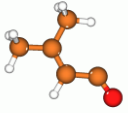
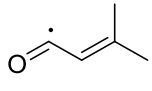
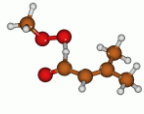


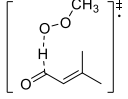
Figure 3S. Reaction profile of H-atom abstraction by ROO• radicals from the aldehyde (path A) or allylic (path B) portions of citral, computed at different levels of theory: (‡) M05/6-311+g(2df,2p); (&) M06-2X/6-311++G(d,p); (#) CBS-QB3. At each level of theory reported values refer to reactants calculated at the same level of theory.

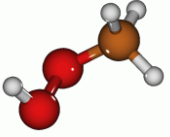
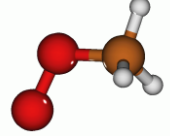
Optimized cartesian coordinates.

structure	M05/6-311+g(2df,2p) level	M06-2X/6-311++G(d,p)
 	C,-0.0386775409,-0.2085792758,-0.0152371439 C,-0.0337818348,-0.0861545804,1.3153082942 H,0.9277824274,-0.3328007314,-0.4999190371 C,1.2507388604,-0.130805633,2.0888540554 C,-1.2568152485,0.0975537932,2.1622941682 C,-1.1984467255,-0.1837754265,-0.9583664977 H,1.3971573539,0.7913395493,2.6579480629 H,1.2400102053,-0.9454147628,2.8183158185 H,2.113934842,-0.269077968,1.4400357718 H,-1.1758520533,1.0109368981,2.7573752783 H,-2.1775535721,0.1543782121,1.5877331339 H,-1.3566937943,-0.7256716597,2.8748349185 C,-1.1209754805,0.9678233823,-1.9574181667 H,-1.2181586816,-1.1268247991,-1.5141191861 H,-2.1444238457,-0.1332903492,-0.4198197464 H,-1.9496100844,0.9323238072,-2.6657092158 H,-1.1536046315,1.9309599289,-1.4468248073 H,-0.19289491,0.9314408025,-2.5302780765	C,0.0238135127,-0.3562827801,-0.0541609496 C,-0.003902519,-0.1044937728,1.2567141512 H,0.9918869021,-0.5775382889,-0.5013799216 C,1.2495764681,-0.1534750415,2.0896644901 C,-1.2465904838,0.2514613978,2.0285135156 C,-1.1348325857,-0.3217850443,-1.0131938156 H,1.4391755043,0.8164254996,2.560520946 H,1.1460011377,-0.883844768,2.8986658042 H,2.1206764294,-0.4232117093,1.4916014869 H,-1.1029329182,1.2045068685,2.5472184004 H,-2.1313994201,0.3408501881,1.4003886226 H,-1.4450722744,-0.4997633866,2.7998061395 C,-1.2157397206,1.0152087678,-1.7604875065 H,-1.0168903398,-1.1319665461,-1.7388196586 H,-2.0769410049,-0.5106211063,-0.4948910056 H,-2.0265394336,1.0140371917,-2.4923747117 H,-1.3854513601,1.8337907379,-1.0573044795 H,-0.2814714382,1.2208480131,-2.2883675054
 	C,0.0043171079,-0.1118446269,0.0274843069 C,-0.0076813805,-0.0292770228,1.5175457206 C,1.1813647215,-0.0773113678,2.2388827965 C,1.3600783601,-0.0153968836,3.605799069 C,2.6854421487,-0.0762565062,4.2775632861 C,-1.3529425149,0.1044557187,2.1476976815 H,2.0877340852,-0.1767274233,1.6453761819 H,-0.5809125173,-0.9667623996,-0.3273659624 H,-0.4526601779,0.7756571022,-0.4228641711 H,1.0129595346,-0.2079490646,-0.3715651351 H,-1.8645110602,1.0013709769,1.7844965982 H,-1.9934140433,-0.7415639883,1.8791545309 H,-1.3176140112,0.1607557132,3.2326003899 H,0.4965700932,0.0838913762,4.2536066012 H,2.8745784227,0.8211216623,4.8743447559 H,2.746093157,-0.9212988214,4.9699760066	C,0.0080043115,0.0533155097,-0.0310178262 C,-0.0165944314,0.0196255159,1.4647233528 C,1.3013702084,0.0092480487,2.1824897952 C,-1.2176102288,-0.0014095281,2.168910251 C,-1.3495461925,-0.0327780948,3.5406484946 C,-2.6662326229,-0.0543701325,4.2472476681 H,-2.1345209498,0.0077976061,1.5811010372 H,0.5369635764,0.9420310022,-0.3953442916 H,0.5446021018,-0.8135197168,-0.4347590817 H,-0.9981297903,0.0584029963,-0.4526315376 H,1.4082256805,-0.8844853246,2.8071943201 H,2.134728707,0.0286675544,1.4786227759 H,1.4005761823,0.8749536906,2.8466777846 H,-0.457034128,-0.0427832538,4.159378363 H,-2.7697531374,-0.9470393749,4.873139898 H,-2.7773910545,0.8083789801,4.9125475613

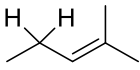
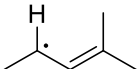
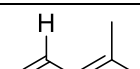
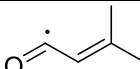
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H,-0.17451233,-3.9232906392,-1.9557028763	H,-0.1841877185,-3.7541959532,-1.6879935949	
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structure	M05/6-311+g(2df,2p) level	M06-2X/6-311++G(d,p)
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 	C,-0.0171986332,0.2813080191,-0.0091535613 C,-0.0412764665,0.1620999989,1.4779107524 C,1.2889106682,0.1538641004,2.1528353082 C,-1.2065147502,0.0694327963,2.1430744222 C,-1.2880364233,-0.0492475433,3.5886348435 O,-2.2371555072,-0.1388852038,4.2921037494 H,-2.1536991675,0.0800906859,1.6066494877 H,0.4931187418,1.2000422457,-0.307394288 H,0.5523931048,-0.5423088649,-0.4459084858 H,-1.014657732,0.2815915254,-0.4419215615 H,1.895008319,-0.6739102489,1.7779095296 H,1.8350535972,1.0698904196,1.9167627959 H,1.1983116314,0.064759197,3.2320455481	C,0.0152662288,0.1347702742,-0.0051509217 C,-0.0157503298,0.0144934397,1.489566065 C,1.3235538904,0.0066456333,2.1641154466 C,-1.1821713022,-0.0779229362,2.1465509544 C,-1.2512677889,-0.1968098291,3.6074026059 O,-2.2080024752,-0.2843483095,4.2932901581 H,-2.1316229078,-0.0680393822,1.6142243816 H,0.5269564829,1.0571248135,-0.2953710427 H,0.5869877755,-0.692996238,-0.4349528684 H,-0.9846484906,0.134950603,-0.4374609504 H,1.9230257777,-0.824113475,1.780565357 H,1.8629517142,0.9265348752,1.9202058992 H,1.2391234802,-0.082491651,3.245296532
	C,-0.1286802151,0.2181525305,0.1876923312 C,0.0186077516,-0.0538148516,1.6497709083 C,1.2497419359,-0.1788795315,2.1791290419 C,1.5761114768,-0.4349748679,3.5765769175 O,2.6715269187,-0.5940114269,4.0258344711	C,0,-0.0949781346,0.2352734869,0.205049831 C,0,0.0312045925,-0.0564529053,1.6721639277 C,0,1.247804721,-0.1859849764,2.2260300717 C,0,1.4985596432,-0.4572915074,3.6445642384 O,0,2.562742083,-0.6254363323,4.1522436094

	<p>C,-1.2677105942,-0.1613053593,2.3983674908 C,1.1272252153,-0.0173306154,7.2305509435 O,0.5676540958,-1.0544457313,6.4432467552\ O,-0.1597658874,-0.5244119258,5.4255884161 H,2.1221914029,-0.0878430457,1.5391266307 H,-0.6780556002,-0.5949272832,-0.2921551755 H,-0.7193289212,1.1232882608,0.0296147337 H,0.8280861842,0.3341433074,-0.3151018385 H,-1.7738006538,0.8071775343,2.3880991849 H,-1.9329717577,-0.8570619962,1.8831225325 H,-1.1664128272,-0.4844015169,3.4276781753 H,0.6102641902,-0.47504514,4.4689975045 H,1.650260136,-0.5231217745,8.0401078545 H,1.8344160908,0.5736837756,6.6457797206 H,0.3404851046,0.6239718765,7.6311309653</p>	<p>C,-1.2768064151,-0.1712599813,2.3998782382 C,1.1727617649,0.0078667533,7.1406764315 O,0.6068232865,-1.077329652,6.4215344088 O,-0.2423773876,-0.583714393,5.469011274 H,2.1450356561,-0.0895531575,1.6206460869 H,-0.6163519943,-0.5876370557,-0.2927843911 H,-0.7031900968,1.1319492008,0.0541711638 H,0.8733944203,0.378850016,-0.2723739393 H,-1.7498741921,0.8148119689,2.4424238569 H,-1.9494625162,-0.8174029211,1.829621473 H,-1.1979675686,-0.5620948827,3.4108066652 H,0.4965359969,-0.4968019669,4.4585221844 H,1.8106384463,-0.447944888,7.8972629051 H,1.7723527057,0.6312591607,6.4737625709 H,0.3829990345,0.597736252,7.6099469569</p>
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structure	M05/6-311+g(2df,2p) level	M06-2X/6-311++G(d,p)
 <p>CH₃OOH</p>	<p>O,-0.073399014,0.0890928529,-0.0028199348 C,-0.0393442106,0.0250012404,1.4032772055 H,1.0207815122,0.0317965031,1.653504671 H,-0.5316563908,0.8886176424,1.8593160274 H,-0.4973002781,-0.8967915491,1.7673106061\ O,-1.4209090244,0.0094049894,-0.407735736\ H,-1.5803568807,0.8970964487,-0.7474874952</p>	<p>O,-0.0847696294,0.1124427797,0.0251591288 C,-0.0233905578,0.000223934,1.4295231669 H,1.0412226132,0.0017916115,1.6649658837 H,-0.5187713039,0.8467495816,1.9123675844 H,-0.4766581977,-0.9372580431,1.7602401144 O,-1.4677814373,0.0455755949,-0.3161452343 H,-1.5581796375,0.8233147039,-0.8789995328</p>
 <p>CH₃OO·</p>	<p>O,-0.0599451116,0.,-0.0111813346 C,-0.0215433411,0.,1.4298586015 H,1.0329434194,0.,1.6915847588 H,-0.5173692876,0.8950579968,1.799521599 H,-0.5173692876,-0.8950579968,1.799521599 O,-1.2673478499,0.,-0.4649460347</p>	<p>O,-0.0611965268,0.,-0.0165773634 C,-0.0268674869,0.,1.4186634375 H,1.0267559526,0.,1.6888578798 H,-0.5271209304,0.8964975298,1.7829637722 H,-0.5271209304,-0.8964975298,1.7829637722 O,-1.2798074596,0.,-0.4612048316</p>

CBS-QB3 enthalpies (in Hartree)

	-235.321269
	-234.691381
	-270.052699
	-269.673976
CH ₃ OOH	-190.589540
CH ₃ OO [•]	-189.954725
H [•]	-0.497457