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Spontaneous reaction of malonyl peroxides with methanol

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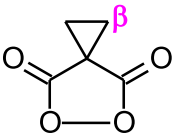
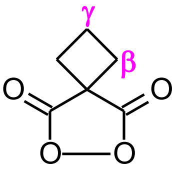
General

The numbers of the compounds are the same as those used in the main text. ^{1}H NMR spectra were recorded on a Bruker AM instrument, 300.13 MHz, at 25°C. In both solvents, $CDCl_3$ and C_6D_6, Me_4Si was used as an internal standard with δ 0.000 ppm. *Ab initio* calculations were performed using Gaussian 09, Revision A.02 (G09).

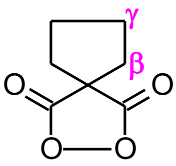
Benzene assisted shifts of signals in ^{1}H NMR spectra



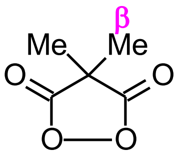
1a



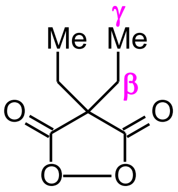
1b



1c



1d



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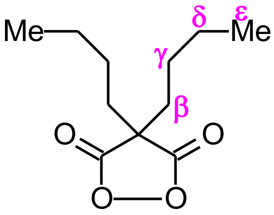
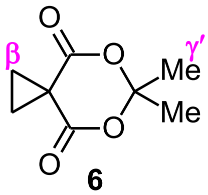


1f



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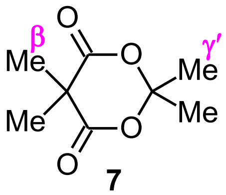

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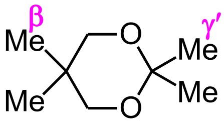

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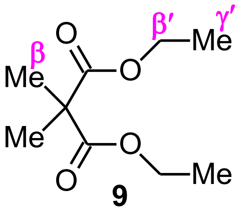


9

Table S1

Benzene assisted shifts for MPOs and relatives[a]

Compound	Proton signals	δ, ppm		Δδ
		$CDCl_3$	C_6D_6	$(C_6D_6\text{-}CDCl_3)$[b]
Malonyl peroxides				
1a	β-CH_2	2.11	0.89	-1.22
1b	β-CH_2	2.69	1.72	-0.97
	γ-CH_2	2.34	1.46	-0.88
1c	β-CH_2	2.25	1.44	-0.81
	γ-CH_2	1.98	1.26	-0.72
1d	β-Me	1.59	0.68	-0.91
1e	β-CH_2	1.95	1.30	-0.65
	γ-Me	0.98	0.52	-0.46
1f	β-CH_2	1.90	1.47	-0.43
	γ-CH_2	1.31	1.07	-0.24
	δ-CH_2	1.31	0.90	-0.41
	ε-Me	0.90	0.59	-0.31
Other compounds				
6	β-CH_2	1.98	1.46	-0.52
	γ'-Me	1.82	1.17	-0.65
7	β-Me	1.65	1.34	-0.31
	γ'-Me	1.75	1.08	-0.67
8[c]	β-Me	0.96	0.78	-0.18
	γ'-Me	1.42	1.38	-0.04
	CH_2	3.50	3.32	-0.18
9	β-Me	1.43	1.47	+0.04
	β'-CH_2	4.18	3.95	-0.23
	γ'-Me	1.25	0.91	-0.34

[a] δ of centers are shown for multiplets.

[b] Negative BAS are shifts to high field.

[c] Position of 'carbonyl carbon' in **8** is assumed to be as in **7**.

Table S2

Results of *ab initio* calculations of geometry for MPO **1a** (for the selection of preferable method)

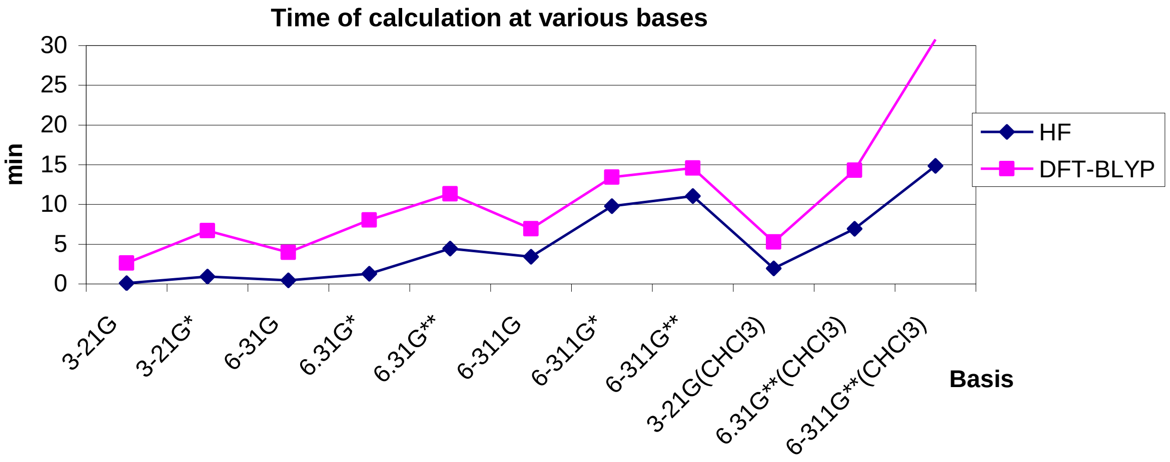
Basis	Calculation time(d), min HF	Calculation time(d), min DFT-BLYP	Free energy, kcal/mol HF	Free energy, kcal/mol DFT-BLYP	Angle OC-C-CO Calculated HF	Angle OC-C-CO Calculated DFT-BLYP	Angle OC-C-CO Calculated - X-ray HF	Angle OC-C-CO Calculated - X-ray DFT-BLYP	Bond O-O, Å Calculated HF	Bond O-O, Å Calculated DFT-BLYP	Bond O-O, Å Calculated - X-ray HF	Bond O-O, Å Calculated - X-ray DFT-BLYP
3-21G	0.07	2.60	-306,391.83	-308,112.26	108.42	109.84	0.82	2.24	1.47	1.53	-0.01	0.05
3-21G*	0.92	6.70	-306,434.18	-308,167.24	108.34	109.76	0.74	2.16	1.47	1.55	-0.01	0.07
6-31G	0.43	3.97	-307,956.78	-309,714.80	107.16	108.59	-0.44	0.99	1.45	1.54	-0.03	0.06
6.31G*	1.28	8.02	-307,965.88	-309,727.90	106.90	108.40	-0.70	0.80	1.45	1.54	-0.03	0.06
6.31G**	4.42	11.30	-307,966.56	-309,728.03	106.91	108.40	-0.69	0.80	1.45	1.54	-0.03	0.06
6-311G	3.40	6.92	-308,037.20	-309,795.66	106.86	108.85	-0.74	1.25	1.44	1.53	-0.04	0.05
6-311G*	9.78	13.40	-308,043.71	-309,802.96	106.66	108.53	-0.94	0.93	1.43	1.53	-0.05	0.05
6-311G**	11.03	14.57	-308,043.80	-309,806.48	106.66	108.70	-0.94	1.10	1.43	1.53	-0.05	0.05
3-21G(CHCl3)	1.93	5.27	-306,398.15	-308,116.41	108.50	109.85	0.90	2.25	1.46	1.53	-0.02	0.05
6.31G**(CHCl3)	6.93	14.28	-307,974.51	-309,734.13	106.93	108.41	-0.67	0.81	1.45	1.54	-0.03	0.06
6-311G**(CHCl3)	14.83	30.73	-308,051.50	-309,803.98	106.43	108.60	-1.17	1.00	1.43	1.53	-0.05	0.05
						Mean:	**-0.35**	**1.30**		**Mean:**	**-0.03**	**0.06**

Published data

Angle OC-C-CO X-ray(a)	Angle OC-C-CO HF 6-31G*(b)	Bond O-O, Å X-ray(a)
107.6	105.2	1.48

Semi-empirical calculation data(c)

Method	OC-C-CO	Bond O-O, Å
PM3	102.85	1.57
PM6	105.28	1.43
PM6(CHCl3)	105.39	1.43



(a) *J. Am. Chem. Soc.* , 2010, **132**, 14409.

(b) *Angew. Chem. Int. Ed.* , 2011, **50**, 10495.

(c) Author's G09 calculations.

(d) Starting from the same file of the molecule.

Conclusions

1. Method DFT-BLYP provides geometric data (at least for this molecule) which are somewhat less close to experimental data than those of HF method.
2. Calculation times for DFT-BLYP method are constantly and often significantly longer than times needed for HF identical calculations.
3. The bases higher than 6.31G* improve the results insignificantly only.

Table S3

Results of *ab initio* calculations of transition states (TS) in the reaction of MPOs with methanol

Item	Molecule(s)	Basis[a]	Medium	Free energy, kcal mol^{-1}	Differences, kcal mol^{-1}
1	**1d** + 1MeOH	6.31G**	vacuum	-380,885.72	0.00
	TS(a)-1d			-380,843.87	**41.85**
	2d			-380,892.49	-6.77
2	**1e** + 1MeOH	6.31G**	vacuum	-429,852.98	0.00
	TS(a)-1e			-429,808.73	**44.25**
	2e			-429,862.79	-9.80
3	**1d** + 1MeOH	6.31G**	PCM MeOH	-380,895.77	0.00
	TS(b)-1d			-380,865.14	**30.63**
	2d			-380,904.12	-8.35
4	**1e** + 1MeOH	6.31G**	PCM MeOH	-429,862.24	0.00
	TS(b)-1e			-429,828.75	**33.50**
	2e			-429,873.10	-10.85
5	**1d** + 2MeOH	6.31G	vacuum	-453,041.09	0.00
	TS(c)-1d			-453,012.96	**28.13**
	2d			-453,051.47	-10.38
6	**1e** + 2MeOH	6.31G	vacuum	-502,007.86	0.00
	TS(c)-1e			-501,976.47	**31.38**
	2e			-502,014.32	-6.46

[a] All calculations were performed using Hartree-Fock method.

Discussion of some calculation results

It has been already stated in the main text that the calculated differences in energy barriers of ~3 kcal mol^{-1} are not large enough for the explanation of more than 800 times difference in the rates of the spontaneous reactions of MPOs **1d** and **1e** with methanol (Table 1 in the main text). Some observed peculiarities of this reaction may be a possible reason of the calculation inefficiency.

1. Calculations of TS in "methanol solution" (model PCM, items 3,4 in Table S3, series **TS(b)**) produced the lowering of energy barriers for ~11 kcal mol^{-1} (in comparison with values in vacuum, items 1,2, series **TS(a)**).

2. Even more significant lowering of energy barriers, for ~13 kcal mol^{-1}, was observed for the reaction model with two methanol molecules (items 5,6, series **TS(c)**). Both methanol molecules participate equaly in TS of this reaction (see Pic. S1). The further lowering of energy barriers, although less significant, was observed in TS models with participation of 3-5 methanol molecules. Quantitative values of these results could not be cited due to inability to find the optimal configuration of TSs with 3-5 independed molecules.

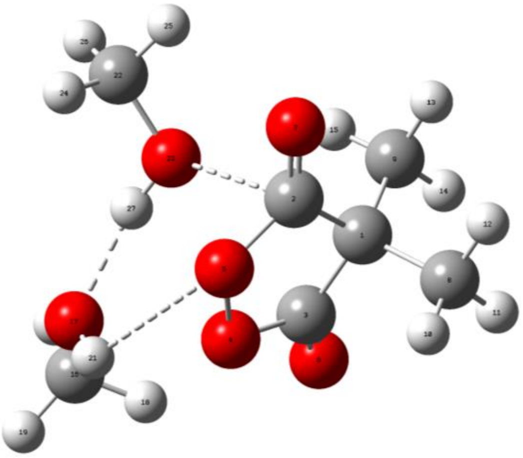


Figure S1 Transition state for the reaction of MPO **1d** with two MeOH molecules.

3. We believe that these results are in accordance with the experimentally found but strange dependence of the reaction rate of MPO spontaneous methanolisis from MPO : MeOH ratio. In a case of 1 : 250 ratio the 50% methanolysis of **1d** needs 5 minutes (item 6, Table 1), however in case 1 : 10 ratio 50% conversion of **1d** was only achieved in 1 hour (item 7). Needless to say, methanol "concentrations" in both cases were practically the same because methanol was the sole solvent. At the 1 : 2 MPO : MeOH ratio the most reactive MPOs **1b**,**d** do not react at all during several days (items 4,8 and some other unpublished experiments).