Electronic Supplementary Information for

Photochemical studies as a function of solvent viscosity. A new photochemical pathway in the reaction of $(\eta^5\text{-}C_5H_4Me)_2Mo_2(CO)_6$ with CCl_4

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Plots of quantum yields for photolysis of $Cp'_2Mo_2(CO)_6$ in various solvents including 20% CCl_4 by volume. In each plot the dashed line is the fit using eq 2 and the solid line is the fit using eq 3.

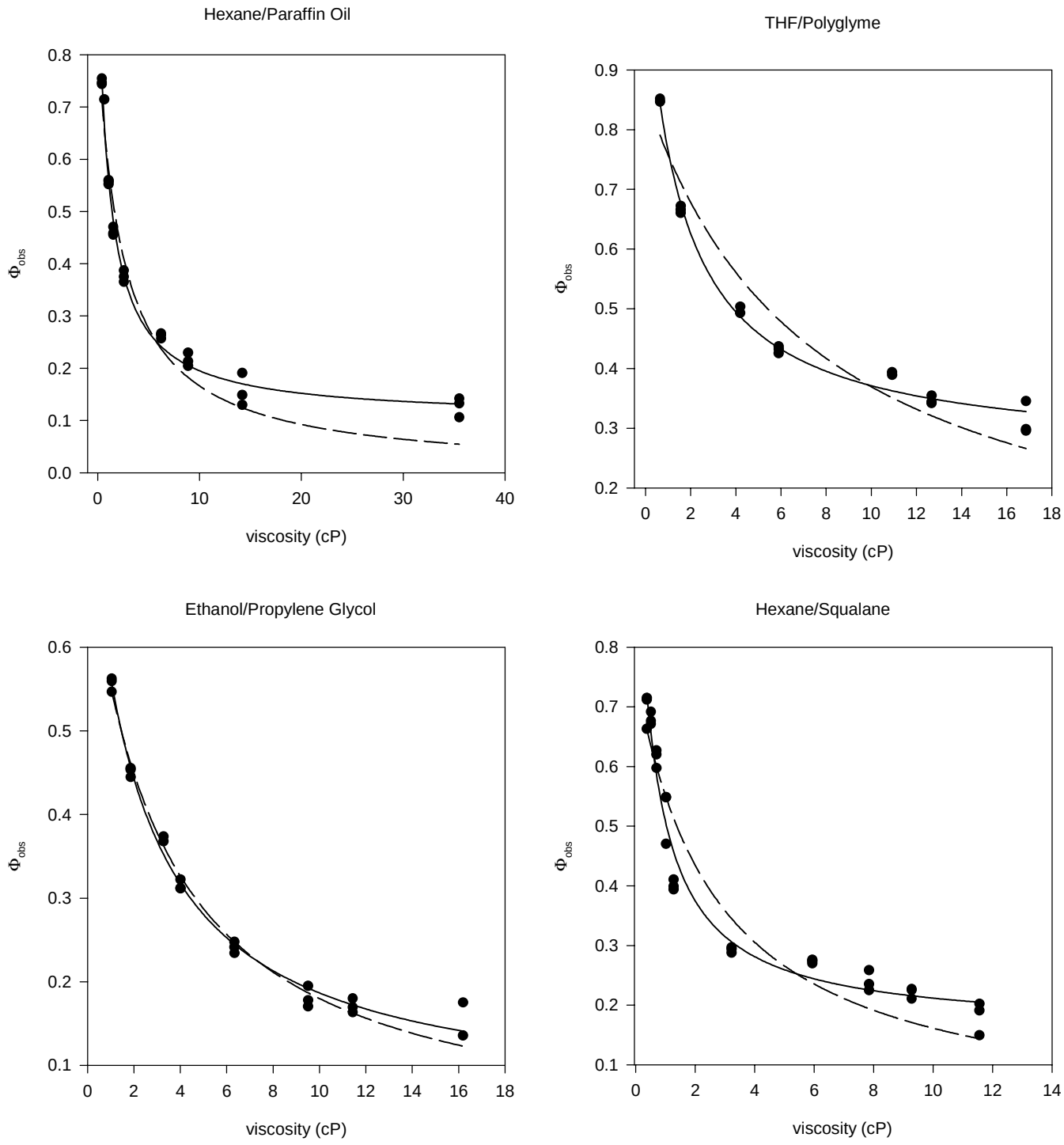

Table 1. Observed quantum yields for photolysis of $Cp'_2Mo_2(CO)_6$ at 546 nm in PDMS-50/CCl_4 mixtures (first 9 entries) and in PDMS-200/CCl_4 (last 14 entries).

% CCl_4 (v/v)	viscosity/cP	ϕ_{obs}
20	18.82	0.25
20	18.82	0.23
20	18.82	0.29
10	31.95	0.17
10	31.95	0.19
10	31.95	0.17
0	48.00	0.01
0	48.00	0.01
0	48.00	0.003
30	62.13	0.24
30	62.13	0.24
30	62.13	0.25
20	79.64	0.23
20	79.64	0.24
20	79.64	0.22
10	133.3	0.19
10	133.3	0.18
7	138.5	0.17
7	138.5	0.16
7	138.5	0.17
0	193.6	0.0004
0	193.6	0.002
0	193.6	0.0005

Table 2. Values of fitting parameters in eq 3 for photolysis of $Cp'_2Mo_2(CO)_6$.

Solvent/CCl_4	ϕ_{pair}	*c*/cP	ϕ_x
PDMS	0.84 ± 0.12	0.35 ± 0.08	0.24 ± 0.004
paraffin oil	0.88 ± 0.03	1.16 ± 0.13	0.10 ± 0.01
squalane	0.90 ± 0.08	0.64 ± 0.15	0.16 ± 0.02
THF/polyglyme	0.84 ± 0.05	1.78 ± 0.44	0.23 ± 0.02
ethanol/propylene glycol	0.74 ± 0.02	2.25 ± 0.29	0.05 ± 0.01

Saturation in CCl_4. The method described in this paper for obtaining F_{cP} requires that all free radicals be trapped (i.e., that no radical cage pairs form by diffusion together of free radicals, the reverse of the k_{dP} step in Scheme I). This condition was confirmed by studying the quantum yields for the reaction of $Cp_2Mo_2(CO)_6$ with CCl_4 in both THF and hexane as a function of $[CCl_4]$. Saturation occurred at about 0.1 M CCl_4, indicative of complete free radical trapping. Experiments in this study used $[CCl_4]$ = 2 M. A decrease in the quantum yield was observed at ≈10 M (neat CCl_4); this downturn is attributed to the increase in viscosity of neat CCl_4 (0.908 cP at 25 °C) compared to the THF solutions (0.456 cP at 25 °C).