Autoxidation of Platinum(IV) Hydrocarbyl Hydride Complexes to Form Platinum(IV) Hydrocarbyl Hydroperoxide Complexes

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Supporting Information

Rate constants for equations 6 from text

Linear regression was used to fit the kinetic data from the autoxidation of **1a** to the rate law:

$$\text{rate} = k_1[\mathbf{1a}] + k_2\, \frac{[\mathbf{1a}][\mathbf{2a}][\text{AIBN}]}{[\mathbf{1a}] + [\mathbf{2a}] + [\mathbf{3a}]} \quad (6)$$

Consistent values were obtained for k_2 with varying concentrations of **1a** (8 – 31 mM) and AIBN

(5-10 mM).

mM **1a**	mM AIBN	k_2 ($M^{-1}s^{-1}$)	+/-	k_1 (s^{-1})	+/-	R^2
15.7	3.5	0.23	0.01	7.83E-05	1.20E-05	0.987
30.5	3.4	0.23	0.01	6.97E-05	1.67E-05	0.969
8.4	3.7	0.23	0.01	5.50E-05	2.28E-05	0.955
13.7	10.2	0.23	0.01	2.61E-06	5.75E-05	0.961
13.7	5.1	0.23	0.01	3.46E-05	2.79E-05	0.911

The k_1 term probably includes a dependence on AIBN, but the values are not precise enough to

determine the nature of the dependence. The uncertainties associated with the k_1 values are too

large to provide any information about the initial formation of the hydroperoxide.

Rate constants for equation 7 from text

For the phenyl compounds, the non-overlapping NMR signals available for integration were of

lower intensity, resulting in worse signal-to-noise ratios. More concentrated solutions could not

be used because of solubility limitations, so the kinetic data for **1b** is noisier leading to less

consistent values for the rate constants. The data are still convincingly in agreement with the

proposed rate law.

$$\text{rate} = k_1[\mathbf{1b}] + k_2[\mathbf{1b}][\mathbf{2b}]_{\text{formed}}^{1/2}[\text{AIBN}]^{1/2} \quad (7)$$

mM 1b	mM AIBN	k_2 (M^{-1}s^{-1})	+/-	k_1 (s^{-1})	+/-	R^2	% conv.
29.6	11.2	0.019	0.001	2.48E-04	1.271E-04	0.981	44
14.8	10.7	0.034	0.001	8.49E-04	2.187E-04	0.979	60
6.4	9.7	0.078	0.004	-5.16E-04	6.659E-04	0.917	75
31.8	6.0	0.039	0.002	-1.65E-03	3.450E-04	0.950	63
14.3	3.5	0.047	0.001	-1.14E-04	1.307E-04	0.968	49
15.7	2.5	0.045	0.001	-2.97E-05	3.739E-06	0.954	64

The average value for k_2, 0.043±0.017 M^{-1}s^{-1} is significantly slower than for the autoxidation of

1a. Again, nothing can be discerned about the k_1 pathway because the associated uncertainties

are so large (the true values should of course be positive, the regression values are just listed to

show that this method is not adequate for determining anything about the slow initial process.).

<u>Reactions with low AIBN concentrations for **1a**</u>

At low concentrations of AIBN, confusing behavior is observed. Increasing the AIBN

concentration from 0.035 mM to 0.07 mM doubles the rate, but the reaction is much faster (k_2 is

more than 2 orders of magnitude larger than at moderate AIBN concentrations described above).

Further increasing the concentration to 2 mM AIBN drastically slows the reaction. The

mechanism of autocatalysis appears to involve reaction of the AIBN radical with the

hydroperoxide **2a**. Perhaps this step is more efficient at lower AIBN concentrations since

coupling of AIBN-derived radicals is more likely at higher concentrations.

mM 1a	mM AIBN	k_2 (M^{-1}s^{-1})	+/-	k_1 (s^{-1})	+/-	R^2
13.6	0.03	80	1.82	4.49E-05	2.20E-05	0.997
13.7	0.07	79	8.70	2.50E-04	2.83E-04	0.940
15.4	2.2	0.79	0.01	7.78E-05	7.93E-06	0.997