Supporting Information

Measurements and Simulations of the Acidity Dependence of the Kinetics of the Iron-Catalyzed Belousov-Zhabotinsky Reaction. Proton-Catalysis in the Electron Transfer Reaction Involving the $[Fe(phen)_3]^{3+}$ Species

Ethan Zars,[1] Rainer Glaser,[1]* Marco Downing[1,2], and Carmen Chicone[2]*

[1]Department of Chemistry, University of Missouri, Columbia, Missouri 65211

[2]Department of Mathematics, University of Missouri, Columbia, Missouri 65211

Table of Contents

Acidity Effects on Intensity Variations

Quantification of the Temporal Evolution of Intensity Variations. The timing parameters are not the only metrics describing the BZ oscillating reaction that are affected by changes in acidity. Figs. 1 and 2 show that the intensities $DCC_{max}(t)$ and $DCC_{min}(t)$ and the amplitude $\Delta I(t) = DCC_{max}(t) - DCC_{min}(t)$ evolve over time and they are affected drastically by the acidity. The $DCC(t)$ value is proportional to the concentration of the oxidized iron catalyst and it is therefore instructive to analyze the $DCC(t)$ value to learn about the iron's redox-cycling.

[Fig. S2 about here]

Temporal variations in the $DCC_{max}(t)$, $DCC_{min}(t)$, and $\Delta I(t)$ values are exemplified in Fig. S2 for reaction KM089. It is seen in Fig. S2 that the $DCC_{max}(t)$ and $DCC_{min}(t)$ stay mostly constant over time and decrease only very slightly. The $\Delta I(t)$ value also stays mostly constant over time and its value remains modest because the reduction of Fe(III) is incomplete. Analogous plots are given for all reactions (Figs. S2-KM%) and all $\Delta I(t)$ values stay below 0.2 or less than 20% of $DCC_{max}(t)$.

[Table S1 about here]

The $DCC_{max}(t)$, $DCC_{min}(t)$, and $\Delta I(t)$ curves are well modelled by linear regression; $DCC_{max}(t) = h_1\, t + I_{max}(0)$, $DCC_{min}(t) = h_2\, t + I_{min}(0)$, and $\Delta I(t) = h_3\, t + \Delta I(0)$. The slopes h_j and the intercepts $I_{max}(0)$, $I_{min}(0)$ and $\Delta I(0)$ are given in Table S5 with their respective R^2 values.

The data presented in Table S1 show that both the $I_{max}(0)$ and $I_{min}(0)$ values are greater at higher acidities with the more pronounced acidity effect on the $I_{min}(0)$ values. Over time the $DCC_{max}(t)$ and $DCC_{min}(t)$ usually decrease ($h_1 < 0$, $h_2 < 0$) and exceptions are observed only for the low-acidity reactions KM036 ($DCC_{min}(t)$ only), KM041, KM043, and KM048. The R^2 value for the regression of $DCC_{min}(t)$ is better than for the regression of $DCC_{max}(t)$ which is likely due to the numerical imperfections in choosing the actual maximum point of the oscillation (see Mathematical Methods).

The $\Delta I(t)$ values almost exclusively become smaller over time and the near-zero h_3 values again result in small R^2 values. This is not a source of concern because the intercept $\Delta I(0)$ of the regression of $\Delta I(t)$ and the $\Delta I'(0)$ value computed as the difference between the intercepts $I_{max}(0)$ and $I_{min}(0)$ are very similar for all reactions.

Acidity Dependence of the Intensity Variations. The data from Table S1 are shown in Fig. S3 as a function of initial sulfuric acid concentration $[H_2SO_4]_0$. The rows of Fig. S3 show plots of intercepts (left) and slopes (right), respectively, for $I_{max}(0)$ and h_1 (top row), for $I_{min}(0)$ and h_2 (center row), and for $\Delta I(0)$ and h_3 (bottom row).

[Fig. S3 about here]

Note that the y-axes of the plots for $I_{max}(0)$, $I_{min}(0)$, and $\Delta I(0)$ are drawn with the same scale. Even though there is some experimental scatter, the data show clear and significant trends. The $I_{max}(0)$ generally increases with increased acidity from $I_{max}(0) \approx 0.90$ to $I_{max}(0) \approx 0.97$. The $I_{min}(0)$ value, however, shows a much steeper increase with increased acidity with values raising from $I_{min}(0) = 0.78$ to $I_{min}(0) = 0.96$ over the acidity range. Consequently, the $\Delta I(0)$ amplitudes strongly correlate and decrease steadily with increasing acidity.

As the acidity increases, the $I_{max}(0)$ values increase less than the $I_{min}(0)$ values and, hence, the decrease in the amplitudes $\Delta I(0)$ is primarily due to the $I_{min}(0)$ variations. For example, at the low acidity of $[H_2SO_4]_0 = 0.36$ mol·L^{-1} the DCC(t) values range between $I_{min}(0) = 0.7753$ and $I_{max}(0) = 0.9314$ with $\Delta I(0) = 0.1530$. At the high acidity of $[H_2SO_4]_0 = 1.20$ mol·L^{-1} the DCC(t) values range from the much higher $I_{min}(0) = 0.9616$ to $I_{max}(0) = 0.9701$ with a modest intensity change of only $\Delta I(0) = 0.0086$. Hence, the relative changes $\Delta I(0)/I_{max}(0)\cdot 100\%$ range from 16.4% at $[H_2SO_4]_0 = 0.36$ mol·L^{-1} to a mere 0.9% at $[H_2SO_4]_0 = 1.20$ mol·L^{-1}.

These data allow for several important conclusions and these are (1) that the reduction of Fe(III) is never complete at any of the acidities ($\Delta I(0) \ll I_{max}(0)$), (2) that the overall extend of the Fe(III) reduction is less complete at higher acidity ($\Delta I(0)$ inversely correlated with acidity), and

(3) that the oxidation of Fe(II) is definitely incomplete at the lower acidities ($I_{max}(0)$ increases with acidity).

The conclusions derived with the $I_{max}(0)$, $I_{min}(0)$, and $\Delta I(0)$ data actually hold very well for any time over the course of a specific reaction. We quantified the temporal changes of $DCC_{max}(t)$, $DCC_{min}(t)$, and $\Delta I(t)$ by the slopes h_i and their values are shown as a function of $[H_2SO_4]_0$ in the plots in the right column of Fig. S3. The reactions at lower acidities feature small numbers of oscillations and the associated h_i values are somewhat prone to experimental error, but the h_i values for the reactions with acidities of $[H_2SO_4]_0 > 0.5$ mol·L^{-1} are reliable. Reactions that start with high values of $I_{max}(0)$ and $I_{min}(0)$ also show a quicker decrease in both values but the magnitude of the redox-cycling $\Delta I(t)$ essentially remains unchanged over time for a given acidity ($h_3 \approx 0$).

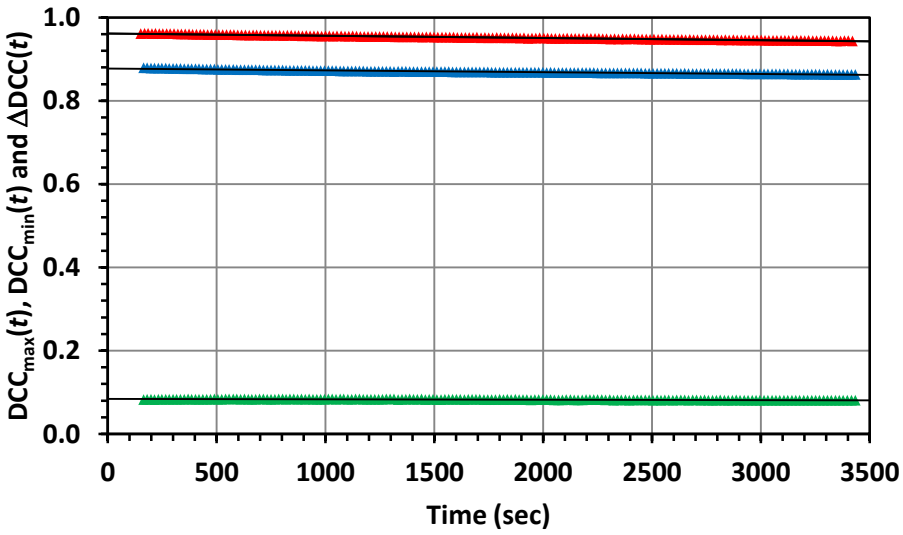

Figure S2. Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta I(t)$ as a function of reaction time t for reaction KM089 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta I(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta I(t) = h_3 \cdot t + \Delta I(0)$.

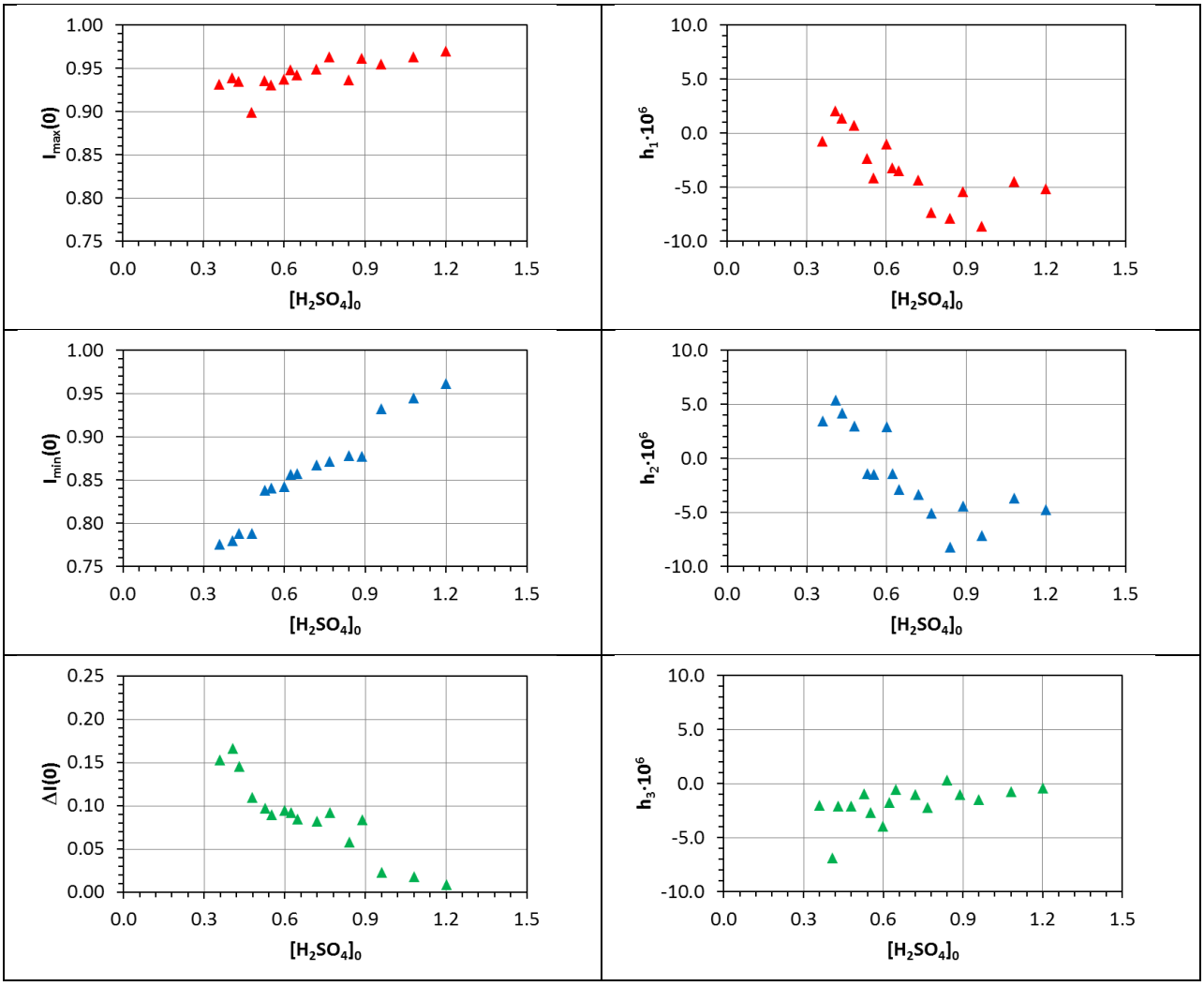

Figure S3. DCC intensities as a function of initial sulfuric acid concentration $[H_2SO_4]_0$. Top row: $I_{max}(0)$ values (left) and h_1 values (right). Middle row: $I_{min}(0)$ values (left) and h_2 values (right). Bottom row: $\Delta I(0)$ values (left) and h_3 values (right).

Table S1. Linear regression for the $DCC_{max}(t)$, $DCC_{min}(t)$, and Amplitude values for all reactions.

Reaction	$DCC_{max}(t)$			$DCC_{min}(t)$			$\Delta I(t)$			
	$h_1 \cdot 10^6$	$I_{max}(0)$	R^2	$h_2 \cdot 10^6$	$I_{min}(0)$	R^2	$h_3 \cdot 10^6$	$\Delta I(0)$[a]	R^2	$\Delta I'(0)$[b]
KM036	-0.7913	0.9314	0.0260	3.4407	0.7753	0.9765	-2.0608	0.1530	0.1189	0.1561
KM041	2.0366	0.9389	0.2029	5.3770	0.7796	0.9793	-6.8806	0.1667	0.9670	0.1593
KM043	1.3991	0.9346	0.0481	4.1796	0.7880	0.9957	-2.0975	0.1452	0.0646	0.1466
KM048	0.7180	0.8992	0.0183	2.9881	0.7883	0.9218	-1.1821	0.1093	0.0581	0.1109
KM053	-2.3599	0.9352	0.8901	-1.4244	0.8384	0.8101	-0.9480	0.0970	0.4510	0.0968
KM055	-4.1823	0.9307	0.5455	-1.4789	0.8408	0.7337	-2.7026	0.0899	0.3178	0.0899
KM060	-1.0528	0.9369	0.2264	2.8762	0.8422	0.4457	-3.9318	0.0948	0.6489	0.0947
KM062	-3.2356	0.9481	0.9268	-1.4572	0.8559	0.6886	-1.7778	0.0924	0.5750	0.0922
KM065	-3.4649	0.9418	0.9718	-2.8838	0.8574	0.9810	-0.5799	0.0846	0.4228	0.0845
KM072	-4.3446	0.9485	0.9923	-3.3315	0.8668	0.9886	-1.0108	0.0819	0.7765	0.0818
KM077	-7.3757	0.9633	0.9899	-5.1274	0.8711	0.9927	-2.2442	0.0924	0.8778	0.0922
KM084	-7.8880	0.9362	0.9716	-8.2031	0.8781	0.9901	0.3085	0.0582	0.0363	0.0581
KM089	-5.4253	0.9614	0.9895	-4.4170	0.8773	0.9669	-1.0128	0.0842	0.8271	0.0841
KM096	-8.6471	0.9549	0.9931	-7.1374	0.9320	0.9811	-1.5066	0.0229	0.8758	0.0229
KM108	-4.5038	0.9628	0.9971	-3.7226	0.9449	0.9692	-0.7751	0.0179	0.6263	0.0179
KM120	-5.1838	0.9701	0.9960	-4.7643	0.9616	0.9953	-0.4145	0.0086	0.3770	0.0086

[a] $\Delta I(t) = DCC_{max}(t) - DCC_{min}(t)$

[b] $\Delta I'(0) = I_{max}(0) - I_{min}(0)$

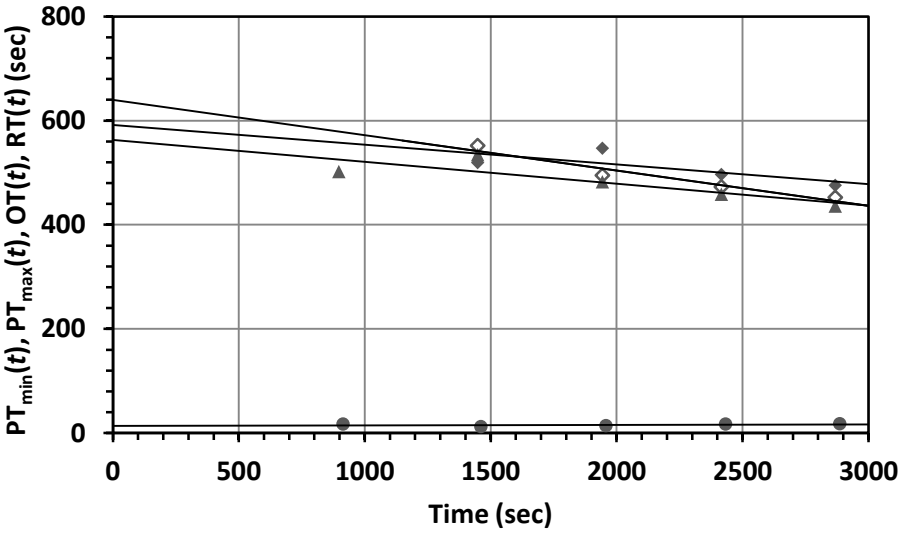

Figure S1-KM036. Values of $PT_{min}(t)$, $PT_{max}(t)$, $OT(t)$, and $RT(t)$ as a function of reaction time t for reaction KM036 (green in Figs. 1 and 2). Unfilled diamonds indicate $PT_{min}(t)$ and filled diamonds indicate $PT_{max}(t)$, circles indicate $OT(t)$, and triangles indicate $RT(t)$. The regressions lines also are shown for $PT_{min}(t) = m_1 \cdot t + PT_1(0)$, $PT_{max}(t) = m_2 \cdot t + PT_2(0)$, $OT(t) = m_3 \cdot t + OT(0)$ and $RT(t) = m_4 \cdot t + RT(0)$.

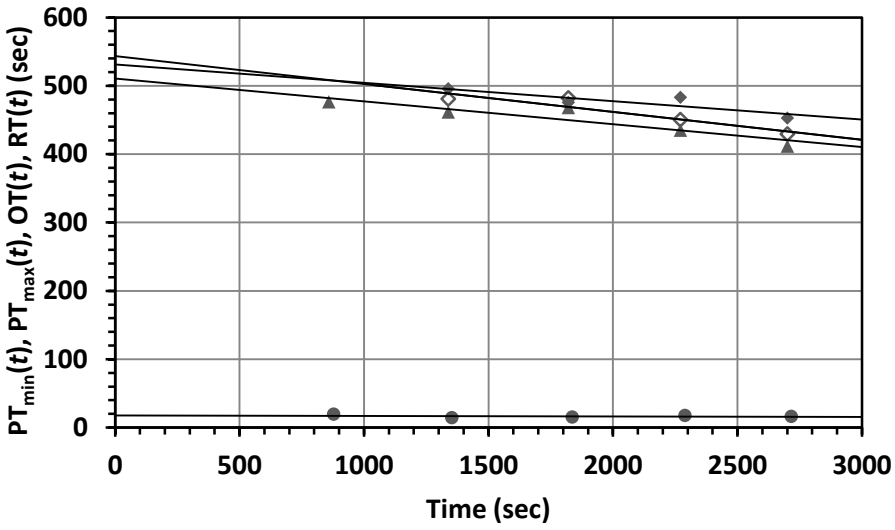

Figure S1-KM041. Values of $PT_{min}(t)$, $PT_{max}(t)$, $OT(t)$, and $RT(t)$ as a function of reaction time t for reaction KM041 (green in Figs. 1 and 2). Unfilled diamonds indicate $PT_{min}(t)$ and filled diamonds indicate $PT_{max}(t)$, circles indicate $OT(t)$, and triangles indicate $RT(t)$. The regressions lines also are shown for $PT_{min}(t) = m_1 \cdot t + PT_1(0)$, $PT_{max}(t) = m_2 \cdot t + PT_2(0)$, $OT(t) = m_3 \cdot t + OT(0)$ and $RT(t) = m_4 \cdot t + RT(0)$.

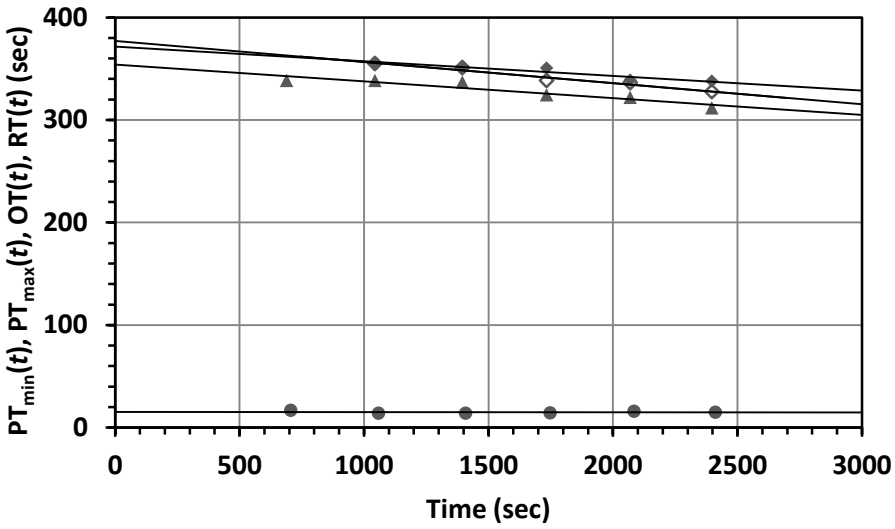

Figure S1-KM043. Values of $PT_{min}(t)$, $PT_{max}(t)$, $OT(t)$, and $RT(t)$ as a function of reaction time t for reaction KM043 (green in Figs. 1 and 2). Unfilled diamonds indicate $PT_{min}(t)$ and filled diamonds indicate $PT_{max}(t)$, circles indicate $OT(t)$, and triangles indicate $RT(t)$. The regressions lines also are shown for $PT_{min}(t) = m_1 \cdot t + PT_1(0)$, $PT_{max}(t) = m_2 \cdot t + PT_2(0)$, $OT(t) = m_3 \cdot t + OT(0)$ and $RT(t) = m_4 \cdot t + RT(0)$.

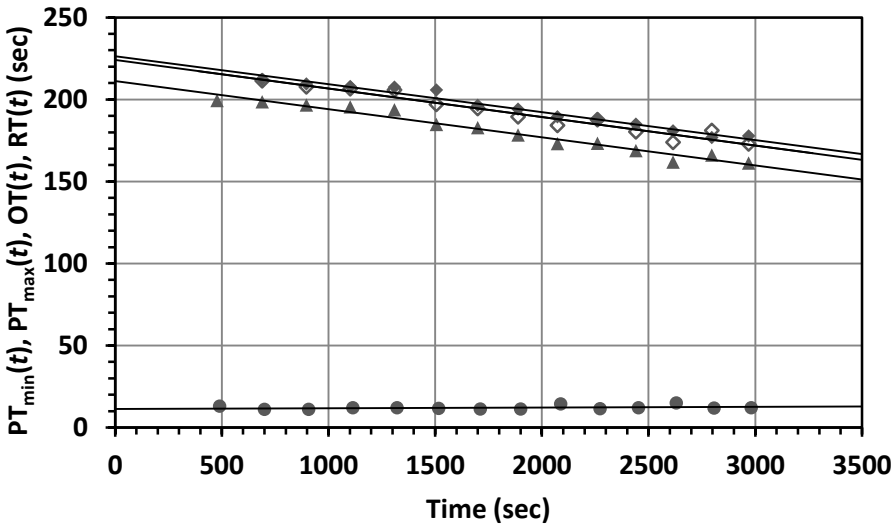

Figure S1-KM048. Values of $PT_{min}(t)$, $PT_{max}(t)$, $OT(t)$, and $RT(t)$ as a function of reaction time t for reaction KM048 (green in Figs. 1 and 2). Unfilled diamonds indicate $PT_{min}(t)$ and filled diamonds indicate $PT_{max}(t)$, circles indicate $OT(t)$, and triangles indicate $RT(t)$. The regressions lines also are shown for $PT_{min}(t) = m_1 \cdot t + PT_1(0)$, $PT_{max}(t) = m_2 \cdot t + PT_2(0)$, $OT(t) = m_3 \cdot t + OT(0)$ and $RT(t) = m_4 \cdot t + RT(0)$.

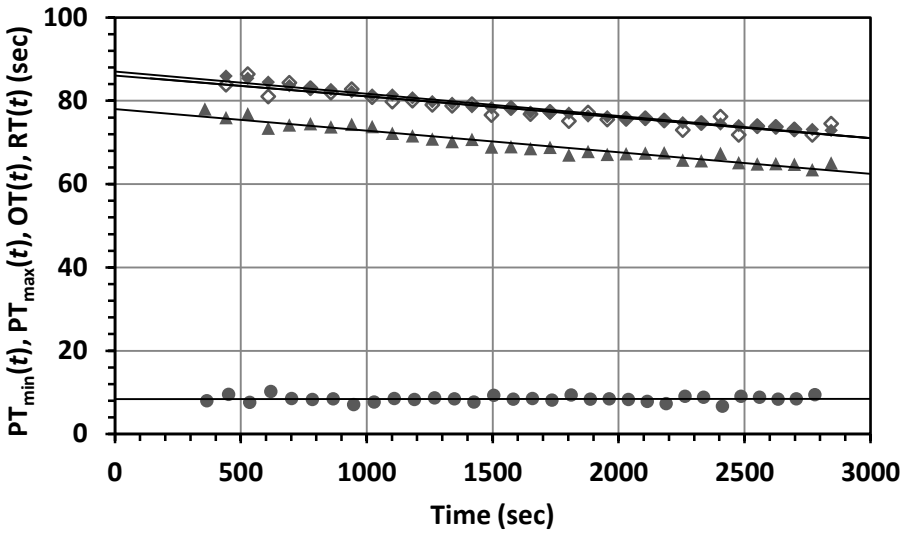

Figure S1-KM053. Values of $PT_{min}(t)$, $PT_{max}(t)$, $OT(t)$, and $RT(t)$ as a function of reaction time t for reaction KM053 (green in Figs. 1 and 2). Unfilled diamonds indicate $PT_{min}(t)$ and filled diamonds indicate $PT_{max}(t)$, circles indicate $OT(t)$, and triangles indicate $RT(t)$. The regressions lines also are shown for $PT_{min}(t) = m_1 \cdot t + PT_1(0)$, $PT_{max}(t) = m_2 \cdot t + PT_2(0)$, $OT(t) = m_3 \cdot t + OT(0)$ and $RT(t) = m_4 \cdot t + RT(0)$.

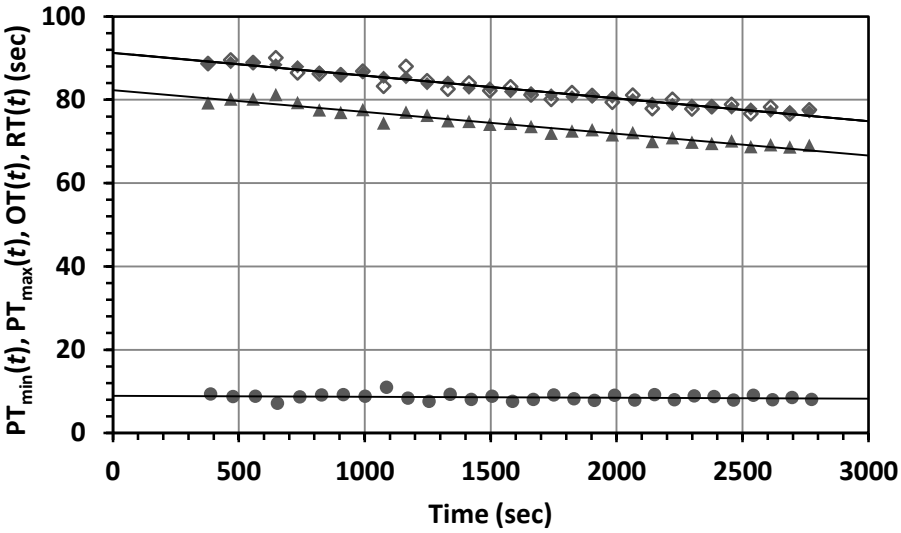

Figure S1-KM055. Values of $PT_{min}(t)$, $PT_{max}(t)$, $OT(t)$, and $RT(t)$ as a function of reaction time t for reaction KM055 (green in Figs. 1 and 2). Unfilled diamonds indicate $PT_{min}(t)$ and filled diamonds indicate $PT_{max}(t)$, circles indicate $OT(t)$, and triangles indicate $RT(t)$. The regressions lines also are shown for $PT_{min}(t) = m_1 \cdot t + PT_1(0)$, $PT_{max}(t) = m_2 \cdot t + PT_2(0)$, $OT(t) = m_3 \cdot t + OT(0)$ and $RT(t) = m_4 \cdot t + RT(0)$.

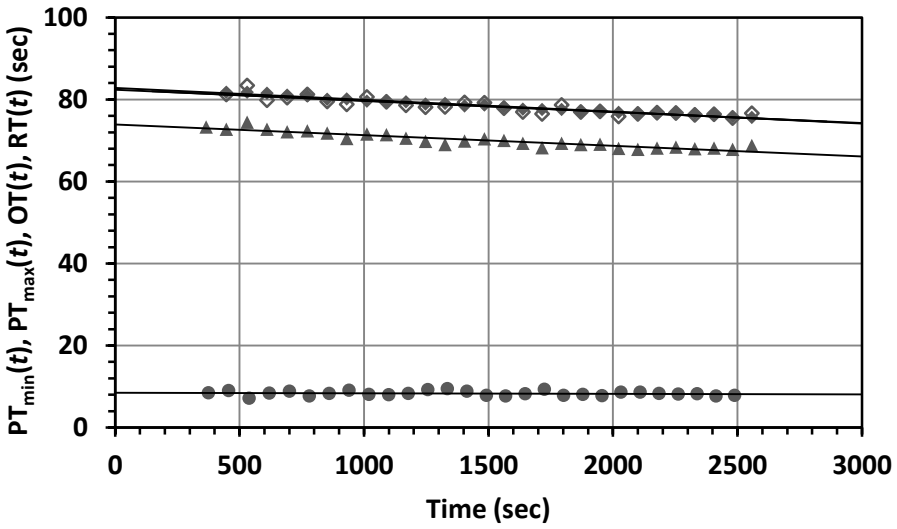

Figure S1-KM060. Values of $PT_{min}(t)$, $PT_{max}(t)$, $OT(t)$, and $RT(t)$ as a function of reaction time t for reaction KM060 (green in Figs. 1 and 2). Unfilled diamonds indicate $PT_{min}(t)$ and filled diamonds indicate $PT_{max}(t)$, circles indicate $OT(t)$, and triangles indicate $RT(t)$. The regressions lines also are shown for $PT_{min}(t) = m_1 \cdot t + PT_1(0)$, $PT_{max}(t) = m_2 \cdot t + PT_2(0)$, $OT(t) = m_3 \cdot t + OT(0)$ and $RT(t) = m_4 \cdot t + RT(0)$.

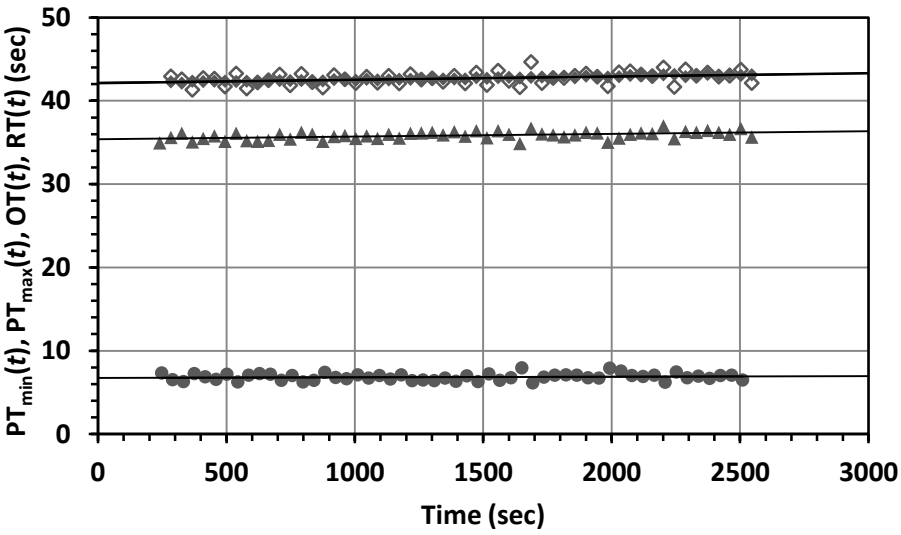

Figure S1-KM065. Values of $PT_{min}(t)$, $PT_{max}(t)$, $OT(t)$, and $RT(t)$ as a function of reaction time t for reaction KM065 (green in Figs. 1 and 2). Unfilled diamonds indicate $PT_{min}(t)$ and filled diamonds indicate $PT_{max}(t)$, circles indicate $OT(t)$, and triangles indicate $RT(t)$. The regressions lines also are shown for $PT_{min}(t) = m_1 \cdot t + PT_1(0)$, $PT_{max}(t) = m_2 \cdot t + PT_2(0)$, $OT(t) = m_3 \cdot t + OT(0)$ and $RT(t) = m_4 \cdot t + RT(0)$.

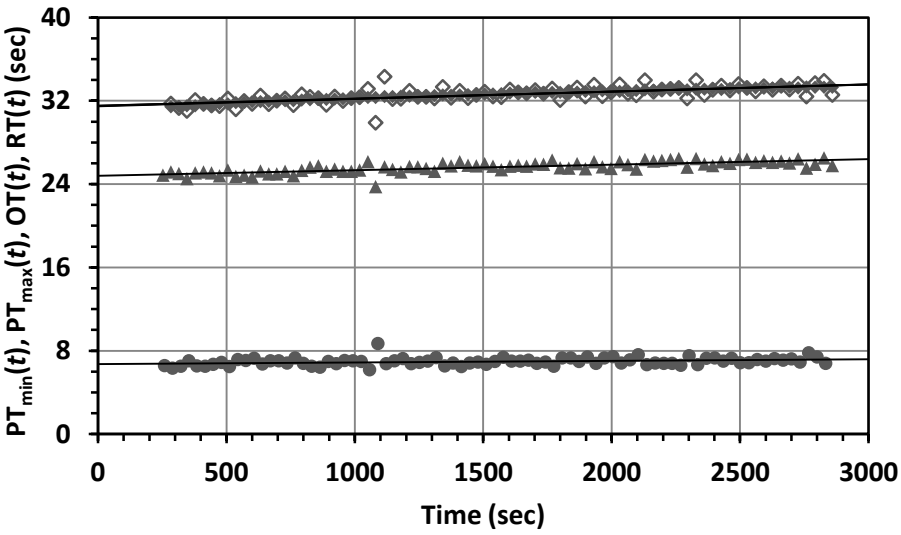

Figure S1-KM072. Values of $PT_{min}(t)$, $PT_{max}(t)$, $OT(t)$, and $RT(t)$ as a function of reaction time t for reaction KM072 (green in Figs. 1 and 2). Unfilled diamonds indicate $PT_{min}(t)$ and filled diamonds indicate $PT_{max}(t)$, circles indicate $OT(t)$, and triangles indicate $RT(t)$. The regressions lines also are shown for $PT_{min}(t) = m_1 \cdot t + PT_1(0)$, $PT_{max}(t) = m_2 \cdot t + PT_2(0)$, $OT(t) = m_3 \cdot t + OT(0)$ and $RT(t) = m_4 \cdot t + RT(0)$.

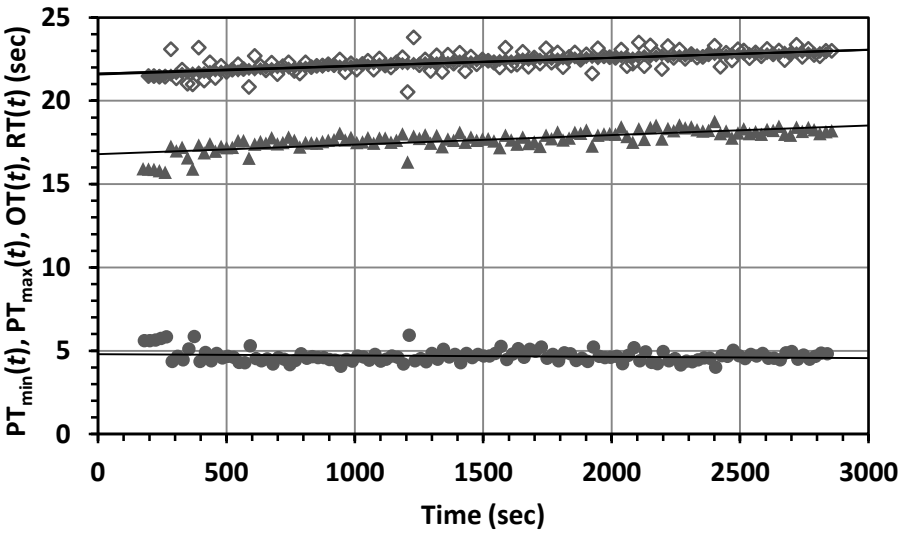

Figure S1-KM077. Values of $PT_{min}(t)$, $PT_{max}(t)$, $OT(t)$, and $RT(t)$ as a function of reaction time t for reaction KM077 (green in Figs. 1 and 2). Unfilled diamonds indicate $PT_{min}(t)$ and filled diamonds indicate $PT_{max}(t)$, circles indicate $OT(t)$, and triangles indicate $RT(t)$. The regressions lines also are shown for $PT_{min}(t) = m_1 \cdot t + PT_1(0)$, $PT_{max}(t) = m_2 \cdot t + PT_2(0)$, $OT(t) = m_3 \cdot t + OT(0)$ and $RT(t) = m_4 \cdot t + RT(0)$.

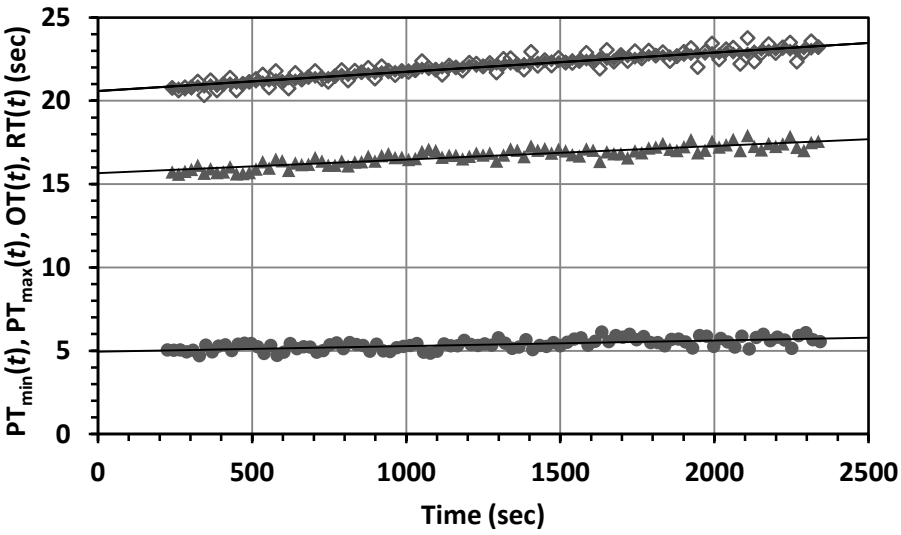

Figure S1-KM084. Values of $PT_{min}(t)$, $PT_{max}(t)$, $OT(t)$, and $RT(t)$ as a function of reaction time t for reaction KM084 (green in Figs. 1 and 2). Unfilled diamonds indicate $PT_{min}(t)$ and filled diamonds indicate $PT_{max}(t)$, circles indicate $OT(t)$, and triangles indicate $RT(t)$. The regressions lines also are shown for $PT_{min}(t) = m_1 \cdot t + PT_1(0)$, $PT_{max}(t) = m_2 \cdot t + PT_2(0)$, $OT(t) = m_3 \cdot t + OT(0)$ and $RT(t) = m_4 \cdot t + RT(0)$.

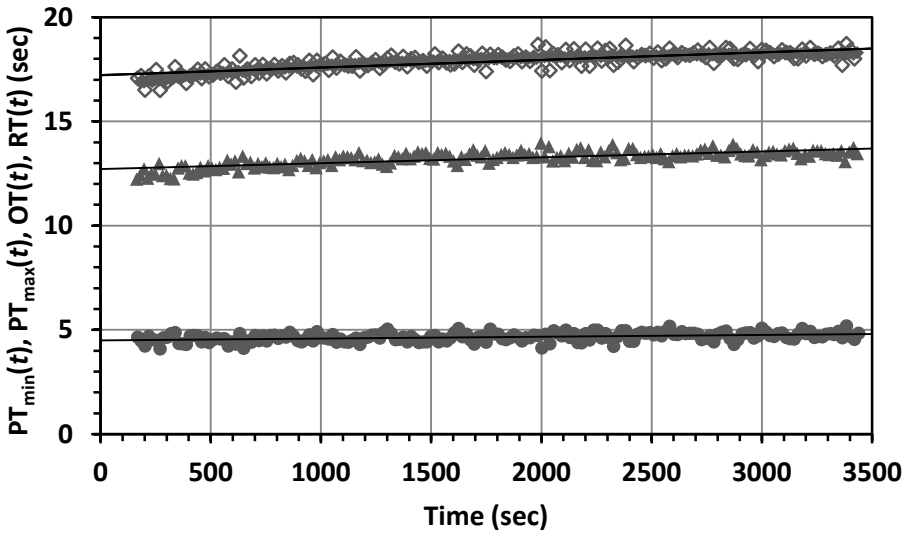

Figure S1-KM089. Values of $PT_{min}(t)$, $PT_{max}(t)$, $OT(t)$, and $RT(t)$ as a function of reaction time t for reaction KM089 (green in Figs. 1 and 2). Unfilled diamonds indicate $PT_{min}(t)$ and filled diamonds indicate $PT_{max}(t)$, circles indicate $OT(t)$, and triangles indicate $RT(t)$. The regressions lines also are shown for $PT_{min}(t) = m_1 \cdot t + PT_1(0)$, $PT_{max}(t) = m_2 \cdot t + PT_2(0)$, $OT(t) = m_3 \cdot t + OT(0)$ and $RT(t) = m_4 \cdot t + RT(0)$.

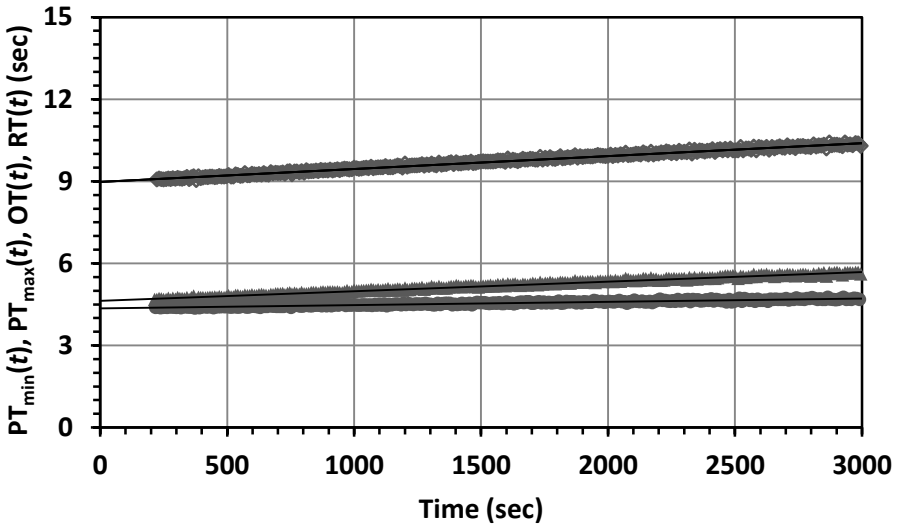

Figure S1-KM096. Values of $PT_{min}(t)$, $PT_{max}(t)$, $OT(t)$, and $RT(t)$ as a function of reaction time t for reaction KM096 (green in Figs. 1 and 2). Unfilled diamonds indicate $PT_{min}(t)$ and filled diamonds indicate $PT_{max}(t)$, circles indicate $OT(t)$, and triangles indicate $RT(t)$. The regressions lines also are shown for $PT_{min}(t) = m_1 \cdot t + PT_1(0)$, $PT_{max}(t) = m_2 \cdot t + PT_2(0)$, $OT(t) = m_3 \cdot t + OT(0)$ and $RT(t) = m_4 \cdot t + RT(0)$.

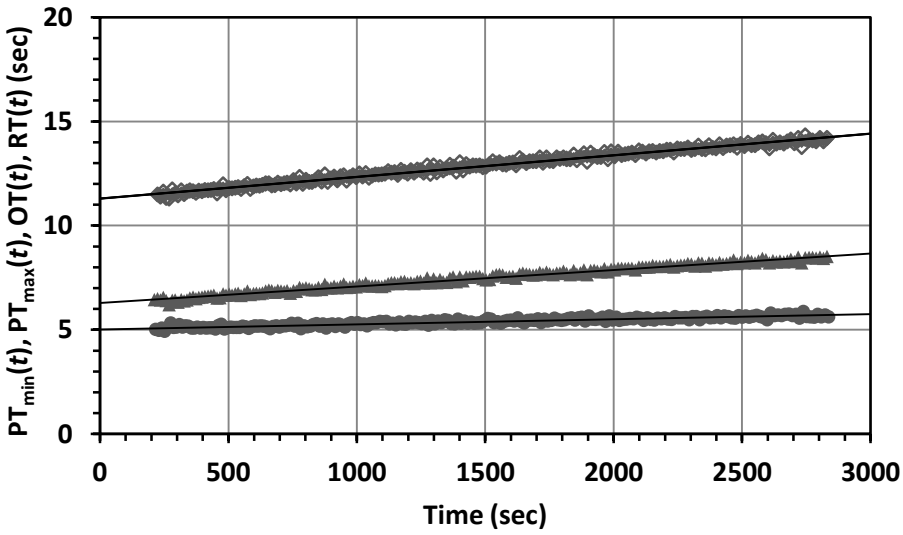

Figure S1-KM108. Values of $PT_{min}(t)$, $PT_{max}(t)$, $OT(t)$, and $RT(t)$ as a function of reaction time t for reaction KM108 (green in Figs. 1 and 2). Unfilled diamonds indicate $PT_{min}(t)$ and filled diamonds indicate $PT_{max}(t)$, circles indicate $OT(t)$, and triangles indicate $RT(t)$. The regressions lines also are shown for $PT_{min}(t) = m_1 \cdot t + PT_1(0)$, $PT_{max}(t) = m_2 \cdot t + PT_2(0)$, $OT(t) = m_3 \cdot t + OT(0)$ and $RT(t) = m_4 \cdot t + RT(0)$.

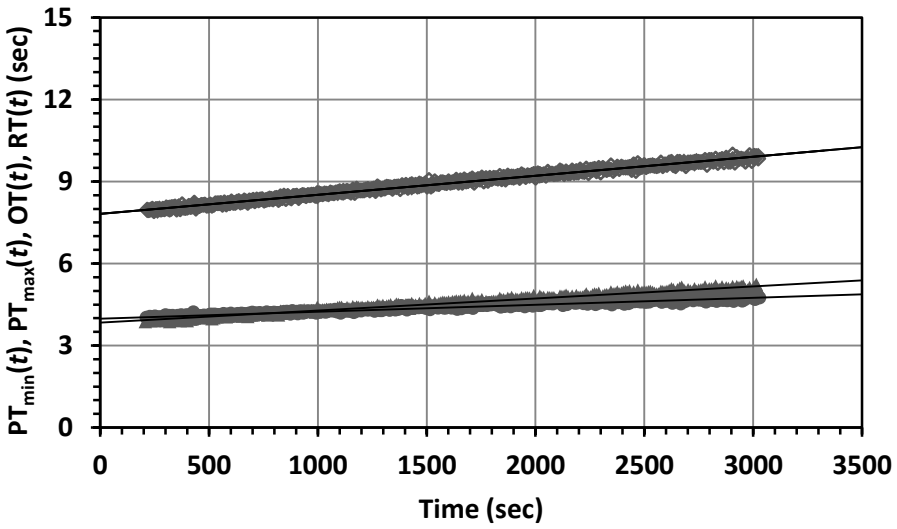

Figure S1-KM120. Values of $PT_{min}(t)$, $PT_{max}(t)$, $OT(t)$, and $RT(t)$ as a function of reaction time t for reaction KM120 (green in Figs. 1 and 2). Unfilled diamonds indicate $PT_{min}(t)$ and filled diamonds indicate $PT_{max}(t)$, circles indicate $OT(t)$, and triangles indicate $RT(t)$. The regressions lines also are shown for $PT_{min}(t) = m_1 \cdot t + PT_1(0)$, $PT_{max}(t) = m_2 \cdot t + PT_2(0)$, $OT(t) = m_3 \cdot t + OT(0)$ and $RT(t) = m_4 \cdot t + RT(0)$.

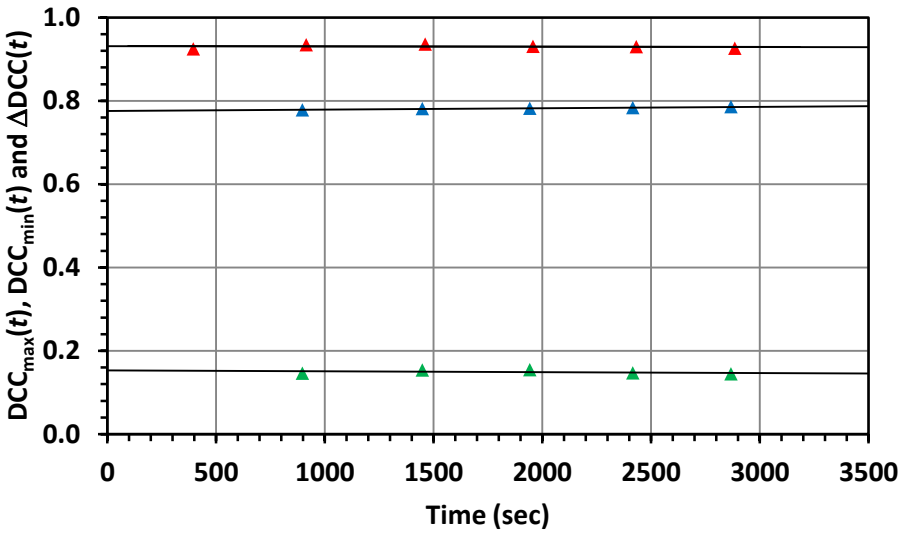

Figure S2-KM036 Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta DCC(t)$ as a function of reaction time t for reaction KM036 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta DCC(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta DCC(t) = h_3 \cdot t + \Delta I(0)$.

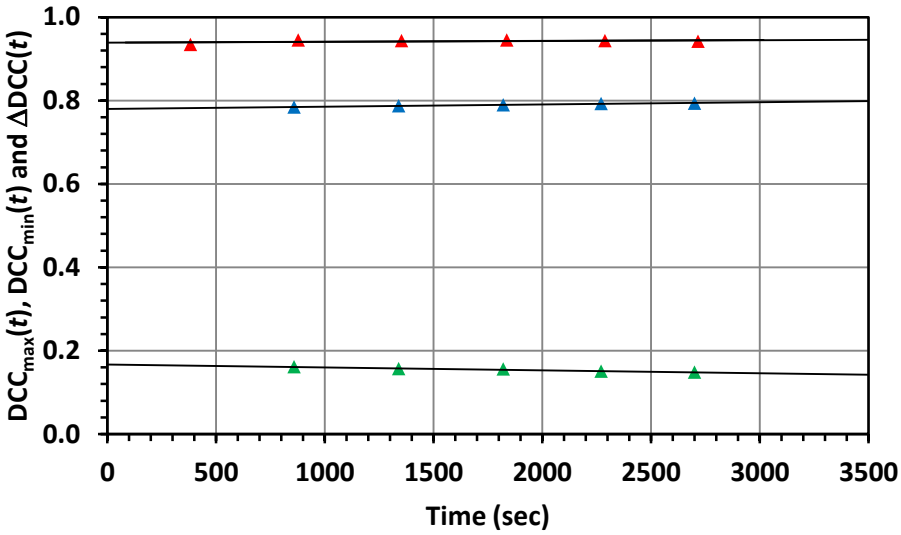

Figure S2-KM041 Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta DCC(t)$ as a function of reaction time t for reaction KM041 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta DCC(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta DCC(t) = h_3 \cdot t + \Delta I(0)$.

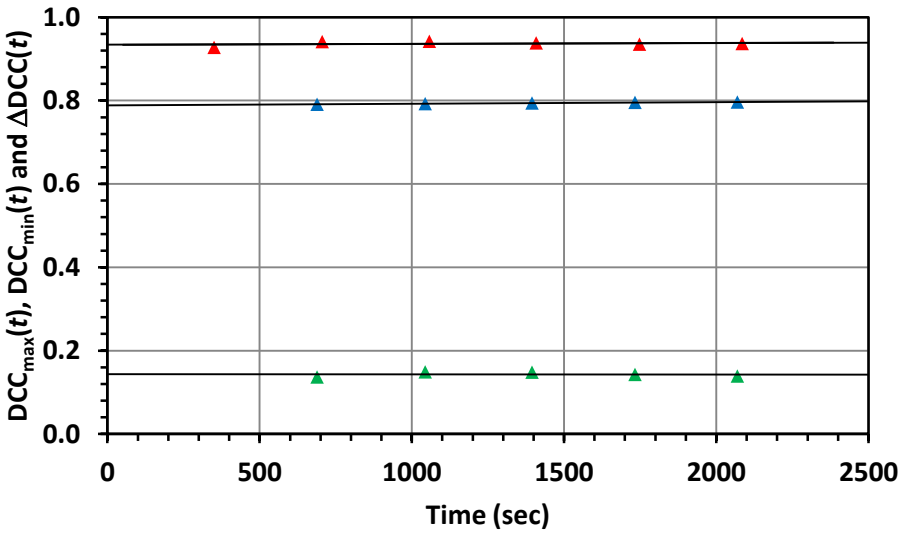

Figure S2-KM043 Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta DCC(t)$ as a function of reaction time t for reaction KM043 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta DCC(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta DCC(t) = h_3 \cdot t + \Delta I(0)$.

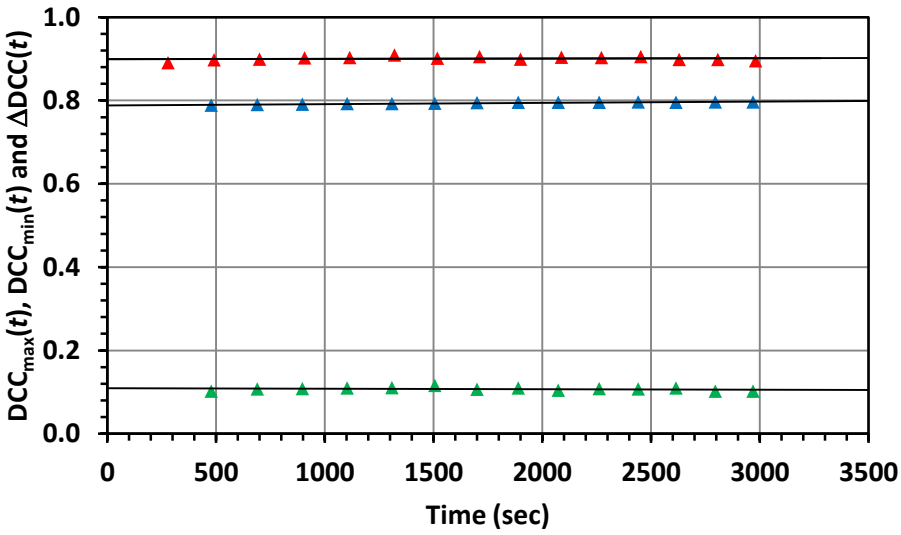

Figure S2-KM048 Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta DCC(t)$ as a function of reaction time t for reaction KM048 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta DCC(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta DCC(t) = h_3 \cdot t + \Delta I(0)$.

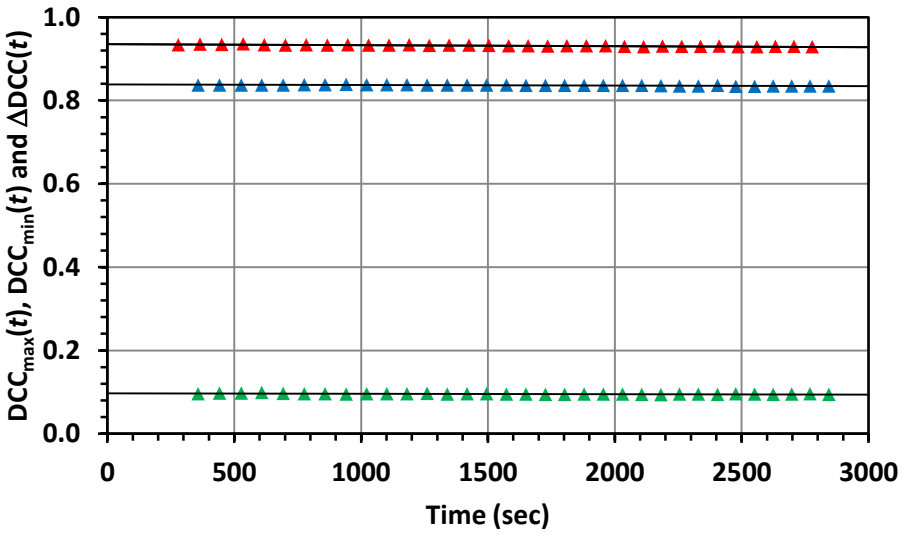

Figure S2-KM053 Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta DCC(t)$ as a function of reaction time t for reaction KM053 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta DCC(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta DCC(t) = h_3 \cdot t + \Delta I(0)$.

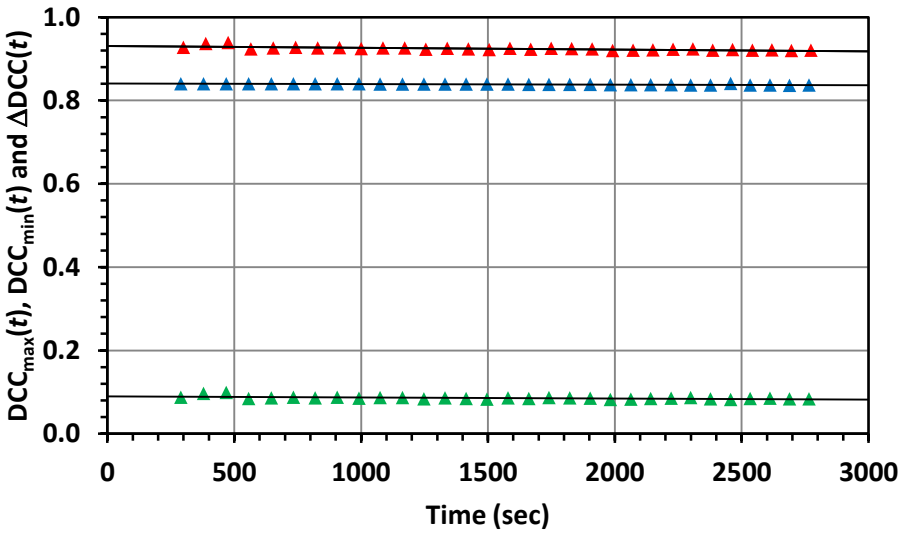

Figure S2-KM055 Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta DCC(t)$ as a function of reaction time t for reaction KM055 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta DCC(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta DCC(t) = h_3 \cdot t + \Delta I(0)$.

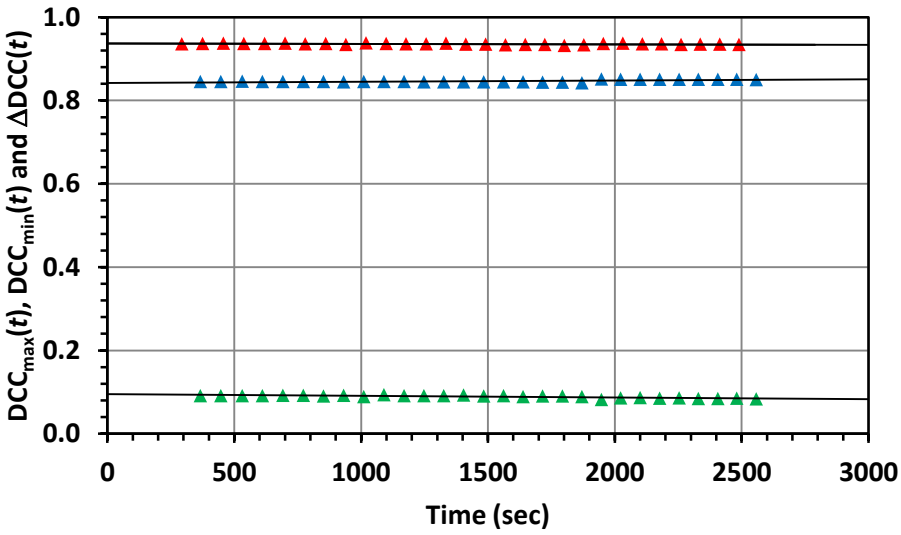

Figure S2-KM060 Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta DCC(t)$ as a function of reaction time t for reaction KM060 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta DCC(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta DCC(t) = h_3 \cdot t + \Delta I(0)$.

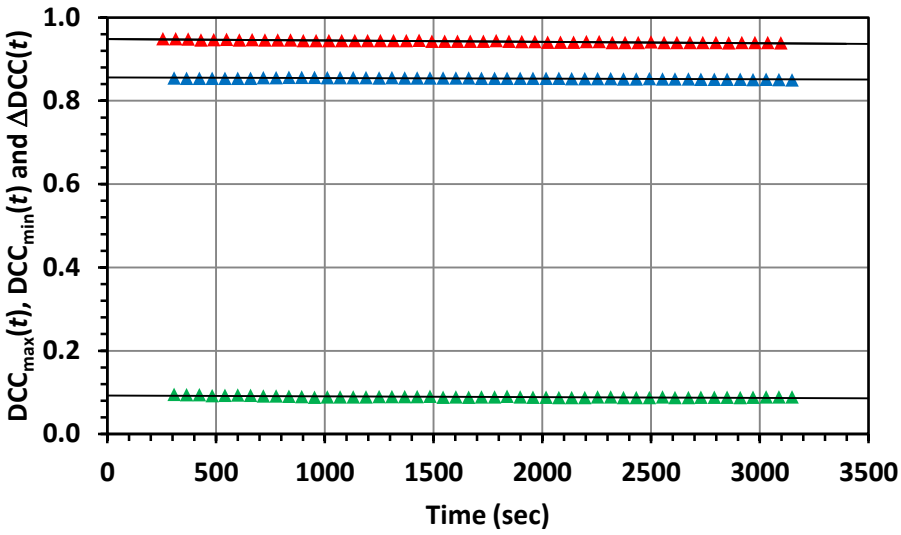

Figure S2-KM062 Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta DCC(t)$ as a function of reaction time t for reaction KM062 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta DCC(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta DCC(t) = h_3 \cdot t + \Delta I(0)$.

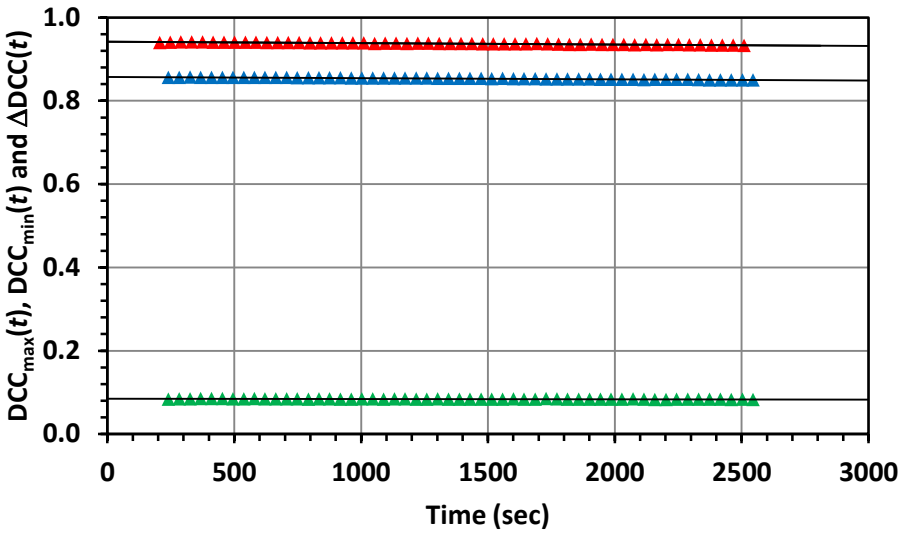

Figure S2-KM065 Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta DCC(t)$ as a function of reaction time t for reaction KM065 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta DCC(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta DCC(t) = h_3 \cdot t + \Delta I(0)$.

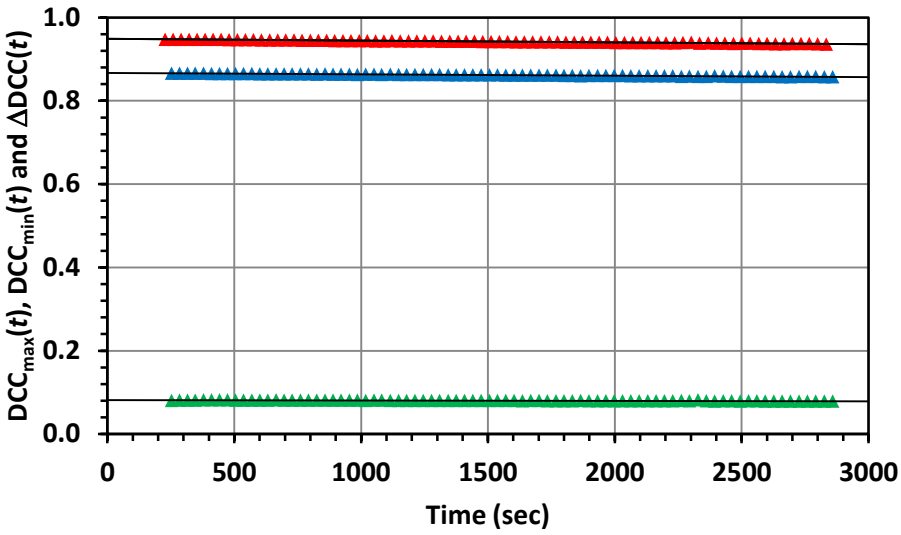

Figure S2-KM072 Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta DCC(t)$ as a function of reaction time t for reaction KM072 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta DCC(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta DCC(t) = h_3 \cdot t + \Delta I(0)$.

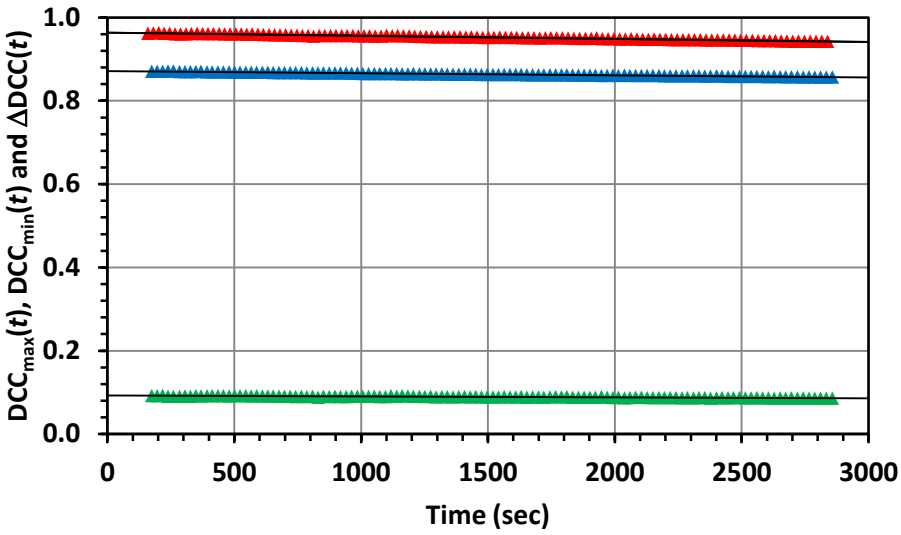

Figure S2-KM077 Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta DCC(t)$ as a function of reaction time t for reaction KM077 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta DCC(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta DCC(t) = h_3 \cdot t + \Delta I(0)$.

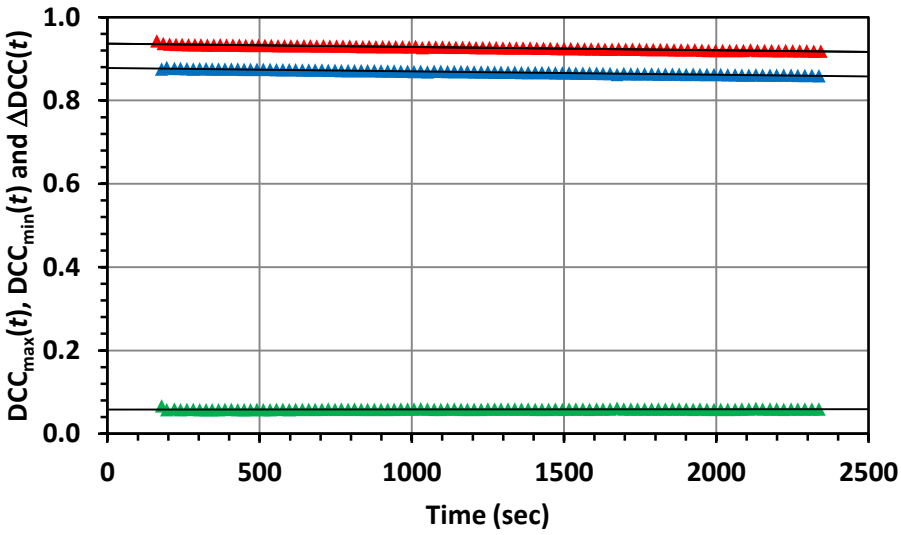

Figure S2-KM084 Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta DCC(t)$ as a function of reaction time t for reaction KM084 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta DCC(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta DCC(t) = h_3 \cdot t + \Delta I(0)$.

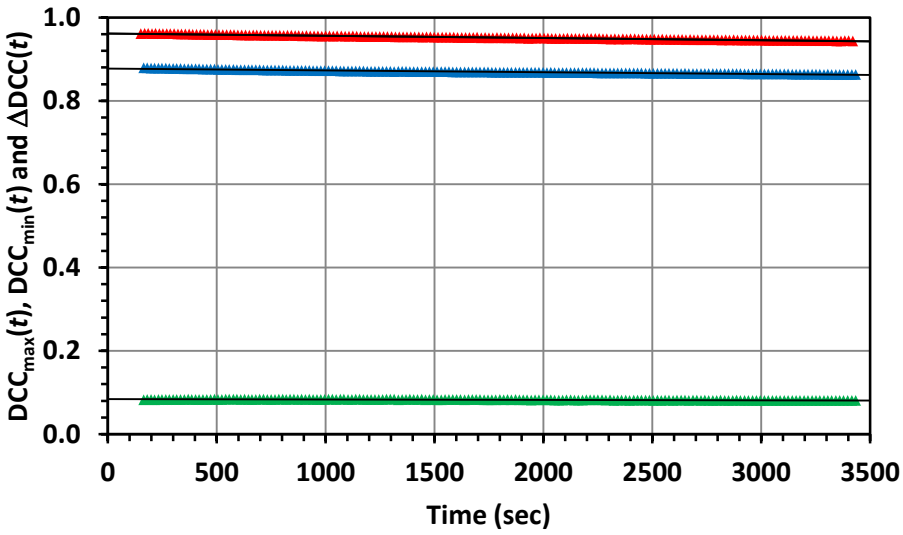

Figure S2-KM089 Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta DCC(t)$ as a function of reaction time t for reaction KM089 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta DCC(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta DCC(t) = h_3 \cdot t + \Delta I(0)$.

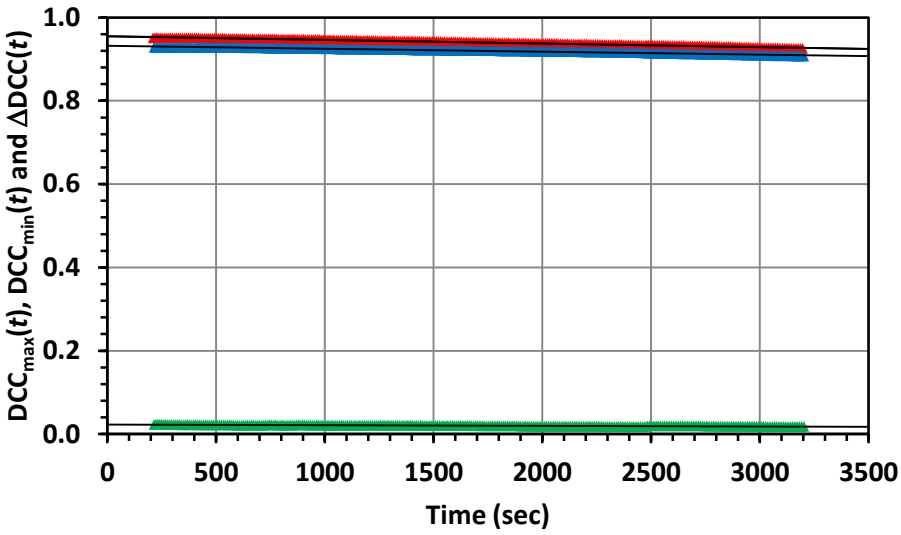

Figure S2-KM096 Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta DCC(t)$ as a function of reaction time t for reaction KM096 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta DCC(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta DCC(t) = h_3 \cdot t + \Delta I(0)$.

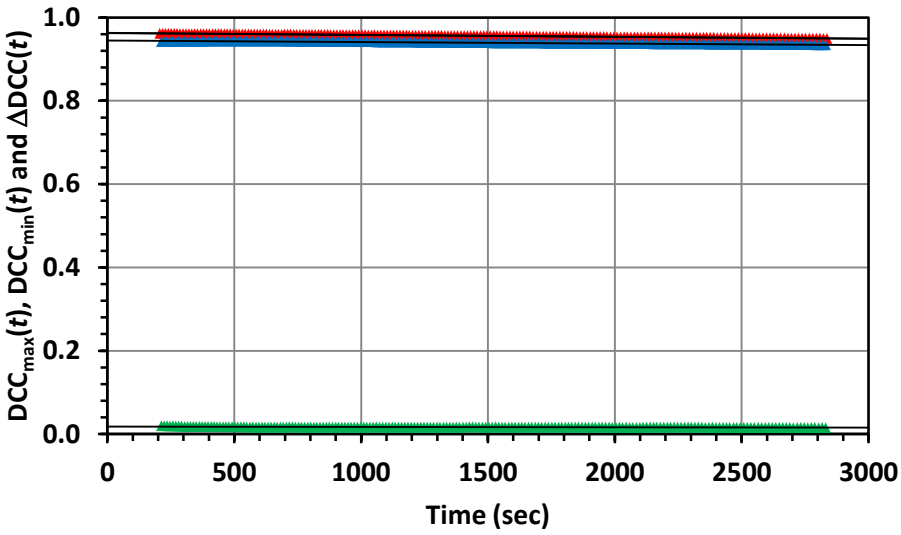

Figure S2-KM108 Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta DCC(t)$ as a function of reaction time t for reaction KM108 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta DCC(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta DCC(t) = h_3 \cdot t + \Delta I(0)$.

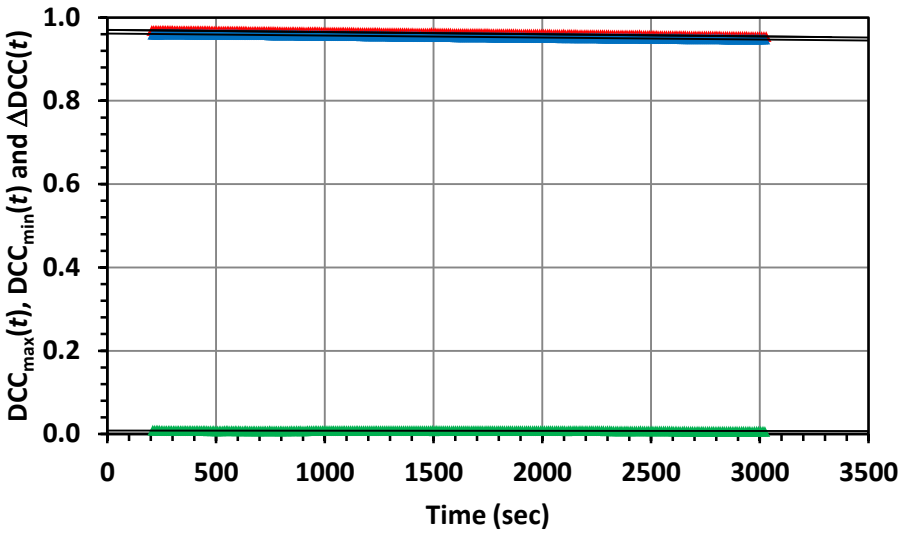

Figure S2-KM120 Values of $DCC_{max}(t)$, $DCC_{min}(t)$ and $\Delta DCC(t)$ as a function of reaction time t for reaction KM120 (green in Figs. 1 and 2). Red triangles indicate $DCC_{max}(t)$, blue triangles indicate $DCC_{min}(t)$, and green triangles indicate $\Delta DCC(t)$. The regressions lines also are shown for $DCC_{max}(t) = h_1 \cdot t + I_{max}(0)$, $DCC_{min}(t) = h_2 \cdot t + I_{min}(0)$, and $\Delta DCC(t) = h_3 \cdot t + \Delta I(0)$.

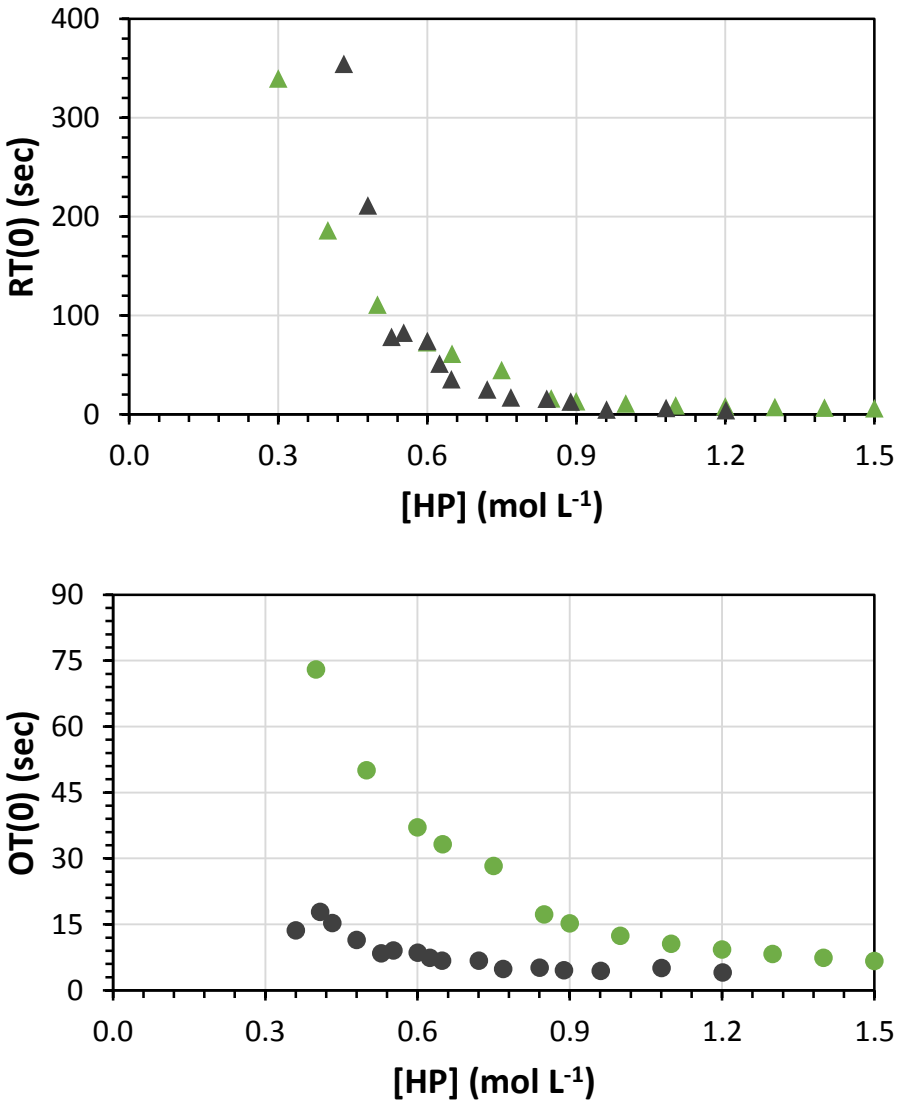

Figure S3. Comparison of the reduction times (RT, top) and oxidation times (OT, bottom) determined by the simulation BZR2 (green) with the experimental data (black) as a function of initial sulfuric acid concentration $[H_2SO_4]_0$ (mol·L^{-1}).