Electron Solvation in Methanol Revisited

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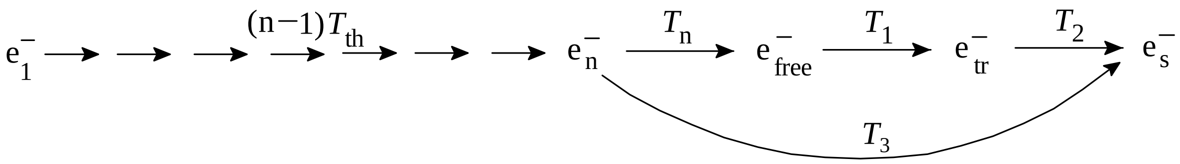
Appendix: Solution of the differential equations associated with mechanism 2



(2)

Let us denote the concentrations of different species involved in mechanism 2 by c marked with the corresponding subscript. The rate constants can be defined as the inverse of the characteristic times; $k_{\mathrm{i}} = \dfrac{1}{T_{\mathrm{i}}}$.

The system of linear differential equations related to mechanism 2 can be written as follows:

$$\frac{dc_1}{dt} = -k_{\mathrm{th}} c_1 \qquad \text{(A.1)}$$

$$\frac{dc_2}{dt} = k_{\mathrm{th}} c_1 - k_{\mathrm{th}} c_2 \qquad \text{(A.2)}$$

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$$\frac{dc_{\mathrm{n}-1}}{dt} = k_{\mathrm{th}} c_{\mathrm{n}-2} - k_{\mathrm{th}} c_{\mathrm{n}-1} \qquad \text{(A.3)}$$

$$\frac{dc_{\mathrm{n}}}{dt} = k_{\mathrm{th}} c_{\mathrm{n}-1} - \left(k_{\mathrm{n}} + k_3\right) c_{\mathrm{n}} \qquad \text{(A.4)}$$

$$\frac{dc_{\mathrm{free}}}{dt} = k_{\mathrm{n}} c_{\mathrm{n}} - k_1 c_{\mathrm{free}} \tag{A.5}$$

$$\frac{dc_{\mathrm{tr}}}{dt} = k_1 c_{\mathrm{free}} - k_2 c_{\mathrm{tr}} \tag{A.6}$$

$$\frac{dc_{\mathrm{s}}}{dt} = k_2 c_{\mathrm{tr}} + k_3 c_{\mathrm{n}} \tag{A.7}$$

The initial conditions to be considered are

$$c_1\big|_{\mathrm{t=0}} = c_0 \, ,$$

$$c_2\big|_{\mathrm{t=0}} = c_3\big|_{\mathrm{t=0}} = \cdots = c_{\mathrm{n}}\big|_{\mathrm{t=0}} = c_{\mathrm{free}}\big|_{\mathrm{t=0}} = c_{\mathrm{tr}}\big|_{\mathrm{t=0}} = c_{\mathrm{s}}\big|_{\mathrm{t=0}} = 0 \tag{A.8}$$

Let the unknown concentration functions in the above system of differential equations be replaced by their Laplace-transforms, keeping in mind the initial conditions. To get the corresponding Laplace-transformed equations, we have to replace the differential operator by a formal multiplication operator (Rodiguin *et al.*, 1964) $\mathrm{P} = \frac{d}{dt}$. The resulting equations are:

$$Pc_1 - Pc_0 = -k_{\mathrm{th}} c_1 \tag{A.9}$$

$$Pc_2 = k_{\mathrm{th}} c_1 - k_{\mathrm{th}} c_2 \tag{A.10}$$

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$$Pc_{\mathrm{n}} = k_{\mathrm{th}} c_{\mathrm{n-1}} - \left(k_{\mathrm{n}} + k_3\right) c_{\mathrm{n}} \tag{A.11}$$

$$Pc_{\mathrm{free}} = k_{\mathrm{n}} c_{\mathrm{n}} - k_1 c_{\mathrm{free}} \tag{A.12}$$

$$Pc_{\mathrm{tr}} = k_1 c_{\mathrm{free}} - k_2 c_{\mathrm{tr}} \tag{A.13}$$

$$Pc_{\mathrm{s}} = k_2 c_{\mathrm{tr}} + k_3 c_{\mathrm{n}} \tag{A.14}$$

In mechanism 2 there is no feedback present, thus equations (A.9)-(A.14) can be solved in succession as ordinary algebraic expressions. As a result we can calculate the Laplace-transforms of the concentration functions in terms of P.

Solving eq. (A.9) for c_1 and eq. (A.10) for c_2 we have:

$$c_1 = \frac{Pc_0}{P + k_{\mathrm{th}}} \tag{A.15}$$

$$c_2 = \frac{k_{\mathrm{th}} c_1}{P + k_{\mathrm{th}}} \tag{A.16}$$

Let us substitute eq. (A.15) in eq. (A.16) to get c_2:

$$c_2 = \frac{Pc_0 k_{\mathrm{th}}}{\left(P + k_{\mathrm{th}}\right)^2} \tag{A.17}$$

Continuing this procedure step by step, we can determine the following Laplace-transformed functions:

$$c_{\mathrm{n-1}} = \frac{Pc_0 k_{\mathrm{th}}^{\mathrm{n-2}}}{\left(P + k_{\mathrm{th}}\right)^{\mathrm{n-1}}} \tag{A.18}$$

$$c_{\mathrm{n}} = \frac{k_{\mathrm{th}} c_{\mathrm{n-1}}}{P + k_{\mathrm{n}} + k_3} \tag{A.19}$$

$$c_{\mathrm{n}} = \frac{Pc_0 k_{\mathrm{th}}^{\mathrm{n-1}}}{\left(P + k_{\mathrm{n}} + k_3\right)\left(P + k_{\mathrm{th}}\right)^{\mathrm{n-1}}} \tag{A.20}$$

$$c_{\mathrm{free}} = \frac{k_{\mathrm{n}} c_{\mathrm{n}}}{P + k_1} \tag{A.21}$$

$$c_{\mathrm{free}} = \frac{P c_0 k_{\mathrm{n}} k_{\mathrm{th}}^{\mathrm{n}-1}}{(P + k_1)(P + k_{\mathrm{n}} + k_3)(P + k_{\mathrm{th}})^{\mathrm{n}-1}} \tag{A.22}$$

$$c_{\mathrm{tr}} = \frac{k_1 c_{\mathrm{free}}}{P + k_2} \tag{A.23}$$

$$c_{\mathrm{tr}} = \frac{P c_0 k_{\mathrm{n}} k_1 k_{\mathrm{th}}^{\mathrm{n}-1}}{(P + k_1)(P + k_2)(P + k_{\mathrm{n}} + k_3)(P + k_{\mathrm{th}})^{\mathrm{n}-1}} \tag{A.24}$$

$$c_{\mathrm{s}} = \frac{k_2 c_{\mathrm{tr}} + k_3 c_{\mathrm{n}}}{P} \tag{A.25}$$

$$c_{\mathrm{s}} = \frac{c_0 k_{\mathrm{th}}^{\mathrm{n}-1}}{(P + k_{\mathrm{th}})^{\mathrm{n}-1}} \left(\frac{k_{\mathrm{n}} k_1 k_2}{(P + k_1)(P + k_2)(P + k_{\mathrm{n}} + k_3)} + \frac{k_3}{(P + k_{\mathrm{n}} + k_3)} \right) \tag{A.26}$$

The concentration functions for e_1^- to e_n^- can be determined by an inverse Laplace-transformation of the above functions. The inverse Laplace-transform for $\frac{P}{(P+a)^n}$ is $\frac{t^{n-1}}{(n-1)!} e^{-at}$.

Applying this in eq. (A.18) we get the concentration functions for e_1^- to $\mathrm{e}_{\mathrm{n}-1}^-$:

$$c_{\mathrm{j}} = \frac{c_0 (k_{\mathrm{th}} t)^{\mathrm{j}-1}}{(\mathrm{j}-1)!} e^{-k_{\mathrm{th}} t} \qquad \mathrm{j} = 1 \ldots \mathrm{n} - 1 \tag{A.27}$$

The overall concentration of the species included in the thermalization process is:

$$c_{\mathrm{hot}} = \sum_{j=1}^{n-1} c_j = c_0 e^{-k_{\mathrm{th}} t} \sum_{j=0}^{n-2} \frac{(k_{\mathrm{th}} t)^j}{j!} \tag{A.28}$$

The inverse Laplace-transform for $\frac{P}{(P+a_1)(P+a_2)^n}$ is $\frac{1}{(a_2-a_1)^n}\left(e^{-a_1 t}-e^{-a_2 t}\sum_{i=0}^{n-1}\frac{((a_2-a_1)t)^i}{i!}\right)$.

Applying this in eq. (A.20) we get the following concentration function for e_n^-:

$$c_\mathrm{n}=c_0\left(\frac{k_\mathrm{th}}{k_\mathrm{th}-(k_\mathrm{n}+k_3)}\right)^{\mathrm{n}-1}\left(e^{-(k_\mathrm{n}+k_3)t}-e^{-k_\mathrm{th}t}\sum_{i=0}^{n-2}\frac{((k_\mathrm{th}-(k_\mathrm{n}+k_3))t)^i}{i!}\right) \qquad \text{(A.29)}$$

To determine the concentration functions for the remaining species included in the mechanism, we use direct integration. Eqs. (A.5) and (A.6) are special cases of the inhomogeneous equation

$$\frac{dy}{dt}+p(x)y=r(x) \qquad \text{(A.30)}$$

The solution of this equation is (Fraleigh, 1990)

$$y=\exp\left[-\int_0^t p(x)dx\right]\left(c+\int_0^t r(y)\exp\left[\int_0^y p(z)dz\right]dy\right) \qquad \text{(A.31)}$$

Rewriting (A.4) and (A.5) in the form of (A.30), we get:

$$\frac{dc_\mathrm{free}}{dt}+k_1 c_\mathrm{free}=k_\mathrm{n}c_\mathrm{n} \qquad \text{(A.32)}$$

$$\frac{dc_\mathrm{tr}}{dt}+k_2 c_\mathrm{tr}=k_1 c_\mathrm{free} \qquad \text{(A.33)}$$

Writing the solutions of the differential equations in the form of (A.31), we have to evaluate the following integral:

$$\int_0^t x^m e^{-ax}dx=\frac{m!}{a^{m+1}}\left[1-e^{-at}\sum_{i=0}^{m}\frac{(at)^i}{i!}\right] \qquad \text{(A.34)}$$

The resulting solutions can be given as:

$$c_{\mathrm{free}} = c_0 k_{\mathrm{n}} \left(\frac{k_{\mathrm{th}}}{k_{\mathrm{th}} - (k_{\mathrm{n}} + k_3)} \right)^{n-1} \Bigg(\frac{1}{k_1 - (k_{\mathrm{n}} + k_3)} \left[e^{-(k_{\mathrm{n}} + k_3)t} - e^{-k_1 t} \right] -$$

$$- \sum_{i=0}^{n-2} \frac{\left(k_{\mathrm{th}} - (k_{\mathrm{n}} + k_3)\right)^i}{\left(k_{\mathrm{th}} - k_1\right)^{i+1}} \left[e^{-k_1 t} - e^{-k_{\mathrm{th}} t} \sum_{j=0}^{i} \frac{\left((k_{\mathrm{th}} - k_1)t\right)^j}{j!} \right] \Bigg) \tag{A.35}$$

$$c_{\mathrm{tr}} = c_0 k_{\mathrm{n}} k_1 \left(\frac{k_{\mathrm{th}}}{k_{\mathrm{th}} - (k_{\mathrm{n}} + k_3)} \right)^{n-1} \Bigg(\frac{1}{k_1 - (k_{\mathrm{n}} + k_3)} \cdot$$

$$\cdot \left[\frac{e^{-(k_{\mathrm{n}} + k_3)t} - e^{-k_2 t}}{k_2 - (k_{\mathrm{n}} + k_3)} - \frac{e^{-k_1 t} - e^{-k_2 t}}{k_2 - k_1} \right] - \sum_{i=0}^{n-2} \frac{\left(k_{\mathrm{th}} - (k_{\mathrm{n}} + k_3)\right)^i}{\left(k_{\mathrm{th}} - k_1\right)^{i+1}} \cdot \tag{A.36}$$

$$\cdot \Bigg(\frac{e^{-k_1 t} - e^{-k_2 t}}{k_2 - k_1} - \sum_{j=0}^{i} \frac{\left(k_{\mathrm{th}} - k_1\right)^j}{\left(k_{\mathrm{th}} - k_2\right)^{j+1}} \left[e^{-k_2 t} - e^{-k_{\mathrm{th}} t} \sum_{k=0}^{j} \frac{\left((k_{\mathrm{th}} - k_2)t\right)^k}{k!} \right] \Bigg) \Bigg)$$

Finally the concentration function for the solvated electron can be calculated from:

$$c_{\mathrm{s}} = c_0 - c_{\mathrm{hot}} - c_{\mathrm{n}} - c_{\mathrm{free}} - c_{\mathrm{tr}} \tag{A.37}$$