**Supporting**

**1s. Results of modeling and deconvolution of heat flow experimental kinetic curves acquired in isothermal conditions**

The initial experimental heat flow over time curves are can be found in *Supporting/Flow-Calorimetry/Main-Experiment/Source.* The results of simulations when a single autocatalytic process was taken as model are presented in *Supporting/Flow-Calorimetry/Main-Experiment/pdf*. The results of statistical processing and assessment of data reproducibility can be found in *Supporting/Flow-Calorimetry/Stat*.

Deconvolution was performed by computer simulation of combinations of two independent and two consecutive autocatalytic reactions with varying values of thermal effects and kinetic parameters and minimization of the standard deviation from the experimental curve using the Broyden–Fletcher–Goldfarb–Shanno algorithm (BFGS) [1a] implemented in our computer program [1b], as well as Nelder–Mead [1c] method implemented in the R statistics software package for statistical analysis and processing [2]. The initial values for the first approximation were taken from the DSC-TGA data (endothermic reaction). Figures 1s.1-6 show the results of deconvolution. The model of two independent autocatalytic processes was found to describe the experimental dependencies more accurately.

Table 1s.1. The result of the deconvolution of the heat flow measured during the isothermal decomposition of 2-nitrobenzenediazonium triflate **1a** using the model of two independent autocatalytic processes.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **T оС** | **k1** | **k2** | **C01** | **C02** | **dH1** | **dH2** | Quality |
| 75 | 0.5222 | 0.0480 | 0.00133 | 0.00304 | 48.5 | -500.6 | 7.3·10-10 |
| 80 | 0.4046 | 0.0489 | 0.00111 | 0.00230 | 30.7 | -441.0 | 7.1·10-9 |
| 85 | 0.9554 | 0.0611 | 0.00070 | 0.00272 | 32.5 | -453.9 | 1.3·10-8 |

Table 1s.2. The result of the deconvolution of the heat flow measured during the isothermal decomposition of 2-nitrobenzenediazonium triflate **1a** using the model of two consecutive autocatalytic processes.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **T оС** | **k1** | **k2** | **C01** | **C02** | **dH1** | **dH2** | Quality |
| 75 | 0.4679 | 0.0642 | 0.00191 | 0.00204 | 39.2 | -520.7 | 1.1·10-9 |
| 80 | 0.5791 | 0.0435 | 0.00122 | 0.00263 | 36.7 | -493.9 | 6.1·10-9 |
| 85 | 1.0512 | 0.0631 | 0.00075 | 0.00259 | 31.8 | -483.4 | 1.3·10-8 |

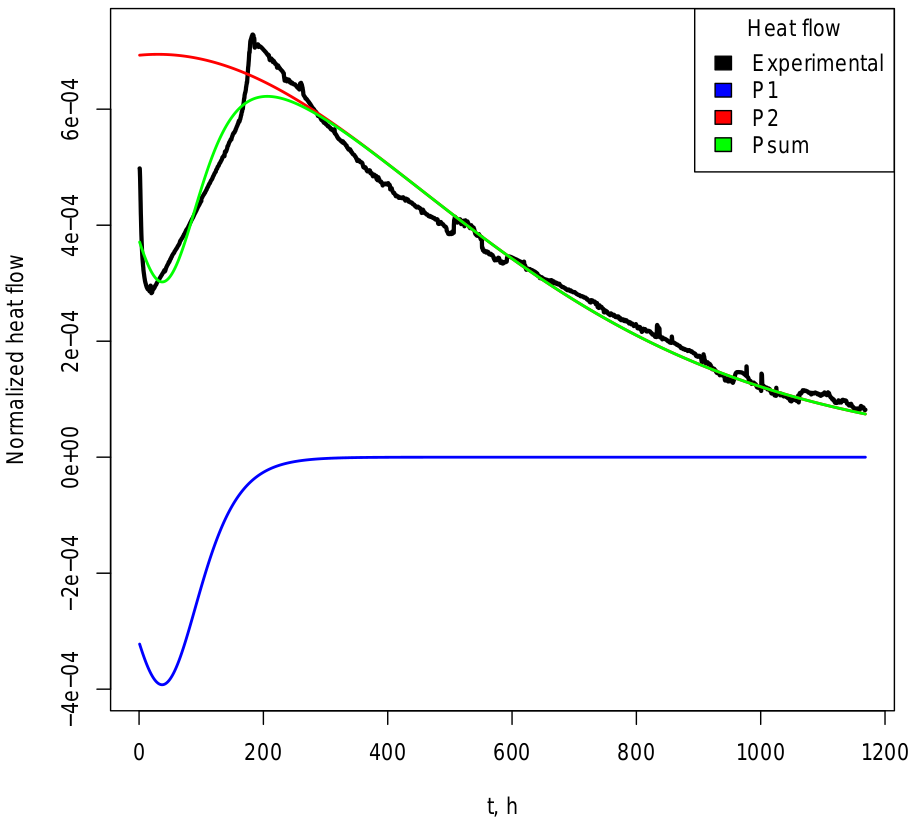


Figure 1s.1. The heat flow experimental curve and its deconvolution results for the isothermal decomposition of 2-nitrobenzenediazonium triflate **1a** at 75 оС. The deconvolution was done using the model of two independent autocatalytic processes.

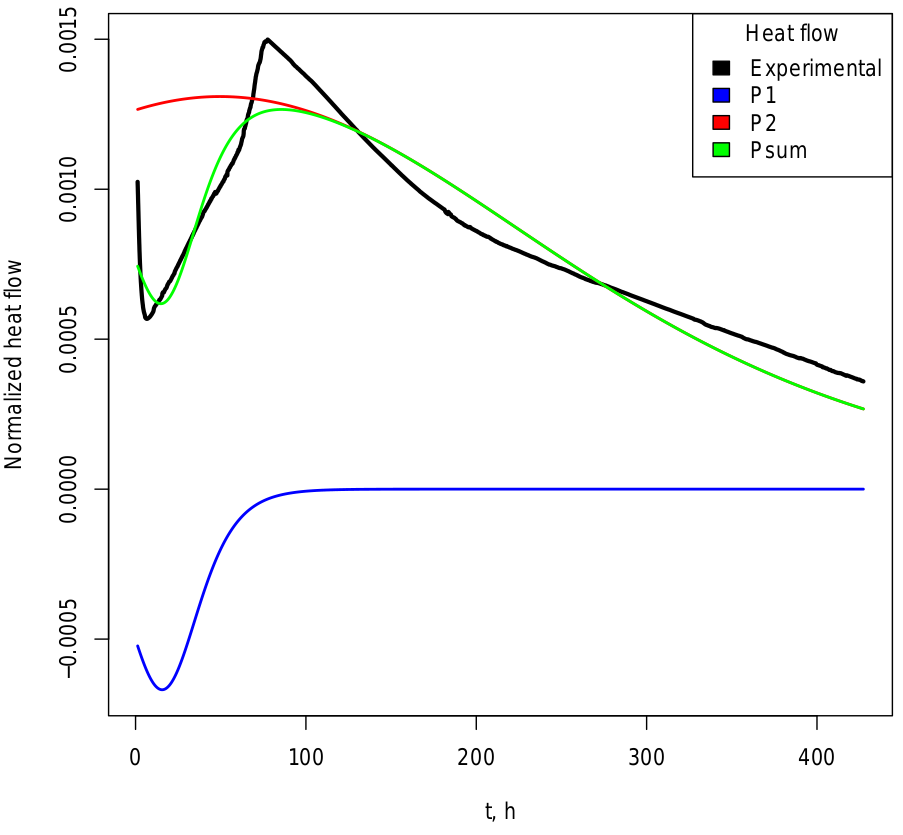


Figure 1s.2. The heat flow experimental curve and its deconvolution results for the isothermal decomposition of 2-nitrobenzenediazonium triflate **1a** at 80 оС. The deconvolution was done using the model of two independent autocatalytic processes.

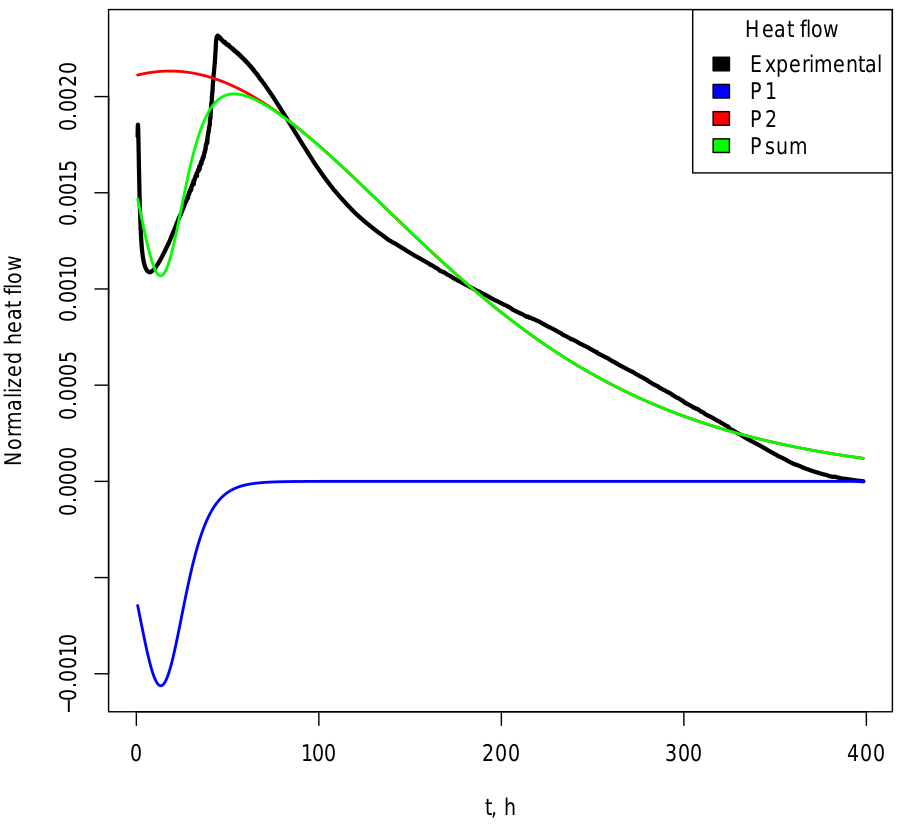


Figure 1s.3. The heat flow experimental curve and its deconvolution results for the isothermal decomposition of 2-nitrobenzenediazonium triflate **1a** at 85 оС. The deconvolution was done using the model of two independent autocatalytic processes.

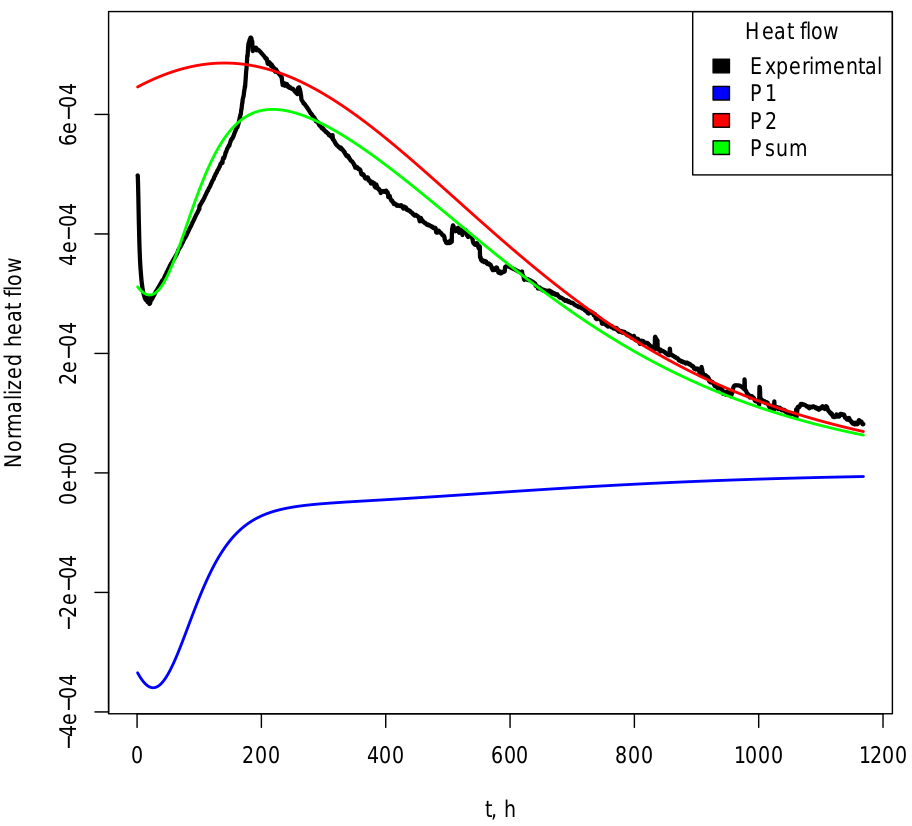


Figure 1s.4. The heat flow experimental curve and its deconvolution results for the isothermal decomposition of 2-nitrobenzenediazonium triflate **1a** at 75 оС. The deconvolution was done using the model of two consecutive autocatalytic processes.

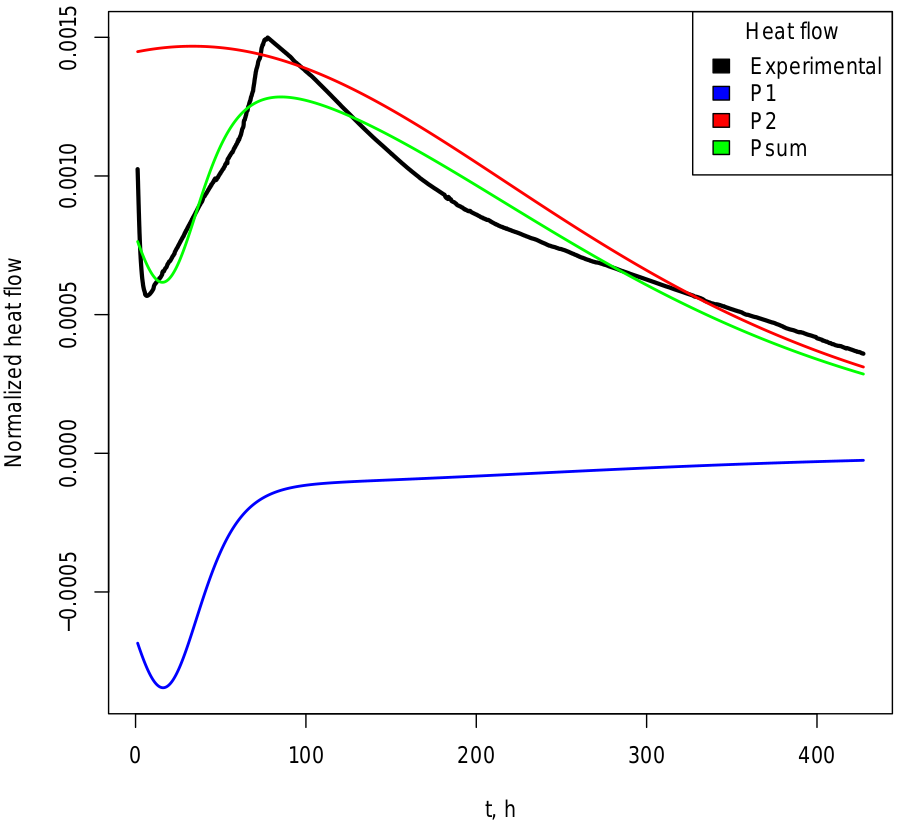


Figure 1s.5. The heat flow experimental curve and its deconvolution results for the isothermal decomposition of 2-nitrobenzenediazonium triflate **1a** at 80 оС. The deconvolution was done using the model of two consecutive autocatalytic processes.

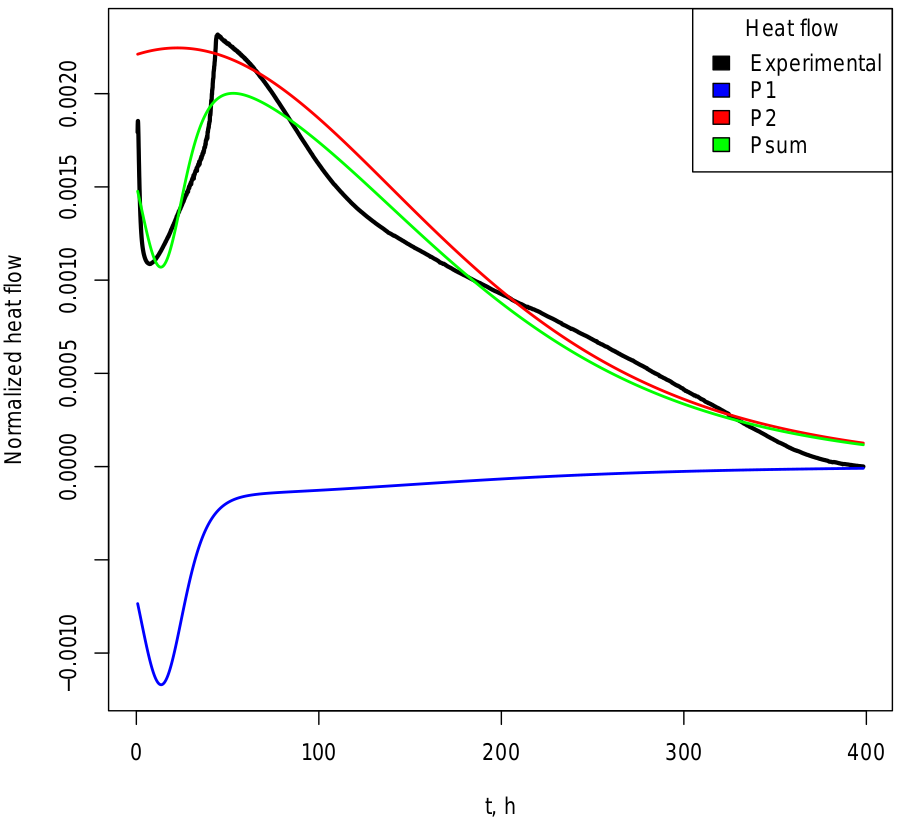


Figure 1s.6. The heat flow experimental curve and its deconvolution results for the isothermal decomposition of 2-nitrobenzenediazonium triflate **1a** at 85 оС. The deconvolution was done using the model of two consecutive autocatalytic processes.

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**Supporting 2s. GC-MS spectra of the decomposition products of diazonium salts studied**



Figure 2s.1 The decomposition products of DS **1a** according to GC-MS data.



Figure 2s.2 The decomposition products of DS **1b** according to GC-MS data. (Peak at 9.246 min corresponds to compound 3-NO2-C6H4-OSO2CF3, Fig. 21)



Figure 2s.3 The decomposition products of DS **1c** according to GC-MS data. (Peak at 13.314 min corresponds to compound 4-NO2-C6H4-OSO2CF3, peak at 14.912 min corresponds to compound 1-iodo-4-nitrobenzene, Fig. 22)



Figure 2s.4 The decomposition products of DS **1d** according to GC-MS data. (Peak at 8.337 min corresponds to compound 4-CH3О-C6H4-OSO2CF3, Fig. 23)



Figure 2s.5 The decomposition products of DS **2** according to GC-MS data. (Peak at 6.750 min corresponds to 1-fluoro-4-nitrobenzene, peak at 10.642 min corresponds to 1-iodo-4-nitrobenzene, Fig. 24)



Figure 2s.6 The decomposition products of DS **3** according to GC-MS data. (Peak at 6.307 min corresponds to 1-fluoro-4-nitrobenzene, peak at 10.515 min corresponds to 1-iodo-4-nitrobenzene, Fig. 25)



Figure 2s.7 The major product of decomposition of DS **1b** according to GC-MS data. Fragmentation pattern corresponds to 3-NO2-C6H4-OSO2CF3 M/Z: 271, 161, 95, 92, 69, 64.





Figure 2s.8 The major products of decomposition of DS **1c** according to GC-MS data. Fragmentation patterns correspond to 4-NO2-C6H4-OSO2CF3 M/Z: 271, 177, 95, 69 and 1-iodo-4-nitrobenzene M/Z: 249, 203, 76.



Figure 2s.9 The major product of decomposition of DS **1d** according to GC-MS data. Fragmentation pattern corresponds to 3-CH3O-C6H4-OSO2CF3 M/Z: 256, 123, 69, 52.





Figure 2s.10 The major products of decomposition of DS **2** according to GC-MS data. Fragmentation patterns correspond to nitrobenzene M/Z: 123, 77, 51 and 1-iodo-4-nitrobenzene M/Z: 249, 203, 76, 50.





Figure 2s.11 The major products of decomposition of DS **3** according to GC-MS data. Fragmentation patterns correspond to 1-fluoro-2-nitrobenzene M/Z: 141, 111, 95, 75, 50 and 1-iodo-4-nitrobenzene M/Z: 249, 203, 76.

**Supporting 3s. LS-MS spectra of the decomposition products of diazonium salts studied**

The acquired LS-MS spectra can be found in *Supporting/LC-MS*. To view and analyze the data the free OpenMS software can be used (<https://www.openms.de/>).

**Supporting 4s. Results of quantum-chemical calculations**

The .out files for quantum chemical calculations can be found in *Supporting/Quant/Out*. The files containing structures with optimized geometries are given in *Supporting/Quant/Mol*.