

Reactions Leading to CO and CO₂ Evolution in the Briggs-Rauscher Reaction

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Abstract

Recently periodic CO and CO₂ evolutions were discovered in the classical oscillatory Briggs-Rauscher (BR) reaction [1]. As these products are not included in the present mechanism of the reaction we started a systematic research to find reaction routes which could lead to these products.

The intensity of the gas evolution is rather low at the start, nevertheless oscillations in the gas evolution can be observed already at the beginning of both experiments. First the amplitude of the oscillations is very small but increases gradually suggesting a supercritical Hopf bifurcation. The gas evolution has a non-oscillatory component as well, which also increases from the start of the experiment. Both the gas evolution and the amplitude of the oscillations reach a maximum between 400 and 500 s (this happens somewhat earlier for the CO evolution) then the amplitude decreases rapidly. Soon the oscillations disappear - probably again with a supercritical Hopf bifurcation - but the monotonic gas evolution survives and continues with a decreasing intensity in the long post-oscillatory regime.

In this poster we report that the source of the non-oscillatory CO and CO₂ evolution is the decarbonylation and decarboxylation reactions of diiodomalonic acid produced in the BR reaction. To prove this, iodomalonic (IMA) and diiodomalonic (I₂MA) were produced. It was found that IMA is relatively stable, only I₂MA decomposes. Moreover, I₂MA can iodinate malonic acid producing two molecules of IMA. It is rather probable that positively charged iodonium ion (I⁺) or its hydrated form play a role in this process. I⁺ transfer between double bonds were already reported [2]. Mechanistic schemes are suggested for the various reactions.

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References

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