

## Dynamical Behavior During the Oxidation of Aniline with Bromate

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Spontaneous oscillations occur during the oxidation of aniline with bromate in sulfuric acid (a Körös-Orban System). In a continuous flow, stirred tank reactor besides a simple relaxation oscillation of large amplitude, a small amplitude oscillation of higher frequency was observed, so were various dynamical phenomena which can be understood as a combination of the two simple oscillations. For some regions of parameter space, the appearance of deterministic chaos seems probable. The role of metal impurities is discussed.

**Keywords:** Aniline – Reaction dynamics – Oscillations – Chaos – Impurities

For a large number of aromatic compounds, an oscillating reaction pathway was observed during the oxidation with bromate in the absence of metal catalysts in a batch reactor [1]. To characterize the dynamics of this type of reaction we investigated the systems containing aniline, phenole, and gallic acid, respectively, in a continuous flow, stirred tank reactor (CSTR). We found complex regimes in the case of aniline, reminiscent of the Belousov-Zhabotinsky (BZ) reaction with cerium as catalyst [2].

For CSTR runs two feed stock solutions containing aniline in sulfuric acid and potassium bromate were pumped at equal flow rates using two HPLC pumps to guarantee constant flux. The reaction took place under well-stirred conditions at 30 °C, the reaction volume was 22 ml. Similar to the BZ reaction we traced the potentials of a bromide selective and a platinum electrode versus a silver/silverchloride reference electrode [3].

After a short induction period (with the solution being violet), stable oscillations occur which are accompanied by a change of color from yellow to brown. Precipitation of uncharacterized reaction products limits undisturbed observation to about 5 hours. For the system with reactant concentrations as given in the legend of Fig. 1, the reaction dynamics was studied

as a function of residence time  $\tau$ , which is defined as reaction volume divided by total flow.

At residence times of 8.8 min, we found simple large amplitude relaxation oscillations with an average frequency of  $0.0037 \text{ sec}^{-1}$  (Figure 1 a). Similar to the BZ reaction (cf. [2]), with decreasing  $\tau$  these oscillations were followed by complex oscillations of significantly higher period, which can be described as a combination of large and small amplitude oscillations. Figure 1 b shows an example for  $\tau = 2.2 \text{ min}$ . At still lower residence times ( $\tau = 2.0 \text{ min}$ ), the small amplitude oscillation remained as a stable limit cycle with a frequency of  $0.057 \text{ sec}^{-1}$  (Figure 1 c). The first composite regime appearing as the result of a bifurcation of the large limit cycle (Fig. 1 a), at increasing flow, was a two-peak oscillation, where by every large peak was followed by one small peak. Further increase led to a stepwise increase of the number of small peaks (e.g. 2, 3, etc.).

At a sulfuric acid concentration of 1 M (other concentrations as in Fig. 1), the first complex type was a sequence of three large peaks followed by one small peak. Using the notation  $N^m$  for a regime consisting of  $N$  large peaks and  $m$  consecutive small peaks (cf. [4]), the sequence at these concentrations with increasing flow can be written as  $3^1, 3^2, 2^2$  (all of them periodic), i.e., there is an increasing number of small peaks and a decreasing number of large peaks, which is what can be observed in the case of the BZ reaction [4].

In analogy with BZ results, we suggest that for 0.7 M sulfuric acid deterministic chaos may be found during the oxidation of aniline, e.g. between the com-

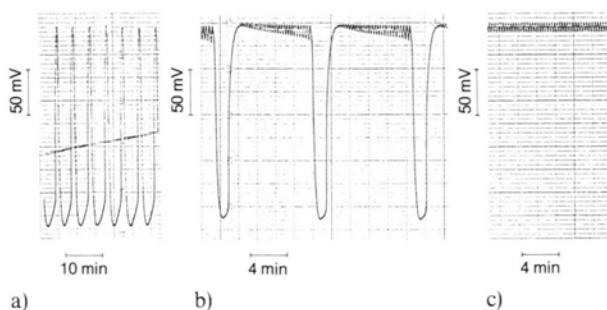


Fig. 1. Oscillations of the redox potential as a function of time. Concentrations in the reactor before any reaction: 0.004 M aniline, 0.7 M sulfuric acid, 0.1 M potassium bromate. a)  $\tau = 8.8 \text{ min}$ , b)  $\tau = 2.2 \text{ min}$ , c)  $\tau = 2.0 \text{ min}$ .

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Table 1. Plasma emission spectroscopic determination of metal content in the reaction solution with concentrations as given in the legend of Figure 1.

Metal	Wavelength (nm)	Concentration		Detection limit ( $\mu\text{g/l}$ )
		( $\mu\text{g/l}$ )	(mol/l)	
V	292.40	< 1	—	1.0
Cr	283.56	< 4	—	4.0
Mn	259.37	4.8	$0.9 \cdot 10^{-8}$	0.4
Fe	259.94	130	$2.3 \cdot 10^{-6}$	3.8
Ce	418.66	< 270	—	270

plex  $1^1$  and  $1^2$  or  $1^2$  and  $1^3$  regimes. This prediction was also obtained from model equations for this type of reaction [5] based on kinetic investigations [6] showing that there is no difference in principal between the catalyzed BZ reaction and the uncatalyzed oxidation of aromatic compounds. Our results strongly confirm these theoretical considerations.

Between two periodic regimes, at intermediate flow rates, we observed aperiodic behavior several times. To guarantee reproducibility, however, the experimental conditions have to be improved further. The complex types of behavior often are not a simple function of the residence time, especially as the slowly precipitated products seem to superimpose an irreversible component which causes additional dependence of the dynamics on the flow rate at the beginning of the reaction.

Furthermore, the effect of small amounts of metal ions as well as impurities of aniline have to be consid-

ered. As to the role of metals, we analyzed the reaction solution using plasma emission spectroscopy. The results for some important elements are presented in Table 1. The BZ catalyst cerium could not be detected with this method. Iron is known to suppress oscillations at concentrations from  $10^{-3}$  to  $10^{-4}$  M [1]. A most recent investigation revealed the redox couple  $\text{Fe}^{2+}/\text{Fe}^{3+}$  to be a cocatalyst of the BZ reaction which has an influence on the dynamics in the ppm range [7]. The present system thus opens up a new field of study of the redox couple's contribution to the phenomenology of BZ-type oscillations. Manganese ions can induce oscillations out of some stable steady states near the critical flow, according to the work of Körös et al. [8]; however, we did not observe a qualitative influence of manganese ions on the shape and type of oscillation. At present we are not able to definitely exclude or quantitatively describe the cocatalyzing or stabilizing effect of metal ion impurities. A future investigation will further elucidate the relationship between catalyzed and uncatalyzed bromate oscillators.

Using phenole or gallic acid instead of aniline we could not obtain stable oscillations in CSTR runs. Only the manganese-catalyzed phenole system also exhibited a sequence of regimes (at constant flow rate) during the period of several hours, including small amplitude, large amplitude oscillations and the mixed type  $2^1$  [9].

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- [1] E. Körös and M. Orban, *Nature London* **273**, 371 (1978). — M. Orban and E. Körös, *J. Phys. Chem.* **82**, 1672 (1978). — M. Orban and E. Körös, in: *Synergetics — Far From Equilibrium*, A. Pacault and C. Vidal (eds.), Berlin 1979.
- [2] J. L. Hudson, M. Hart, and D. Marinko, *J. Chem. Phys.* **71**, 1601 (1979).
- [3] K. Wegmann and O. E. Rössler, *Z. Naturforsch.* **33A**, 1179 (1978).
- [4] J. Maselko and H. L. Swinney, *Phys. Scr.* **52**, 269 (1984).

- [5] P. Richetti and A. Arneodo, *Phys. Lett.* **109A**, 359 (1985).
- [6] M. Orban, E. Körös, and R. M. Noyes, *J. Phys. Chem.* **83**, 3056 (1979).
- [7] K. G. Coffman, W. D. McCormick, Z. Noszticzius, R. H. Simoyi, and H. L. Swinney, *J. Chem. Phys.* **86**, 4418 (1987).
- [8] E. Körös, M. Orban, I. Habon, *J. Phys. Chem.* **84**, 559 (1980).
- [9] G. Baier, Diploma thesis, University of Tübingen, 1985.