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pH Oscillations in a Semibatch Reactor[1]

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Oscillating chemical reactions serve as dynamical models both for biological rhythms and for certain technological processes. These systems and other interesting nonlinear dynamical phenomena in chemistry are usually studied either in a closed (batch) reactor or in an open (continuous flow stirred tank (CSTR)) reactor. Most natural and industrial processes, however, take place in "reaction vessels" other than batch reactors or CSTRs. A commonly used procedure consists of the controlled continuous admission of one reactant to a reaction vessel in which the other reactants are already present. No outflow is used, and when the reactor is full, the input flow is stopped.

One industrial example of the use of this "semibatch reactor" is the production of oxalic acid by the action of nitrogen dioxide on hydrolyzed starch,[3] an exothermic and autocatalytic reaction which can lead to thermokinetic oscillations with potentially hazardous consequences. Waste treatment protocols in which materials are allowed to accumulate in a holding tank or pond before the addition of a substance designed to convert them to less toxic substances are another instance of the use of semibatch systems. Finally, therapeutic administration of drugs under continuous-flow conditions constitutes still another way in which this configuration is employed.

In contrast to the CSTR and batch reactors, there has been no systematic exploitation of semibatch reactors in the study of exotic reactions. Hess and Boiteux[4] applied this configuration to an investigation of glycolysis. The catalyzed oxidation of benzaldehyde to benzoic acid was discovered to be oscillatory when a continuous oxygen transfer from the gas phase to the liquid reaction mixture was maintained.[5] The oscillatory reduction of bromate by H_2[6] and the oxidation of NADH by O_2[7] have also been studied. Recently, oscillatory kinetics have been found in the gas-phase reaction between H_2 and Cl_2 under semibatch conditions.[8]

We suggest that the semibatch reactor is a potentially powerful tool for the experimental study of reactions known to exhibit oscillatory kinetics in a CSTR, because it can provide valuable information for better understanding of the mechanisms of these reactions. We examine here several reactions known to be oscillatory in a CSTR, and we demonstrate that they maintain their oscillatory character in the semibatch reactor. We restrict the present experiments to the class of pH-regulated oscillators.[9]

The hydrogen peroxide oxidation of thiosulfate ions oscillates in the presence of catalytic amounts of Cu(II) when carried out in a CSTR.[10] We were not able to find oscillatory behavior in the semibatch configuration using the initial concentrations that produce oscillations in a CSTR.[10] However, by modifying the reactant concentrations, we were able to obtain pH–time curves of the sort shown in Figure 1a. The pH first goes through a minimum during a long preoscillatory period. Then it starts to oscillate with increasing amplitude. The length of the induction period and the number of oscillations depend on the reactant concentrations.

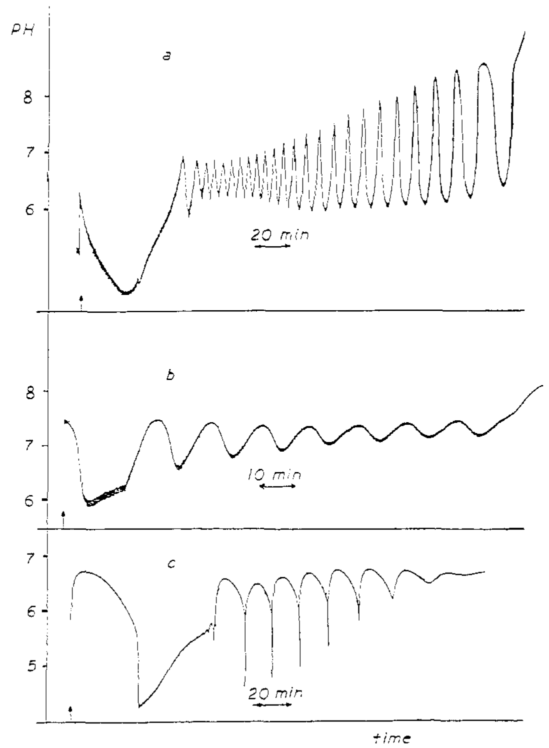

Figure 1. Semibatch pH oscillations observed under various conditions: (a) A solution of 0.05 M $Na_2S_2O_3$ containing 0.07 M NaOH is flowed, at 0.159 mL/min using a peristaltic pump, into 300 mL of a solution containing 0.10 M H_2O_2 and 8.83×10^{-6} M $CuSO_4$ that is placed in a 500-mL Erlenmeyer flask and magnetically stirred at 300 rpm. (b) A 0.1 M sodium sulfide solution is flowed into 300 mL of a 0.33 M hydrogen peroxide solution at 0.185 mL/min. (c) A solution containing 0.02 M Na_2SO_3, 0.015 M $Na_2S_2O_3$, and 0.0050 M H_2SO_4 is introduced at 0.159 mL/min into 300 mL of 0.05 M sodium iodate. $T = 24 \pm 1$ °C.

The initial pH of a reactant mixture showing oscillations in a CSTR and that of the semibatch oscillatory mixture differ significantly. The latter contains sodium hydroxide, while some acid must be introduced into the CSTR. This difference can be explained by taking into account the fact that there are two different reaction routes for the oxidation of thiosulfate by hydrogen peroxide:

$$2S_2O_3^{2-} + H_2O_2 \rightarrow S_4O_6^{2-} + 2OH^- \qquad (1)$$

$$S_2O_3^{2-} + 4H_2O_2 \rightarrow 2SO_4^{2-} + 2H^+ + 3H_2O \qquad (2)$$

While no detailed mechanism has yet been suggested for this system, the competition between the production of OH^- and of H^+ has been assumed to be responsible for the oscillation in CSTR.[10] The hydrogen ion producing reaction (eq 2) predominates when hydrogen peroxide is in excess. In the semibatch configuration, since it is the H_2O_2 that is present initially, the excess of hydrogen peroxide is always much higher in the reacting mixture than it is during the CSTR experiments. In order to make reaction 1 competitive, introduction of hydroxide ion is necessary. This experimental finding supports the earlier qualitative explanation of oscillations in this reaction[10] and can help in developing a detailed mechanism.

We now turn to the reaction between hydrogen peroxide and hydrogen sulfide, which is also an oscillatory reaction in a CSTR.[11] A mechanism has recently been proposed which accounts for both the oscillations and the kinetic behavior under batch conditions.[12] We used this mechanism to calculate the expected kinetic behavior in the semibatch. Under appropriate semibatch conditions, oscillatory pH–time curves were obtained. Our experiments support

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the prediction of the model. A typical result is presented in Figure 1b, which is obtained when a sodium sulfide solution is introduced into a hydrogen peroxide solution already present in the flask. Note that the roles of the reactants are not symmetric; no oscillatory conditions could be found in which the H_2O_2 solution was added to the sulfide solution. This asymmetry appears to be a general feature of oscillatory semibatch systems.

The well-known Landolt reaction, the iodate oxidation of hydrogen sulfite, is an important component process of a number of pH oscillators. When the Landolt reaction takes place in the presence of thiosulfate, pH-regulated oscillations can occur both in CSTR[13] and in batch.[14] However, the batch oscillation is strongly damped, and only two or three periods can be observed. Under semibatch conditions, we are able to obtain damped oscillation with many more cycles of oscillation (Figure 1c). The period of the oscillations in this reaction is extremely sensitive to the temperature in the CSTR mode.[13] This unusual sensitivity is not observed either in batch or in semibatch. Further semibatch investigation of the temperature sensitivity of this reaction may lead to an explanation of the peculiar temperature effect.

While the potential of the semibatch reactor for studies of nonlinear chemical dynamics remains largely unexplored, we believe that these initial investigations as well as those of refs 4–8 suggest that this technique merits further investigation as a tool in the arsenal of the chemical dynamicist.

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The First Unambiguous Synthesis of Poly(alkyl/aryloxothiazenes). A Novel Route to Precursors and Synthesis of Polymers

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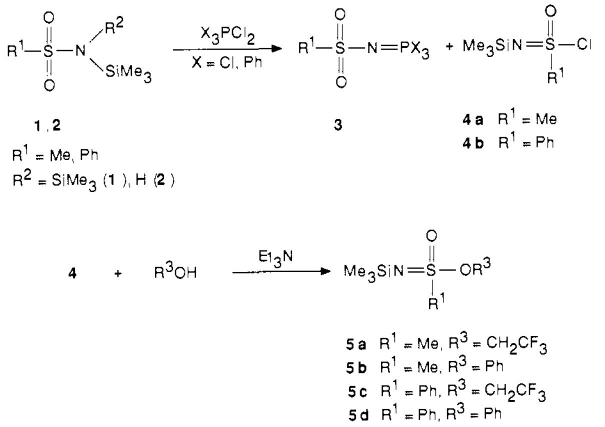
Recent years have seen a resurgence in interest in inorganic polymers. One reason for this is that several existing inorganic polymers, and their hybrids with organic polymers, possess properties not exhibited by conventional carbon-based macromolecules. The synthesis of poly(oxothiazenes),[1] polymers with an alternating sulfur(VI)–nitrogen backbone, has been reported sporadically by various groups since the early 1960s.[2-9] However, the polymers in several of these reports either were low molecular weight oligomers or were simply inferred without substantiation of their polymeric identity. We now report a general synthesis of linear, high molecular weight alkyl and aryl poly(oxothiazenes), $[N{=}S(O)R]_n$, in two steps from N-silylated sulfonamides.[10] The synthesis of *N*-silylsulfonimidates[11] and their condensation to poly(oxothiazenes) in a manner analogous to the condensation of *N*-silylphosphoranimines to polyphosphazenes[12] are shown in Schemes I and II.

Scheme I



Scheme II

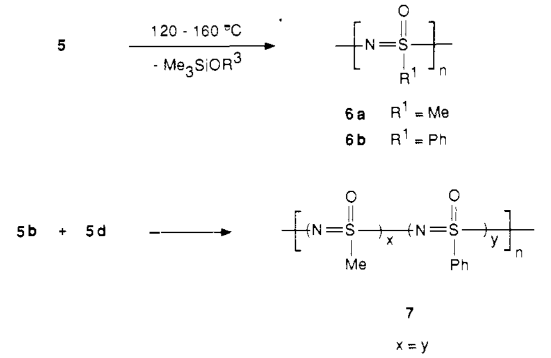


Table I. Molecular Weight and T_g of Poly(oxothiazenes)

sulfonimidate	polymer	temp, °C	mol wt[a] M_w	mol wt[a] M_n	T_g, °C
5a	**6a**	160	51 812	5898	55–65
5b	**6a**	120	408 982	31 671	–
5c	**6b**	170	10 471	3509	–
5d	**6b**	120	194 614[b]	138 116	85
			14 110	12 242	
5b + 5d	7	140	256 000	36 630	72

[a] Molecular weights (in DMF) are relative to polystyrene and are, therefore, only estimates. [b] Bimodal distribution.

The conversion of N-silylated sulfonamides (**1**, **2**) to sulfonimidoyl chlorides **4** was accomplished via reaction with halophosphoranes of the type X_3PCl_2. The course of the reaction was found to be dependent on the polarity of the solvent used and the steric bulk of the phosphorus reagent. While the bis(silyl) sulfonamide **1a** (R^1 = Me) and PCl_5 in refluxing CCl_4 yielded only **3** (evidenced by a S–Me doublet due to phosphorus coupling in the ^1H NMR spectrum), the same reaction in $CHCl_3$ produced a 1:1 mixture of **3** and *N*-(trimethylsilyl)methanesulfonimidoyl chloride (**4a**). The downfield ^1H NMR chemical shift (δ 3.5) of

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(1) Early nomenclature described these polymers as "poly(oxosulfurnitrides)". However, we have chosen to introduce the "oxothiazene" nomenclature for the repeat unit $[N{=}S(O)R]$ consisting of a sulfur(VI)–nitrogen skeletal unit with oxygen as a "fixed" substituent on sulfur because of close structural similarity with the well-recognized phosphazene unit $[N{=}PR_2]$, and because of reasonings similar to those used by Allcock for his preference of the phosphazene nomenclature, as discussed in the following: Allcock, H. R. *Phosphorus-Nitrogen Compounds*: Academic Press: New York, 1972; pp 7–13.

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