
PERMANGANATE CHEMICAL OSCILLATORS WITH CYCLIC DIKETONES

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Permanganate chemical oscillators with 1,3-cyclopentanedione, 1,3-cyclohexanedione and dimedone (5,5-dimethyl-1,3-cyclohexane-dione) in a CSTR (continuous-flow, stirred tank reactor) are described. The oscillatory systems under study are remarkable in that the oscillations are well developed, but no kinetic bistability has been found. Presumably, bistability may not be a pre-requisite for oscillations to occur.

Key words: Chemical oscillations; Permanganate oscillators; Oscillatory oxidation of cyclic diketones by permanganate.

Halogenate (iodate, bromate, chlorite etc.) oscillators constitute the majority of chemical oscillators. This group of oscillators is based on the well-known Belousov–Zhabotinskii reaction, the most frequently studied chemical oscillator so far, and by the Bray–Liebhafsky reaction disclosed more than 70 years ago^{1,2}. The group of chlorite oscillators has been disclosed and elucidated by a group of scientists centered around De Kepper, Epstein and Kustin³ at Brandeis University. The oscillatory autooxidation of benzaldehyde⁴ is a special case, and gas evolution oscillators⁵ form a special group. A taxonomy of chemical oscillators including members of a mechanistically related family has been developed by Epstein⁶. More recently, Simoyi⁷ began to report on a class of oscillators based on sulfur chemistry.

Transition metal-based oscillators seem to constitute a new family of chemical oscillators, within which the manganese-chemistry based chemical oscillators^{8–22} form the first group. They can be divided into two subgroups:

a) Permanganate oscillators based on the reduction of MnO_4^- ions by an appropriate reducing agent in a continuous-flow, stirred tank reactor (CSTR), and

b) manganese oscillators based on the oxidation of Mn^{2+} ions by an appropriate oxidizing agent in a CSTR.

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So far, the first subgroup, based on the reduction of MnO_4^- ions in a CSTR, includes only one oscillator with a cyclic diketone, viz. ninhydrine⁹. We sought for additional oscillators involving cyclic diketones, with a view to extending this subgroup and gaining a deeper insight into their behaviour. The outcome of our efforts is the subject of the present paper.

EXPERIMENTAL

Glass CSTRs (ref.⁸) (27.6 cm^3) with a mantle connected to a TB 150 ultrathermostat (Medingen) were used. The oscillatory reaction in a flowing, well stirred solution was monitored voltamperometri-

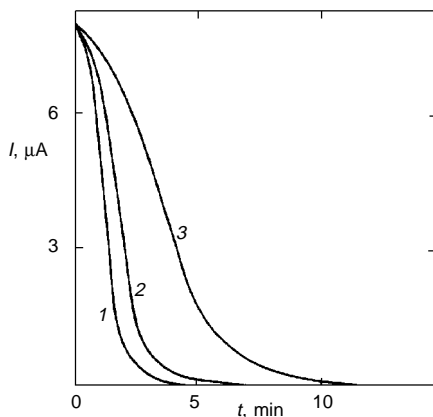


FIG. 1

Autocatalytic reduction of MnO_4^- ions at 20°C : conditions: $[\text{KMnO}_4]_0 = 3 \cdot 10^{-5} \text{ mol dm}^{-3}$, $[\text{H}_3\text{PO}_4]_0 = 1 \cdot 10^{-3} \text{ mol dm}^{-3}$; initial concentration of diketone: $7 \cdot 10^{-5} \text{ mol dm}^{-3}$; 1 dimedone, 2 1,3-cyclohexanedione, 3 1,3-cyclopentanedione

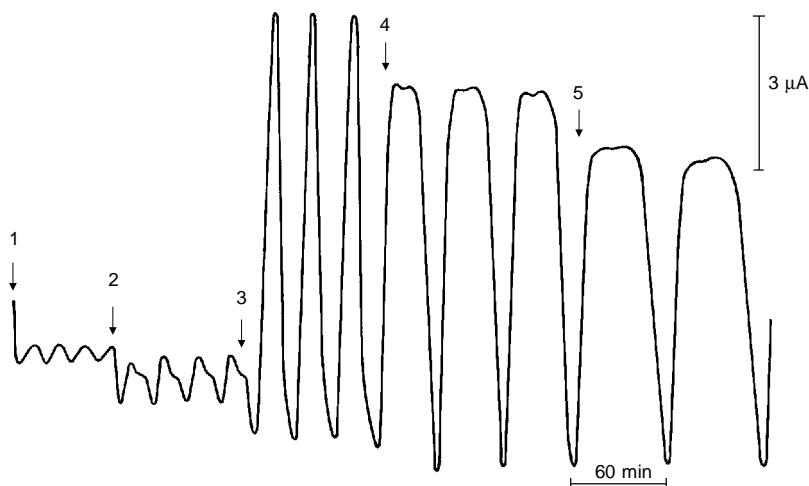


FIG. 2

The permanganate chemical oscillator with dimedone: $[\text{KMnO}_4]_0 = 3 \cdot 10^{-5} \text{ mol dm}^{-3}$, $[\text{H}_3\text{PO}_4]_0 = 2 \cdot 10^{-3} \text{ mol dm}^{-3}$, $[\text{D}]_0 = 7 \cdot 10^{-5} \text{ mol dm}^{-3}$, $T = 20^\circ\text{C}$; $k_0 \text{ (s}^{-1}\text{)}$: 1 $8.7 \cdot 10^{-3}$, 2 $6.7 \cdot 10^{-3}$, 3 $5.3 \cdot 10^{-3}$, 4 $4.1 \cdot 10^{-3}$, 5 $3.2 \cdot 10^{-3}$

cally on an LP7 Polarograph (Laboratorni pristroje, Prague, Czechoslovakia) fitted with a static platinum electrode. The reactors were equipped with propellers with a stirring frequency of $2\,250\text{ min}^{-1}$.

The experimental procedure was the same as in our earlier work^{20,21}.

RESULTS AND DISCUSSION

The reduction of MnO_4^- ions by 1,3-cyclopentanedione, 1,3-cyclohexanedione and dimedone (D) has an autocatalytic character (Fig. 1). Carbon dioxide and water are the final diketone oxidation products provided that permanganate is present in a stoichiometric excess. Although we failed to observe kinetic bistability in the CSTR, we succeeded to find conditions under which chemical oscillations occur (Fig. 2). The oscillations, monitored voltamperometrically, mostly correspond to those of manganese between oxidation states +7 and +4 in a solution of phosphoric acid at an optimum concentration of $2 \cdot 10^{-3}\text{ mol dm}^{-3}$. Systems in which D is replaced by cyclopentanedione or cyclohexanedione exhibit a similar oscillatory behaviour. As in the systems studied previously⁸⁻²², the presence of H_2PO_4^- ions is necessary to stabilize the colloids, $(\text{MnO}_2)_{\text{col}}$, as products of the MnO_4^-

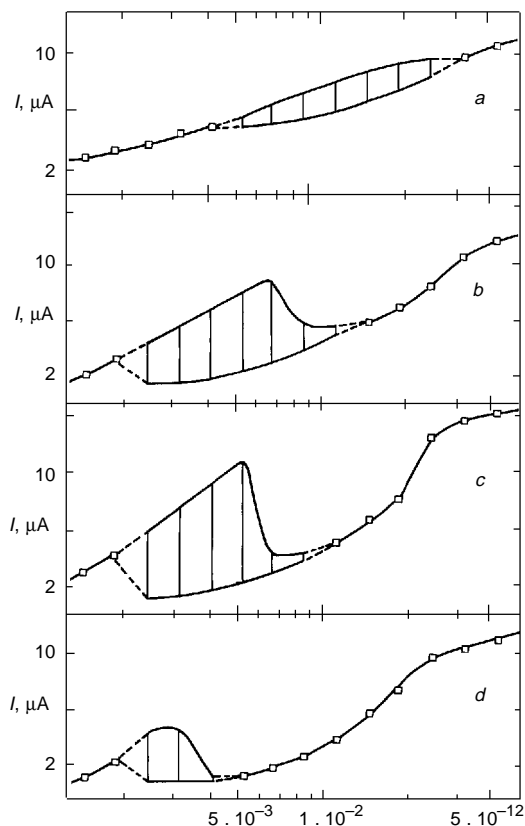


FIG. 3

Amplitude of oscillations at $20\text{ }^\circ\text{C}$ in dependence on the initial H_3PO_4 concentration: $[\text{KMnO}_4]_0 = 3 \cdot 10^{-5}\text{ mol dm}^{-3}$, $[\text{D}]_0 = 7 \cdot 10^{-5}\text{ mol dm}^{-3}$; $[\text{H}_3\text{PO}_4]_0$ (mol dm^{-3}): a $1 \cdot 10^{-3}$, b $1.5 \cdot 10^{-3}$, c $2 \cdot 10^{-3}$, d $3 \cdot 10^{-3}$; \square steady state; amplitude of oscillations is demonstrated by section lining

reduction. The effect of H_3PO_4 concentration on the oscillatory behaviour of the system under study is shown in Fig. 3. A canard²³ is observed at a concentration of H_3PO_4 of $2 \cdot 10^{-3} \text{ mol dm}^{-3}$; this is usually interpreted as an abrupt change in the period and amplitude of the oscillatory system within a very narrow range of the control parameter. According to Peng and coworkers²³, canards indicate some false bifurcations in the chemical systems, because the qualitative dynamical features remain unchanged during the transition: limit cycle oscillations occur before and after the canard. The concentration of $3 \cdot 10^{-3} \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$ seems to be too high (Fig. 3), which may be due to the fact that the optimum degree of stabilization of $(\text{MnO}_2)_{\text{col}}$ has been exceeded. Small changes in H_3PO_4 concentration (Figs 2 and 4) cause rather large changes in the character of the oscillations. Within the H_3PO_4 concentration range of $1.4 \cdot 10^{-3}$ to $1.7 \cdot 10^{-3} \text{ mol dm}^{-3}$, the oscillations are complex and relatively regular, but the transition between high-amplitude and low-amplitude oscillations is characterized by an irregularity or some kind of chaotic behaviour (Fig. 5). We tried to analyze this chaotic behaviour by means of a one-dimensional map, but no deterministic chaos could be proved. Perhaps,

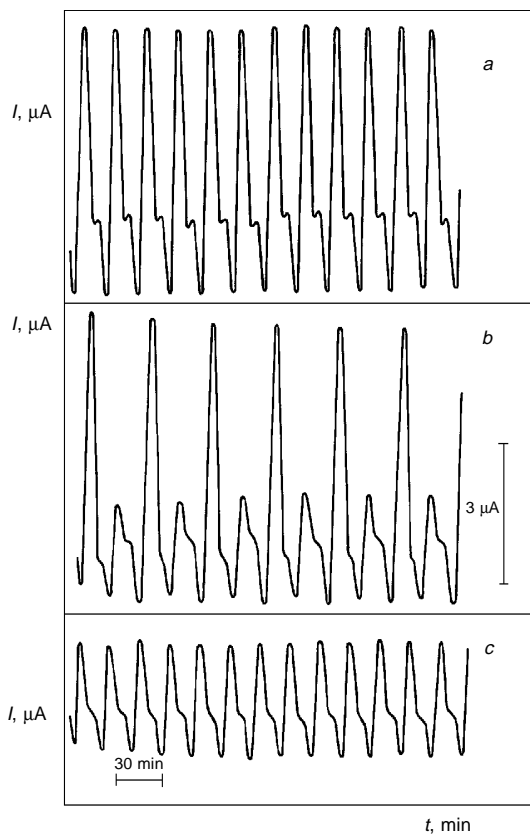


FIG. 4

Regular complex oscillations of the MnO_4^- -dimedone- H_3PO_4 system at 20°C : $k_0 = 6.71 \cdot 10^{-2} \text{ s}^{-1}$, $[\text{KMnO}_4]_0 = 3 \cdot 10^{-5} \text{ mol dm}^{-3}$, $[\text{D}]_0 = 7 \cdot 10^{-5} \text{ mol dm}^{-3}$, $[\text{H}_3\text{PO}_4]_0$ (mol dm^{-3}): a $1.4 \cdot 10^{-3}$, b $1.55 \cdot 10^{-3}$, c $1.7 \cdot 10^{-3}$

the explanation is similar to that suggested by Gyorgyi and Field for the BZ systems²⁴, namely that our permanganate oscillator inside the reactor bulk phase is also dynamically coupled with the in-flow reagents.

It is noteworthy that we could observe oscillations but no bistability in the systems under study. Until now, we found such behaviour only for the permanganate oscillator with oxalacetic acid as the substrate²¹. Presumably, bistability is not necessarily a prerequisite for oscillations: bistability and oscillations are both consequences of chemical feedback, which may or may not occur simultaneously.

Since the permanganate oscillator with D shows a relatively rich, dynamical behaviour in a CSTR, we tried to represent it in the $[\text{KMnO}_4]_0-k_0$, $[\text{D}]_0-k_0$ and $[\text{H}_3\text{PO}_4]_0-k_0$ planes (Fig. 6). In the first two planes, the regions of oscillations are relatively large, whereas in the third plane, viz. $[\text{H}_3\text{PO}_4]_0-k_0$, the oscillations are limited, especially at high k_0 values. This indicates that the concentration of phosphoric acid, or H_2PO_4^- ions, is a critical parameter in the permanganate oscillations. The narrow interval of H_3PO_4 concentrations, $1.25\text{--}1.5 \cdot 10^{-3} \text{ mol dm}^{-3}$, seems to be the optimum concentration of H_3PO_4 for the oscillations. The optimum H_3PO_4 concentration implies an optimum degree of the stabilization of $(\text{MnO}_2)_{\text{col}}$ colloids which, on the one hand, slowly undergo

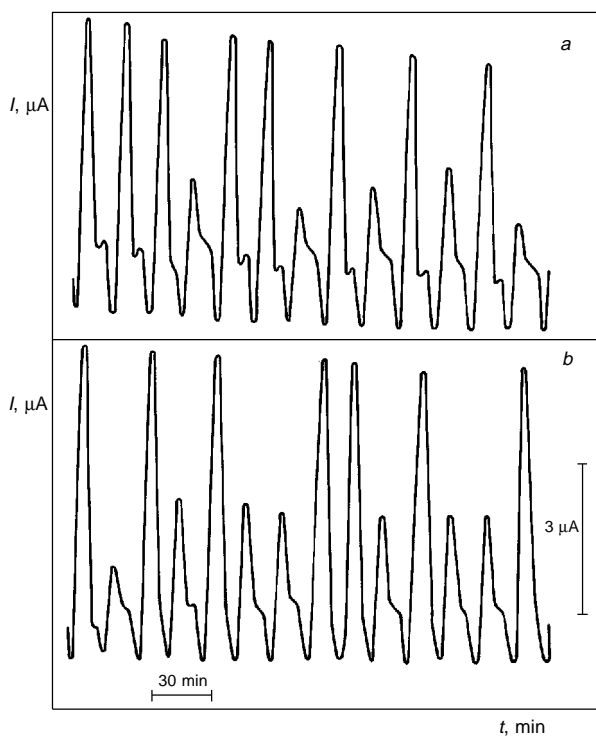
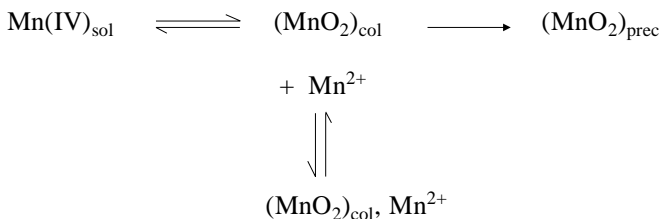


FIG. 5

Irregular complex oscillations of the MnO_4^- -dimedone- H_3PO_4 system at 20°C : $k_0 = 6.71 \cdot 10^{-3} \text{ s}^{-1}$, $[\text{KMnO}_4]_0 = 3 \cdot 10^{-5} \text{ mol dm}^{-3}$, $[\text{D}]_0 = 7 \cdot 10^{-5} \text{ mol dm}^{-3}$; $[\text{H}_3\text{PO}_4]_0$ (mol dm^{-3}): a $1.45 \cdot 10^{-3}$, b $1.65 \cdot 10^{-3}$

irreversible precipitation and, on the other hand, can form $\text{Mn(IV)}_{\text{sol}}$ species reversibly, but can also adsorb Mn^{2+} ions on their surfaces (see Scheme 1).

We suggest that the underlying mechanism of the oscillators under study consist in the alternation of two processes, viz. the autocatalytic reduction of MnO_4^- ions by a



SCHEME 1

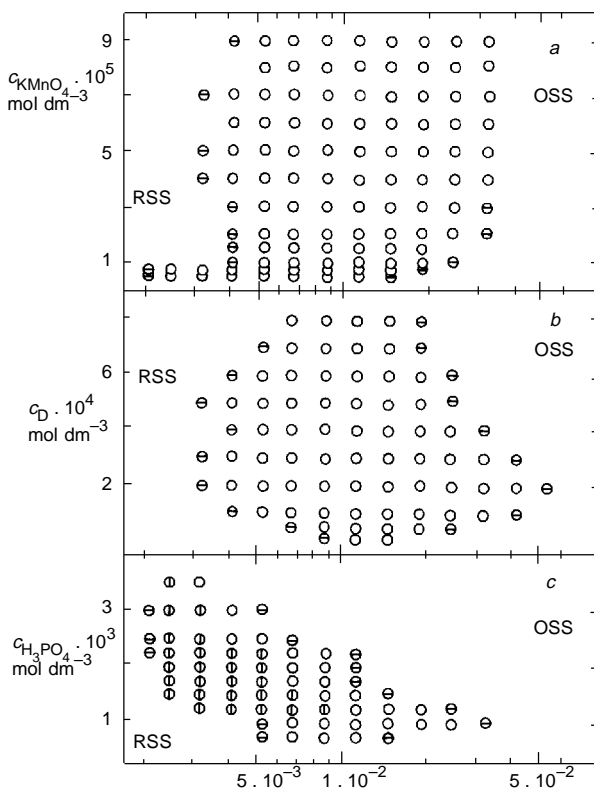


FIG. 6

Phase diagrams ($T = 20^\circ\text{C}$) in the planes: *a* $[\text{KMnO}_4]_0 - k_0$, *b* $[\text{D}]_0 - k_0$ and *c* $[\text{H}_3\text{PO}_4]_0 - k_0$; $[\text{D}]_0 = 8 \cdot 10^{-5} \text{ mol dm}^{-3}$, *a* $[\text{H}_3\text{PO}_4]_0 = 1 \cdot 10^{-3} \text{ mol dm}^{-3}$; *b* $[\text{KMnO}_4]_0 = 3 \cdot 10^{-5} \text{ mol dm}^{-3}$, $[\text{H}_3\text{PO}_4]_0 = 1 \cdot 10^{-3} \text{ mol dm}^{-3}$; *c* $[\text{KMnO}_4]_0 = 3 \cdot 10^{-5} \text{ mol dm}^{-3}$, $[\text{D}]_0 = 7 \cdot 10^{-5} \text{ mol dm}^{-3}$; \odot sustained oscillations, \circ damped oscillations, \ominus canard behaviour, OSS oxidized steady state, RSS reduced steady state

reducing substrate as a positive feedback, and autoinhibition due to the adsorption of Mn^{2+} on the surface of colloids $(MnO_2)_{col}$, as a negative feedback.

The complex reaction mechanism of permanganate oscillators in general remains to be elucidated and mathematically simulated. This will be the subject of a forthcoming project to be addressed by our laboratory.

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