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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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PHYSICAL CHEMISTRY

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PERIODIC OXIDATION REACTIONS IN THE LIQUID PHASE

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Chemical reactions that are periodic in time are of great interest from the standpoint of chemical kinetics and especially biology ([1,2]). However, up to the present time only periodic reactions occurring at a phase boundary or in the gas phase have been studied in relatively great detail ([3,4]). In the case of the liquid phase, only isolated reactions of this type have been described, whose mechanism has remained uninvestigated ([5–7]). We have succeeded in showing that there exists a whole group of periodic reactions analogous to the reaction first described by Belousov ([7]).

Fig. 1. Oscillations of light absorption ($\lambda \sim 3650$ Å, UFS-6 filter) caused by oscillations in the concentration of Ce^{4+} ions.

$KBrO_3$ oxidizes substances possessing an active methylene group ([8]) (malonic acid, acetoacetic ester, etc.) in the presence of a catalyst, namely ions of transition-valence metals: cerium or manganese. In this process, periodic oscillations occur in the concentrations of the oxidized and reduced forms of the catalyst. These oscillations can arise at definite ratios of the concentrations of the initial substances, which, however, can be varied over wide limits. The reaction proceeds in a strongly acidic medium. The frequency and form of the oscillations depend on the concentrations of the initial substances, the acidity of the medium, and the temperature. Measurements were carried out in cuvettes with a working volume of 3 cm^3 under continuous stirring. Light absorption was measured in the near ultraviolet and violet regions of the spectrum, which was determined mainly by the concentration of Ce^{4+} or Mn^{3+} ions, respectively. In this way, sufficiently stable relaxation oscillations were recorded (Fig. 1).

Fig. 2. Recording of the initial portion of the reaction (by light absorption). Initial concentrations (g-mole): [KBrO3] = 0.067; [C3H4O4] = 1; [Ce] = 0.001; t = 18°. Solvent 3N H2SO4

Figure 2: Fig. 2. Recording of the initial portion of the reaction (by light absorption). Initial concentrations (g-mole): [KBrO3] = 0.067; [C3H4O4] = 1; [Ce] = 0.001; t = 18°. Solvent 3N H2SO4

Under certain conditions, the stability of the frequency was $\sim 1\%$ or better, and the stability of the amplitude over several tens of periods was $\sim 1\%$.

The main details of the mechanism of this group of reactions can be described using as an example the most fully studied reactions of bromomalonic acid (BMA) and malonic acid (catalyst—cerium). In the case of BMA, the following main reactions occur in the system:

$$Ce^{3+} \xrightarrow{BrO_3^-} Ce^{4+}, \tag{1}$$

$$Ce^{4+} \xrightarrow{C_3H_3BrO_4} Ce^{3+} + Br^-. \tag{2}$$

Reaction (1) is autocatalytic, i.e., a reaction whose basis is the multiplication of active intermediate particles. These particles apparently are intermediate products of the reduction of BrO_3^- (for example, BrO_2^- and, possibly, free radicals). The Br^- liberated as a result of reaction (2), in small concentrations, is a strong competitive inhibitor of reaction (1), which has a chain character. Therefore, as long as Ce^{4+} is present in the system and, as a result of reaction (2), rele—

is Br^-, reaction (1) cannot begin. As a result, all the cerium passes into the trivalent state. After this, a rapid reaction (1) occurs, a large amount of Ce^{4+} is formed, and the cycle begins again.

Reactions (1) and (2) were each studied separately. In this case, the accumulation of Ce^{4+} in reaction (1) had an autocatalytic character, but the addition of Ce^{4+} from outside had no effect on the course of the reaction. Reaction (2) is first order with respect to $[Ce^{4+}]$. The formation of Br^- in reaction (2) was demonstrated by the precipitation of AgBr upon addition of $AgNO_3$. The inhibiting action of Br^- can be shown by the following experiment. If a small amount of Br^- is continuously introduced through a capillary into a system that is in an oscillatory regime,

Fig. 2. Recording of the initial portion of the reaction (by light absorption). Concentrations of the initial substances (g-mole): $[KBrO_3] = 0.067$; $[C_3H_4O_4] = 1$; $[Ce] = 0.001$; $t = 18°$. Solvent: $3N$ H_2SO_4.

then the oscillations are interrupted and all the cerium remains in the trivalent state. After the supply of Br^- is stopped, the oscillations resume. An analogous

result can be obtained by adding Ce^{4+} through a capillary; however, in such an experiment the parameters of the system change because of the substantial increase in the cerium concentration. It should be noted that during the oscillations free Br_2 could not be detected. In addition to color oscillations, oscillations of the potential with an amplitude of the order of 100 mV can be recorded in the system by means of a platinum electrode. This potential is analogous to the oxidation-reduction potential of an equilibrium system.

If malonic acid is used as the reducing agent, then in the initial portion of the reaction a stationary concentration $[Ce^{4+}]$ is established, which slowly changes with time (Fig. 2). This stationary state arises as a result of the simultaneous course of reaction (1) and the reaction:

$$Ce^{4+} \xrightarrow{C_3H_4O_4} Ce^{3+}. \qquad (2a)$$

In parallel, bromination of malonic acid occurs by the reduction products of BrO_3^-, which appear in the course of reaction (1), and BMA is formed. After some amount of BMA has accumulated, the system passes into an oscillatory regime, during which reactions (2) and (2a) proceed in parallel.

Oscillations under similar conditions were also obtained with the use of other reducing agents possessing an active methylene group, or compounds that readily form one upon oxidation (see Table 1). This group is readily brominated and is responsible for the occurrence of reactions of types (2) and (2a). The substances studied had different activities. For example, when oxaloacetic acid was used, oscillations could be obtained only by using relatively low concentrations of the reducing agent. In this case the oscillations rapidly died out. Some substances possessing an active methylene group, in particular acetylacetone or barbituric acid, do not give oscillations at all under similar conditions. On the other hand, if malic acid, which does not possess an active methylene group, is taken as the reducing agent, the reaction proceeds differently from that described above, and under certain conditions two-frequency oscillations can be obtained (Fig. 3). Malic acid in the course of this reac-

Table 1

No.	Reducing agent	Concentration, gram-mol. of reducing agent	Concentration, gram-mol. of $KBrO_3$	Catalyst (input concentration 0.001 gram-mol.)	Frequency, $Hz \cdot 10^{-2}$	Notes
1	Malonic acid-$COOH \cdot CH_2 \cdot COOH$	0.27	0.067	Ce	1.6	
1	Malonic acid-$COOH \cdot CH_2 \cdot COOH$	0.27	0.067	Mn	2.2	
2	Bromomalonic acid-$COOH \cdot CHBr \cdot COOH$	0.13	0.067	Ce	0.9	
2	Bromomalonic acid-$COOH \cdot CHBr \cdot COOH$	0.27	0.13	Mn	3.1	Solvent composed of 2.5 cm^3 of glacial acetic acid and 0.5 cm^3 of 3N H_2SO_4
3	Acetoacetic ester-$terCH_3CO \cdot CH_2COO \cdot C_2H_5$	0.26	0.067	Ce	6.7	
3	Acetoacetic ester-$terCH_3CO \cdot CH_2COO \cdot C_2H_5$	0.26	0.067	Mn	17	

No.	Reducing agent	Concentration, gram-mol. of reducing agent	Concentration, gram-mol. of $KBrO_3$	Catalyst (input concentration 0.001 gram-mol.)	Frequency, $Hz \cdot 10^{-2}$	Notes
4	Oxaloacetic acid- COOH· $COCH_2$· COOH	0.01	0.067	Ce	16	Oscillations rapidly die out
4	Oxaloacetic acid- COOH· $COCH_2$· COOH	0.02	0.067	Mn	9	
5	Malic acid- COOH· CHOH×× CH_2COOH	0.27	0.067	Ce	1.1	Frequency determined in the regime of single-frequency oscillations
5	Malic acid- COOH· CHOH×× CH_2COOH	0.27	0.067	Mn	3.3	

No.	Reducing agent	Concentration, gram-mol. of reducing agent	Concentration, gram-mol. of $KBrO_3$	Catalyst (input concentration 0.001 gram-mol.)	Frequency, $Hz \cdot 10^{-2}$	Notes
6	Acetonedicarboxylic acid- COOH· CH_2COCH_2××COOH	0.15	0.067	Ce	6	Acetonedicarboxylic acid was obtained from citric acid and was not dried. The concentration was determined approximately
6	Acetonedicarboxylic acid- COOH· CH_2COCH_2××COOH	0.12	0.067	Mn	5	
7	Citric acid- COOH· $CH_2C(OH)$××(COOH)· CH_2COOH	0.33	0.067	Ce	1.2	During the reaction a precipitate forms
7	Citric acid- COOH· $CH_2C(OH)$××(COOH)· CH_2COOH	0.27	0.067	Mn	0.8	

Note. All experiments were carried out in 3N H_2SO_4 at $t \sim 16^\circ$. In those cases where there was initially a transient process, the frequency was determined after

Fig. 3. Two-frequency oscillations when malic acid is used as the reducing agent (by light absorption)

Figure 3: Fig. 3. Two-frequency oscillations when malic acid is used as the reducing agent (by light absorption)

it had become established. Standard reagents were used. Because of the small working volume, the accuracy of determining the initial concentration is 10%.

apparently is converted into oxaloacetic acid. Thus, using different but similar-type reducing agents and two different catalysts with close oxidation-reduction potentials, in all cases we obtain a reaction in the course of which stable relaxation oscillations of the concentrations of intermediate products occur, owing to definite relationships in the kinetics of the individual stages of the reaction.

Considering the scheme presented above, we see that the oscillations arise as a result of the presence of an autocatalytic reaction, from whose products, as a result of subsequent reactions, its own inhibitor is produced. It should be noted that existing mathematical models of chemical oscillation generators are constructed from coupled autocatalytic or autoinhibitory reactions [9,10]. All these mathematical models use the equations of homogeneous chemical kinetics. However, for stable oscillations to exist it is necessary that the coefficients in these equations be constant, which corresponds to constant concentrations of the initial components or to their constant inflow. This requirement, in the opinion of some authors [3], is difficult to fulfill in a homogeneous phase, which is the reason why chemical oscillations are not observed there. But for the existence

Fig. 3. Two-frequency oscillations when malic acid is used as the reducing agent (by light absorption)

For stable oscillations it is sufficient that the concentrations of the initial substances change negligibly during the time of one oscillation, i.e., the system must be quasi-open. This requirement can be realized in a homogeneous catalytic system. In our case, a sufficient duration (several hundred periods) and stability of the oscillations can be ensured by the smallness of the catalyst concentration in comparison with the concentration of the initial substances (1 : 1000). This ensures a small consumption of substance per cycle. When the initial products are supplied from outside, i.e., in a truly open heterogeneous system, the oscillations can continue for an arbitrarily long time.

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Note: Figure translations are in progress. See original paper for figures.