

Influence of Low-Frequency Sonolysis on the Kinetics of Liquid-Phase Chemical Reactions Involving Associates

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Abstract: The influence of low-frequency sonolysis on the kinetics of liquid-phase bimolecular liquid-phase reactions was studied by mathematical modeling with due regard for the association of starting reagents into dimers and trimers. With increasing frequency and amplitude of low-frequency sonic waves (up to some critical value), we observed the disappearance of trimers and concomitant cessation of the reaction. This observation offers an additional tool for controlling reaction rate by the external action of low-frequency vibrations.

Keywords: Chemical reaction, Kinetics, Liquid medium, Reagent association, Low-frequency action.

1. INTRODUCTION

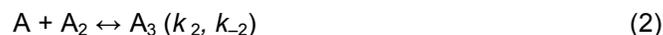
Previously, we have proposed [1] that some anomalies in the kinetics of bimolecular liquid-phase reactions can be explained by formation of the associates of starting reagents. This circumstance has to be taken into account in mathematical modeling oriented on optimization of most important processes in chemical engineering. Earlier, the effect of sonolysis on the reaction kinetics in liquids was explored mostly for high-frequency acoustic waves [2, 3]. Meanwhile, noticeable chemical effects were also reported for low-frequency (10–100 Hz) acoustic waves [4–6]. Deeper insight into the mechanism of this phenomenon can be reached via mathematical modeling of such reactions [1, 7, 8]. Presently, the theory for low-frequency sonolysis of liquid reactive mixtures is just at the first steps of its development [9, 10].

In this communication, we report on the effect of low-frequency sonolysis on the stability of liquid-phase bimolecular reactions with due regard for the association of starting reagents. With increasing frequency and amplitude of low-frequency sonic waves up to some critical value, we observed the disappearance of trimers and concomitant cessation of the reaction. This observation offers an additional tool for controlling reaction rate by the external action of low-frequency vibrations.

2. MATHEMATICAL MODEL

As shown recently [10] on an example of modelling bimolecular reactions yielding urethanes [11], the

reaction $A + B \rightarrow C$ can be described by dynamic equations with two degrees of freedom. Reagent A was assumed to form dimer A_2 and trimer A_3 by the following scheme:



where k_i and k_{-i} stand for the rate constants of direct (i) and reverse ($-i$) reactions.

Reagent B takes part in the reaction:



Product C is obtained in the reaction:



For frequency 1–100 Hz, the wavelength of acoustic wave does not exceed 15 m. The amplitude of pressure p_0 is independent of ν and is defined by intensity I of acoustic waves as $p \propto I^{0.5}$. The strain/compression waves induced in the solution by acoustic waves with frequency ν affect the rate constant $k(\nu)_{-i}$ for dissociation of the associates under the action of strain σ . According to [12], the latter can be written in the form:

$$k(\nu)_{-i} = k_{-0} \exp[(-E_{-i} + \gamma\sigma)/RT] \quad (i = 1, 2) \quad (6)$$

where γ is a structure-sensitive coefficient and $\sigma = p \sin(2\pi\nu t)$.

The kinetic equations for the system under consideration have the form:

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$$\begin{aligned} d[A_2]/dt &= k_1[A]^2 - k(v)_{-1}[A_2] - k_2[A][A_2] + k(v)_{-2}[A_3] - \\ & k_3[A][A_2][A_3] \quad (7) \\ d[A_3]/dt &= k_2[A][A_2] + k_3[A][A_2][A_3] - k(v)_{-2}[A_3] - \\ & k_4k_5[B]^2[A_3]\{k_{-4} + k_5[A_3]\}^{-1} \end{aligned}$$

Under simplifying assumptions that in (6) $T = \text{const}$ and $E_i = \text{const}$, system (7) can be rewritten in a form convenient for calculations:

$$\begin{aligned} dx/dt &= \mu - a_1 \exp[p \sin(2\pi vt)]x - ax + by - uxy \quad (8) \\ dy/dt &= ax - by + uxy - m y(g + y)^{-1} \end{aligned}$$

where $x = [A_2]$, $y = [A_3]$, $\mu = k_1[A]^2$, $a_1 = k_{-1}$, $a = k_2[A]$, $b = k_{-2}$, $u = k_3[A]$, $m = k_4[B]^2$, and $g = k_{-4} k_5^{-1}$.

We also assume that a change in $k(v)$ during compression can be neglected in view of low compressibility of liquids. Moreover, the associates can

be formed in case of some favorable mutual disposition of the reagents, which is infringed due to diffusion and formation of voids under the action of tension strain. With increasing separation between the reactive species, the reaction may transfer to a mode of diffusion control. Slow association at the stage of compression is known in the literature [4].

On the other side, at high v the monomers formed upon dissociation of associates have no enough time to quit the cage or resume a favorable mutual disposition of the reagents: so that the association at higher v proceeds faster. Since the diffusion, conformational transitions, and cage effect are neglected in our model, its predictions should be regarded just as qualitative ones.

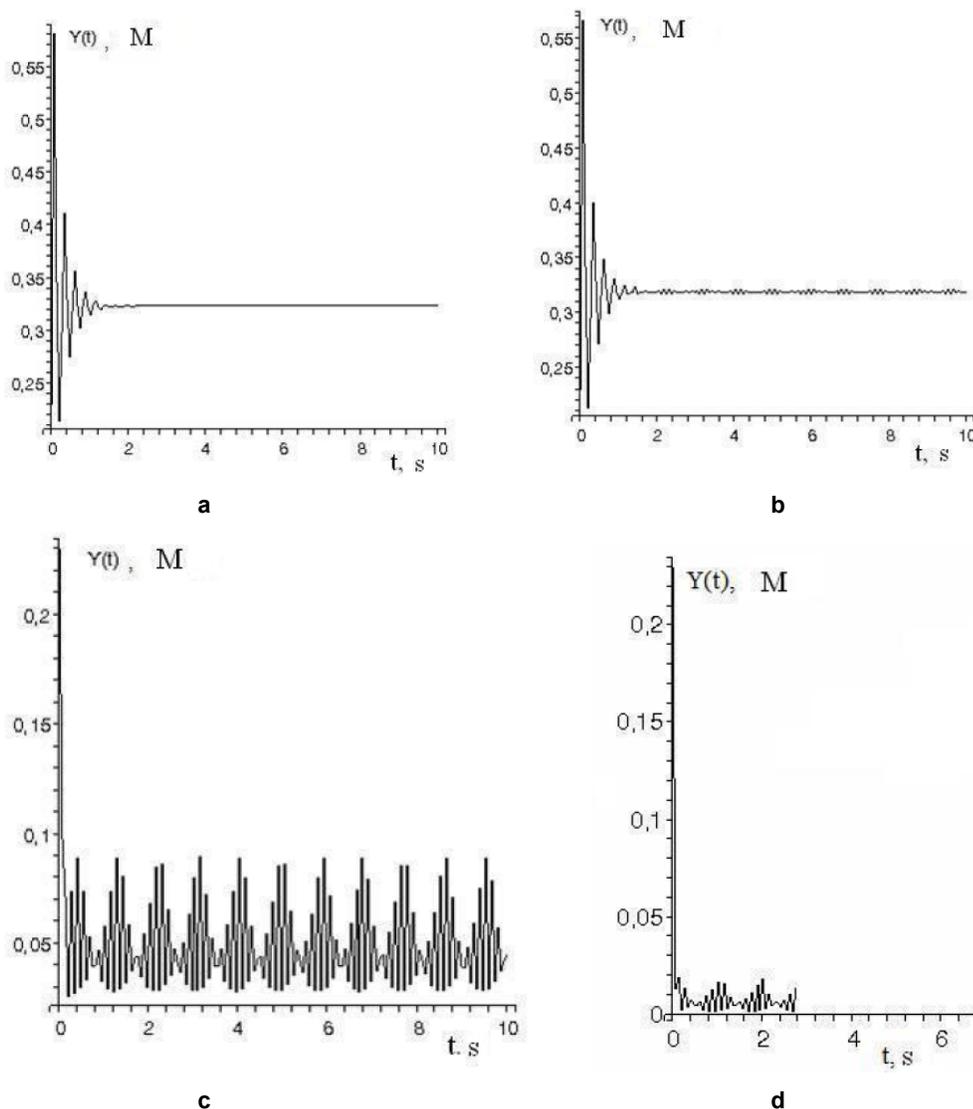


Figure 1: Variation in concentration $y = [A_3]$ with time t for frequency $\omega = 50.24 \text{ s}^{-1}$ and amplitude $p = 1$ (a), 5 (b), 10 (c), and 20 (d).

3. RESULTS AND DISCUSSION

In order to escape cumbersome calculations, we solved the problem for a situation when $[A] = [B] = \text{const}$, $[A_2]_0 = 1.8 \text{ M}$, and $[A_3]_0 = 0.23 \text{ M}$. In this case, the expression for rate w for formation of product C can be represented [11] as:

$$w = d[C]/dt = k_4 k_5 [B]^2 [A_3] \{k_{-4} + k_5 [A_3]\}^{-1} \quad (9)$$

Accordingly, the expression for effective rate constant (k_{eff}) acquires the form:

$$k_{\text{eff}} = k_4 k_5 \{k_{-4} + k_5 [A_3]\}^{-1} [A_3] [A]^{-1} [B].$$

We studied the behavior of associates upon variation in p and $\omega = 2\pi\nu$. Other system parameters were the same as in [9, 10]. Figure 1 presents the results obtained for trimer A_3 ; similar behavior exhibited the kinetic curves for A_2 and w .

In system (8), we varied all system parameters. Below we will discuss the results obtained for $\mu = 16.8 \text{ M s}^{-1}$ and $a_1 = 0.005 \text{ s}^{-1}$, $a = 0.5 \text{ M s}^{-1}$, $g = 1.6 \text{ M}$, $b = 1 \text{ c}^{-1}$, $u = 40 \text{ M}^{-2} \text{ s}^{-1}$, $m = 100 \text{ M s}^{-1}$, $x(0) = 1.8 \text{ M}$, and $y(0) = 0.23 \text{ M}$.

Trimer concentration $[A_3]$ is seen (Figure 1a) to be independent of t for p up to 5. At higher p , we observe some oscillations in $[A_3]$ (Figure 1b). At $p = 10$ (Figure 1c), the oscillations become asymmetric and self-swinging. Around $p = 20$, the yield of $[A_3]$ goes down to zero and hence to the completion of the reaction.

4. CONCLUSIONS

The above results suggest that sonolysis can be used as an additional tool for controlling the liquid-phase reactions involving the associates of starting reagents.

ACKNOWLEDGMENT

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