PROCEEDINGS OF THE YEREVAN STATE UNIVERSITY

Chemistry and Biology 2016, № 2, p. 17–22

Chemistry

STUDY OF INFLUENCE OF SOME ADDITIVES ON THE RATE OF CUMENE AUTOXIDATION: II. INFLUENCE OF UNSATURATED CYANO-LACTON AND DIMETHYL SULFOXIDE

N. M. BEYLERIAN [*], P. G. MINASYAN[**]

Chair of Organic Chemistry YSU, Armenia

The influence of 2-cyano-3,4,4-trimethyl-2-butene-4-olyd (unsaturated cyano-lactone, UCL) and DMSO on the rate of initiated with AIBN of cumene (CU) autoxidation in chlorobenzene solution by gasometric method is studied. It is established that in the presence of UCL (for reaction order n=0.6) the stationary reaction rate R_{st} can be described by empirical rate law. In the case of DMSO (n=0.5) a classical rate law of radical-chain reactions in the stationary regime is occurring. In both cases the reaction begins after some induction period, τ. With increasing of $[UCL]_0$ τ is decreasing up to 0, when $[UCL]_0 \geq 2 \cdot 10^{-3}\, M$. It is shown also that DMSO decreases R_{st}, which, probably, can be explained by DMSO and CU competition to react with $ROO^{\bullet}$ free radicals, which are being formed in the reaction propagation step.

Keywords: cumene autoxidation, radical reactions, unsaturated cyano-lacton, DMSO as antioxidator.

Introduction. Radical reactions play a very important role in human's vital activity. It concerns the manufacture of a great deal of chemical compounds, also the health of human life. The reveal of participation of free radicals in many kinds of chemical processes and the control of their activity is very important and is an actual problem. Nature solves this problem using materials, which have natural origin, for example vegetables and fruits containing vitamins. The antioxidant properties of some vitamins are very well established [1–3]. There are some interesting studies carried out in this field in Armenia too [4]. Naturally it is reasonable to make use of such materials and their influence study on model reactions to reveal their efficiency.

In [5] the influence of vitamins B_C and B_1 on kinetics of cumene (CU) autoxidation, which is chosen as a model radical-chain reaction, is studied. In the present paper experimental data concerning the influence of the cited 2-cyano-3,4,4-trimethyl-2-butene-4-olyd (unsaturated cyano-lactone, UCL) and DMSO on the rate of the above mentioned model reaction are presented and discussed. UCL and DMSO are not of natural origin, but they possess biologic activity. The expediency of their choice is discussed.

[*] E-mail: bnorayr@mail.ru [**]E-mail: parandzemminasyan@mail.ru

Experimental Part. To study above mentioned reactions gasometric method is used. The oxygen consumed during the reaction proceeding was determined by means of a manometer. The liquid height change (Δh) in the manometer was determined at the reaction run. It is expressed in $mm \cdot s^{-1}$. In all experiments the same manometer was used. The distilled CU was purified as follows: the mixture of CU with fresh portions of "chemically pure" H_2SO_4 was shaken several times until the added H_2SO_4 remained colourless. Then the CU was shaken with bidistilled water until the pH of the water became to the pH of the used water. The CU autoxidation was initiated with AIBN, which was twice recrystallised from ethanol solution.The reactions are carried out in chlorobenzene solution. C_6H_5Cl was "chemically pure" grade. The UCL is synthesized and purified at the Chair of Organic Chemistry of YSU. All experiments are carried out at 353 *K*.

Results and Discussion.

I. Kinetics of Initiated with AIBN–CU Autoxidation in Chlorobenzene Solution in the Presence of UCL. The use of UCL is well grounded. From its formula it follows that the molecule contains unsaturated lactone ring. Many organic compounds of natural origin, e.g. vitamin C, also contain such a ring [6].

It is well known that vitamin C is a very powerful antioxidant [6]. Recent works confirm this conclusion [7–9]. So, it is very probable that UCL also will reveal antioxidant properties. Preliminary studies have confirmed that conclusion. Methods of synthesizing and chemical properties of the UCL are described in [10–19].

Note that the cited UCL does not directly react with potassium persulfate, which is a powerful oxidant [14]. So, it is unprobable the direct bimolecular reaction between UCL and hydroperoxides (and peroxides), which may be formed during organic compounds autoxidation.

1. *R_{st} Dependence on $[CU]_0$.* The obtained kinetic data are presented in Fig. 1.

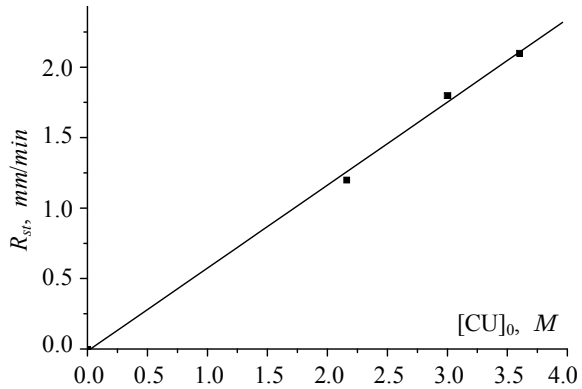


Fig. 1. R_{st} dependence on $[CU]_0$. $[AIBN]_0=5\cdot10^{-3}$ *M*, $[UCL]_0= 5\cdot10^{-3}$ *M*.

From Fig. 1 it follows that $R_{st} \sim [CU]_0$. The kinetic curves show that reaction begins after some induction period τ, which does not depend on $[CU]_0$ and has an experimental value $\tau = 11 \pm 1$ *min*.

2. *R_{st} Dependence on $[AIBN]_0$.* $[CU]_0=3.6$ *M*, $[UCL]_0= 5\cdot10^{-3}$ *M*.

Table 1

$[AIBN]_0\cdot10^{-3}$, *M*	2.5	5.0	7.5
R_{st}, *mm/min*	1.6	2.3	3.0

From the presented data it follows that $R_{st} \sim [\mathrm{AIBN}]_0^n$, where $n \cong 0.6$ ($0.5 < n < 0.7$). So,

$$R_{st} = k[\mathrm{AIBN}]^n [\mathrm{CU}]_0. \quad (1)$$

The conclusion is: UCL practically does not act on the classical mechanism of radical-chain reactions concerning the autoxidation of hydrocarbons (the reaction up to the beginning of chain branching is not driven).

2. *R_{st} Dependence on $[UCL]_0$.*

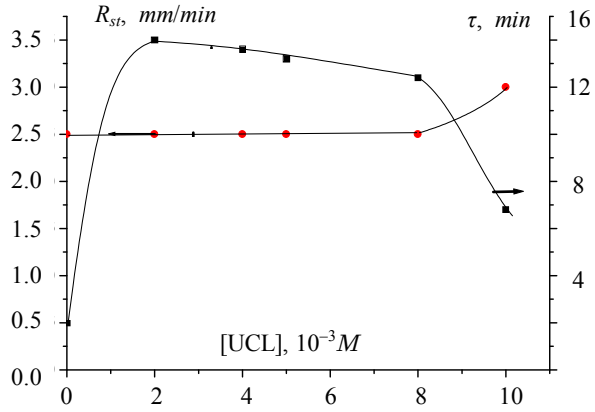


Fig. 2. R_{st} dependence on $[UCL]_0$.
$[AIBN]_0=5\cdot10^{-3}$ *M*,
$[CU]_0$= 3.6 *M*.

From data presented in Fig. 2 it follows that:

(i) UCL has antioxidant activity;

(ii) $\tau = f([UCL]_0)$ is not linear;

(iii) at $[UCL]_0 \geq 1\cdot10^{-2}$ *M* τ decreases and R_{st} increases. Probably autoxidation of UCL begins as a usual organic compound parallel to CU. This results in τ decrease and R_{st} increases.

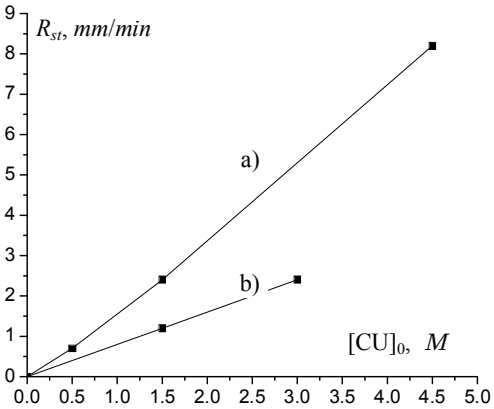


Fig. 3. R_{st} dependence on $[CU]_0$.
$[AIBN]_0=1\cdot10^{-3}$ *M*.
a) [DMSO] = 0;
b) [DMSO]=1.5 *M*.

II. Kinetics of Initiated with AIBN–CU Autoxidation in Chlorobenzene Solution in the Presence of DMSO. DMSO with the title "dimexidium" forms part in some drugs, parfums [11]. It favors drugs penetration through membrane [15]. Some supplementary information concerning DMSO biologic properties are presented in [16]. Dialkyl sulfoxides, including DMSO, are sulfurcontaining

inhibitors for radical reactions [17]. Making use of ESR method DMSO influence on the rate of catalyzed by Ti(III) and Fe(II) H_2O_2 decomposition is studied [18]. It is shown that the reaction

$$HO^{\bullet} + Me_2SO \rightarrow Me_2S(O^{\bullet})OH \qquad (2)$$

occurs very fast. This reaction theoretically is discussed in [15]. DMSO has applications in cell biology, also as cryoprotective [16, 21].

From this brief review it follows that DMSO has applications in life and it is very reactive with respect to free radicals as $HO^{\bullet}$.

Taking into consideration the presented literature data DMSO influence on the kinetics of CU autoxidation is studied.

All reactions are carried out in chlorobenzene solution.

1. *R_{st} Dependence on $[CU]_0$ in Absence and in Presence of DMSO.*

Using the obtained experimental data R_{st} dependence on $[CU]_0$ in absence and in presence of DMSO is drawn up (Fig. 3).

It follows that:

(i) DMSO influence is noticeable at $[DMSO]_0 > 1$ *M*;

(ii) even in DMSO presence $[R_{st}]_0 \sim [CU]_0$.

Note that in DMSO presence the studied reactions are beginning with some delay.

2. *R_{st} Dependence on $[AIBN]_0$* . The obtained kinetic data are brought in Tab. 2.

Table 2

R_{st} dependence on $[AIBN]_0$. $[CU]_0$=3.0 M, $[DNSO]_0$=1.5 M

$[AIBN]_0^{1/2} \cdot 10^2$, $M^{1/2}$	5.0	7.1	10.0
R_{st}, *mm/min*	1.2	1.6	2.3

It is easy to show that $[R_{st}]_0 \sim [AIBN]_0^{1/2}$. So,

$$R_{st} = k[AIBN]^{1/2}[CU]. \qquad (3)$$

This equation is identical with the classic rate law of radical-chain reactions.

3. *R_{st} Dependence on $[DMSO]_0$.* The obtained kinetic data are presented in Tab. 3.

Table 3

R_{st} dependence on $[DNSO]_0$. $[CU]_0$=3.0 M, $[AIBN]_0 = 1 \cdot 10^{-3}$ M

$[DMSO]_0$, *M*	0	0.60	1.13	1.50	2.0
R_{st}, *mm/min*	3.3	3.0	2.8	2.3	0.62

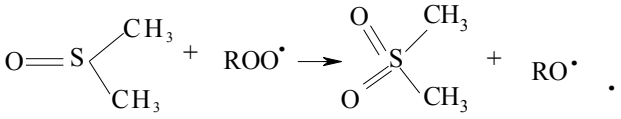
As was mentioned at $[DMSO]_0 > 1.0$ *M* the reaction begins with some delay. For example, at $[DMSO]_0$=1.5 *M*, $[AIBN]_0 = 1 \cdot 10^{-3}$ *M*, $[CU]_0$=3.0 *M*, τ=26 *min*.

From Tab. 3 it follows, that DMSO acts not only on the reaction initiation rate, but also on the R_{st}. With increase of $[DMSO]_0$ R_{st} decreases, its action is noticeable at $[DMSO]_0 \geq 2.0$ *M* .

We assume that it may be the result of DMSO reaction with $ROO^{\bullet}$ radical, which takes place in the reaction propagation stage:

$$\left.\begin{array}{l} R^{\bullet} + O_2 \rightarrow RO^{\bullet} \\ RO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \end{array}\right\}, \qquad (4)$$
$$ROOH \rightarrow RO^{\bullet} + HO^{\bullet},$$

here $R^{\bullet} = C_6H_5 - \overset{\bullet}{C}(CH_3)_2$,



$$(RH, DMSO) \xrightarrow{R^{\bullet}_X} \text{molecular products}.$$

$R^{\bullet}_X$ is any radical, which is in the reaction medium. This Scheme shows that DMSO competes with CU (RH) to react with free radicals $ROO^{\bullet}$.

It must be noted that only $R^{\bullet}$ free radical reacts with O_2. The decrease of O_2 consumption rate results in R_{st} decrease, because it is being determined by measuring the quantity of expended O_2.

Conclusion.

1. The unsaturated cyano lactone is a better inhibitor than DMSO. The function $\tau = f([UCL]_0)$ is not linear.

2. At $[UCL]_0 \geq 1 \cdot 10^{-2}$ *M* the reaction induction period decreases, but at the same time the cumene autoxidation rate increases. It is assumed that occurs parallel to cumene UCL autoxidation.

3. DMSO is comparatively a weak inhibitor for radical-chain reactions. Its inhibitory effect is noticeable at $[DMSO]_0 > 1$ *M*. Simultaneously it decreases the over-all rate of initiated cumene autoxidation rate. It is conditioned by the possibility of DMSO reaction with $ROO^{\bullet}$ and $RO^{\bullet}$ free radicals.

The authors express their thanks to E.R. Saroukhanian, who has taken part in the fulfillment of experiments.

Received 03.05.2016

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