Thermal stability of *cis* isomer of 3-methyl-2-penten-4-yn-1-ol

[a]A. ŠKODA, [b]L. VOJČEK, [b]D. MRAVEC, and [b]J. ILAVSKÝ

[a]*Slovakofarma, CS-920 27 Hlohovec*

[b]*Department of Organic Technology, Faculty of Chemical Technology,*
Slovak Technical University, CS-812 37 Bratislava

The products and kinetics of thermal conversion of *cis* isomer of 3-
-methyl-2-penten-4-yn-1-ol in the range of 117 to 136 °C have been studied.
The inhibition effects of hydroquinone, Ionol, and Tetrol at the conditions
followed were shown to be the same.

Изучены продукты и кинетика термической конверсии *цис*-изомера
3-метил-2-пентен-4-ин-1-ола в интервале температур 117—136 °C. По-
казано, что гидрохинон, Ионол и Тетрол оказывают одинаковое инги-
бирующее влияние в данных условиях.

In the latest years, considerable attention has been paid to acetylene alcohols,
mainly due to their applicability in pharmaceutical and food industry. For
example, 3-methyl-2-penten-4-yn-1-ol (*I*) is an intermediate in the synthesis of
vitamin A (retinyl acetate) [1—4]. Owing to unsaturated nature, this compound
easily polymerizes, especially in the atmosphere of free oxygen and under
thermal stress [5, 6] (*e.g.* in distillation purification). This fact cannot be neglec-
ted with regard to high price of this compound. The authors in [5] tested the
inhibitors of polymerization used in industry for stabilization of *I* in the atmo-
sphere of oxygen at temperatures up to 70 °C. Of these, the most effective was
proved hydroquinone.

In the present work the thermal stability of *I* was followed in the temperature
range of 117 to 136 °C and, contrary to the previous work [5], in the atmosphere
of an inert gas. The aim was to find out the thermal stability of *I*, mainly from
the point of view of thermal stress required at technological conditions, espe-
cially in its rectification purification. The effects of hydroquinone, 2,6-di-*tert*-bu-
tyl-4-methylphenol (Ionol), and 3,3,3′,3′-tetramethyl-1,1′-spirobiindan-5,6,5′,6′-
-tetrol (Tetrol) as stabilizers of *I* were compared from the aspect of their possible
technological utilization.

Experimental

3-Methyl-2-penten-4-yn-1-ol (*cis* isomer), minimum 98 % purity (Slovakofarma, Hlo-
hovec), heptanol, anal. grade, tetrachloromethane, pure grade, hydroquinone, pure

grade (all Lachema, Brno), Ionol, Tetrol (J. Dimitrov Chemical Works, Bratislava), and helium, anal. grade (BASF, GFR) were used.

The content of *I* in the samples was determined by gas chromatography. Tetrachloromethane was used as the solvent and heptanol as the internal standard. Chrom-5 chromatograph with flame-ionization detector and glass column (3 m × 4 mm) of 10 % Carbowax 20 M on Chromaton N AW DMCS (0.125—0.160 mm) were used; working temperature 130 °C, injection port temperature 140 °C, and detector temperature 160 °C. The flow rate of nitrogen was 50 cm^3 min^{-1}, of hydrogen 26 cm^3 min^{-1}, and of air 500 cm^3 min^{-1} The average error of determination was ± 1.5 %. HPLC comparative measurements were performed on a column (250 mm × 4 mm) of Partisil 10 m, Silica (Pye—Unicam) using cyclohexane—2-propanol ($\varphi_r = 9:1$) as the mobile phase; flow rate 1.0 cm^3 min^{-1} Detection was provided with a UV detector at $\lambda = 222$ nm. The method of external standard was applied. The results obtained were in the range of accuracy of determination.

DTA was performed on a Q-1500 Derivatograph (MOM, Budapest) in the temperature interval of 20 to 600 °C.

Working procedure

Into 20 cm^3 glass ampoules splashed with helium *I* was added without and/or with the inhibitor (1.00 mass %). The ampoules after sealing were put into the thermostat tempered to the respective temperature. The ampoules were withdrawn from the thermostat at time intervals, cooled down rapidly to 5 °C and the reaction mixtures were analyzed by gas chromatography. The compound *II* used for measurement was isolated from the reaction mixture of thermal conversion of *I* by dissolving the reaction mixture in tetrachloromethane and cooling the solution to *ca.* 5 °C to give the precipitate of *II* which was filtered in an inert atmosphere. The filtration cake was washed with tetrachloromethane and dried under reduced pressure.

Results and discussion

The effect of temperature of 117 to 136 °C on conversion of *I* was investigated. All experiments were carried out within 300 min in the atmosphere of helium.

The conversion of *I* without addition of the inhibitor was followed in the first series of experiments. Time dependences of conversion degree of *I* at the temperatures followed are presented in Fig. 1. Further information about the course of thermal reaction of *I* was obtained by evaluation of DTA records of *I* and of the polymerization product *II*. On the DTA record of *I* a significant exothermal reaction can be observed at 117 °C and an endothermal change at 234 °C which is observed also on the DTA record of *II*. It concerns probably the state conversion of the component *II*.

Fig. 1. Time dependence of conversion degree of *I* at the temperatures followed without inhibitor (○ 120 °C, □ 128 °C, △ 136 °C).
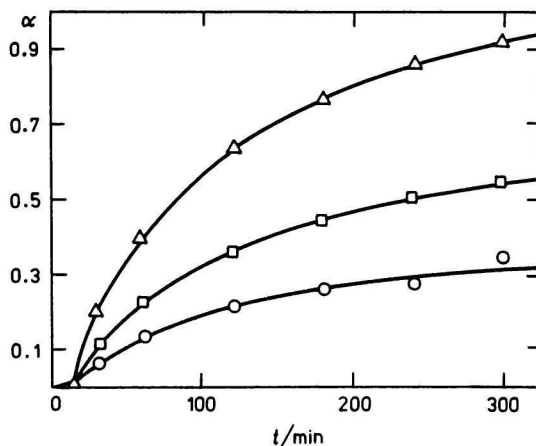
The inhibitory effects of hydroquinone, Ionol, and Tetrol on thermal conversion of *I* were followed in the atmosphere of an inert gas. The experiments were carried out at 136 °C which is the highest temperature achieved during rectification in the distillation device. The results are presented in Fig. 2.

Fig. 2. Time dependence of conversion degree of *I* at 136 °C with addition of 1 mass % of inhibitor (× without inhibitor, △ hydroquinone, ○ Ionol, □ Tetrol).
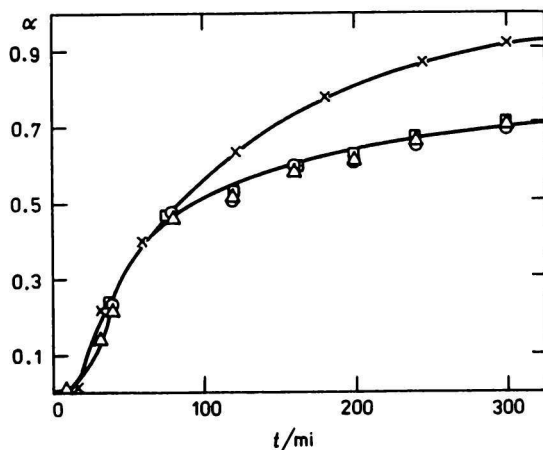
It was shown that the inhibitors tested exhibited practically the same effect. In accordance with the knowledge [5] about the formation and effects of peroxy radicals on the conversion of *I* (the formation of which was not prevented in preparation of *I* for experiments) it can be assumed that the effects of the inhibitors used lay mainly in neutralization of peroxy radicals present in *I*. Therefore, the further experiments were conducted in the presence of hydroquinone.

The time dependences of conversion degree of I at distinct temperatures in the range of 117 to 136 °C are illustrated in Fig. 3. These dependences show a significant induction period.
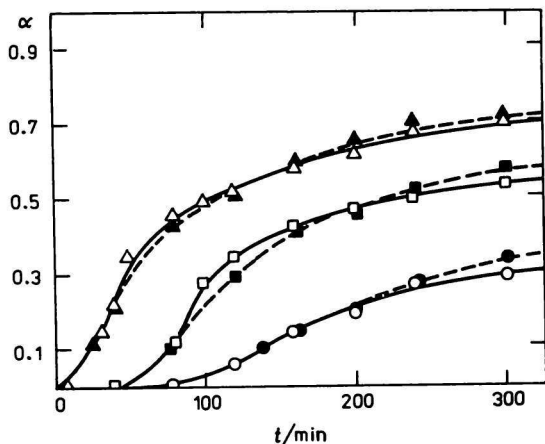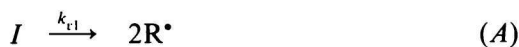

Fig. 3. Time dependence of conversion degree of I at the temperatures followed with addition of 1 mass % of hydroquinone into the reaction mixture. Comparison of experimental and calculated data.
○ Experimental values (117 °C),
● calculated values (117 °C).
□ Experimental values (131 °C),
■ calculated values (131 °C).
△ Experimental values (136 °C),
▲ calculated values (136 °C).

In evaluation of experimental results we looked for a rate equation which suited best the experimental results. A model of the reaction scheme corresponding to the conception of radical mechanism was used

$$ I \xrightarrow{k_{v1}} 2R^{\bullet} \qquad (A) $$

$$ I + R^{\bullet} \xrightarrow{k_{v2}} R'^{\bullet} \qquad (B) $$

$$ R^{\bullet} + R'^{\bullet} \xrightarrow{k_{v3}} II \qquad (C) $$

By action of heat I decomposes to two radicals $R^{\bullet}$ which recombine with a further molecule of I. At termination a neutral molecule II is formed. Using approximation of stabilized reaction rates of initiation (A) and termination (C) and also approximation of low concentration of active intermediate [7], for the rate of concentration change of I the following rate equation can be derived

$$ \frac{\mathrm{d}c_I}{\mathrm{d}t} = -k_{v1}c_I - k_{v2}k_{v1}^{1/2}k_{v3}^{-1/2}c_I^{3/2} \qquad (1) $$

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which is simplified by substitution

$$k = k_{v2} k_{v1}^{1/2} k_{v3}^{-1/2} \tag{2}$$

to

$$\frac{\mathrm{d}c_I}{\mathrm{d}t} = -k_{v1} c_I - k c_I^{3/2} \tag{3}$$

The constants k_{v1} and k in eqn (3) were calculated by numerical solution (Chebyshevov method) of this differential equation for the experimental results of time dependence of the conversion degree of I presented in Fig. 3. An Atari 800 XL microcomputer with a standard program was used. The calculated values (Table 1) represent arithmetic means of the constants calculated for two parallel sets of experimental results. Used were the values of constants where the relative average error of determination was lower than 5 %.

Table 1

Calculated values of reaction rate constants in dependence on temperature

θ °C	$k_{v1} \cdot 10^5$ s^{-1}	$k \cdot 10^8$ $s^{-1} mol^{-0.5} m^{1.5}$
117	1.5	1.92
127	4.7	3.97
131	9.3	5.35
136	17.3	7.15

The suitability of the suggested reaction scheme is evident from coincidence of the experimental values and the values calculated after eqn (3) (Fig. 3).

It was shown that at temperature conditions corresponding to technological conditions required in production and treatment of I, mainly in rectification, it is advisable to work in the presence of hydroquinone. In evaluation of kinetic measurements the effect of hydroquinone was not included into the reaction scheme. Assumed was only its function in removal of peroxy radicals contained in I.

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