Russian Journal of Organic Chemistry, Vol. 39, No. 1, 2003, pp. 29–32. Translated from Zhurnal Organicheskoi Khimii, Vol. 39, No. 1, 2003, pp. 41–43.
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Effect of the Reaction Products on the Rate of Oxidation of Crotonaldehyde

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Received February 27, 2002

Abstract—Study of the oxidation of crotonaldehyde revealed an appreciable inhibitory effect of the products on the process. Analysis of the kinetic data obtained over a wide range of reaction conditions (c_0 1.5–3.3 M, p_{O_2} 1–16 atm, T 293–309 K) showed that the overall oxidation process (with account taken of the inhibitory effect of the products) is described by the equation: $W_{CA} = k^*_{ap}\, c_{CA}\, (p_{O_2})^{0.6}\, (1 + 0.17\,\Delta c^{\tau}_{CA})^{-1}$, where k^*_{ap} is the apparent rate constant, and Δc^{τ}_{CA} is the decrease of the aldehyde concentration by a moment τ.

Crotonic acid and its esters are used in the preparation of copolymers for various applications (specialty rubbers, latexes, adhesives, plastics, modifying agents, etc.). Some crotonic acid esters are biologically active compounds which possess insecticide, ascaricide, and herbicide properties.

The simplest procedure for the preparation of crotonic acid is based on oxidation of crotonaldehyde with molecular oxygen under atmospheric pressure. The most appropriate medium for the oxidation is ethyl acetate [1]. The oxidation of crotonaldehyde in ethyl acetate was studied in detail in [2–4]. It was shown that the efficiency of crotonaldehyde oxidation can be increased to a considerable extent by raising the oxygen pressure to a certain value ($p^{\lim}_{O_2}$). This limiting oxygen pressure linearly increases as the temperature rises. Kinetic equations were found which satisfactorily describe the kinetics of oxidation of crotonaldehyde with molecular oxygen over a wide range of temperature (T 286–333 K), concentration (c_0 1.2–7.6 M), and pressure (p_{O_2} 0.21–16 atm) conditions [Eq. (1)]:

$$W_{CA} = k^{CA}_{ap}\, c_{CA}\, (p_{O_2})^{0.6}. \qquad (1)$$

However, Eq. (1) does not take into account possible effect of products which accumulate during the oxidation process. In order to estimate this effect, the kinetic dependences like $c_{CA} = f(\tau)$ were converted into $W_{CA} = \varphi(\tau)$ by numerical differentiation. As a result, it became possible to calculate the apparent reaction rate not only in the initial period (when the reaction mixture still contains no oxidation products) but also at any stage of the process. The data obtained are summarized in table. It is seen that the apparent rate constant for oxidation of crotonaldehyde notably decreases as the reaction progresses. When the conversion of crotonaldehyde attains 50%, k_{ap} decreases by about 10–12%. Thus, although Eq. (1) describes the overall kinetics of the reaction under study with an accuracy sufficient for practical purposes, it does not reflect all fine details of this complicated multistep process. Decrease in the apparent rate constant of crotonaldehyde oxidation may be attributed to inhibitory effect of some reaction products, which is not taken into consideration by Eq. (1). Insofar as the inhibitory effect increases as the concentration of crotonaldehyde decreases, just the latter parameter can be used to interrelate with the former. Then, the kinetic equation for consumption of crotonaldehyde during the oxidation process may be written as

$$W_{CA} = k^*_{ap}\, c_{CA}\, (p_{O_2})^{0.6}\, (1 + k_i\, \Delta c^{\tau}_{CA})^{-1}. \qquad (2)$$

Here, k_i is a constant which takes into account inhibitory effect of the oxidation products, and Δc^{τ}_{CA} is the decrease of the crotonaldehyde concentration by a moment τ from the reaction onset. When Δc^{τ}_{CA} tends to zero, Eq. (2) is transformed into Eq. (1).

Let us denote the rate $k^*_{ap}\, c_{CA}\, (p_{O_2})^{0.6}$ (which does not take into account the inhibitory effect of oxidation product) as W^{d}_{CA} (estimated rate). Then, Eq. (2) is transformed into linear Eq. (3):

$$W^{d}_{CA} = W_{CA} + W_{CA}\, k_i\, \Delta c^{\tau}_{CA}$$

and

$$(W^{d}_{CA} - W_{CA})/W_{CA} = k_i\, \Delta c^{\tau}_{CA}. \qquad (3)$$

Using Eq. (3), the value of k_i may be determined by the graphical method. Figures 1 and 2 show the plots of $(W^{d}_{CA} - W_{CA})/W_{CA}$ versus Δc^{τ}_{CA}. These plots are linear throughout a wide range of temperature and crotonaldehyde concentration. The straight lines are characterized by similar slopes equal to 0.17±0.03. Hence the overall kinetics of crotonaldehyde oxidation is described by Eq. (4).

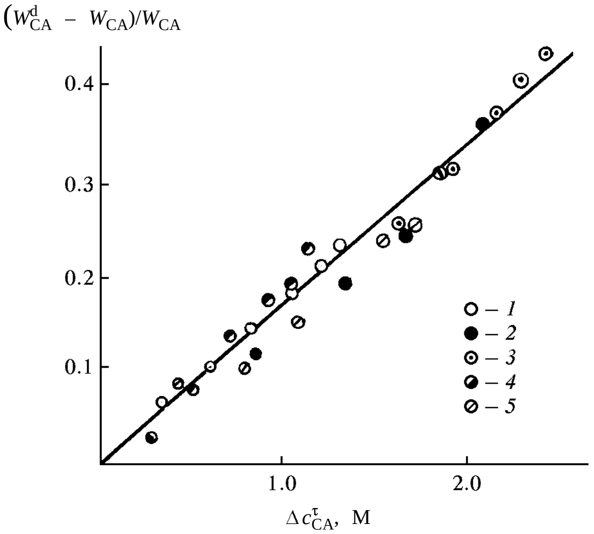

Fig. 1. Inhibitory effect of the products on the oxidation of crotonaldehyde at (*1*, *2*, *3*) 309 and (*4*, *5*) 300 K; c^{0}_{CA} = 2.46 M; p_{O_2}, atm: (*1*, *4*) 1, (*2*) 4, (*3*) 7, (*5*) 3.

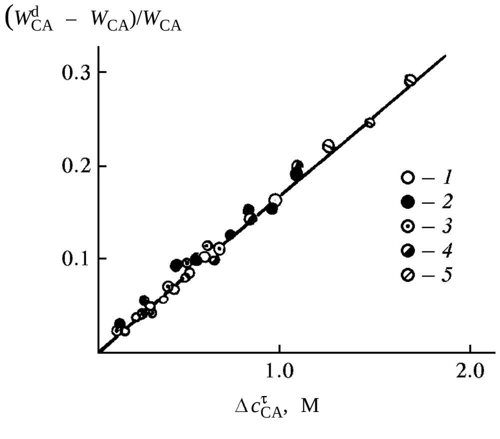

Fig. 2. Inhibitory effect of the products on the oxidation of crotonaldehyde at (*1*, *2*) 293 and (*3*, *4*, *5*) 295 K: (*1*) p_{O_2} = 1 atm, c^{0}_{CA} = 2.46 M; (*2*, *4*) p_{O_2} = 2 atm, c^{0}_{CA} = 2.46 M; (*3*) p_{O_2} = 2 atm, c^{0}_{CA} = 1.5 M; (*5*) p_{O_2} = 2 atm, c^{0}_{CA} = 3.69 M.

$$W_{CA} = k^{*}_{ap}\, c_{CA}\, (p_{O_2})^{0.6}\, (1 + 0.17\Delta c^{\tau}_{CA})^{-1}. \qquad (4)$$

Using Eq. (4), we can calculate the apparent rate constant k^{*}_{ap} with account taken of inhibitory effect of the reaction products:

$$k^{*}_{ap} = W_{CA}(1 + 0.17\Delta c^{\tau}_{CA})(c_{CA})^{-1}(p_{O_2})^{-0.4}$$
$$= k^{CA}_{ap}(1 + 0.17\Delta c^{\tau}_{CA}).$$

The data given in table indicate that k^{*}_{ap} almost does not change during the process. This means that Eq. (4) sufficiently reliably reflects inhibitory effect of the products and properly describes the overal kinetics of the crotonaldehyde oxidation process. Analogous analysis of the kinetics of formation of the major crotonaldehyde oxidation products, crotonic and peroxycrotonic acids, showed that the inhibition constant of these reactions has a similar value.

EXPERIMENTAL

A 70-ml stainless steel reactor was charged with 45 ml of a solution of crotonaldehyde in ethyl acetate. The reactor was connected to a gas-supplying system, hermetically sealed, purged three times with argon, and an argon pressure of 3 atm was set. The reactor was placed in a water bath equipped with a temperature-control unit. The temperature was measured using a thermocouple and was recorded with the aid of a KSP-4 potentiometer. When the reactor attained a required temperature, excess argon pressure was released, and oxygen was bubbled through the solution at a flow rate of 3.5 l/h to a specified pressure. The mixture was stirred with a magnetic stirrer. Preliminary experiments showed that a speed of stirring of 1200 rpm is sufficient for the process to occur in the kinetic mode.

The reaction mixture was analyzed by chemical and cromatographic methods, as well as by IR spectroscopy [3]. Apart from the major oxidation products, crotonic and peroxycrotonic acids, the mixture contained propionaldehyde, formic and propionic acids, propenyl formate, and epoxypropyl formate. The overall yield of the minor products did not exceed 15% (on the reacted crotonaldehyde). It was difficult to study the kinetics of formation of minor products because of their low concentration. Therefore, we examined only the overall kinetics of consumption of crotonaldehyde and formation of crotonic and peroxycrotonic acids.

The experimental kinetic dependences $c_i = f(\tau)$ were approximated by the Chebyshev orthogonal

Kinetics of oxidation of crotonaldehyde

τ, min	c_{CA}, M	$W_{\mathrm{CA}} \times 10^2$, mol l^{-1} min^{-1}	$k_{\mathrm{ap}}^{\mathrm{CA}} \times 10^2$	$W_{\mathrm{CA}}^{\mathrm{d}} \times 10^2$, mol l^{-1} min^{-1}	$k_{\mathrm{ap}}^{*} \times 10^2$
T = 309 K, p_{O_2} = 1 atm					
0	2.46	1.57	0.64	1.57	0.64
30	2.10	1.26	0.60	1.34	0.64
60	1.84	1.07	0.58	1.18	0.64
90	1.62	0.91	0.56	1.04	0.64
120	1.42	0.77	0.54	0.91	0.63
150	1.26	0.67	0.54	0.81	0.65
180	1.14	0.59	0.53	0.73	0.65
T = 309 K, p_{O_2} = 7 atm					
0	2.46	4.78	0.60	4.78	0.60
30	1.40	2.58	0.57	2.70	0.65
60	0.84	1.29	0.48	1.62	0.61
90	0.55	0.81	0.46	1.06	0.61
120	0.32	0.45	0.44	0.62	0.60
150	0.16	0.22	0.45	0.31	0.63
180	0.06	0.08	0.42	0.12	0.60
T = 300 K, p_{O_2} = 3 atm					
0	2.46	1.86	0.39	1.86	0.39
30	2.00	1.39	0.36	1.51	0.39
60	1.64	1.13	0.36	1.24	0.41
90	1.35	0.89	0.34	1.02	0.40
120	1.10	0.73	0.36	0.83	0.43
150	0.90	0.55	0.32	0.68	0.40
180	0.76	0.46	0.31	0.57	0.40
210	0.62	0.36	0.32	0.47	0.42
T = 295 K, p_{O_2} = 2 atm					
0	1.50	0.52	0.23	0.52	0.23
60	1.21	0.40	0.22	0.42	0.23
120	0.99	0.32	0.21	0.35	0.23
180	0.83	0.26	0.20	0.29	0.22
0	2.46	0.93	0.25	0.93	0.25
60	2.00	0.70	0.23	0.76	0.25
120	1.63	0.54	0.22	0.62	0.25
180	1.38	0.44	0.21	0.52	0.25
0	3.69	1.47	0.26	1.47	0.26
60	3.30	1.05	0.23	1.18	0.26
120	2.48	0.80	0.21	0.98	0.25
180	2.06	0.63	0.20	0.81	0.25
T = 293 K, p_{O_2} = 2 atm					
0	2.46	0.66	0.18	0.66	0.18
60	2.19	0.56	0.17	0.59	0.18
120	1.89	0.46	0.16	0.51	0.18
180	1.51	0.35	0.15	0.41	0.18
210	1.38	0.31	0.15	0.37	0.17

polynomial, and numerical differentiation of the latter gave analytical time dependence of the reaction rate (W_i, mol l^{-1} min^{-1}): $W_i = \varphi(\tau)$, where $\varphi(\tau) = f'(\tau)$.

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