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Role of Peroxy Compounds in Oxidation of Crotonaldehyde with Molecular Oxygen

O. E. Fedevich, S. S. Levush, E. V. Fedevich, and Yu. V. Kit

L'vivs'ka Politekhnika National University, Lviv, Ukraine

Lviv State Agricultural University, Lviv, Ukraine

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Abstract—Oxidation of crotonaldehyde with molecular oxygen and the role of percrotonic acid accumulating in the process were studied.

Crotonic acid (CAc) and its derivatives are used as comonomers in production of rubbers, latexes, adhesives, and plastics. Some crotonic acid esters exhibit insecticidal or herbicidal properties.

The main synthetic route to CAc is oxidation of crotonaldehyde (CAl). In oxidation of CAl with molecular oxygen at atmospheric [1, 2] or elevated [3] pressure, peroxy compounds accumulate in concentrations comparable with that of the forming CAc.

Our goal was to examine the possibility of using peroxides accumulating in the oxidate to raise the yield of CAc.

EXPERIMENTAL

Pure-grade CAl was distilled before use on a laboratory column (10 TP, reflux ratio 2); the fraction with bp 375–376 K was collected. Crotonaldehyde was kept under argon at 253 K. An additional purification was performed by steam distillation, with the collection of the azeotrope (75.7 wt % CAl, 24.3 wt % H_2O), from which water was frozen out at 223 K, and CAl was dried over $MgSO_4$ and distilled on a column. A chromatographically pure CAl was thus obtained (bp 375 K, d_4^{20} 0.853 g cm^{-3}). The optimal medium for CAl oxidation, from the viewpoint of CAc yield, is ethyl acetate [1]. We used ethyl acetate of analytically pure grade ; it was dried over $CaCl_2$ and distilled before use.

Qualitative and quantitative analyses were performed by chemical methods [4], gas chromatography, and IR spectroscopy. Chromatographic analyses were carried out on a Tsvet-100 chromatograph (2000 × 3-mm column; sorbent Polysorb-1, 0.1–0.25 mm; column and vaporizer temperatures 423 and 463 K, respectively; thermal conductivity detector). In the oxidate, we determined the content of CAl and CAc. The total content of carbonyl compounds was determined by the hydroxylamine method [4], and the total content of acids, by titration with 0.1 N NaOH in the presence of phenolphthalein. The content of peroxides was determined by iodometric titration in glacial acetic acid.

The gas–chromatographic analysis gives the total content of crotonic and percrotonic (PCAc) acids, because PCAc transforms into CAc in the vaporizer. To confirm this conclusion, we performed absolute calibration with respect to CAc in the system CAc–ethyl acetate. Percrotonic acid was prepared by oxidation of CAc in ethyl acetate at a low temperature. For example, in oxidation of CAl at 12°C to 15% conversion, the content of PCAc in the sum of acids reaches 93%. Such an oxidate gives a chromatographic peak of CAc, whose area corresponds to the total calculated amount of PCAc and CAc and is consistent with the total acid content determined by chemical analysis.

In oxidation of CAl under various conditions, the oxidate always contains PCAc and CAc (Table 1). The PCAc : CAc ratio decreases with increasing temperature, oxidation time, and partial oxygen pressure. Peroxy compounds disappear from the oxidate upon prolonged storage (100–150 h). The approximate composition of the oxidate stored for 150 h at 20°C is as follows (wt %): ethyl acetate 75.04, CAl 8.97, CAc 12.46, propionaldehyde 0.40, propionic acid 0.50, formic acid 1.20, propenyl formate 0.60, and 1,2-epoxypropenyl formate 0.60.

Table 1. Influence of the oxygen pressure and temperature on oxidation of CAl in ethyl acetate* (c^0_{CAl} = 2.46 M)

$p_{\mathrm{O_2}}$, atm	τ, min	c_{CAl}, M	X_{CAl}, %	c_{PCAc}	c_{CAc}	S_{PCAc}	S_{CAc}	$S_{\Sigma\,\mathrm{CAc+PCAc}}$
				M		%		
T = 300 K								
1	35	2.09	15.0	0.25	0.06	67.6	14.8	82.4
	60	1.99	19.1	0.32	0.08	67.9	17.6	85.5
	120	1.60	35.0	0.55	0.18	65.1	19.9	85.0
	180	1.23	50.0	0.70	0.33	56.9	27.1	84.0
4	30	1.95	20.7	0.33	0.08	64.7	15.7	80.4
	60	1.83	25.6	0.40	0.12	63.5	19.0	82.5
	120	1.12	54.5	0.78	0.33	58.2	24.6	82.8
	180	0.61	75.2	0.96	0.54	51.9	29.2	81.1
T = 309 K								
1	30	1.93	21.5	0.33	0.09	62.2	17.0	79.2
	60	1.64	33.3	0.53	0.17	64.6	19.9	84.5
	120	1.17	52.4	0.75	0.33	58.1	25.7	83.8
	180	0.68	72.4	0.95	0.53	53.3	29.8	83.1
16	30	1.66	32.5	0.42	0.18	52.5	22.5	75.0
	60	1.07	56.5	0.81	0.34	59.0	23.7	82.7
	120	0.59	76.0	1.07	0.47	57.7	24.8	82.5
	180	0.38	84.6	1.00	0.66	49.0	31.0	80.0

* ($p_{\mathrm{O_2}}$) O_2 pressure, (τ) time from the start of the reaction, (c) concentration, (X) conversion, and (S) selectivity.

According to [5], CAc is formed by a parallel-consecutive mechanism directly from CAl and via PCAc. Table 1 shows that the selectivity of CAc formation grows with conversion, and the selectivity of PCAc formation decreases. Apparently, the consecutive formation CAc via PCAc is the major pathway.

According to the classical autooxidation scheme, peroxy compounds accumulating in oxidation of unsaturated aldehydes are mainly the corresponding per acids. As shown by Boboleva *et al.* [6], the poor selectivity of CAc formation in autooxidation of CAl at elevated temperature is due to consumption of PCAc in side processes, rather than to cleavage of the C=C bond in the course of oxidation. They believe that PCAc not only transforms into CAc, but also undergoes a radical decomposition:

$$\mathrm{RC(O)OOH} \rightarrow \mathrm{RC(O)O^{\cdot}} + {}^{\cdot}\mathrm{OH},$$

$$\mathrm{RC(O)O^{\cdot}} \rightarrow \mathrm{CO_2} + \mathrm{R^{\cdot}}.$$

With decreasing temperature, the decomposition decelerates [6], and the selectivity with respect to the sum of CAc and PCAc increases. Thus, by-products formed in CA oxidation mainly arise from radical decomposition of PCAc. There are also indications [7] that H_2O_2, diacyl peroxides, and polyperoxides are also formed in oxidation of unsaturated aldehydes along with per acids. Quantitative data on the composition of peroxy compounds in oxidation of CAl are lacking. This stimulated us to evaluate the content of undesirable stable peroxides in oxidation of CAl. For this purpose, after completion of the experiments and determination in oxidates of CAc and sum of peroxy compounds, the oxidates were stored for a long time at room temperature, after which the content of peroxides, CAc, and CAl was determined. The results are listed in Table 2.

It is seen that 95–98% of peroxides accumulated by the end of experiments are unstable and undergo consecutive transformations at room temperature. This means that thermally stable peroxides incapable of reacting with CAl are formed in oxidation of CAl in very low amounts (≤0.04 M). Presumably, the peroxides in the oxidate are mainly PCAc and certain amount of H_2O_2. The content of H_2O_2 in the oxidate must not be significant, since, as seen from Table 2, in some experiments (nos. 8, 10, 12, 13, 15), when the content of CAl exceeds that of peroxides, CAl transforms into CAc within the storage time in the amount equivalent to the content of peroxy compounds in the oxidate. This means that all the peroxides in the oxidate oxidize CAl to CAc. At the same time, hydrogen peroxide oxidizes CAl to CAc only in the presence of catalysts, Se^{4+} compounds [7]. Hence, hydroperoxides accumulating in oxidation of CAl with molecular

Table 2. Composition of CAl oxidate before and after storage at 293–295 K*

Run no.	Storage time, days	c^0_{CAl}	$c^0_{\Sigma\,\mathrm{CAc+PCAc}}$	c^0_{HP}	c^τ_{CAl}	$c^\tau_{\Sigma\,\mathrm{CAc+PCAc}}$	c^τ_{HP}
		M					
1	90	0.52	1.84	1.09	0.02	2.34	0.04
2	88	0.34	1.98	1.31	0.01	2.28	0.05
3	88	0.17	2.04	1.20	0.03	2.18	0.03
4	86	0.48	1.84	1.23	0.02	2.28	0.03
5	82	0.59	1.65	0.85	0.04	2.20	0.02
6	79	0.90	1.35	0.79	0.10	2.10	0.02
7	51	0.94	1.38	0.84	0.06	2.10	0.03
8	49	1.12	1.21	0.63	0.52	1.80	0.02
9	44	0.69	1.71	1.18	0.01	2.36	0.05
10	41	1.13	1.20	0.63	0.54	1.75	0.03
11	37	0.33	1.86	1.02	0.01	2.18	0.04
12	37	1.63	0.84	0.67	0.95	1.52	0.02
13	37	1.23	1.14	0.86	0.43	1.92	0.03
14	35	0.74	1.50	0.84	0.01	2.20	0.04
15	35	3.30	1.30	0.57	2.75	1.83	0.02

* (c^0) Content after oxidation, (c^τ) content after storage, (ΣCAc + PCAc) sum of acids, and (HP) hydroperoxides.

oxygen under the experimental conditions consist mainly of PCAc, which oxidizes CAl to CAc in the course of storage of the oxidate at room temperature, transforming itself into CAc. In the absence of a sufficient amount of CAl in the oxidate, PCAc also transforms into CAc (Table 2, run nos. 1, 2, 4, 9, 11, 14), but less selectively.

The fact that PCAc, one of the major products of CAl oxidation, virtually quantitatively transforms into CAc on keeping the oxidate at room temperature and oxidizes in the process an equimolar amount of CAl can be used to achieve the maximum yield of CAc. Oxidation of CAl with molecular oxygen should be performed up to accumulation of the maximum concentration of PCAc in the oxidate. In so doing, the concentration of unchanged CAl should only slightly exceed the PCAc concentration (Table 2, run nos. 6, 7). In the course of storage, CAl virtually quantitatively transforms into CAc in the reaction with PCAc.

For practical synthesis of CAc, it is necessary to find the optimal temperature for decomposition of PCAc in the oxidate, because at room temperature the reaction is too slow. The kinetics of PCAc and CAl consumption and CAc accumulation in the oxidate was studied at 318 and 333 K. After oxidation for 100 min at 309 K, the oxygen supply was stopped, the system was purged with argon and then heated to the required temperature, and the oxidate composition was monitored. The results of some experiments are shown as example in Fig. 1. As seen from Fig. 1a,

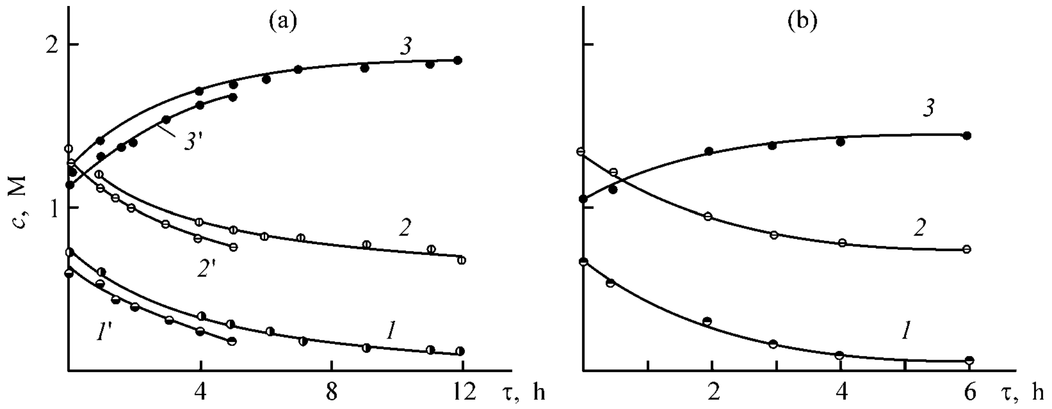

Fig. 1. Kinetic curves of (*1*, *1'*) consumption of PCAc, (*2*, *2'*) consumption of CAl, and (*3*, *3'*) accumulation of the sum of CAc and PCAc at (a) 318 and (b) 333 K. (c) Concentration and (τ) time. (*1*, *1'*, *2*, *2'*, *3*, *3'*) Results of replicate runs.

Table 3. Characteristics of the oxidate after oxidation and storage (CAl content at the beginning of experiments 2.46 M, oxidation time 180 min, storage for 7 h at 318 K)

T,* K	p_{O_2}, atm	c^0_{CAl}	c^0_{PCAc}	c^0_{CAc}	x_{CAl}	$S_{\Sigma\,CAc + PCAc}$	c^τ_{CAl}	c^τ_{PCAc}	c^τ_{CAc}	x_{CAl}	S_{CAc}
		M			%		M			%	
300	1	1.23	0.70	0.33	50.0	84.0	0.52	0.02	1.69	79.7	87.1
300	2	0.96	1.03	0.47	61.0	83.0	0.05	0.03	2.28	98.0	94.6
300	4	0.61	0.96	0.54	75.2	81.1	0.02	0.02	2.05	99.1	84.0
309	1	0.68	0.95	0.53	72.4	83.1	0.03	0.03	2.09	98.8	86.0
309	16	0.38	1.00	0.66	84.6	80.0	0.01	0.03	1.99	99.6	81.2

* (T) Oxidation temperature.

the concentrations of CAl and PCAc decrease to a similar extent, with the total concentration of CAc and PCAc growing simultaneously. For example, in 7 h, the PCAc concentration decreased by 0.61 M; that of CAl, by 0.59 M; and that of the sum of CAc and PCAc increased by 0.6 M. Within the same time, 9.6 ml of CO_2 and 2.4 ml of CO evolved from the oxidate (30 ml). Hence, at 318 K only 1–2% of PCAc is spent for side reactions (initiated radical decomposition), whereas 98–99% of PCAc reacts with CAl to form CAc.

At 333 K (Fig. 1b), PCAc is consumed considerably faster, and the process is complete within approximately 4 h. However, the relative contribution of PCAc decomposition grows. For example, 15 ml of CO_2 and 5.4 ml of CO evolved from the reactor in 4 h. Percrotonic acid is consumed noticeably faster than CAl: in 4 h, the PCAc concentration decreased by 0.62 M, and that of CAl, by 0.56 M. The total concentration of CAc and PCAc grew by only 0.54 M (87% of the consumed PCAc).

Apparently, to ensure the most efficient utilization of PCAc and maximum yield of CAc, the oxidate should be kept at relatively low temperatures. Table 3 illustrates the variation of the oxidate composition at 318 K in the course of 7 h. It is seen that oxidation of CAl to CAc with PCAc occurs more selectively than oxidation with molecular oxygen to CAc and PCAc. Table 3 shows that the maximum efficiency is reached when the concentrations of the accumulated PCAc and unchanged CAl in the oxidate by the end of autooxidation are approximately equal. This situation is attained at ~60% conversion of CAl. In the course of storage, unchanged CAl is oxidized with PCAc, and the total selectivity with respect to CAc reaches 94%.

The results of these studies allowed development of an efficient procedure for preparing CAc [8].

CONCLUSION

To achieve the maximum yield of crotonic acid, it is appropriate to perform oxidation of crotonaldehyde with molecular oxygen at 300–310 K to 55–65% conversion of crotonaldehyde, when the concentrations of perctoronic acid and unchanged crotonaldehyde in the oxidate become approximately equal. The unchanged crotonaldehyde is subsequently oxidized with percrotonic acid at 315–320 K within 7.0–7.5 h.

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