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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Oxidation of 2-Methoxy-3,6-dichloropropenylbenzene with Ozone

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Abstract—Oxidation of 2-methoxy-3,6-dichloropropenylbenzene with ozone in acetic acid and carbon tetrachloride was studied.

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Ozonolysis is one of the most promising methods for oxidation of hydrocarbons containing double bonds. In this study, we examined the formation of 2-methoxy-3,6-dichlorobenzaldehyde by ozonation of 2-methoxy-3,6-dichloropropenylbenzene (DCPB). 2-Methoxy-3,6-dichlorobenzaldehyde can serve as a starting compound for preparing 2-methoxy-3,6-dichlorobenzoic acid and its derivatives used in agriculture as herbicides [1–3]. It is known that the efficiency of ozonolytic conversion of olefins is determined by the decomposition of intermediate ozonolysis products, ozonides. In this study, we examined the thermal stability of ozonides formed by ozonation of 2-methoxy-3,6-dichloropropenylbenzene and the effect of acidity on their decomposition.

EXPERIMENTAL

2-Methoxy-3,6-dichloropropenylbenzene was purified by vacuum distillation under argon. Carbon tetrachloride (CCl_4) was successively treated with ozone, dried over $CaCl_2$, and distilled in argon. Methanesulfonic acid (CH_3SO_3H) and *p*-toluenesulfonic acid (*p*-$TolSO_3H$) of chemically pure grade were used without purification. Ozone was prepared from oxygen in a ozonizer with an output capacity of 0.5 g of ozone per hour at an oxygen consumption of 4 l h^{-1}.

The ozonation of DCPB and isolation of products of its conversion were carried out as follows. A solution of the olefin in acetic acid or CCl4 was purged with an ozone–oxygen mixture fed into the lower part of a reactor. The ozone content at the inlet and outlet of the reactor was determined spectrophotometrically at $\lambda = 300$ nm (ozone extinction coefficient 95 l mol^{-1} cm^{-1}) [4]. After the breakthrough of ozone through the reactor, the ozonation was stopped.

The intermediate compounds containing peroxy groups were determined by spectrophotometric iodometric titration [5]. The concentration of intermediates containing peroxy groups (–O–O–) was calculated by the equation

$$[\text{–O–O–}] = AV_{\text{as}}/(\varepsilon l V_{\text{s}}),$$

The extinction coefficient of I_3^- at $\lambda = 360$ nm is $\varepsilon = 28\,000$ l mol^{-1} cm^{-1}, the optical cell width is 1 cm, the volume of the solution being analyzed V_{as} = 2.5–3.0 ml, and the introduced sample volume V_{s} = 2–10 μl.

The decomposition products of ozonized compounds were examined by ^1H and ^{13}C NMR, IR, and UV spectroscopies, and also by GLC. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AM-300 NMR spectrometer (300 and 75 MHz, respectively).

Ozonation of the olefin in acetic acid solutions. 2-Methoxy-3,6-dichloropropenylbenzene (27.4 mol, 6.06 g) was dissolved in glacial acetic acid (50 ml) and ozonized at 315 K. In the course of the ozonation, the reaction mixture was sampled at regular intervals and the samples were titrated iodometrically. The reaction mixture was ozonized for 3 h . After the ozonation was complete, the ozonide concentration in the reaction mixture was 0.12 M.

Ozonation of the olefin in acetic acid containing water and *p*-toluenesulfonic acid. The initial mix-

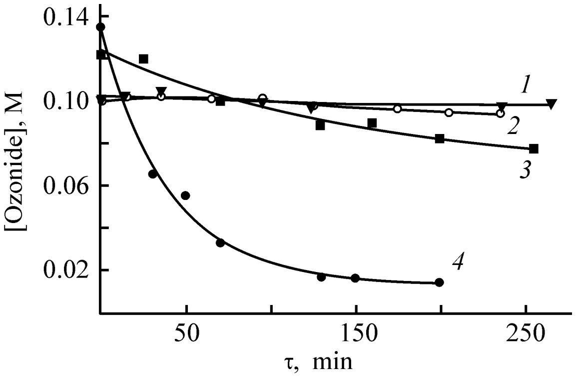


Fig. 1. Kinetic curves of ozonide decomposition in CH3COOH. (τ) Time. Temperature, K: (*1*) 298, (*2*) 326, (*3*) 347, and (*4*) 347 in the presence of $[CH_3SO_3H]$ = 1.1×10^{-2} M.

ture to be ozonized (50 ml) contained olefin (6.06 g) dissolved in an acetic acid solution containing *p*-$TolSO_3H$ (0.1 g) and H_2O (3.2 g). The ozonation was carried out at 315 K. After a lapse of 2 h 35 min, the ozonide concentration in the reaction mixture reached 0.2 M.

Ozonation of the olefin in CCl_4. In these experiments, solutions of the olefin in CCl_4 (50 ml) containing 6.06 g of the olefin were ozonized at 295 K. Although the ozone breakthrough occurred 40 min after the start of the reaction, the ozonation was continued for 3 h. Under these conditions, the ozonide content in the reaction mixture did not exceed 0.1 M.

Rate constant of ozonide decomposition in an acetic acid solution at various temperatures and sulfonic acid concentrations

T, K	$[RSO_3H]$, M	$[Ozonide]_0$, M	k_{eff}, s^{-1}
290	–	0.03*	$(5 \pm 0.2) \times 10^{-7}$
298	–	0.01	$(7.5 \pm 2.1) \times 10^{-7}$
347	–	0.04	$(2.3 \pm 0.4) \times 10^{-5}$
	[Methanesulfonic acid]:		
347	0.5×10^{-2}	0.12	$(4.0 \pm 0.5) \times 10^{-5}$
	0.9×10^{-2}	0.16	$(4.2 \pm 0.5) \times 10^{-5}$
	3.1×10^{-2}	0.07	$(7.3 \pm 0.5) \times 10^{-5}$
	5.0×10^{-2}	0.14	$(11.4 \pm 1.5) \times 10^{-5}$
	7.0×10^{-2}	0.14	$(12.9 \pm 1.6) \times 10^{-5}$
	[*p*-Toluenesulfonic acid]:		
347	0.6×10^{-2}	0.03	$(4.6 \pm 0.7) \times 10^{-5}$
	1.8×10^{-2}	0.07	$(7.5 \pm 0.7) \times 10^{-5}$
	2.9×10^{-2}	0.06	$(8.1 \pm 0.7) \times 10^{-5}$
	6.8×10^{-2}	0.07	$(14.7 \pm 0.8) \times 10^{-5}$

* In CCl_4.

The thermal stability of ozonides formed by ozonation of the olefin was examined as follows. A portion of the reaction mixture was taken from the reactor and dissolved in acetic acid. This solution was placed in a temperature-controlled reactor equipped with a water-cooled reflux condenser and a stirrer. At certain intervals, the reaction mixture was sampled drawn and the concentration of the peroxy groups in was determined iodometrically. This experiment was continued until the degree of decomposition of the ozonide reached no less than 70%. To elucidate how the acidity affects the kinetics of acid-catalyzed decomposition of ozonides, weighed portions of the sulfonic acid were added to the reaction mixture.

Thermal stability of 2-methoxy-3,6-dichloropropenylbenzene ozonide. The thermal decomposition of the ozonide was examined in acetic acid solutions at 288–347 K. As can be seen from Fig. 1, 2-methoxy-3,6-dichloropropenylbenzene ozonide is stable at room temperature for several hours. We found that the addition of water (3.3 M) does not affect the kinetics of degradation of the ozonide. With increasing temperature, the ozonide stability decreases. Noticeable decomposition of the ozonide begins at 347 K. The kinetic curve of thermal decomposition of the ozonide is linear in the coordinates of equation of a first-order reaction, which allows calculation of the effective rate constant k_{eff} of the ozonide decomposition (see table). These data show that this rate constant is independent of both the initial ozonide concentration and solvent type, and its value is close to that of decomposition of 1-hexene ozonide [4].

Acid-catalyzed decomposition of ozonide. We found that addition of methane and *p*-toluenesulfonic acids (RSO_3H) accelerates the decomposition of the ozonide. Acetic acid used as the solvent (pK_a 4.75) [6] is weaker than methane- and *p*-toluenesulfonic acids (pK_a 0 and 0.7, respectively) [7]. The table shows that the ozonide decomposition is noticeably accelerated in the presence of methanesulfonic acid. The kinetic curve of ozonide decomposition in the presence of methanesulfonic acid is linear in the coordinates of equation of a first-order reaction, which allows calculation of the effective rate constant k_{eff} of ozonide decomposition. The effective rate constants k_{eff} of ozonide decomposition in the presence of sulfonic acids at varied temperature are listed in the table. Thus, with the content of sulfonic acid in acetic acid solutions increasing within the entire concentration range, the stability of ozonides decreases, with k_{eff} weakly dependent on the initial ozonide concentration. Figure 2 shows that k_{eff} linearly depends on the sulfonic acid concentration. These correlations suggest that the rate of ozonide decomposition is described by the linear equation

$$W = k_{\text{eff}}[\text{ozonide}] = (k_0 + k_c[\text{RSO}_3])[\text{ozonide}]_0,$$

where k_0 is the rate constant of ozonide decomposi tion in the absence of sulfonic acid, and k_c, the rate constant of ozonide decomposition catalyzed by sulfonic acid.

The rate constants of ozonide decomposition in acetic acid containing a sulfonic acid were calculated from our experimental data for $[\text{ozonide}]_0$ = 0.16–0.03 M and are as follows: in the presence of *p*-toluenesulfonic acid, $k_0 = (3.5 \pm 1.5) \times 10^{-5}$ s^{-1}, $k_c = (1.5 \pm 0.3) \times 10^{-3}$ l mol^{-1} s^{-1}; and in the presence of methanesulfonic acid, $k_0 = (2.8 \pm 1,5) \times 10^{-5}$ s^{-1} and $k_c = (1.5 \pm 1.3) \times 10^{-3}$ l mol^{-1} s^{-1}.

It should be noted that the rate constant of acid-catalyzed decomposition of 2-methoxy-3,6-dichloropropenylbenzene ozonide determined in this study reasonably agrees with the rate constant of decomposition of 1-hexene ozonide catalyzed by *p*-toluenesulfonic acid in the presence of the accumulated aldehyde, 7.4×10^{-4} s^{-1} [8].

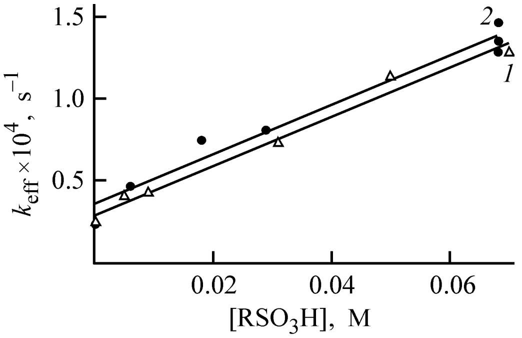


Fig. 2. Plot of k_{eff} vs. RSO$_3$H concentration at 347 K. (*1*) CH$_3$SO$_3$H and (*2*) *p*-TolSO$_3$H.

After the completion of the ozonide decomposition, the products of oxidative conversion of DCPB were isolated by two different methods. In the first method, water was added to the reaction mixture and the resulting yellow oily precipitate was treated with saturated aqueous Na$_2$SO$_4$ and cooled to 273 K. A grayish precipitate formed under these conditions was filtered off, washed with benzene, and dried. The ^{1}H and ^{13}C NMR spectra of this product formed in a yield of 98% were found to be identical to those of 2-methoxy-3,6-dichlorobenzaldehyde.

In the second method, acetic acid was distilled off from the reaction mixture, and the resulting precipitate was dissolved in CCl$_4$. This solution was filtered and CCl$_4$ was distilled off. The ^{1}H NMR spectrum of the resulting product formed in 96% yield contains a signal at 10.4 ppm belonging to the aldehyde group. The ^{13}C NMR spectra show that the product of oxidation of DCPB is 2-methoxy-3,6-dichlorobenzaldehyde.

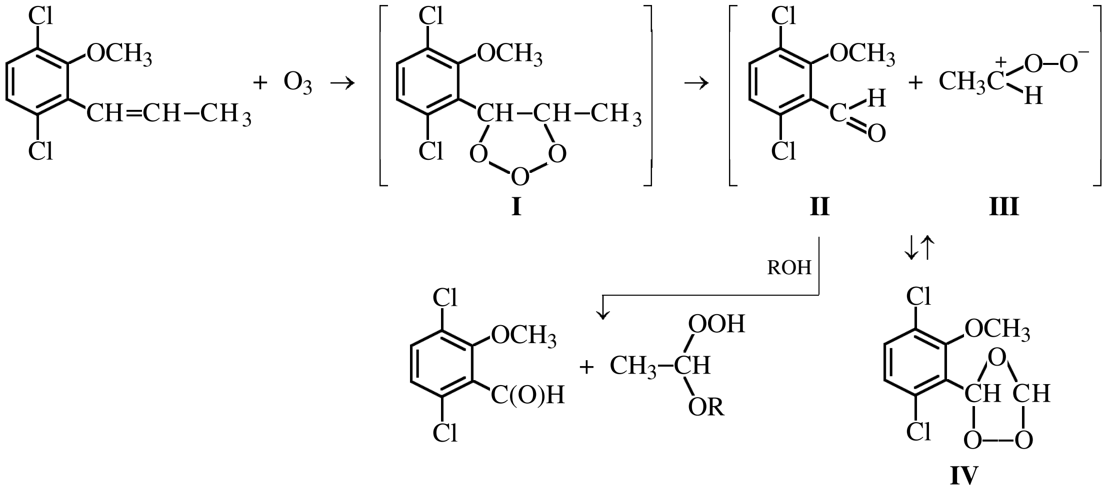
^{1}H NMR spectrum of 2-methoxy-3,6-dichlorobenzaldehyde

Proton	–OCH$_3$	–C(O)H	≥CH	≥CH
δ, ppm:				
calculation	3.84	10.57	7.32	7.23
experiment	3.8–395	10.2–10.4	7.3–7.5	7.1–7.2

^{12}C NMR spectrum of 2-methoxy-3,6-dichlorobenzaldehyde

C atom	–OCH$_3$	H–C≤	H–C≤	≥C–Cl	≥C–Cl	≥C–OR	≥CH=O
δ, ppm:							
calculation	62.49	127.0	134.6	122.8	137.3	156.05	190.4
experiment	62.84	127.1	134.9	121.1	134.9	156.12	188.5

Our experimental results can be adequately described within the framework of the known mechanism of ozonation of unsaturated compounds [4]:



Chemical scheme of ozonation.

In this scheme, molozonide **I** formed by the reaction of ozone with the double bond is very unstable and decomposes to yield aldehyde **II** and carbonyl oxide **III**. Owing to the cell effect, some portion of carbonyl oxide has no time to escape into the bulk and reacts with the aldehyde to form more stable ozonide **IV**. This is evident from the fact that, if the components of the reaction mixture containing active oxygen are not decomposed, the aldehyde yield does not exceed 70%. At the same time, the yield of the product containing the –O–O– group increases in the course of ozonation and, after the reaction is complete, it is approximately 20% of the initial olefin amount.

Thus, the main part of aldehyde is formed by direct ozonation of 2-methoxy-3,6-dichlorobenzene. A small portion of the aldehyde (up to 20% of the initial olefin) is converted to ozonide by the reaction with the simultaneously formed carbonyl oxide. After decomposition of the ozonide in the presence of *p*-toluenesulfonic acid, 2-methoxy-3,6-dichlorobenzaldehyde is formed in a yield of up to 98%.

CONCLUSIONS

(1) The ozonation of 2-methoxy-3,6-dichloropropenylbenzene yields 2-methoxy-3,6-dichlorobenzaldehyde (up to 70%) and the corresponding ozonide.

(2) Strong acids catalyze the ozonide decomposition.

(3) The main ozonation product in acetic acid, formed in 98% yield after completion of decomposition of the ozonide, is 2-methoxy-3,6-dichlorobenzaldehyde.

REFERENCES

1. Mel'nikov, N.N., Novozhilov, K.V., and Belan, S.R., *Pestitsidy i regulyatory rosta rastenii: Spravochnik* (Pesticides and Plant Growth Regulators: Handbook), Moscow: Khimiya, 1995.
2. RF Patent 2106782.
3. RF Patent 2070877.
4. Razumovskii, S.D. and Zaikov, G.E., *Ozon i ego reaktsii s organicheskimi soedineniyami* (Ozone and Its Reactions with Organic Compounds), Moscow: Nauka, 1974.
5. Safiullin, R.L., Enikeeva, L.R., and Komissarov, V.D., *Kinet. Katal.*, 1989, vol. 30, no. 5, pp.1040–1044.
6. *Spravochnik khimika* (Chemist's Handbook), Nikol'skii, B.P., Ed., Moscow: Khimiya, 1964, vol. 3.
7. *Organic Chemistry of Sulfur, Oae, S.*, Ed., New York: Plenum, 1977.
8. Yur'ev, Yu.N., Razumovskii, S.D., Berezova, L.D., and Zelikman, E.S., *Zh. Org. Khim.*, 1975, vol. 11, no. 1, pp. 7–11.