Organic Process Research & Development **2007,** *11,* 1025–1031

Ozonolysis of Acetic Acid 1-Vinyl-hexyl Ester in a Falling Film Microreactor

Norbert Steinfeldt,* Radwan Abdallah,† Uwe Dingerdissen, and Klaus Jähnisch*

Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Aussenstelle Berlin, Richard-Willstätter-Str. 12, Berlin D-12489, Germany

Abstract:

Ozonolysis of acetic acid 1-vinyl-hexyl ester was carried out in a falling film microreactor in a continuous fashion. The influence of reaction variables (e.g., olefin concentration, ozone initial partial pressure, gas velocity, temperature and liquid flow rate) on the product formation in the liquid phase was studied over a wide range of operating conditions. Based on the obtained results, a formal reaction scheme for the ozonolysis of acetic acid 1-vinyl-hexyl ester is suggested. The acetic acid 1-formyl-hexyl ester and the corresponding carbonyl oxide are the main products of the cleavage of the primary formed ozonide. The secondary ozonide acetic acid 1-[1,2,4]trioxolan-3-yl-hexyl ester is formed by consecutive reaction of the acetic acid 1-formyl-hexyl ester and the carbonyl oxide.

Introduction

During recent years microreaction technology has gained increasing importance for academic research as well as for process development in the chemical industry.[1] The benefits of microstructured devices for chemical reactions have been demonstrated in many examples.[2] The selectivity of final products can be increased by efficient heat and/or mass transfer, and the risk potential can be significantly reduced by low hold-up.

In contrast to reactions in the liquid phase and solid-material-catalyzed gas-phase reactions, only few examples are given for gas/liquid reactions using microstructured devices. The advantages of microreactor technology become particularly evident if exothermic reactions with toxic or corrosive gases (e.g., Cl_2, F_2, Br_2, SO_2, SO_3)[3] or reactions with formation of explosive intermediates or products are applied.[4] Additionally, examples for fast hydrogenation of olefins[5] or nitrocompounds also have been published.[6]

The reaction of ozone with olefins can be considered as a typical gas/liquid reaction characterized by a high exothermicity and by the formation of explosive intermediates. Ozonides and/or hydroperoxides are generated in the liquid phase, and furthermore explosive mixtures of solvent vapours with oxygen and ozone are present in the gas phase.[7] Despite the high risk potential the ozonolysis of olefins is industrially performed as a synthesis step in semibatch processes for the production of drugs[8] and fine chemicals. Typical examples are the formation of glyoxylic acid from maleic acid dimethyl ester and the formation of pelargonic acid and azelaic acid from oleic acid.[9]

The reaction mechanism that is generally accepted for olefins[10] is shown in Scheme 1. In the first step a primary ozonide **2** is formed[11] by cycloaddition of ozone with the olefin **1**. As a result of its instability, the primary ozonide **2** undergoes fast cleavage to aldehydes or ketones **4** and zwitterions (carbonyl oxides) **3**.[12] If the solvent does not participate in the reaction, aldehyde **4** and zwitterion **3** react in a consecutive reaction to form the monomeric secondary ozonide **5**.[10] Alternatively, the zwitterions may dimerize to diperoxide **6** or polymerize to yield peroxides **7** with higher molecular weight.[10] Unsymmetrical olefins afford two different aldehydes or ketones and two different zwitterions, respectively. Therefore, different secondary ozonides can be generated (Scheme 2).[13] The ratio in which the different secondary ozonides are formed depends on the ratio olefin/solvent,[13] whereas the direction of the cleavage of the primary ozonides is strongly influenced by the substituents.[14] Electron-donating substituents stabilize the carbonyl oxide, whereas electron-withdrawing substituents destabilize it. Therefore, carbonyl compounds with electron-acceptor substituents are formed predominantly. As already stated, the ozonolysis of an olefin is an exothermic reaction, and the reaction heat (in

* To whom correspondence should be addressed. E-mail: norbert.steinfeldt@catalysis.de or klaus.jaehnisch@catalysis.de.

† Present affiliation: BASF AG Ludwigshafen.

(1) Hessel, V.; Hardt, S.; Löwe, H. *Chemical Micro Process Engineering*; Wiley-VCH: Weinheim, 2004.

(2) (a) Jähnisch, K.; Hessel, V.; Löwe, H.; Baerns, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 381. (b) Mason, P. B.; Proce, K. E.; Steinbacher, J. L.; Bogdan, A. R.; McQuade, D. T. *Chem. Rev.* **2007**, *107*, 2300.

(3) (a) Jähnisch, K.; Baerns, M.; Hessel, V.; Ehrfeld, W.; Haverkamp, W.; Löwe, H.; Wille, C.; Guber, A. *J. Fluorine Chem.* **2000**, *105*, 117. (b) Ehrich, H.; Linke, D.; Morgenschweis, K.; Baerns, M.; Jähnisch, K. *Chimia* **2002**, *56*, 647. (c) Chambers, R. D.; Spink, R. C. H. *Chem. Commun.* **1999**, *10*, 883. (d) Chambers, R. D.; Holling, D.; Rees, A. J.; Sandford, G. *J. Fluorine Chem.* **2003**, *119*, 81.

(4) (a) Wada, Y.; Schmidt, M. A.; Jensen, K. F. *Ind. Eng. Chem. Res.* **2006**, *45*, 8036. (b) Jähnisch, K.; Dingerdissen, U. *Chem. Eng. Technol.* **2005**, *28*, 426.

(5) (a) Kobayashi, J.; Mori, Y.; Okamoto, K.; Akiyama, R.; Ueno, M.; Kitamori, T.; Kobayashi, S. *Science* **2004**, *304*, 1305. (b) Abdallah, R.; Meille, V.; Shaw, J.; Wenn, D.; de Bellefon, C. *Chem. Commun.* **2004**, 372.

(6) Yeong, K. K.; Gavriilidis, A.; Zapf, R.; Hessel, V. *Catal. Today* **2003**, *81*, 641.

(7) Ragan, J. A.; am Ende, D. J.; Brenek, S. J.; Eisenbeis, S. A.; Singer, R. A.; Tickner, D. L.; Teixeira, J. J., Jr.; Vanderplas, B. C.; Weston, N. *Org. Process Res. Dev.* **2003**, *7*, 155.

(8) Van Ornum, S. G.; Chapeau, R. M.; Pariza, R. *Chem. Rev.* **2006**, *106*, 2990.

(9) Weissermel, K.; Arpe, H.-J. *Industrielle Organische Chemie*; Wiley-VCH: Weinheim, 1998.

(10) (a) Criegee, R. *Angew. Chemie, Int. Ed.* **1975**, *14*, 745. (b) Murray, R. W. *Acc. Chem. Res.* **1968**, *1*, 313. (c) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York, 1978; Vol. I.

(11) Bailey, P. S.; Thompsen, J. A.; Shoulders, B. A. *J. Am. Chem. Soc.* **1966**, *88*, 4098.

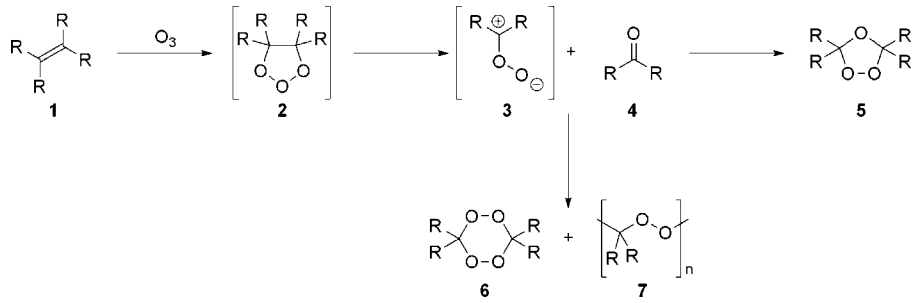
(12) Bailey, P. S.; Rustaiyan, A.; Ferrel, T. M. *J. Am. Chem. Soc.* **1976**, *98*, 638.

(13) Loan, L. D.; Murray, R. W.; Story, P. R. *J. Am. Chem. Soc.* **1965**, *87*, 737.

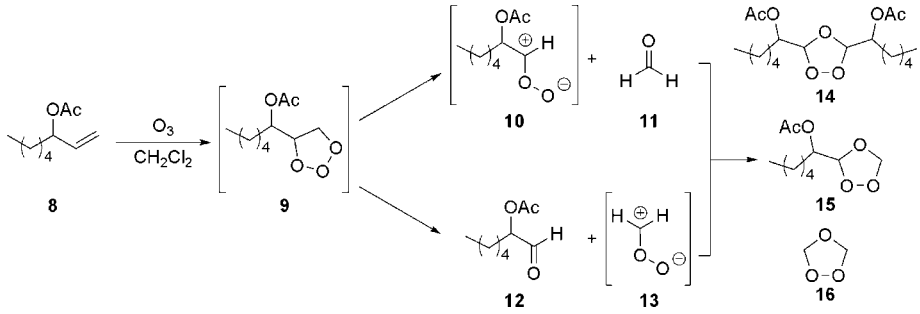
(14) Dowideit, P.; von Sonntag, C. *Environ. Sci. Technol.* **1998**, *32*, 1112.

10.1021/op7000673 CCC: $37.00
Published on Web 11/03/2007

Scheme 1



Scheme 2



the order of 100 kcal/mol) arises from the formation and the cleavage of the primary ozonide.[15]

Ozonolysis reactions of olefins have been studied mainly in semibatch reactors by varying olefins and organic solvents at temperatures between −150 and −20 °C. However, the influence of reaction conditions on olefin conversion and product selectivities in organic solvents is described only scarcely.[16]

The present work deals with the ozonolysis of acetic acid 1-vinyl-hexyl ester **8** in a falling film microreactor with CH_2Cl_2 as solvent. This olefin was chosen as a model olefin for two reasons: (1) the substituent of the olefin has a UV-active chromophoric acetoxy group and the reaction mixture can be analyzed by HPLC more easily, and 2) there is little information about the influence of a substituent in the α-position to the olefinic C–C double bond on the product distribution.

Acetic acid 1-vinyl-hexyl ester **8** reacts with ozone (Scheme 2) to form the primary ozonide **9**, which is cleaved to acetic acid 1-formyl-hexyl ester **12**, formaldehyde **11**, and the corresponding carbonyl oxides **10** and **13**. Aldehydes and carbonyl oxides can react in a subsequent reaction to the secondary ozonides **14**, **15** and **16**.

For fast gas/liquid reactions, such as the ozonolysis of olefins,[17] reactors with a high interfacial area and a low liquid-phase hold-up are required to obtain high gas absorption rates because the reaction will take place only in a small zone of the liquid near the gas/liquid interface.[18] In the falling film microreactor, film thicknesses under 100 μm can be obtained that lead to high values of the specific interfacial area related to the volume of the liquid phase in the reactor.

The aim of this study was to demonstrate the safe operability of microstructured reactors for olefin ozonolysis under continuous flow conditions at temperatures higher than −60 °C and to elucidate the influence of reaction variables (olefin concentration, ozone partial pressure, temperature) on the olefin conversion and product distribution.

Experimental Section

Materials. *Acetic Acid 1-Vinyl-hexyl Ester* ***8.*** A 51 g (0.5 mol) portion of acetic anhydride was added dropwise under stirring at 0 °C within 30 min to a solution of 12.8 g (0.1 mol) of 1-octen-3-ol in 95 g (1.2 mol) pyridine (96.6 mL).[19] After complete addition the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was then diluted with 250 mL of methyl-*tert*-butyl ether, extracted 5 times each with 100 mL of sulphuric acid (5%) and then washed with saturated $NaHCO_3$ solution. The resulting solution was dried over sodium sulphate, filtered, and evaporated with a rotary evaporator. The residue is distilled in vacuum. Bp_7: 74 °C to yield 15 g (86%). ^{1}H NMR: δ 0.88 (t, ^3J = 7.0 Hz, 3 H, CH_3), 1.31 (m, 6 H, CH_2), 1.57 (m, 2 H, $C\underline{H}_2$-CH-O), 2.06 (s, 3 H, CH_3-CO), 5.16 (m, 1 H, CH-O), 5.23 (m, 2 H, CH=C$\underline{H}_2$), 5.77 (ddd, ^3J = 17.2 Hz, ^3J = 10.6 Hz, ^3J = 6.2 Hz, 1 H, C$\underline{H}$=CH_2) ppm. ^{13}C{H}NMR: δ 14.0 (CH_3), 21.2 (CH_3-CO), 34.2, 31.6, 24.8, 22.5 (CH_2), 74.9 (CH-O), 115.5 (C=$\underline{C}H_2$), 136.7 ($\underline{C}$=CH_2), 170.3 (C=O) ppm.

Acetic Acid 1-[1,2,4]Trioxolan-3-yl-hexyl Ester ***15.*** In a semibatch reactor 2.38 g (14 mmol) of acetic acid 1-vinyl-hexyl ester **8** was dissolved in 140 mL of dichloromethane. After the mixture cooled to −15 °C, an oxygen/ozone stream (flow rate 100 mL/min) with an ozone concentration of 2.12 mmol/L was introduced under stirring for approximately 60 min. The solution was then concentrated to a volume of approximately 15 mL (caution: danger of explosion) at room temperature, poured onto

(15) Criegee, R. *Chem. unserer Zeit* **1973**, *7*, 75.
(16) Rischbieter, E. Ph. D. Thesis,Technische Universität Carolo-Wilhelmina zu Braunschweig, 2000.
(17) Williamson, D. C.; Cvetanovic, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 3668.
(18) Levenspiel, O. *Chemical Reaction Engineering*; Wiley: New York, 1999.
(19) Michelot, D. *Synthesis* **1983**, 139.

200 g of silica gel, and eluted with dichloromethane. The eluant was evaporated in small portions with extreme caution at room temperature to yield a colourless clear liquid as a mixture of two diastereomers (ratio approximately 1:1). ^{1}H NMR: δ 0.88 (t, ^3J = 6.7 Hz, 6 H, CH_3), 1.33 (m, 12 H, CH_2), 1.55–1.68 (m, 4 H, C$\underline{H}_2$-CH-O), 2.096 (s, 3 H, CH_3-CO), 2.099 (s, 3 H, CH_3-CO), 4.97 – 5.05 (m, 2 H, CH_2-C$\underline{H}$-O), 5.07 (s, 1 H of O-CH_2-O), 5.09 (s, 1 H of O-CH_2-O), 5.16 (s, 1 H of O-CH_2-O), 5.17 (d, ^3J = 4.4 Hz, 1 H, O-CH-O), 5.18 (s, 1 H of O-CH_2-O), 5.19 (d, ^3J = 5.5 Hz, 1 H, O-CH-O) ppm. ^{13}C{H}NMR: δ 13.9 ($2CH_3$), 20.89 and 20.91 ($\underline{C}H_3$-CO), 22.4 ($2CH_3$), 24.5 and 24.7, 29.22 and 29.23, 31.47 and 31.52 (CH_2), 71.2 and 71.3 (CH-O), 94.1 and 94.2 (O-CH_2-O), 102.1 and 102.2 (O-CH-O), 170.1 and 170.3 (C=O) ppm.

Acetic Acid 1-Formyl-hexyl Ester ***12.*** A 12 g (70 mmol) portion of acetic acid 1-vinyl-hexyl ester **8** was dissolved in 120 mL of dichloromethane in a semibatch reactor. After the mixture cooled to −20 °C, an oxygen/ozone stream (flow rate 100 mL/min) with an ozone concentration of 2.12 mmol/L was introduced under stirring for approximately 90 min (the reaction was controlled by TLC), then 43 mL (540 mmol) of dimethyl sulphide was added, and the mixture was stirred overnight at −20 °C. The mixture was then evaporated under vacuum, and the residue was purified by column chromatography (eluant: heptane/ethylacetate 5:1) to yield a colourless liquid. Its NMR spectra were identical to those given in the literature.[20] ^{1}H NMR: δ 0.89 (t, ^3J = 6.8 Hz, 3 H, CH_3), 1.32 (m, 4 H, CH_2), 1.42 (m, 2 H, CH_2), 1.69 – 1.79 (m, 1 H of C$\underline{H}_2$-CH-O), 1.80 – 1.88 (m, 1 H of C$\underline{H}_2$-CH-O), 2.18 (s, 3 H, CH_3-CO), 4.99 (dd, ^3J = 8.4 Hz, ^3J = 4.7 Hz, 1 H, CH-O), 9.52 (s, 1 H, CH=O) ppm.

2-Acetoxy-heptanoic Acid ***17.*** A 1.7 g portion of acetic acid 1-vinyl-hexyl ester **8** was dissolved in 100 mL of dichloromethane in a semibatch reactor. After the mixture cooled to −25 °C, an oxygen/ozone stream (flow rate 100 mL/min) with an ozone concentration of 2.12 mol/L was introduced until the solution was blue (excess of ozone). After 20 h at −20 °C the mixture was concentrated (caution: danger of explosion) in vacuum. The residue was purified by column chromatography (eluants: dichlormethane was used to separate the ozonide and ethylacetate was used to separate the acid) to yield 1.1 g (60%) of 2-acetoxy-heptanoic acid. Its NMR spectra were identical to those given in the literature.[21] ^{1}H NMR: δ 0.90 (t, ^3J = 6.9 Hz, 3 H, CH_3), 1.31 (m, 4 H, CH_2), 1.44 (m, 2 H, CH_2), 1.85 (m, 2 H, C$\underline{H}_2$-CH-O), 2.15 (s, 3 H, CH_3-CO), 4.90 (1 H, CH-O) ppm.

Analytics. The quantitative analysis of the reaction mixture was carried out by HPLC and NMR methods. NMR spectra were recorded in deuterochloroform on a Varian unit plus NMR spectrometer operating at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR) using TMS as internal standard. HPLC analyses were carried out using an HPLC apparatus (Merck Hitachi L6200; Diode Array Detector L-4500) equipped with a LiChrospher 100, RP18 (5 μm, T = 25 °C, a water/acetonitrile (30/70) flow of 1 mL/min and a wavelength of 220 nm). The concentrations of acetic acid 1-vinyl-hexyl ester **8** (olefin) and acetic acid 1-[1,2,4]trioxolan-3-yl-hexyl ester (ozonide) **15** were determined by HPLC. The concentration of acetic acid 1-formyl-hexyl ester **12** (aldehyde) could not be determined by HPLC because of instability. Therefore a combined method using results of HPLC and NMR was used for the determination of aldehyde concentration. In the reaction mixture the chemical shift (δ in ppm) of the C-H proton for the acetyl group shows different values for the olefin **8** (2.036), ozonide **15** (2.070 and 2.074), aldehyde **12** (2.155) and acid **17** (2.15). If the olefin or ozonide concentration for the same solution is known from HPLC, then the aldehyde concentration can be calculated from the ratio of the NMR proton intensities of the acetyl group of the aldehyde to that of the olefin or ozonide multiplied by olefin or ozonide concentrations. The error of this method for determining the aldehyde concentration is about 5% as indicated by a few repeated experiments.

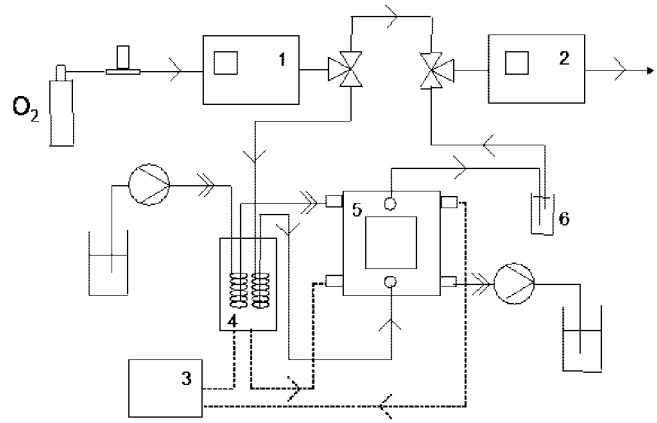


Figure 1. **Experimental setup for the ozonolysis reaction: (1) ozone generator; (2) ozone analyzer; (3) cryostat; (4) heat exchanger; (5) falling film microreactor; (6) cooling finger.**

Olefin conversion X_{olefin} and product selectivity S_i were calculated using the following formulas:

$$X_{\text{olefin}} = 1 - \frac{C_{\text{olefin}}^{\text{outlet}}}{C_{\text{olefin}}^{\text{inlet}}} \quad (1)$$

$$S_i = \frac{C_i^{\text{outlet}}}{C_{\text{olefin}}^{\text{inlet}} - C_{\text{olefin}}^{\text{outlet}}} \quad (2)$$

where i = aldehyde, ozonide.

Ozonolysis. The experimental setup for the ozonolysis is shown schematically in Figure 1. The ozonolysis reaction was carried out in a falling film microreactor (Institut für Mikrotechnik Mainz GmbH, Figure 2). The characteristics of the falling film microreactor are presented in Table 1.

Oxygen, dosed by a mass flow controller (Bronkhorst), was fed through the ozone generator (Fischer OZ 500/2). The ozone content in the oxygen stream was analyzed by an ozone analyzer (Fisher Ozotron 23). The olefin dissolved in dichloromethane was pumped into the falling film microreactor by a gear pump. The liquid passed through the falling film reactor by gravity and was pumped out of the falling film reactor by a second gear pump. The ozonolysis reaction was carried out in counter-

(20) Kern, W.; Spiteller, G. *Tetrahedron* **1996**, *52*, 4347.
(21) Kusakabe, M.; Kitano, Y.; Kobayashi, Y.; Sato, F. *J. Org. Chem.* **1989**, *54*, 2085.

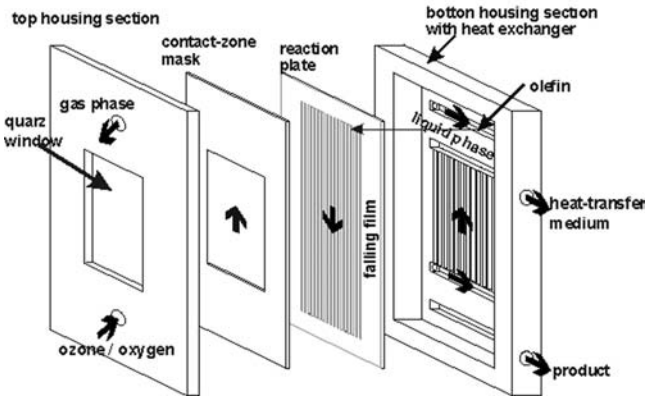


Figure 2. **Construction of the falling film microreactor (source: IMM, Mainz[22]).**

Table 1. **Characteristics of the falling film microreactor**

volume of gas room (cm^3)	11
reaction channels	
number	32
length of contact zone (mm)	66
width (mm)	0.6
height (mm)	0.2
total channel volume (cm^3)	0.25

Table 2. **Experimental operation conditions**

solvent	CH_2Cl_2
liquid flow rate (mL/min)	0.5–15
gas flow rate (mL/min)	100–520
initial olefin concentration (mol/L)	0.03–0.2
initial ozone concentration (g/m^3)	20 – 100
temperature (°C)	−50 – 0
total pressure (bar)	1.023

current flow of gas and liquid phases. The temperature of the cooling medium and the reaction mixture at the inlet and outlet of the falling film microreactor was measured with thermocouples. After having achieved the reaction temperature, ozone was passed into the microreactor. Two samples were collected at steady-state conditions at different reaction times and analyzed at room temperature.

The global absorption rate of ozone q_{O_3} was calculated from the concentration of ozone at the reactor inlet and outlet and the gas flow rate of the ozone/oxygen mixture by means of the following equation:

$$q_{O_3} = (c^{i}_{O_3} - c^{o}_{O_3})\dot{V}_G \tag{3}$$

The mean residence time of the liquid phase in the falling film microreactor was calculated by the following formula:

$$\tau = \frac{V}{\dot{V}_{liq}} = \frac{\delta l}{\dot{V}_{liq}} \tag{4}$$

where V is the volume of the liquid phase in the falling film microreactor and $\dot{V}_{liq}$ is the liquid flow rate. The film thickness δ inside the single microchannel was calculated using eq 5.[23] In this equation the perimeter $2\pi R$ of the falling film reactor was replaced by the wetted width B of the microchannels.

$$\delta = \left[\frac{3\dot{V}_{liq}\,\mu_{liq}}{\rho_{liq}\,gB}\right]^{\frac{1}{3}} \tag{5}$$

The film thickness δ calculated by eq 5 gives reasonable agreement with experimentally determined film thicknesses.[24]

In contrast to conventional falling film reactors, where the residence time of the liquid phase can be changed by variation of the height of the column at constant liquid flow rate, the liquid-phase residence time in the falling film microreactor can be changed only by variation of the liquid flow rate. However, with variation of the liquid flow rate the film thickness is also changed. Therefore, it has to be mentioned, that it is impossible to vary the contact time by the same film thickness in the falling film microreactor.

For the calculation of film thickness at different temperatures, the physical data of CH_2Cl_2 were used. This is an allowed approximation because in comparison to the olefin the solvent CH_2Cl_2 was used in great excess. Viscosity data of CH_2Cl_2 for the corresponding temperature were taken from the literature[25] and fitted by the following function:

$$\mu_{CH_2Cl_2}(T) = -6.9\times10^{-6}T(°C) + 5.47\times10^{-4} \tag{6}$$

The density and the flow rate of the liquid phase inside the reactor are also dependent on temperature. The flow rate of the liquid phase in the falling film microreactor for different temperatures was calculated by

$$\dot{V}_{liq}(T) = \frac{\rho_{CH_2Cl_2}(20\ °C)\cdot\dot{V}_{liq}(20\ °C)}{\rho_{CH_2Cl_2}(T)} \tag{7}$$

and for the density of CH_2Cl_2 depending on temperature, the following formula was used.[25]

$$\rho_{CH_2Cl_2}(T) = -0.0017T(°C) + 1.3641 \tag{8}$$

The range of reaction parameters applied is given in Table 2.

Results and Discussion

Influence of Reaction Parameters on the Olefin Conversion. The influence of the liquid flow rate on olefin conversion at constant gas flow rate and constant ozone inlet partial pressure

(22) Hessel, V.; Ehrfeld, W.; Golbig, K.; Haverkamp, V.; Löwe, H.; Storz, M.; Wille, C.; Guber, A.; Jähnisch, K.; Baerns, M.; *Microreaction Technology: Industrial Prospects*; Ehrfeld, W., Ed.; Springer-Verlag: Berlin, 2000; p 526.
(23) van Dam, M. H. H.; Corriou, J.-P.; Midoux, N.; Lamine, A.; Roizard, S. C. *Chem. Eng. Sci.* **1999**, *54*, 5311.
(24) Yeong, K. K.; Gavriilidis, A.; Zapf, R.; Kost, H.-J.; Hessel, V.; Boyde, A. *Exp. Therm. Fluid Sci.* **2006**, *30*, 463.
(25) Perry, R. H., Green, D. W., Eds.; *Perry's Chemical Engineers' Handbook*, 6th ed.; McGraw-Hill: New York, 1984.

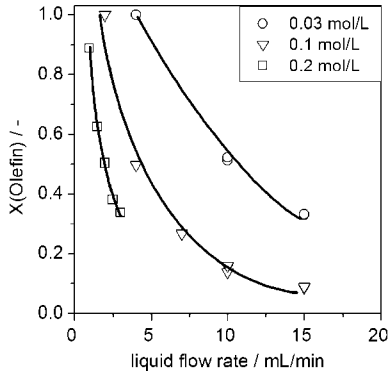


Figure 3. **Olefin conversion versus liquid flow rate ($T = -20$ °C, $p_{O_3} = 4.9–5.1$ kPa, gas flow rate = 100–107 mL/min).**

is presented in Figure 3 for three different olefin concentrations. The results show that independent of the olefin concentration the olefin conversion decreases with increasing liquid flow rate. The maximum liquid flow rate for complete olefin conversion increases with decreasing olefin concentration from about 0.5 mL/min (0.2 mol/L) to about 4 mL/min (0.03 mol/L). The olefin conversion is affected by the molar inlet ozone/olefin ratio, the liquid-phase residence time and the film thickness of the liquid phase. With increasing liquid flow rate the molar ozone/olefin inlet ratio and the liquid-phase residence time decrease while the film thickness increases. The influence of liquid-phase residence time and film thickness on olefin conversion can be eliminated if the olefin conversion for different olefin concentrations is compared at the same liquid flow rate. For the same liquid flow rate the olefin conversion decreased with increasing olefin concentration. This shows that the observed olefin conversion is determined mainly by the molar inlet ratio of ozone to olefin. The measured olefin conversion was always lower than the theoretical olefin conversion determined from the ozone/olefin inlet ratio. This is in good agreement with the results of the ozone measurements at the reactor outlet. None of the experiments presented in Figure 3 showed complete ozone conversion, even if a clear excess of olefin was applied at the reactor inlet.

To evaluate whether the mass transfer from the gas to the liquid phase influences the molar ozone absorption rate and the olefin conversion, experiments with higher gas flow rates (up to 520 mL/min) at constant liquid flow rate and ozone inlet concentration were carried out (Figure 4). With increasing gas flow rate the ozone conversion decreased from 72% at 100 mL/min to 30% at 520 mL/min. At the same time the olefin conversion increased from 35% to 70%. The molar ozone absorption rate increases from 9×10^{-4} to 1.9×10^{-3} mol/s. These results show that the ozone absorption rate and the olefin conversion depend strongly on the gas side mass transfer. The results are in agreement with previous studies on mass transfer carried out with an identical falling film microreactor where the gas-phase mass transfer coefficient increases with increasing gas flow rate.[26]

The molar ratio of the ozone absorption rate from the gas phase to the liquid phase and the olefin converted per unit of time in the liquid phase is shown in Figure 5. Linear regression

(26) Commenge, J. M.; Rode, S.; Framboisier, X.; Obein, T.; Schanen, V.; Pitiot, P.; Matlosz, M.;Proceedings of IMRET 5, 2003.

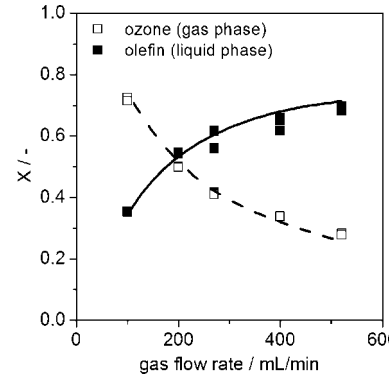


Figure 4. **Influence of the gas flow rate on the ozone and olefin conversions, respectively ($T = -20$ °C, $p_{O_3} = 2.3$ kPa, initial olefin concentration = 0.03 mol/L, liquid flow rate = 7 mL/min).**

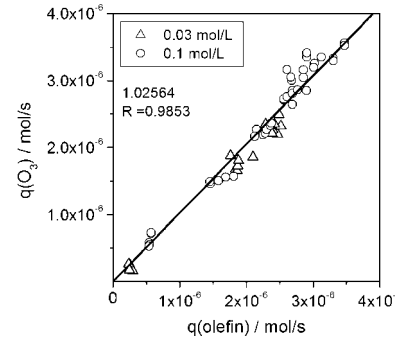


Figure 5. **Global ozone absorption rate vs converted mole of olefin per time ($T = -50$ to 0 °C, $p_{O_3} = 4.88$ kPa, gas flow rate = 100–270 mL/min, liquid flow rate = 1–15 mL/min, initial olefin concentration = 0.03 and 0.1 mol/L).**

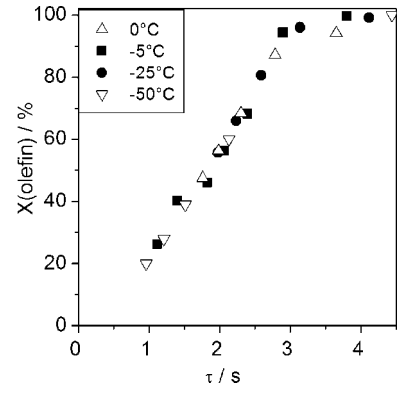
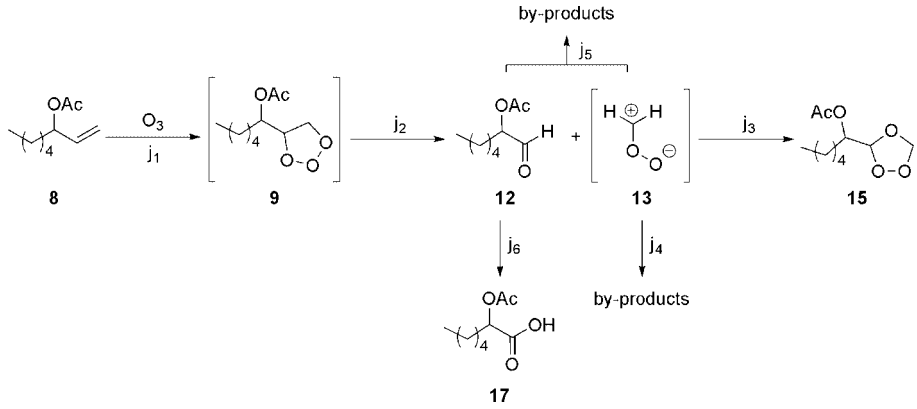


Figure 6. **Olefin conversion versus mean liquid-phase residence time at four different temperatures (initial olefin concentration = 0.1 mol/L, p_{O_3}= 4.8 kPa).**

analysis of the points gives a value of 1.02 for the slope. These results indicate that ozone is consumed only by reaction of ozone with the olefin molecules. Consecutive reactions only play a minor role under the applied conditions. This result is in agreement with preliminary studies in which indicated that ozone is stable in dichloromethane for longer times without appreciable reactions between ozone and dichloromethane.

The dependence of olefin conversion on the liquid-phase mean residence time at different temperatures is shown in Figure 6. The residence time was calculated from the liquid flow rate using the physical values of dichloromethane at the corresponding temperature. For a constant temperature, the olefin conver-

Scheme 3



sion increased approximately linearly with increasing mean residence time. Comparison of the olefin conversion at different temperatures shows no dependency of olefin conversion on temperature for the temperature range studied. It is therefore assumed that the chemical reaction of ozone with the olefin, even at low temperatures, is much faster than the mass transfer of ozone from the gas to the liquid phase. In contrast to the chemical reaction, the mass transfer has only a low dependence on temperature and therefore the rate of mass transfer is only slightly influenced by temperature. These results support the above conclusion that the measured olefin conversion is strongly influenced by the gas-phase mass transfer.

Influence of Reaction Parameters on Product Selectivities. The products of the ozonolysis reaction of olefin **8** were aldehyde **12**, ozonide **15**, and 2-acetoxy-heptanoic acid **17** (Scheme 3). The ozonides **14** and **16** as well as formaldehyde **11** (see Scheme 2) were not detected. At residence times longer than necessary for complete olefin conversion, a slightly decreasing concentration of the aldehyde and the formation of a further compound was observed. This new compound was identified by NMR spectroscopy as acid **17** resulting from reaction of the aldehyde **12** with ozone. This reaction is clearly slower than the reaction of the olefin with ozone.

Influence of Olefin Concentration. The influence of the olefin concentration on the product selectivity was studied for two different olefin concentrations (0.03 and 0.1 mol/L) at constant ozone inlet partial pressure, gas velocity and temperature (Figure 7). A different degree of olefin conversion was obtained by variation of the liquid-phase flow rate. At very low olefin conversion (<10%) a high aldehyde (>90%) and a low ozonide (<10%) selectivity was obtained for both olefin concentrations. With increasing olefin conversion, the ozonide selectivity increases and aldehyde selectivity decreases. Comparing the product selectivities at the same value of olefin conversion but different olefin concentration, generally, for aldehyde **12** a higher selectivity was observed in case of lower olefin concentration (0.03 mol/L). In contrast to that, for ozonide **15** a higher selectivity was detected at higher olefin concentration (0.1 mol/L).

However, the formation of side products increases with increasing olefin concentration, i.e., a lower ozone/olefin ratio in the reactor. For the olefin concentration of 0.1 mol/L the sum of the aldehyde and ozonide selectivities at low olefin conversion (<10%) is about 100%. For an olefin conversion of 100% the sum of these two product selectivities decreases to about 70%. It is assumed that the selectivity loss is due to side reactions of the aldehyde **12** and to overoxidation of the aldehyde **12** to the corresponding acid **17** as a result of the long residence time in the presence of an oxidative media.

Effect of Inlet Ozone Partial Pressure. The effect of the inlet ozone partial pressure on product selectivities was studied for three different ozone inlet partial pressures at constant gas velocity, temperature and an olefin concentration of 0.1 mol/L (Figure 8). The olefin conversion at each ozone partial pressure was adjusted by variation of the liquid flow rate. Olefin conversion was limited by the ozone/olefin inlet ratio, and full olefin conversion was achieved only for the highest inlet partial pressure value (4.9 kPa). Compared at a similar degree of olefin conversion an increase of the ozone partial pressure from 0.96 to 4.9 kPa has no influence on the product distributions.

Effect of Temperature. The selectivity–conversion plot for two temperatures is shown in Figure 9. A reduction of the temperature from −25 to −50 °C did not influence the product selectivity compared at the same olefin conversion. This result can only be explained with the assumption that all steps in the reaction network of the olefin ozonolysis in the liquid phase have approximately the same dependence on temperature.

Formal Reaction Scheme. Based on the observed dependencies of product selectivities on olefin conversion, a formal reaction scheme for the ozonolysis of 3-acetoxy-1-octene **8** in dichloromethane is suggested (Scheme 3).

Ozone reacts with olefin **8** to the primary ozonide **9**, which is immediately cleaved to acetic acid 1-formyl-hexyl ester **12** and the carbonyl oxide **13** (reaction path j_1 and j_2). The nearly exclusive formation of the long-chain aldehyde **12** from the primary ozonide **9** is attributed to the presence of the acetoxy group in vicinity to the olefinic double bond; **12** and **13** are the primary products as indicated by the high aldehyde **12** selectivity (>90%) at low olefin conversion. This surprising result is probably caused by the low reactivity of this aldehyde **12** due to the electron-withdrawing property of the acetoxy group in the vicinity of the carbonyl group and/or the steric effect of the acetoxy group.[27] Therefore recombination to the secondary ozonide **15** does not occur predominantly. The formed carbonyl oxide **13** gives side products (j_4) that were not identified. In the case of higher olefin conversion, the selectivity of aldehyde

(27) Marshall, J. A.; Garofalo, A. W. *J. Org. Chem.* **1993**, *58*, 3675.

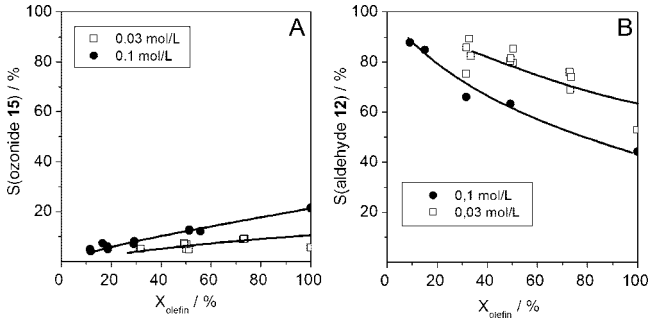


Figure 7. **Selectivity of ozonide 15 (left) and aldehyde 12 (right) versus olefin conversion at different olefin concentrations (T = −20 °C, p_{O_3} = 4,88 kPa, gas flow rate = 100 mL/min).**

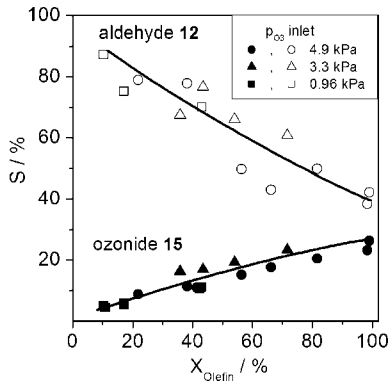


Figure 8. **Selectivity of ozonide 15 and aldehyde 12 versus olefin conversion at different ozone inlet partial pressures (initial olefin concentration = 0.1 mol/L, T = −20 °C, gas flow rate = 100 mL/min).**

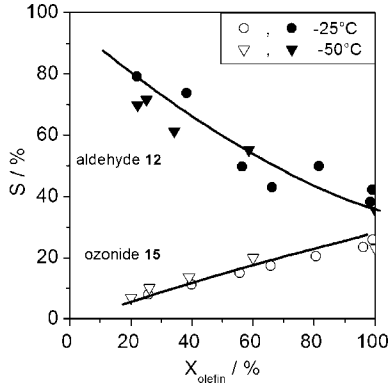


Figure 9. **Selectivity of ozonide 15 and aldehyde 12 versus olefin conversion at different temperatures (initial olefin concentration = 0.1 mol/L, p_{O_3} = 4.8 kPa, gas flow rate = 100 mL/min).**

12 decreases, indicating subsequent transformations. One of these is the formation of the secondary ozonide, which proceeds via the reaction path j_3 by 1,3-dipolar cycloaddition of the aldehyde **12** and carbonyl oxide **13**. Further consecutive side reactions of the aldehyde lead to formation of unidentified oligomeric side products (reaction path j_5). This is concluded by a decrease in the mass balance of the identified products at higher olefin conversion. At complete olefin conversion the formed acetic acid 1-formyl-hexyl ester **12** can also react with the ozone/oxygen mixture and lead to the formation of the carboxylic acid **17** (reaction path j_6). However, this reaction is clearly slower than the reaction of the olefin with ozone.

Conclusions

The ozonolysis of acetic acid 1-vinyl-hexyl ester in dichloromethane can be carried out with a minimized risk potential in a falling film microreactor in a continuous manner over a temperature interval of −50 to 0 °C. The primary ozonide formed cleaves nearly exclusively to the longchain aldehyde **12** and the corresponding carbonyl oxide **13**. With increasing olefin conversion the selectivity of aldehyde **12** decreases while that of ozonide **15** increases. Olefin and ozone are consumed in an equimolar ratio. In the range of operating conditions no effect of temperature (−50 to 0 °C) and ozone partial pressure (0.96 to 4.9 kPa) was observed on the product selectivities compared at the same value of olefin conversion. The formation of unidentified by-products depends both on olefin concentration and olefin conversion and increases with increasing olefin conversion and olefin concentration (0.03 to 0.1 mol/L).

NOTATIONS

B	wetted width (width of a channel x number of channels, m)
D_H	hydraulic perimeter (m)
D_{diff}	diffusion coefficient (m^2/s)
g	gravitational acceleration (m/s^2)
l	length of a single microchannel (m)
S	selectivity
V	volume of the liquid phase in the falling film microreactor (m^3)
$\dot{V}_{liq}$	liquid-phase flow rate (mL/min)
$\dot{V}_G$	gas-phase flow rate (mL/min)
X	conversion
ρ_G	gas density (kg/m^3)
ρ_{liq}	density of the liquid phase (g/cm^3)
μ_G	gas viscosity (kg/(m·s))
μ_{liq}	viscosity of the liquid phase (kg/(m·s))
δ	film thickness of the liquid phase (m)

Acknowledgment

The work was funded by the German Federal Ministry of Economics and Technology (BMWi) over the German Federation of Industrial Research Associations "Otto von Guericke" e.V. (AiF). The authors also thank the GVT working party 1 "Reaction Technology and Mixing" for supporting and stimulating discussions.

Received for review March 21, 2007.

OP7000673