J. of Korean Ind. & Eng. Chemistry,
Vol.3, No.4, December 1992, 579-587

Ozone Oxidation of Trans-3-hexene with/without Pyridine

Chul G. Kim* and Won P. Hong

Dept. of Chemical Engineering, Chungnam National University, Taejeon 305-764, Korea
*National Science Museum, Taejeon 305-338, Korea

(Received October 30, 1991, Accepted August 27, 1992)

Pyridine 존재여부에 따른 Trans-3-hexene의 오존 산화 반응

김 철 규* · 홍 원 표

충남대학교 공과대학 화학공학과
*국립중앙과학관

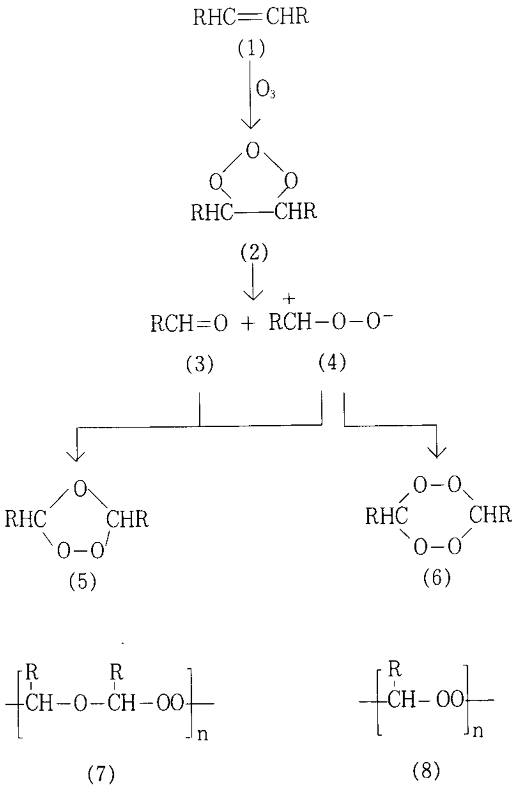
(1991년 10월 30일 접수, 1992년 8월 27일 채택)

Abstract: It was explored, whether the usual course of the ozonolysis of olefins can be modified with the help of pyridine. In the first step, the ozone oxidation of trans-3-hexene was performed with and without pyridine in the inert solvents n-pentane and dichloromethane. In addition, base catalyzed decompositions of monomeric and polymeric ozonides were also examined to identify the reaction mechanism. The reaction products were identified by modern analytical tools. The results of this work showed that reactions of ozone with olefins in the absence of pyridine in aprotic solvents gave, one hand, dominantly peroxidic products, namely monomeric and polymeric ozonides. The other hand, they in the presence of pyridine gave only the non-peroxidic products, namely propionaldehyde and rearranged propionic acid without peroxidic products. It seems, also, that the pyridine-catalyzed isomerization of the Criegee zwitterion of trans-3-hexene to give propionic acid takes place in the ozone oxidation of trans-3-hexene.

요 약: 올레핀의 오존화 반응에서 보여지는 통상의 반응경로가 pyridine의 도움으로 modification될 수 있는지 여부가 검토되었다. 먼저, trans-3-hexene의 오존 산화 반응이 aprotic non-participating solvent인 n-pentane과 dichloromethane을 사용하여 시험되었다. 덧붙여, 올레핀의 오존 산화 반응에서 pyridine의 역할과 반응기구를 검토하기 위하여, monomeric과 polymeric ozonides의 염기성 촉매 분해반응이 시험되었다. 본 연구에서 반응 과정의 고찰뿐만 아니라 생성물의 정량, 정성 분석을 위하여 현대적인 분석 기기들이 사용되었다. 본 연구의 결과로서, Pyridine 무존재하 aprotic solvent에서 올레핀과 오존의 반응으로 주로 과산화물인 monomeric이나 polymeric ozonides가 생성되었으며, pyridine 존재하에서는 과산화물의 생성없이 propionaldehyde와 Criegee zwitterion의 자리옮김 생성물인 propionic acid가 주생성물이었다. 또한, trans-3-hexene의 오존 산화 반응에서 pyridine의 촉매작용에 의하여 trans-3-hexene의 Criegee zwitterion의 propionic acid로 이성화되는 것으로 사료된다.

1. Introduction

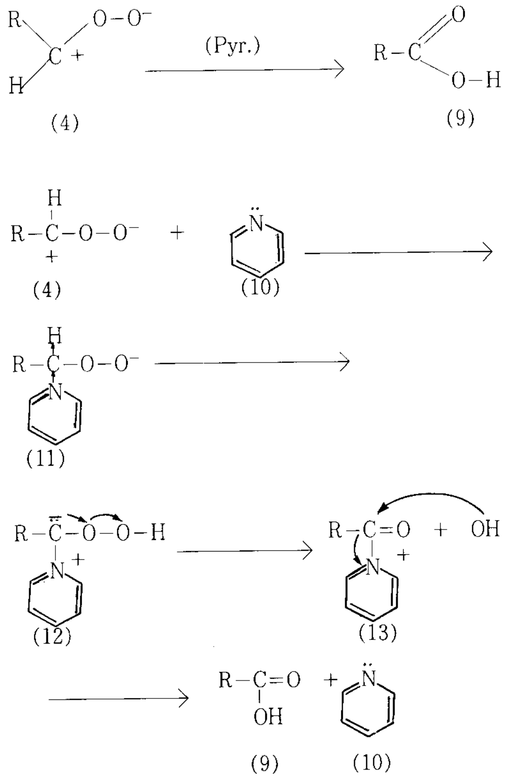
Ozone is a strong oxidizing agent for olefins(1), and it attacks selectively only the double bonds. The reaction results eventually in the cleavage of double bonds, and it proceeds stepwise with the formation of a series of peroxidic intermediates: In the first step, a 1, 2, 3-trioxolane(2) is formed by a (2+3)-cycloaddition between ozone and an olefinic substrate(1). Compounds of type(2) are, however, very labile and undergo spontaneous decomposition even at temperatures below -100℃ to give two fragments, viz. a carbonyl compound(3) and a zwitterion(4), also called carbonyl oxide. Due to its nature as a zwitterion, (4) is not stable and tends to react in such a way, that neutral compounds result. Ordinarily, i.e. in the absence of trapping agents for (4), the latter undergoes a (2+3)-cycloaddition with (3) to give a 1, 2, 4-trioxolane (5), also called ozonide. However, if the carbonyl compound(3) is too unreactive for a cycloaddition, two or several species of type(4) combine to give dimeric (6) or oligomeric peroxides (8), or (4) combines with (3) to give polymeric ozonides (7)[1]:



Scheme 1. Criegee mechanism for the ozonolysis of olefins.

It is a common feature of compounds of type (5), (7) that they are peroxidic and, hence, of limited stability. This imposes considerable limitations on their utility as industrial products, and for that reason, ozonolysis reactions have long been disregarded as a potential oxidation technique in industrial chemistry.

In recent years, however, it could be shown, that certain carbonyl oxide intermediates(4) can be induced to react in such a way that stable, non-peroxidic products can be obtained by the judicious selection and application of specific catalysts. One example for such reactions is the pyridine-catalyzed rearrangement of mono-substituted carbonyl oxides (4) to give carboxylic acids(9): This type of reaction has been discovered by the K. Griesbaum and the following rationalization for the course of this reaction has been advanced[2, 3];



Scheme 2. Postulated role of pyridine in ozone oxidations of olefins in aprotic, non-participating solvents.

However, pyridine has been employed as a unique reducing agent in ozonolysis.[1, 4-6]; it was assumed that attack of pyridine on the Criegee carbonyl oxide(4) occured to give an aldehyde or ketone and pyridine oxide. The reaction has appeared to be much complicated[7] and been not fully understood, yet.

The arguments for this are very important and must be also closed by systematical studies in details. Under this viewpoint, the ozone oxidation of trans-3-hexene was tested with and without pyridine in the inert solvents, such as n-pentane, dichloromethane, whether the usual course of the ozonolysis of olefins can be modified with the help of pyridine.

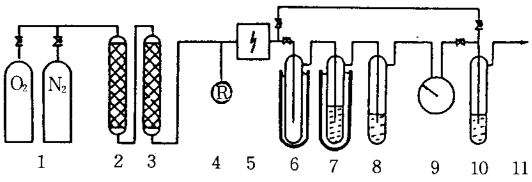
2. Experimental section

2. 1. General procedures

2. 1. 1. Ozone oxidation apparatus and experimental method

The ozone was generated by electric discharge in an oxygen stream, using a Sander or a Fischer 500 ozone generator. Ozone concentration in oxygen, which served also as carrier gas, averaged 0.5-1 mmol/ℓ. The ozone concentraion was determined by percolation of the ozone-oxygen mixture through a 2% aqueous solution of potassium iodine and titration of the liberated iodine with a 0.1 N aqueous sodiumthiosulfate solution.

For the ozone oxidation reaction the following procedure has been used: A mixture consisting of ca. 0.5-1.0g of the alkene to be ozonized and of the standard 1,1,2,2-tetrachloroethane(TCE) and, if applicable, the appropriate amount of pyridine was dissolved in ca. 100ml of either n-pentane or dichloromethane and transferred into the reactor 7 (Fig. 1). Then the stirred solution was cooled to the desired reaction temperature and ozone oxidation was started. In all experiments, the gas stream passed through the reactor had a flow rate of 20 ℓ/hr and contained 0.5mmol of ozone per liter of O_3/O_2-gas. After completion of the ozone oxidation which was recognized by the appearance of iodine in flask 8, the O_3/O_2-stream was stopped and reactor 7 was purged with nitrogen.



1. Gas cylinder(O_2, N_2) 2. Drying tube(silica gel) 3. Drying tube($CaCl_2$)
4. Manometer 5. Ozone generator 6. Cold trap(-78℃)
7. Reactor 8. KI solution bottle(2%wt) 9. Gasometer
10. NaOH solution bottle(10%wt) 11. Hood

Fig. 1. Apparatus for ozone oxidations.

For immediate ^{1}H-NMR analysis, a sample of 2-5ml of the reaction mixture was removed and concentrated by removing the solvent at room temperature and ca. 15 Torr. The residue was dissolved in acetone-d_6 or in $CDCl_3$. The main portion of the reaction mixture was transferred into a rotary evaporator, and the solvent was largely removed at room temperature and reduced pressure of ca. 15 Torr. The concentrated crude reaction product was, in each case, analyzed by ^{1}H-NMR spectroscopy. The residue was submitted to further separation and analysis.

In some cases, the concentrate from the ozone oxidation reaction was separated by flash chromatography on silica gel in order to isolate individual compounds.

2. 1. 2. Methods of analysis

Calculation of product yields by means of ^{1}H-NMR analysis was done in the following way: On completion of ozone oxidation a sample was removed. From this, the major part of the solvent was evaporated and replaced by acetone-d_6 or $CDCl_3$. Then, the NMR spectrum was recorded with tetramethylsilane(TMS) as reference. The spectra were recorded on a Bruker WM 250 spectrometer.

2. 2. Ozone oxidation of trans-3-hexene(14) in n-pentane and in the absence of pyridine

A mixture of 0.535g (6.36mmol) of (14) and 0.107g (0.636mmol) of TCE in 100ml of n-pentane was ozonized at 0℃. A sample for ^{1}H-NMR analysis was taken immediately after completion of the reaction. Its crucial part was depicted in Fig. 2 A. The assignment of the products (15), (17), (18) and (19) are based on the ^{1}H-NMR data given below.

The major portion of the crude product was kept at room temperature for ca. 1 hr, and decanted from the polymeric ozonide (18). From the decanted solution the solvent was evaporated and from the residue ozonide (17) was isolated by flash chromatography (column 1×30cm, 20 g silica gel; pentane, diethyl ether 30:1). From the polymeric ozonide (18), the residual solvent was evaporated at room temperature and ca. 15 Torr.

3, 5-diethyl-1, 2, 4-trioxolane(17): Colorless liquid, Yield: 0.152 g (1.15mmol), 18.11%, ^{1}H-NMR (250MHz, $CDCl_3$/TMS) δ=5.16(m, 1H), 1.74(m, 2H), 0.99(m, 3H). ^{13}C-NMR(CW)(63MHz, $CDCl_3$/TMS): δ=104.91(d), 25.45(t), 23.95(t), 7.88(m). MS: m/e=132(rel. intensity=15.0%) M^+, 103(73.8%) $(M-CHO)^+$, 85(2.0%), 74(42.4%) $C_3H_6O_2^+$, 45(20.2%), 29(73.8%) CH_2CH_3. IR(KBr/Film) : 2920, 1450, 1320, 1100, 900cm^{-1}.

Reduction of ozonide (17:) A solution of 20mg of (17) and of triphenylphosphine in 1ml of $CDCl_3$ was kept at room temperature for 3 days, ^{1}H-NMR analysis showed only the signals of (15).

Polymeric ozonide (18): Colorless viscous liquid, Yield; 0.363 g, ^{1}H-NMR (250MHz, $CDCl_3$/TMS) δ =5.48(m, 1H), 1.66(m, 2H), 1.06(m, 3H). ^{13}C-NMR (BB) (63MHz, $CDCl_3$/TMS) δ=110.82(m), 107.19(m), 105.55(m), 25.82(m), 23.09(m), 9.26(m). IR(KBr/Film): 2880, 1700, 1450, 1350, 1070, 940cm^{-1}.

Reduction of (18): A solution of 20mg of (18) and triphenylphosphine in 1ml of $CDCl_3$ was kept at room temperature for 10 days. ^{1}H-NMR analysis showed only the signals of (15).

Propionaldehyde(15) (Commercially available): ^{1}H-NMR(250MHz, $CDCl_3$/TMS) δ=9.72(t, 1H), 2.48(m, 2H), 1.12(t, 3H).

Propionic acid(19) (Commercially available): ^{1}H-NMR(250MHz, $CDCl_3$/TMS) δ=2.40(m, J=7.5Hz, 2H), 1.16(t, J=7.5Hz, 3H).

2. 2. 1. Base catalyzed decompositions of ozonide (17) and of polymeric ozonide(18)

a) with Pyridine: A solution containing 17mg of ozonide (17) in 1ml of $CDCl_3$ was admixed with one half equimolar amount of pyridine and kept at room temperature. ^{1}H-NMR analysis after 25 days showed its complete decomposition and the presence of (15) and (19) in a molar ratio of 15:85.

b) with Triethylamine: Solutions containing 17mg of either ozonide (17) or polymeric ozonide (18) in 1ml of $CDCl_3$ were admixed with a few drops of triethylamine and kept at room temperature. ^{1}H-NMR analysis of the sample containing ozonide (17) after 4 days showed its complete disappearance and the presence of (15) and (19) in a ratio of 34:65. Similarly, analysis of the sample containing the polymeric ozonide (18) after 2 days contained (15) and (19) in a ratio of 22:78.

c) with DMSO: A solution containing 17mg of (17) in 1ml of $CDCl_3$ was admixed with equimolar amounts of DMSO-d_6. ^{1}H-NMR analysis after 2 months showed the complete disappearance of (17) and the presence of (15) and (19) in a ratio of 23:77.

2. 3. Ozone oxidation trans-3-hexene(14) in the presence of pyridine

A mixture of 0.5 g (6.36mmol) trans-3-hexene

(14), 0.503 g (6.36mmol) of pyridine, and 1.068 g (6.36mmol) of TCE in 100mℓ n-pentane of CH_2Cl_2 was ozonized at 0℃. Samples for ^1H-NMR analysis were taken immediately after completion of the reactions. Their crucial part was depicted in Fig. 2 B, C.

3. Results and discussion

In order to establish the effect exerted by pyridine and by solvent polarity, the ozonolysis of trans-3-hexene(14) was carried out in the non-polar solvent n-pentane both in the absence and presence of pyridine, and in the polar solvent dichloromethane in the presence of pyridine. Fig. 2 shows crucial parts of the ^1H-NMR spectra of the concentrated raw reaction products obtained from these three ozone oxidations. The spectrum of Fig. 2 A shows two different signal groups, centered around 5.16 ppm, around 5.37 ppm and 5.52 ppm. They have been tentatively assigned to the CH-groups of the peroxidic compounds(17) and (18), respectively. Confirmation of these assignments is provided by the experiments described in this report. The spectrum of Fig. 2 B shows the same signals, albeit in considerably weaker intensities. The spectrum of Fig. 2 C, finally, shows no signals of peroxidic ozonolysis products.

In addition, Fig. 2 B and C show the presence of pyridine to the exclusion of pyridine-N-oxide, which means that pyridine has not been altered during the ozone oxidation of (14).

It can be clearly seen from these experiments, that the presence of pyridine changes the product slate in the ozone oxidation of (14) such that formation of the peroxidic products (17) and (18) is disfavored. Furthermore, the change from a non-polar to a polar solvent enhances this effect to the point that no peroxidic materials are formed any more[8-10].

For further structure proof, ozonide (17) and the polymeric ozonide (18) have been isolated and characterized. Isolation of (17) was achieved by vacuum distillation at room temperature and collection at -30℃. The polymeric ozonide was left as the residue of this distillation.

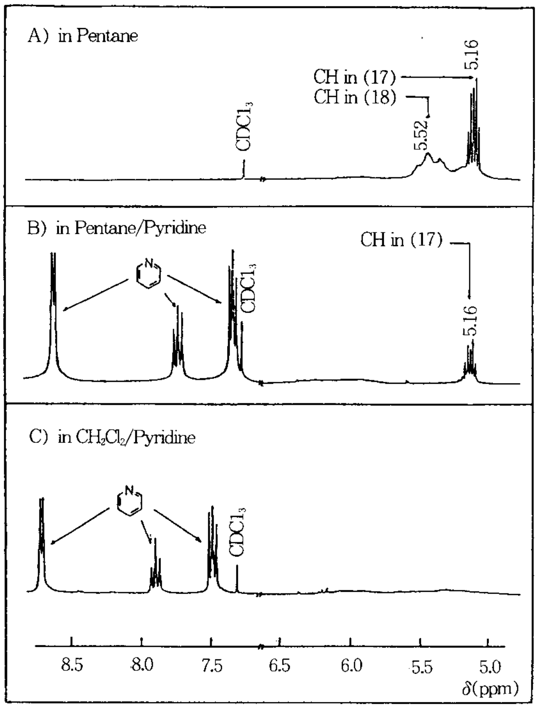
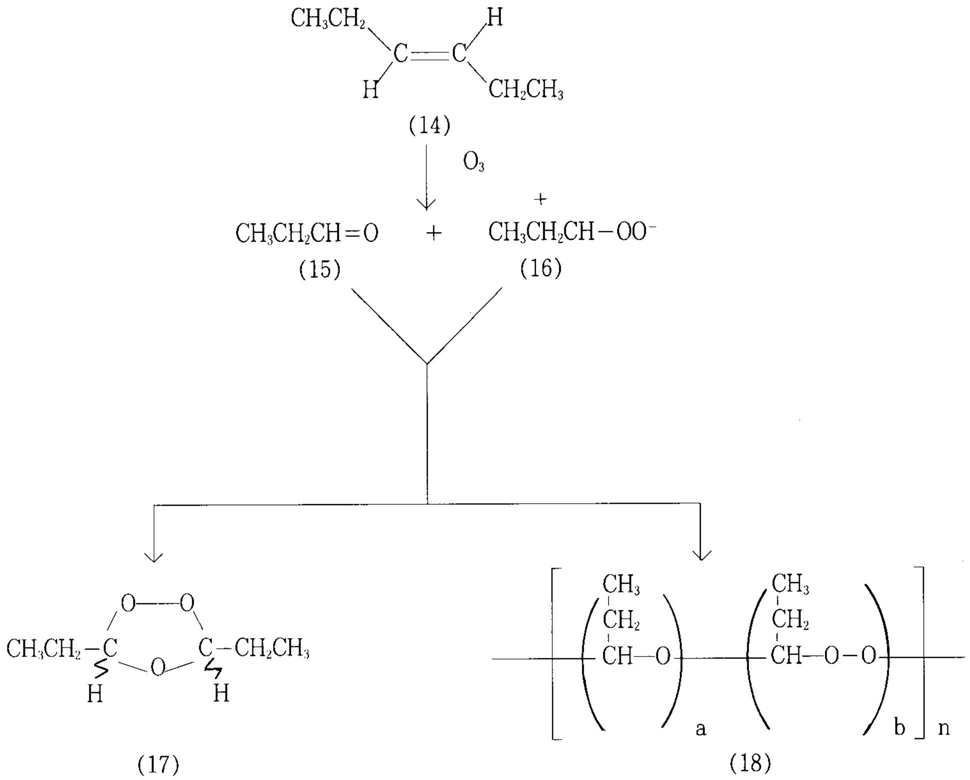


Fig. 2. Details of ^1H-NMR spectra of crude products obtained from ozone oxidation of (14) in pentane(A), in pentane/pyridine(B), and in CH_2Cl_2/pyridine(C).

Ozonide (17) is a colorless, peroxidic liquid. The ^1H-NMR spectrum showed signals centered at ca. 0.99ppm for the CH_3-groups, at 1.74ppm for the CH_2-groups and at 5.16ppm for the CH-groups. However, these signals were not of the expected multiplicity, but they were more complicated. This is ascribed to the fact, that there is a mixture of cis-and trans-ozonide (17)[11-13]. The CW-^{13}C-NMR spectrum of (17) showed a multiplet centered at 7.88ppm for the CH_3-carbon, two triplets centered at 23.94 and 25.45ppm for the CH_3-carbons and a doublet centered at 104.91ppm for the CH-carbon. The IR spectrum of (17) showed no absorp-tion in the carbonyl region. The EI-mass spectrum of (17) showed no absorption in the carbonyl region. The



Scheme 3. Peroxidic products from the ozone oxidation of trans-3-hexene (14).

EI-mass spectrum of (17) showed the peaks for M^+ at m/e=132, [[M-CH_2CH_3]$^+$ at m/e=103, [M-$CH_3CH_2CH=O$]$^+$ at m/e=74, [$CH_3CH_2CH=O$]$^+$ at m/e=58 and [CH_3CH_2]$^+$ at m/e=29.

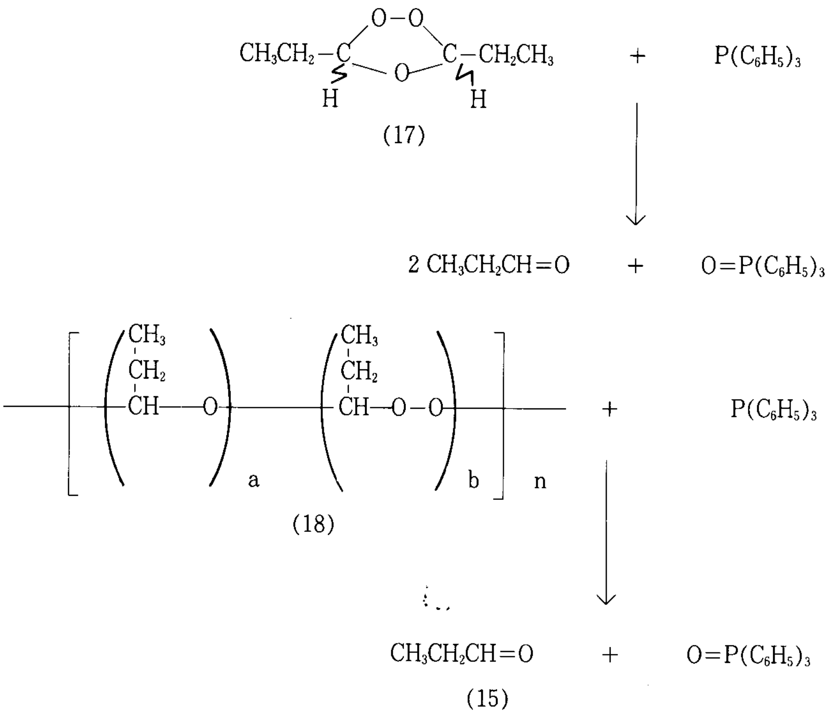
Reduction of ozonide (17) with triphenylphosphine in $CDCl_3$ at room temperature gave propionaldehyde(15) as the sole product of reduction, as evidenced by ^{1}H-NMR analysis, and in line with the expectation[14].

Polymeric ozonide (18) was a colorless, viscous liquid. The ^{1}H-NMR spectrum showed a multiplet centered at 1.06 ppm for the CH_3-groups, a multiplet at 1.66 ppm for the CH_2-groups and a multiplet centered at 5.43 ppm for the CH-groups. The BB-^{13}C-NMR spectrum of (18) showed signals at 9.26 ppm for the CH_3-carbon, at 23.09 and 25.82 ppm for the two different types of CH_2-groups and at 105.55, 107.19 and 110.82 ppm for the three different types of CH-groups, viz (O-CH-O), (O-CH-OO) and (OO-CH-OO). The different relative intensities of the two signals for the CH_2-groups and of the three signals for the CH-groups are due to the fact, that (18) is a random copolymer.

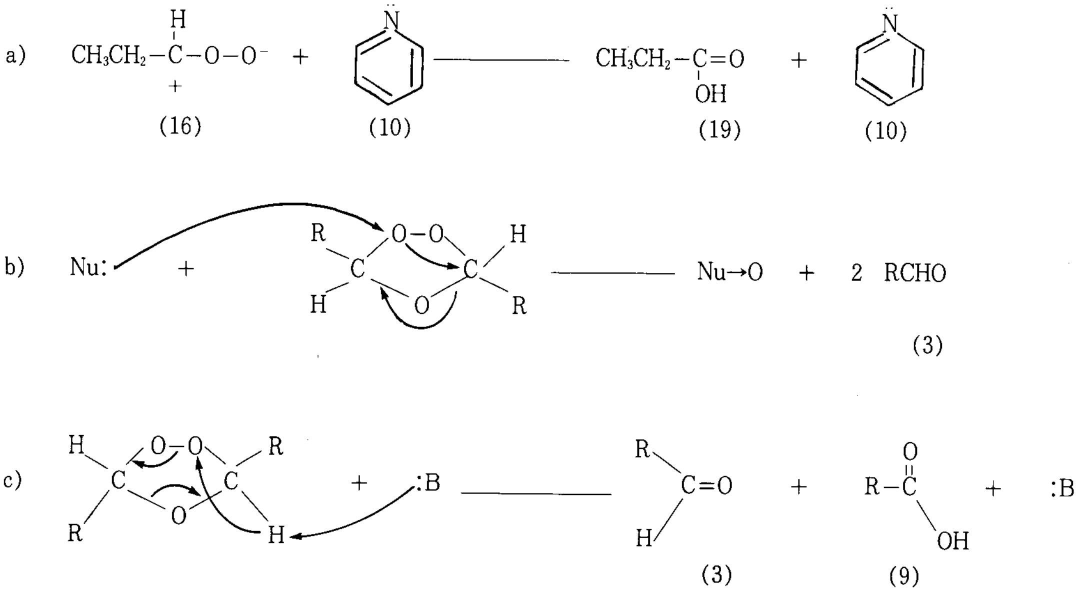
The IR spectrum of (18) showed a carbonyl absorption at ca. 1700 cm^{-1}. This indicates, that there were terminal aldehyde groups and, hence, that the polymeric ozonide(18) is an open-chain material[15].

Reduction of (18) with triphenylphosphine in $CDCl_3$ at room temperature was completed within 10 days. It gave propionaldehyde(15) as the sole reduction product.

The fact, that ozonolysis of (14) in the presence of pyridine produced less or no (17) and (18) as opposed to the ozononlysis of (14) in the absence of pyridine could a priori be due to three different ef-



Scheme 4. Reductions of monomeric and polymeric ozonide (17, 18) with triphenylphosphine.



Scheme 5. Possible reactions in the ozonolysis of trans-3-hexene in the presence of pyridine.

fects. One possibility was a pyridine-catalyzed isomerization of the zwitterion (16) to give propionic acid (19) (scheme 5, a); Since pyridine acts as a neucleophile or acts sometimes as a base[16], we can consider two reductive reactions, namely neucleophilic attact on one of the oxygens of the peroxy linkage and base-catalyzed decomposition of ozonides. The neucleophilic displacement at oxygen, like that of triphenylphosphine, as the second possibility affords 2 mole of aldehyde (3) and 1 mole of pyridine-N-oxide (scheme 5, b)[15]. However, this possibility must be removed as already mentioned because no pyridine-N-oxide has been observed during the ozone oxidation of (14) by the ^{1}H-NMR spectroscopy.

As the third possibility, one had to consider, that (17) and (18) may have been formed even in the presence of pyridine, but that they were subsequently decomposed by the action of pyridine as a base (scheme 5, c)[17-19].

In order to test the latter possibility, we have exposed both (17) and (18) to pyridine and monitored possible events by ^{1}H-NMR spectroscopy. It could be shown, that at room temperature and in $CDCl_3$-solution both (17) and (18) were indeed decomposed by catalysis of pyridine to give mixtures of propionaldehyde(15) and propionic acid(19). But both of these reactions were very slow and required ca. 1 and 2 months, respectively, to go to completion. This shows, that in the ozone oxidation of (14) in the presence of pyridine, the latter indeed interacts with the zwitterion (16) and, thus, prevents or diminishes the formations of peroxidic products like (17) and (18).

Additional tests showed, that ozonide (17) is also decomposed upon addition of triethylamine or of DMSO, which also act as base catalysts to give (15) and (19). The polymeric ozonide (18) was also decomposed to give (15) and (19) in the presence of triethylamine. These reactions were faster than those catalyzed by pyridine, yet not spontaneous in either case.

4. Conclusion

It was tested, whether the usual course of the ozonolysis of olefins can be modified with the help of pyridine. In addition, base catalyzed decompositions of monomeric and polymeric ozonides were also examined to identify the reaction mechanism. The following results are obtained in this work.

1. Reactions of ozone with olefins in the absence of pyridine in aprotic solvents gave, one hand, dominantly peroxidic products, namely monomeric and polymeric ozonides.
2. They, the other hand, in the presence of pyridine gave only the non-peroxidic products, namely propionaldehyde and rearranged propionic acid without peroxidic products.
3. Reaction mechanism studies confirmed, that pyridine catalyzes the isomerization of zwitterionic carbonyl oxide moieties to give the corresponding carboxylic acids.

Acknowledgement

This investigation was supported by the KOSEF, to whom we are grateful. The experiments was conducted while Chul G. Kim was a visiting researcher at Englar-Bunte-Institute, Winter 1990. Chul G. Kim acknowledges with thanks the support provided by Professor Dr. K. Griesbaum, the Englar-Bunte-Institute, the University of Karlsruhe, Germany.

References

1. P. S. Bailey, "Ozonation in Organic Chemistry", Vol. 1, Academic press, New York, 1978.
2. K. Griesbaum, *Chem. Commun.*, 920(1966).
3. K. Griesbaum and G. W. Burton, Preprints of papers, A. C. S. Petroleum Chemistry Division, **13**, 216(1968).
4. P. S. Bailey, *Chem. Rev.*, **58**, 925(1958).
5. G. Slomp, Jr. and J. 1. Johnson, *J. Am. Chem. Soc.*, **80**, 915(1958).

6. G. Slomp, Jr. and J. 1. Johnson, *Adv. Chem. Ser.*, **21**, 162(1959).
7. E. H. Pryde and J. C. Cowan, *Top Lipid Chem.*, **2**, 1(1971).
8. R. W. Murry, R. D. Youssefyeh, G. J. Williams, and P. R. Story, *Tetrahedron*, **24**, 4347(1968).
9. R. W. Murry and V. Ramachandran, *J. Org. Chem.*, **48**, 813(1983).
10. C. Reinhardt, "Solvents and Solvent Effects in Organic Chemistry", 2nd Ed., 69, VCH Verlagsgesellschaft mbH, Weinheim, 1988.
11. G. Schroeder, *Chemische Berichte jahrg.*, **95**, 733 (1961).
12. L. D. Loan, R. W. Murray, and P. R. Story, *J. Am. Chem. Soc.*, **87**, 737(1965).
13. V. Ball, Diplomarbeit, Universitaet Karlsruhe (1990).
14. O. Lorenz and C. R. Parks, *J. Org. Chem.*, **30**, 1976(1965).
15. S. D. Razumovskii, G. A. Niazashvili, I. A. Tutorskii, and Y. N. Yur'ev, *Polym. Sci. USSR (Engl. Transl.)*, **13**, 217(1971).
16. F. A. Corey and R. J. Sundbery, "Advanced Organic Chemistry", Part A, 267, Plenum, New York and London, 1984.
17. N. Kornblum and H. E. De La Mare, *J. Am. Chem. Soc.*, **73**, 880(1951).
18. R. M. Ellam and J. M. Padbury, *Chem. Commun.*, 1094(1971).
19. R. Criegee and H. Korber, *Adv. Chem. Ser.*, **112**, 22(1972).