

CHLORINATION OF ACETIC ACID BY MOLECULAR CHLORINE USING KETENE AND A NEW CATALYST

METİN OBALI

Department of Chemistry, Faculty of Science University of Ankara, Ankara-Turkey

ABSTRACT

A new method was described for the chlorination of acetic acid. Ketene, at definite time intervals and chlorine was continuously passed through a catalyst bed before reacted with acetic acid. The catalyst consist of silver on silicagel.

78-89 % monochloroacetic acid was isolated from liquid phase chlorination of acetic acid for 9 h in the presence of a new catalyst and ketene.

INTRODUCTION

Chlorination of the hydrocarbon chain of carboxylic acids has been the subject of investigation for more than a century. The importance of the subject lies in the preparation of carboxylic acid bearing different functional groups on the hydrocarbon chain in which chlorination mostly is the first step. Long-chain normal aliphatic carboxylic acids constitute the major components of fats and oils in plant and animal tissue. These "fatty acids" are obviously important in the fields of nutrition, medical science and industrial technology. Although, most attention probably has been devoted to the chemistry of the carboxyl group, functionalisation of the hydrocarbon chain have received a good share.

Several procedures for the chlorination of carboxylic acids at the α position are known. Most of them use molecular chlorine with a promoter such as phosphorus trihalide (Hell-Volhard-Zelinsky reaction 1881-1887), thionyl chloride (Harp, et.al. 1975) or chlorosulfonic acid or oleum (Ogata, Sugimoto, 1978-1979) (Ogata, Watanabe, 1980). Methods using N-chlorosuccinimide or CuCl_2 (Louw, 1966) are also known.

In all these procedures at least ten percent of promotor is used and mostly it is a difficult step to separate the promotor from the product. Generally promoters are not reused.

There is no selectivity problem in the chlorination of acetic acid because of one methyl carbon. Among carboxylic acids, acetic acid is the most difficultly chlorinated acid because of inductive effect of carbonyl group and absence of electron releasing alkyl group. We here report a new method for the chlorination of acetic acid by using ketene and a new silver-silicagel catalyst.

EXPERIMENTAL

Unless otherwise stated, all chemicals and solvents were general laboratory or analytical grade. Glacial acetic acid (64-19-7) was obtained from Adapazarı Asit Sanayii (Sakarya-Turkey) 99.6% G.C. purity, contains %0.3 ethyl acetate %0.1 butanol impurity, M.P= 16°, B.P= 116-118°, $D_4^{20} = 1.04$. Chlorine was obtained in cylinder from Koruma Tarım İlaçları A.Ş. (Derince-Kocaeli Turkey).

Preparation of catalyst: 40 g sodium silicate ($D_4^{20} = 1.39$) (water glass) was dissolved in 60 ml water and poured slowly together with equal amounts of 60 ml 6N sulfuric acid, into a vigorously stirred beaker, after addition stirring was continued for 5 min and freshly prepared solution described below was added slowly.

1 g potassium hydroxide was dissolved in 20 ml water and added to 20 ml solution of 2 g silver nitrate. Precipitated silver oxide was complexified by adding adequate amount of ammonium hydroxide dropwise. To this solution was added a solution of 2.25 g of sucrose in 25 ml of water containing two or three drops of nitric acid and immediately the whole solution was mixed with the prepared silicate solution.

The whole content was left overnight for gel formation. Formed gel was put in a cambric bag and dialyzed ten times with distilled water. First dried in the air than in the oven. Oven temperature was raised to 110° gradually to prevent the breaking into pieces of the formed gel. Yield was 14.56 g unactivated catalyst.

Keten was obtained from a generator described by Vogel (1977)

Typical procedure for the chlorination by using catalyst and ketene: 50 ml (0.87 mol) glacial acetic acid was put in a 100 ml three neck-

ked flask. To the middle neck, a gas inlet tube was fitted with a sintered plate at its lower end, filled with 5 g of prepared catalyst above acetic acid level by placing first glass wool. Other two necks were fitted with an all glass syringe and a Dimroth condenser. The exit of the condenser was connected to a pressure regulator and a washing bottle to trap evolved hydrochloric acid and excess chlorine. Chlorine from the cylinder was washed with sulfuric acid and then passed through a pressure regulator and introduced to the top of catalyst bed together with ketene which was produced at certain intervals from a generator. The two gases separated from each other by a T stopcock. Chlorine was passed through the catalyst bed continuously throughout the chlorination. Ketene was introduced only at first ten minutes and two minutes at the end of first, second, third and fourth hours. During ketene introduction, ketene to chlorine mol ratio was kept nearly at 2. Flask was immersed in a paraffin bath which was kept at 180°. Aliquots (0.2 ml) of the reaction mixture were taken out by the use of syringe at given time intervals, and analyzed with G.C. quantitatively by using 50 μ l bromobenzene as internal standart. Relative response factors of acetic acid, methyl esters of monochloroacetic acid and dichloro acetic acid were also determined. All gas chromatographic analyses were carried out with a Spectra Physics Autolab Minigrator, temperature programmer and flame ionization detector connected Perkin Elmer Model F11 chromatography by using 1/8 in 2 m stainless steel column filled with 3% carbowax 20 m on chromosorb 750, 100-120 mesh, with nitrogen carrier gas flow rate 30 ml min⁻¹ at 90° oven temperature. Acetic acid was analyzed directly. F.I.D. response for mono and dichloroacetic acids were so small that they were derivatized by using diazomethane to methyl esters and analyzed, quantitatively as their methyl esters (Schlenk H., Gellerman J.L., 1960).

The reaction products of ketene and molecular chlorine on catalyst bed was analyzed by using Packart-Finnigan 3000 E Quadrupol G C. M S system. Column used in this separation was 3% OV 101 on Gas Chrom 80-100 mesh 2mx2mm glass column, temperature programmed from 50° to 180° at 0.7°C min⁻¹ with helium carrier gas flow rate 20 ml min⁻¹, ionization energy= 70 eV.

RESULTS AND DISCUSSION

For quantitative gas chromatographic analyses relative response factors of acetic acid and methyl esters of mono and dichloroacetic acids to bromobenzene were found: 0.35, 0.57, 0.60 respectively.

In all gas chromatographic quantitative analyses these values were used.

To make a comparison of the catalyst effectiveness in acetic acid chlorination, chlorination was carried out under identical experimental conditions in three ways, a) only chlorine was introduced, b) ketene was also introduced in the same procedure as with the catalyst, c) chlorine was introduced to acetic acid through active catalyst bed without ketene. In case (a) at the end of 30 h monochloroacetic acid yield was only 52.8 % and 11.7 % of dichloroacetic acid was also formed. The result of direct chlorination was given in Figure 1. In the α halogenation of carboxylic acids, two different mechanisms have been proposed that, reaction proceeds via enol or ketene intermediate with little evidence (Little, et.al., 1969) but most workers prefer the intermediacy of enol (Harpp, et.al. 1975) (Rodin and Gershon, 1973). Besides, only one kinetic study for the Hell-Volhard-Zelinsky reaction was reported, in which the rate was said to depend on the concentration of bromine (Kwart, Scalz, 1964) in contrast to the behaviour of enol mechanism in which enol form is in equilibrium with the keto form and rate-determining step is the enolization, hence the rate is independent of the concentration and nature of halogen. In enol mechanism chloroacetyl chloride is intermediate and it is known that reaction of ketene with chlorine gives this compound (Boese, 1940). In strong acidic media chlorination, ketene formation by dehydration of acid have been postulated by Yoshira Ogata et.al. 1(978). In the light of above discussion we decided to use ketene, in which chlorination was carried out with the use of ketene and chlorine together. The results are better than direct chlorination At the end of 10 h monochloroacetic acid yield is 49% and the ratio of the used ketene to acetic acid is only 8-9 %. As it is seen in Figure 3, in much shorter time i.e. 1/3, about the same percent yield is obtained. On the other hand, in an investigation by König and Kolb (1952) chlorination rate increased when the reaction was carried out in a silver plated reactor and known interactions of silver with halogens and double bond gave rise to the idea of trying silver as heterogeneous phase catalyst. As a preliminary work, silver plated ceramic beads were used as catalyst together with ketene and an increase in the reaction rate was observed. Than we prepared silver-silicagel catalyst, but in the first run a reversed effect was observed and product yield was lower than any other chlorination case. At the end of 9 h monochloroacetic acid yield percent was only 4.6. In the second

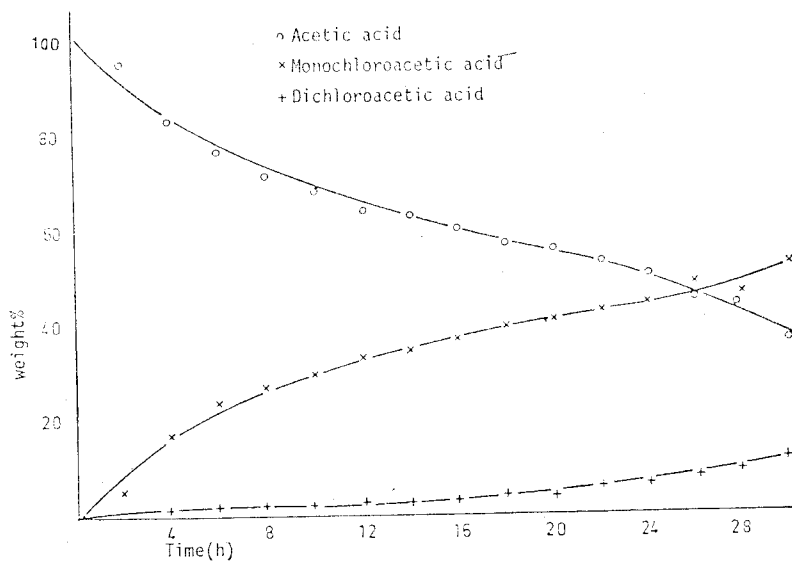


Figure 1. Chlorination of acetic acid by molecular chlorine.

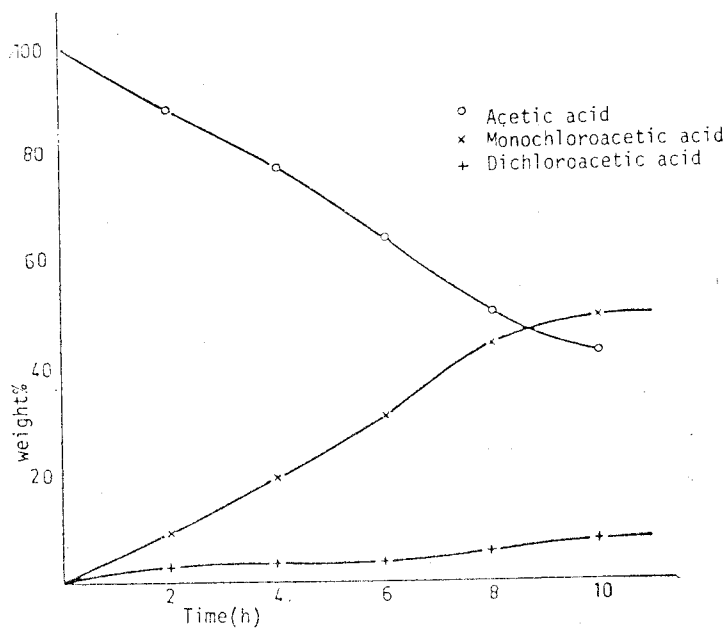


Figure 2. Chlorination of acetic acid with molecular chlorine and ketene.

run it increased to 15.3. Further work showed that, catalyst was gaining its full activity, after chlorine passage through the catalyst continued 18 h. The activity of the catalyst was tested for 270 h and within certain limits no change was observed.

During chlorination of acetic acid with active catalyst and ketene, at the end of 9 h, 87–89 % yield of monochloroacetic acid was obtained together with 7–8 % yield of dichloroacetic acid. Increasing the chlorination time was found to increase the yield of dichloroacetic acid. The increase of catalyst activity with reaction time was given in Figure 3 and chlorination of acetic acid in the presence of active catalyst and ketene was given in Figure 4. The results of using only active catalyst but not ketene, was given in Figure 5. This is the (c) case in our previous discussion. As it is seen, chlorination carried out by using only active catalyst results in the formation of more dichloroacetic acid than other cases, it is 21.8% at the end of 14 h. Comparison of the different chlorination precuderer can be seen in Figure 6.

Rate of chlorination reaction in the presence of ketene and active catalyst was increased with the temperature increase of the paraffine bath of the reaction flask. But after 180°, percent yield of monochloro product was decrease because of decomposition of monochloroacetic acid. All chlorination reactions were carried out in 180° paraffin bath. When ketene and chlorine passed together through active catalyst, mol ratio of ketene to chlorine was kept at approximately 2, because according to Ptil (1959) when ketene ratio increases more, monochloroacetyl chloride formation decreases and excess ketene reacts with evolved hydrogen chloride to give acetyl chloride (Lacey and Blades, 1956).

To find out the reaction products when ketene and chlorine passing through catalyst bed, condensed liquid from the exit of the catalyst was analyzed by GC.MS. system. The condensed mixture was colourless and turned to dark brown colour on standing. This indicates the presence of free radicals. The ion chromatogram was given in Figure 7. As it is seen, major products are chloroacetyl chloride and dichloroacetyl chloride Small amonuts of unexpected 1,2-dichloroethane, dichloroacetone and trichloroacetone are formed.

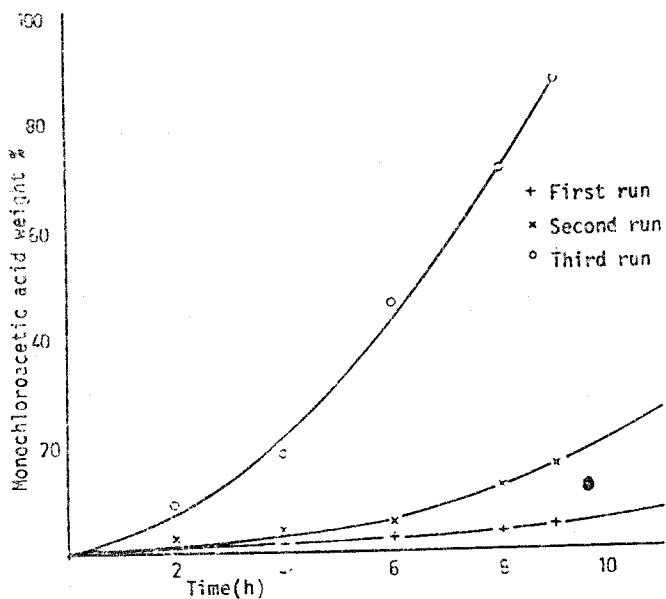


Figure 3. Increase of catalyst activity

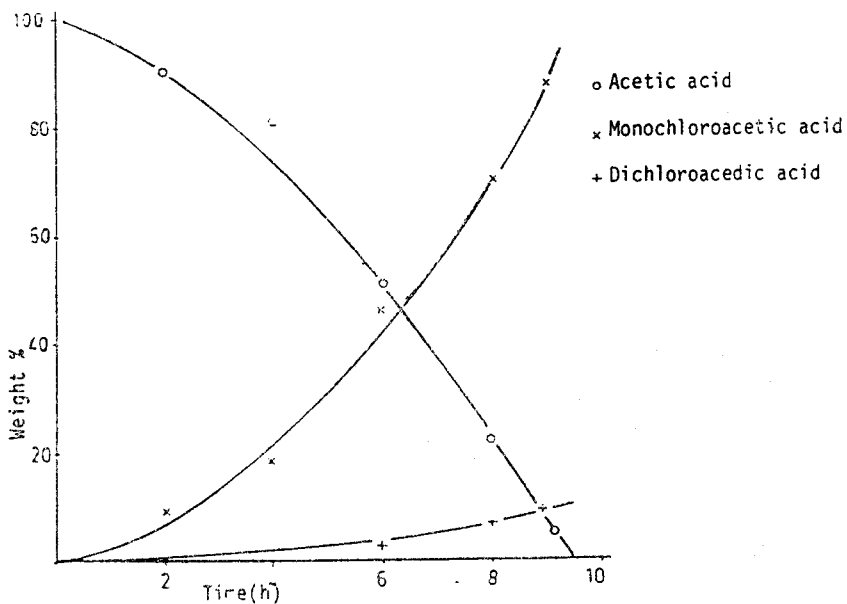


Figure 4. Chlorination of acetic acid with molecular chlorine ketene and active catalyst

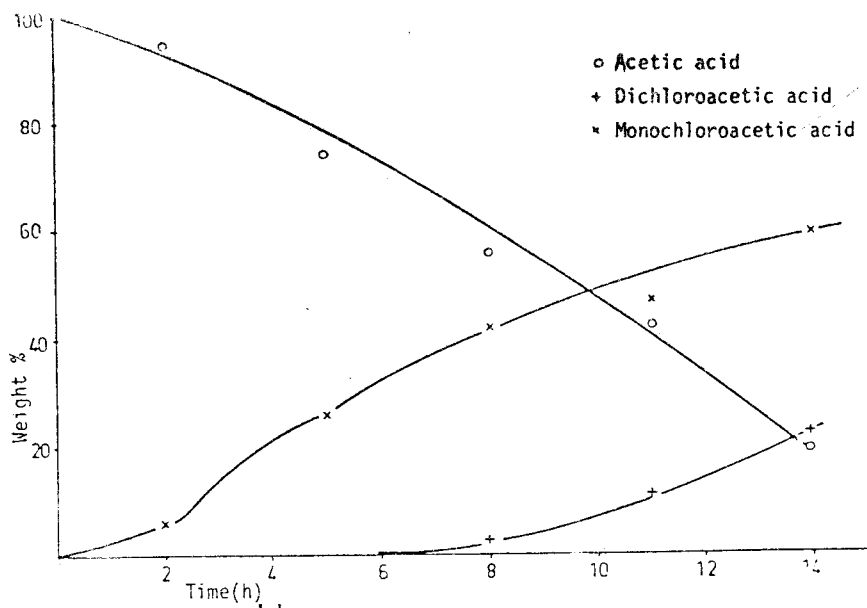


Figure 5. Chlorination of acetic acid with molecular chlorine and active catalyst.

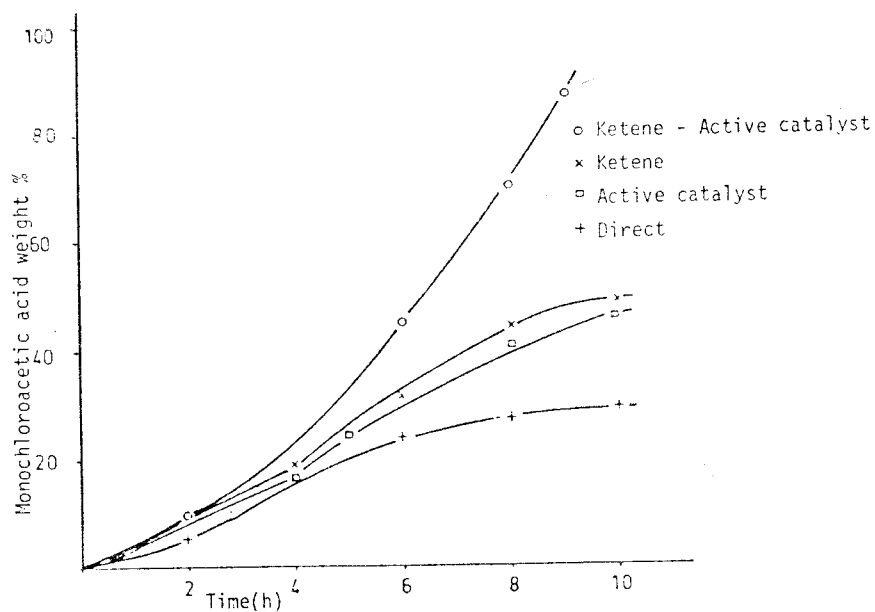


Figure 6. Monochloroacetic acid yield by different chlorination methods of acetic acid.

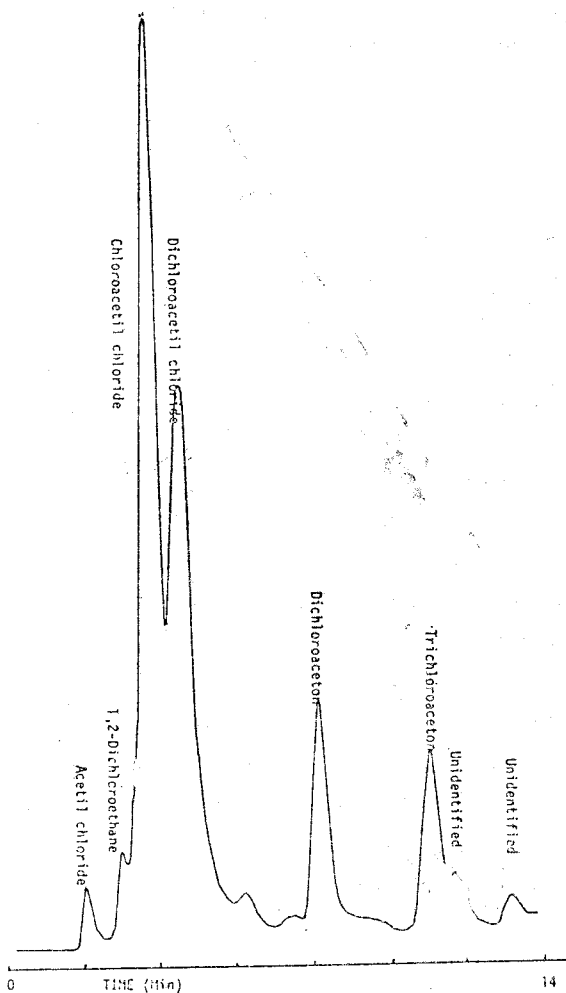


Figure 7. Ion chromatogram of products formed on active catalyst bed from ketene and molecular chlorine.

CONCLUSION

According to acetic acid, 8-9 % (w) of acetone is consumed for the production of ketene in this chlorination process of acetic acid and a silver-silicagel catalyst bed is used. Reaction rate in this method is three times higher than direct chlorination. At end of 9 h chlorination, 87-89% of monochloroacetic acid is produced containing only acetic

acid and dichloroacetic acid as impurity but in other chlorination processes product contains sulfurous or phosphorous catalyzing compounds which are mostly separated with difficulty.

REFERENCES

- BOESE, A.B., *Ind Eng. Chem.*, 32, 16 (1940)
- HARP, D.N., BAO, L.Q., et.al., *J. Org. Chem.*, 40, 3420 (1975)
- HELL, C., *Ber.*, 14, 891, (1881)
- KÖNIC, J., KOLB, H., *Ger. Pat.*, 824, 342 (1952)
- KWART, H., SCALZI, F.V., *J. Am. Chem. Soc.*, 86, 5496 (1964)
- LACEY, R.N., BLADES, A.E., *Brit. Pat.* 735, 902 (1955)
- LITTLE, J.C., et.al., *J. Am. Chem. Soc.*, 91, 7090 (1969)
- LOUW, R., *Chem. Commun.*, 544 (1966)
- OGATA, Y., SUGIMOTO, T., INAISHI, M., *Org. Synth.*, 59, 20 (1979)
- OGATA, Y., WATENABE, S., *Bull. Chem. Soc., Jpn.*, 53, 2417 (1980)
- OGATA, Y., SUGIMATO, T., *J. Org. Chem.* 43, 3684 (1978)
- PRILL, E.J., *U.S. Pat.*, 2, 889, 365 (1959)
- RODIN, R.L., GERSHON, H., *J. Org. Chem.*, 38, 3919 (1973)
- SCHLENK, H., GELLERMAN, J.L., *Anal. Chem.*, 32, 1412 (1960)
- VOGEL, A.I., *Practical Organic Chemistry.*, Longman 3 rd. Ed. p. 373 (1977)
- VOLHARD, J., *Ann.*, 242, 141 (1887)
- ZELINSKY, N., *Ber.*, 20, 2206 (1886)