GLOBAL JOURNAL OF PURE AND APPLIED SCIENCES VOL. 6 NO. 4, SEPTEMBER 2000:697-704
COPYRIGHT (C) BACHUDO SCIENCE CO. LTD. PRINTED IN NIGERIA ISSN 1118-0579

EFFECT OF H_2O_2 AS CATALYST ON PRODUCT DISTRIBUTION ON AR-H OXYCHLORINATION AT LOW TEMPERATURE

J. SOJI ADEYINKA and B. B. MAMEDOV

(Received 17 July 1997; Revision accepted 24 February, 2000)

ABSTRACT

An homogeneous catalytic oxychlorination reaction of aromatic hydrocarbons was carried out on H_2O_2 as catalyst on HCl oxidation for chlorine for chlorination process in situ. Presence of Ar-H in the medium shifted the oxidation rate of the HCl through bond breaking in the Ar-H-Cl upon which chlorine distribution was found to be dependent on H_2O_2 concentration, and temperature. Increase in HCl concentration beyond 30% showed significant effect on the rate of chlorine liberation but no influence on chlorine distribution in the Ar-H, except on branched hydrocarbon groups. Temperature profile showed that 99% of the available chlorine was liberated between 40 – 55^{0}C while only 98% of the liberated chlorine reacted with the aromatic hydrocarbons. Above 60^{0}C over 40% of the liberated chlorine dissolve in the inorganic phase as a result of evaporation of the Ar-H from the reaction zone at that temperature.

Keyword: chlorine, organic phase, pivot radical, temperature, concentration.

INTRODUCTION

Increased concentration of hydrogen chloride gas as by product in organic chlorination processes and its side effect as environmental pollutant has made such HCl to become a chlorine source in the chemical industry. Although Deacons process used hard contact catalysts at slightly elevated temperature (Cu_2O_2 and 350^{O}C) problem of equilibrium shift towards the left at temperature above 250^{O}C and hot spot locations on the catalyst are the disadvantages of such processes (Englin 1969). Thus, there arose a need for better catalyst with better and lower temperature tolerance. Such catalyst, usually liquid homogeneous catalysts made it possible for the reaction process to be

J. SOJI ADEYINKA, Chemical Engg. Department, University of Port Harcourt, Port Harcourt - Nigeria
B. B. MAMEDOV, Department of Petrochemical and Organic Synthesis Azerbaijan Industrial University, Baku - Azerbaijan

carried out at very low temperature ($T \leq 60^{O}C$) with better efficiency and effectiveness without the problems of hot spot location and need for temperature regulation by cooling.

Hydrogen peroxide is a stable one electron donor/acceptor reagent at the catalytic stage. This made the H_2O_2 to be better than the permanganate and the chromate salts often used as catalyst of oxidation. Also, since chlorinated aromatics are highly reactive reagents, they serve as starting raw materials in the pharmaceutical, fine chemical and allied industries. Need for industrial scale production of such products has led to source raw materials (HCl) from alternatively cheap sources becomes very important (Burke 1964, Abramov 1976, Campbell et al 1980, and Allen 1971). Hydrogen peroxide as catalyst for such reaction has not been deeply investigated, as such, very few reports are in existence on its thermodynamics and mechanism. Due to lack of information on these guiding factors, true mechanistic pathways of such reactions was investigated. Since the 3π-bonds in monocyclic benzene and aromatics are evenly distributed and equally reactive, reaction of chlorine at these bonds will take place faster than the reaction of OH or per hydroxyl ($HOO^{\cdot}$) arising from the reaction of hydrogen peroxide and hydrogen chloride especially at the m-position since chlorine is more reactive than

This work presents a kinetic study for product distribution and mechanistic pathway for the transformation of such products using elemental analysis, solvation effect of π-bond, water concentration, and electron distribution as it affected dislocated π-bond.

EXPERIMENT

Pure benzene and toluene from BPI, and hydrochloric acid (15%, 25%, 30% concentration) were variously treated with hydrogen peroxide. All reagents were certified pollution free and experimental operation condition maintained.

$Ar\text{-}H\text{-}H_2O_2\text{-}HCl$ was dosed into the reactor and stirred for six hours continuously in a 1dm three way reactor flask fitted with heat control

HO^{-}. Such attack of chlorine (Cl Cl^{-}) in the position will depend on temperature (activation energy) and the polarity of the medium. Variation in HCl concentration has little effect on the process.

jacket in a closed PTFE vacuum tight apparatus. The mixture was regulated through equal molar dosing of H_2O_2 and HCl into the Ar-H. At the end of the six hours continuous reaction after all the H_2O_2 and HCl had been dosed, the mixture was further stirred for one hour (gently) until the temperature of the system became constant (25°C). The rector and its content were then kept overnight, a separation funnel was used to separate the organic phase from the inorganic phase.

The organic phase was initially sent for chromatographic analysis. Major content of the organic phase was then distilled in a glass jacket to evaporate pure organic component from the soluble inorganic phase. The distilled organic product was analysed for purity and compared with the crude organic phase analysis. The inorganic phase was treated with 0.1N NaOH to evaluate the presence of HCl and its percentage composition in the inorganic phase. The major content of the inorganic phase was then titrated with $Na_2S_2O_3$ to evaluate soluble chlorine in the inorganic phase.

RESULTS AND DISCUSSION

Reaction of hydrogen peroxide on hydrochloric acid is an oxidative process in which the HCl is reduced to chlorine and water. Such chlorine release depended on the concentration of both hydrogen peroxide and the HCl. Table 1, shows the rate of chlorine release at different hydrogen peroxide concentration at constant temperature.

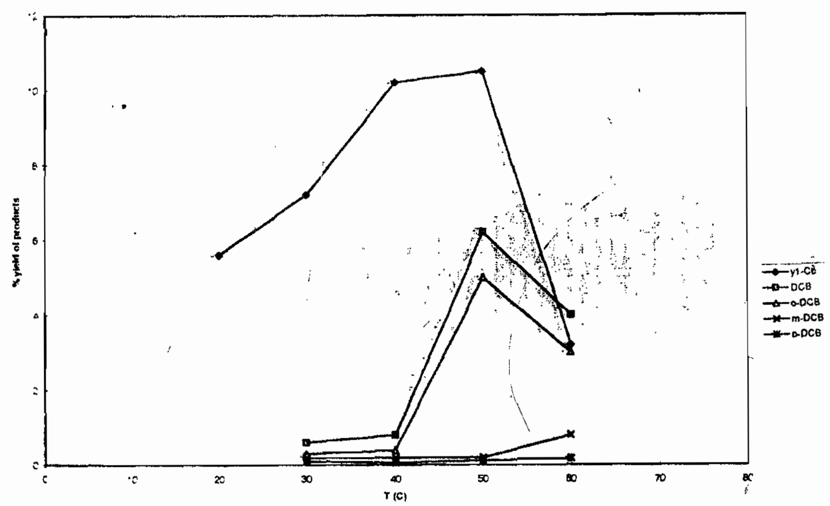
Table 1: Effect of $[H_2O_2]$ on Chlorine Release in H_2O_2-HCl Process

Time(hr) Yield (% Cl_2)	1	2	3	4	5	6	7	8	9	10	11	12	14	16
10												4	5.8	6.5
15										4	6	6.4	6.8	9.6
20									3	5	5.5	7.0	7.8	8.0
25							3.5	5.0	6.0	8.0	8.4	9.0	9.2	
30	3	10	15	18	19		19.4	19.6	19.6	19.6	19.7	19.8		
40	5.0	10	15	17	20	21	21	21.4	21.6	22.0	21.0			
50	12	18	25	26	26	28	28.4	28.4	28.6	28.8				
60	18	30	31	31.6	32	32.8	3.6	34	34	34				

Table 2: Product distribution of oxychlorination of benzene at constant H_2O_2 and 30% HCl

Temp (°C)	20	30	40	50	60
Product (g)					
C_6H_5Cl	5.77	7.22	10.28	10.88	3.25
$C_6H_4Cl_2$	-	0.60	1.22	6.52	4.20
o-DCB	-	0.40	1.02	5.42	2.68
m-DCB	-	0.06	0.02	0.18	0.20
p-DCB	-	0.17	0.18	0.92	1.32
Cl_2	0.10	0.05	0.46	0.31	0.69
HCl	0.12	0.11	0.06	0.13	0.32
H_2O_2	0.70	0.03	0.03	0.07	0.46
C_6H_6	4.10	1.85	4.03	0.53	3.20

Fig.1 Product distribution of Chloro-organic phase at varying temperature.

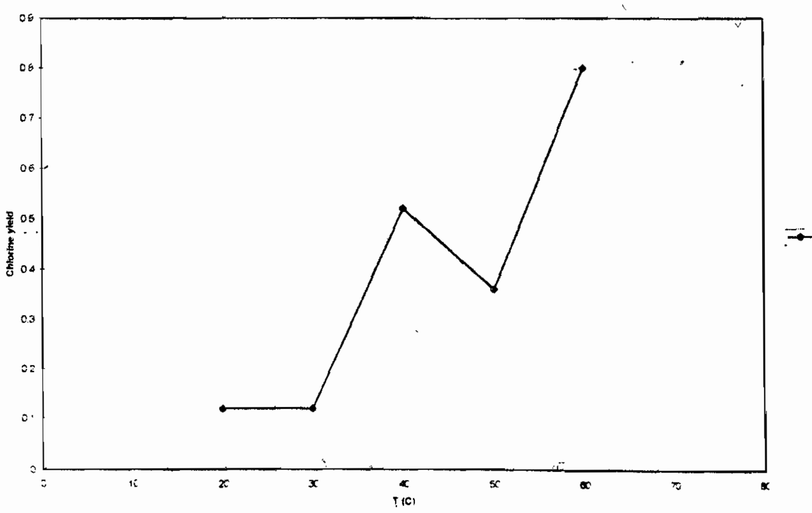


It was observed that when the oxidation reaction was carried out for sixteen hours, increase in H_2O_2 concentration increased chlorine release rate from 40% till 60% within the first six hours of the experiment after which further doses of H_2O_2 had no significant effect.

Figure 1 shows product distribution of the reaction of benzene chlorination. Variation in the o,m,p-position of chlorine on the dichlorobenzene (DCB) shows an indication of the effect of polarity of the medium, the prevailing reaction condition and the effect of Ar-H configuration. Table 2 shows the product distribution of benzene oxychlorination at constant reactant concentration.

Chlorine distribution can be seen as an effect of π-bond dislocation thus leading to a subsequent attack of chlorine at the $_{p,m}$-positions respectively due to the $_o$-position dislocation. This has led to an increase in the DCB at 30°C and above at equimolar ratio of H_2O_2 and HCl at such conditions. Figure 2, shows the concentration of dissolved chlorine as observed from the inorganic phase analyses. This shows that the higher the temperature of the process the higher the rate of chlorine escape into the inorganic phase from the reaction zone. This is as a result of the instability of C_6H_6- Cl_2 complex formed at such high temperature of exothermicity upon which the contact time of chlorine with the Ar-H becomes reduced far below the reaction time. As a result of this, the complex does not

Fig.2 Rate of chlorine diffusion into Inorganic phase at different temperature



transform into chloroorganic products, thus, some of the chlorine dissolved into the inorganic phase (water) (Adeyinka 1985, Jimenez et al 1983). Table 3 shows yield of chlor-aromatic derivative at different hydrogen concentration.

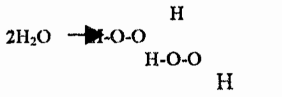
Table 3: Effect of [H_2O_2] on Product Distribution of Different Ar-H

Reagent	Process product	Concentration of H_2O_2 20	30	40	60
Benzene	Conversion	23.0	29	35	25
	MCB	23.0	28	35	25
	PCB	-	6.4	5.1	4.6
Toluene	Conversion	27	18.5	10	7.0
	Isomeric CT	15.8	10.5	5.2	3.2
	P-CT	11.2	8.0	4.8	3.8
Xylene	Conversion	23.0	20.2	18.6	13.1
	PC Xylene	6.8	5.8	4.8	2.4
	p-C Xylene	3.9	4.6	6.3	3.3
o-Xylene	Conversion	17.5	15.8	14.0	11.2
	Isomeric MC-Xylene	14.0	11.8	9.6	7.6
	o-C Xylene	5.5	5.0	4.4	3.8
m-Xylene	Conversion	17.1	13.0	10.0	10.0
	Isomeric m-Xylene	12.4	10.0	7.8	6.6
	m-C Xylene	1.7	3.5	2.3	3.5

From the analysis of the product distribution, it was observed that increase in temperature increased polychlor-atomatic hydrocarbons. This is an evidence of the catalytic activity of H_2O_2 with respect to activation energy reduction at such temperature. This can be associated with the ease of attaining equilibrium as a result of higher oxygen content at increased H_2O_2 upon which peroxides function as electron donor with a radical transition stage. Such proposition of radical formation is supported by the exothermicity of the process. Also chlorine so produced in the system reacts initially with oxygen forming chloroxyl radical ClO^- upon which one electron so transferred proves the radical reaction since there was no phenolic product in the process as a result of (HO^-) absence. Presencne of oxyl radical reacting with hydroxyl ion has been reported for phenol production (Adeyinka 1988). Absence of such phenolic products may be used as a confirmation of the involvement of a radical in the reaction mechanism. Although, chlorine dissolved in the water, such H_2O-Cl did not produce H^+,OCl- since no functional group of such were observed in the products; even though, this ions has higher reactivity than Cl^- or Cl-. Since no such functional group was observed, it was confirmed that the unreacted chlorine dissolved in the water this was in agreement witn tne result of the inorganic phase titration with $Na_2S_2O_3$. As temperature increased, due to exothermicity, chlorine evaporated with unreacted Ar-H especially above 50°C. This led to gaseous phase reaction at which the heat of reaction was reduced at the bottom of the reactor between 60 ± 5°C.. Above (40%) concentration of H_2O_2, high heat of reaction was evolved. This led to reduction in the activation energy of the dichloro aromatic formation. This invariably reduced the yield of monochlorcbenzene especially even

MECHANISTIC STUDY

In a system $A\text{-}H_2O_2\text{-}H_2O$ (where A is a halide – HCl) increase in the H_2O_2-A plays a major role on the exothermicity of the process of the process. The effect of such heat of reaction has led to bond breaking upon which



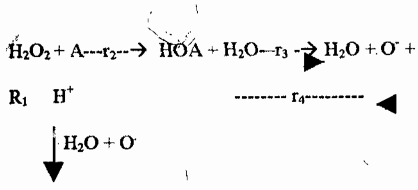
$$2H_2O \rightarrow \begin{matrix} \text{H-O-O} \quad \text{H} \\ \text{H-O-O} \\ \quad\quad \text{H} \end{matrix} \quad [2]$$

Which in the presence of HCl will yield

$$2\text{H-O-O-H} + 2HCl \text{-----} 3H_2O + Cl_2 + O\text{-} \quad [3]$$

at high molar ratio of benzene in the reactor.

Variation of hydrogen chloride concentration above 30% has no significant effect on oxychlorination process since chlorine release rate remained constant but increase in H_2O_2 strongly affected chlorine liberation in the HCl at concentration between 15% and 30% at which such chlorine liberation became constant.



$$H_2O_2 + A \xrightarrow{r_2} HOA + H_2O \xrightarrow{r_3} H_2O + O^{\cdot} + HA \quad [1]$$
$$R_1 \quad H^+ \quad \xleftarrow{r_4} \quad \downarrow H_2O + O^{\cdot}$$

HA (HOCl) depended on the water concentration in the medium thereby increasing the catalytic property of H_2O_2 liberating $O^{\cdot}$ in r1 and r3 through the route

$$H_2O_2 + HCl \xrightarrow{k_2} H_2O + HOCl \quad [3B]$$

HOCl at thermal decomposition or attack of free radicals within the system on HOCl will lead to both chlorine and oxygen radicals respectively.

$$HOCl \xrightarrow{K_3} Cl\text{-} + HO\text{-} \xrightarrow{k_4} H^+ + O\text{-} + Cl\text{-} \quad [4]$$

Presence of HCl in the $HOCl\text{-}H_2O_2$ can also serve as a source for chlorine Production through the mechanistic pathway

$$HOCl + HCl \xrightarrow{k_5} H_2O + Cl_2 \quad [5]$$

$$HCl \xrightarrow{k_6} HO\text{-} + Cl\text{-} \quad [6]$$
$$HO\text{-} + HO \xrightarrow{k_7} H_2O_2 \quad [7]$$
$$H_2O_2 + HCl \xrightarrow{k_8} H_2O + Cl^{\cdot} + HO^{\cdot} \quad [8]$$
$$H_2O_2 + Cl2 \xrightarrow{k_9} 2HOCl \quad [9]$$
$$Cl\text{-} + 0 \xrightarrow{k_{10}} ClO\text{-} \quad [10]$$

From the above kinetic analysis, it was observed that chlorine liberation is a function of H_2O_2 concentration at constant HCl concentration which supported chlorine libieration as seen in table 1, through the empirical equation

(Muganliskii et al 1988,and Muganlinskii 1979)

$$\frac{DCl_2}{dt} = \frac{\beta_2 k_2 k_6 k_8 [HOCl]^{2n}}{k_5 k_9 [H_2O]^{2n}} \quad [11]$$

This kinetic proves that with increase in $[H_2O_2]$ yield of products increased (HOCl,OH,Cl) which reduced the polarity of the medium. Such reduction in polarity (eq. 5 & 8) led to increase in isomerization of poly chlorinated hydrocarbons in the process (Table 3).

CONCLUSION

Direct study of the effect of H_2O_2 concentration on oxychlorination of Ar-H hydrocarbons indicated that no catalytic promoter is needed as in Deacon catalyst; as such product purity and problem of hot spot ocation was not encountered. Presence of water in the medium as norganic phase has no negative effect on the products purity since at he temperature of operation the water-organic phase did not form an aseotropic phase. Also, presence of water reduced chlorine loss into the environment thereby making the plant environmentally friendly. Below 75°C this had very little effect on the reaction medium. As a result of this, low temperature oxychlorination using H_2O_2 will suit olefin and aromatic chlorination process. This observation indicates that homogeneous catalytic oxychlorination has better prospect than the hard contact process where catalyst regeneration, product purification and spent catalyst disposal is required. However, since there is need to maintain temperature distribution in the process, further studies to ascertain in more details the combined effect of concentration and temperature for economic evaluation of the process is in progress.

REFERENCES

Abramov, V.I., 1976. Oxychlorination in Chloro-organic sysnthesis. Review HUUTEXUM 64.XI, 46-49.

Adeyinka, J.S., 1988. Direct Chlorination of ethylene to 1,2-dichloroethane. MSc Thesis Azerbaijan academy of Chemical Sciences, Baku, USSR (Unpubl1.)

Alden, J.A., 1961. Oxychlorination catalysis: Review. Jour of Pure and Applied Chemistry. 21:145-149

Allen, J.A. 1971 Product distribution in Oxychlorination of α-olefinic hydrocarbons. Jour of Pure and Applied chemistry. 12:9-16.

Arnold, C.W. 1952 /synthesis of chloroorganic products from aromatic hydrocaroon Chem. Engrg. Prog. 48(6):239.

Burke, F., 1964. Low temperature chlorination processes Chem. Week 95(8): 93 – 119

Ramsey G, Campbell, B., Ellioit P.D.M.; M. Henry, H.O., Joseph S. N.M.; Harvey, J. U.L. Oxychlorination of Ethylene USA Patent No. 4 206 180 of June 1980.

Englin, A.L. 1969 Towards development of new products in chloro-organic synthesis. Journal of Chemical Society Mendeleev 14(3): 288 – 299.

Husienzade, E.M. 1977. Chlorination of α-olefin in liquid medium, Azerbaijan Chem. Jour. 55(2): 340.

Muganlisnkii, F.F., 1975 Kinetic of Hexachloro cyclopentene on Hard catalysts. Dsc dissertation Azerbaijan Institute Baku, USSR.

Muganlisnkii, F.F., Xas-Mamedov, A., and Adeyinka, J.S. 1988, Effect of Temperature on Chlorine distribution on tripple bonds in chlorohydrin synnthesis from acetylene" Monograph, AZINEFT, Baku USSR.

Sergeev, G.G., 1978, Polar Organic Medium, Proceeding of Chem. Soc. Moscow University, 19(3): 281-285.

Smolina, A.C. 1972, Chlorination of olefine hydrocarbons Chemical Industry 11:807.

Xas-Mamemdov, A and Adeyinka, J.S., 1987. Chlorohydrin Synthesis: AZINEFT 86, Scientific Report