

Research Article

Telomerization of Vinyl Chloride with Chloroform Initiated by Ferrous Chloride-Dimethylacetamide under Ultrasonic Conditions

Hua Qian¹ and Hengdao Quan²

¹School of Chemical Engineering, Nanjing University of Science and Technology, Xiaolingwei 200, Nanjing, Jiangsu 210094, China

²National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan

Correspondence should be addressed to Hua Qian; qianhua@njust.edu.cn

Received 16 October 2014; Revised 10 December 2014; Accepted 3 January 2015

Academic Editor: Oliver Höfft

Copyright © 2015 H. Qian and H. Quan. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Telomerization of vinyl chloride with chloroform was investigated using ferrous chloride-dimethylacetamide system, and 42.1% yield, more than four times the one reported before, was achieved. The addition of ultrasound further improved the reaction and yield was raised to 51.9% with trace byproducts at highly reduced reaction time and temperature. Ferrous chloride-dimethylacetamide under ultrasonic irradiation acts as a very efficient catalyst system for the 1:1 telomerization.

1. Introduction

1,1,3,3-tetrachloropropane is an important intermediate for organic synthesis and is also the last one of twenty-nine possible chloropropanes that was not characterized until 1951 [1]. In the literature, 1,1,3,3-tetrachloropropane can be prepared by the chlorination of 1,1,3-trichloropropane [1] or the reaction of vinyl chloride with chloroform [2–4]. The first method is uncompetitive, for the preparation of 1,1,3-trichloropropane is also difficult and not in favor of environment. The latter is a classic telomerization. Compared with the telomerization of olefin and tetrachloromethane [5–8], chloroform is much less reactive, and the highest yield that has been reported is less than 10% [2].

During the past few years, researchers all confirmed that the effect of solvents was not remarkable [9, 10]; they focused on effective catalyst system [11–16]. Catalysts of telomerization must be able to produce free radicals, such as organic initiator, UV light, electron beam, and oxyreductive initiator, in which amine-metallic salts are widely regarded as an effective initiating system to synthesize halogenated alkanes.

The key to enhance yield is to increase the contacting opportunity of reactants and stabilize the corresponding intermediates. So, different from other researchers' efforts

to search effective initiators, solvent effects and reaction conditions were investigated in our research and a high yield of more than 50% was achieved.

2. Experiments

Vinyl chloride (purity > 99%) was directly used from Sumitomo Seika chemicals Co. Ltd. Chloroform was purified by distillation after water wash, the purity being examined by gas chromatography. Nitrogen was produced in our institute and its purity was more than 99.9%. Other reagents were obtained from Wako Company without further purification.

GC analysis was performed on Shimadzu 17A instrument with an HP CP-PoraBond Q column (25 m × 0.32 mm). Mass spectrum was measured on Shimadzu QP2010 mass spectrometers. ¹H NMR and ¹³C NMR spectra were recorded on JEOL NMR 300 instruments, using TMS as internal standard and CDCl₃ as solvent. UV-visible absorption spectral measurements were carried out using a recording double beam spectrophotometer (Shimadzu, UV-2600, Japan). Sonication was performed in Bransonic 5510J-MT ultrasonic cleaner with the frequency of 42 Hz and an output power of 135 W.

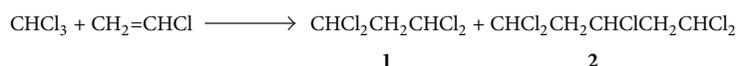
The reaction was carried out in a 500 mL stainless steel autoclave with a magnetic stirrer. Chloroform, initiators, and

TABLE 1: Effects of catalyst systems^a.

Entry	Initiator	Solvents	Conversion ^b (%)	Yield ^b (%)
1	FeCl ₂ ·4H ₂ O, (HOCH ₂ CH ₂) ₃ N	MeOH ^c	73.4	5.7
2	CuCl·2H ₂ O, (HOCH ₂ CH ₂) ₃ N	CH ₃ CN	11.4	8.7
3	FeCl ₂ ·4H ₂ O, (HOCH ₂ CH ₂) ₃ N	CH ₃ CN	22.1	18.3
4	FeCl ₂ ·4H ₂ O, (HOCH ₂ CH ₂) ₃ N	DMF	35.9	24.6
5	FeCl ₂ ·4H ₂ O, (HOCH ₂ CH ₂) ₃ N	DMSO	40.5	28.0
6	FeCl ₂ ·4H ₂ O, (HOCH ₂ CH ₂) ₃ N	DAMC	67.7	40.5
7	FeCl ₂ ·4H ₂ O	DAMC	64.7	42.1

^aThe molar ratio of vinyl chloride, chloroform, catalysts, and solvent is 1:4:0.02:0.2, respectively; reaction time 30 h; temperature 130°C; initial pressure 0.3 MPa.

^bIt is calculated by vinyl chloride. ^cMethanol is the same molar amount as chloroform.



SCHEME 1

solvents were placed in the autoclave. Then autoclave was cooled down by liquid nitrogen and vacuumed to 20 Pa below. Quantitative vinyl chloride was inhaled to the autoclave through vacuum line, and then nitrogen was charged to maintain 0.03 MPa. The autoclave was heated to a prescribed temperature. After the reaction, autoclave was cooled to room temperature and mixtures were washed by water. The organic layer was dried by anhydrous Na₂SO₄, then filtered, and subjected to GC and MS analysis. Unconverted vinyl chloride and excess chloroform were recovered by distillation at atmosphere pressure. Distillation at 20 kPa and 53°C gave the product, transparency liquid with the boiling point of 162°C:

¹H NMR (300 MHz, CDCl₃): δ 3.08–3.12 (t, *J* = 5.0, 2H), 5.89–5.93 (t, 2H);

¹³C NMR (75.5 MHz, CDCl₃): δ 55.29, 68.66;

MS: *m/z* = 145 (M⁺–Cl, 7), 109 (100), 97 (8), 83 (29), 61 (8), 49 (7), 39 (8).

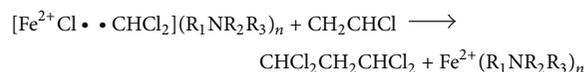
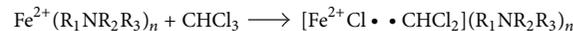
As shown in the NMR spectra, the ¹H-NMR spectrum of the product in CDCl₃ shows two triplets which are assigned as follows: δ 3.08–3.12 (CH₂), δ 5.89–5.93 (CCl₂H). The ¹³C-NMR spectra of the product show two easily recognized signals at about δ 55.29 (CH₂) and δ 68.66 (CCl₂H), respectively.

3. Results and Discussion

In this study of addition reaction of vinyl chloride with chloroform, amine-metallic salts were used as a model compound. In all cases, 1:1 adduct **1** was obtained as the aim product, and the 1:2 adduct **2** was the byproduct, with the structures presented in Scheme 1.

Several catalyst systems with different solvents were examined and the results were summarized in Table 1.

Entry 1 was examined using methanol (MeOH) as solvent according to the patent [15]. The conversion is high, while little aim product was observed, for most vinyl chloride was polymerized to form white spherical solids. Low yield can be explained that methanol is a protonic solvent with the ability of absorbing free radicals, causing hindrance of



SCHEME 2: Catalytic mechanism of ferrous iron.

the telomerization. Compared with entries 2 and 3, ferrous chloride is much more effective than cuprous chloride, so ferrous chloride-diethanolamine was used to evaluate the effect of solvents.

In the previous work, methanol, propanol, heptane, dioxane, and benzene were all tried, and the effects were not remarkable [9, 15, 17, 18]. In our experiment, non-protonic solvents with better solubility of both metallic salt and chloroform, such as acetonitrile (CH₃CN), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and N,N-dimethylacetamide (DAMC), were tried (entries 3–7), and the yield was enhanced to 42.1%.

According to the effective chlorine-transfer mechanism [19], amine can form the complex with ferrous ion, which is the actual initiator. Assuming the existence of such complexes, the reaction scheme shown in Scheme 2 would follow.

Organic amine was used as a stabilizer shown in Scheme 2. The complex as a reaction intermediate would be formed through the interaction of chlorine radical with ferrous ion and the stabilization by coordinated amines. The attack of vinyl chloride on this complex affords trichloropropyl radical, and the resulting radical instantly abstracts chlorine radical from the complex. The presence of such complexes greatly decreases activation energy for the insertion of vinyl chloride into the Cl-CHCl₂ bond. DMAC, as both an effective complexing agent and organic amine, can highly catalyze the telomerization, which was also verified by entry 7.

In order to further confirm our thoughts, UV-visible spectra of solutions of DMAC, FeCl₂·4H₂O, and their mixture in C₂H₅OH were measured as shown in Figure 1, and

TABLE 2: Effects of reaction conditions^a.

Entry	Condition	Temperature (°C)	Initial pressure (MPa)	Time (h)	Conversion ^b (%)	Yield ^b (%)	
						1	2
1	Silent	110	0.3	30	16.9	14.0	1.4
2	Silent	130	0.3	30	64.7	42.1	15.6
3	Silent	130	0.1	30	24.6	21.0	2.2
4	Silent	130	0.3	20	46.0	27.8	3.7
5	Silent	130	0.3	40	69.2	43.6	18.9
6))) ^c	130	0.3	30	73.2	54.1	18.2
7)))	100	0.3	8	52.3	50.1	0.7

^aThe molar ratio of vinyl chloride, chloroform, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and DMAC is 1 : 4 : 0.02 : 0.2. ^bIt is calculated by vinyl chloride. ^cUltrasonic irradiation.

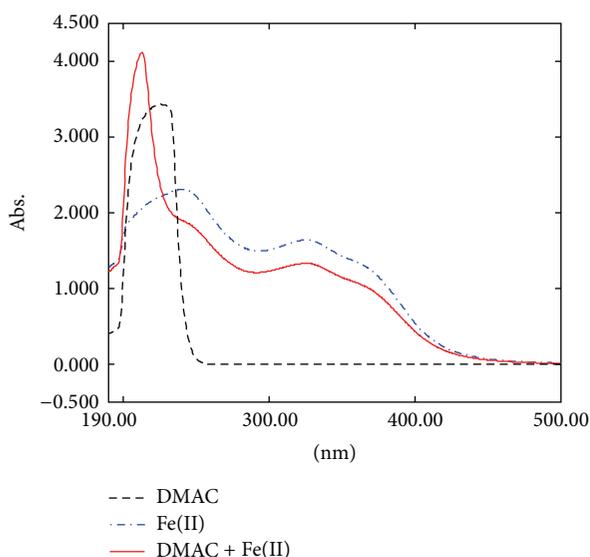


FIGURE 1: UV-visible spectra of reactants.

spectra were recorded against solvent blank from 190 to 500 nm. It was confirmed that the absorption maxima of DMAC, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and their mixture was, respectively, 224 nm, 241 nm, and 213 nm, which indicated that a new complex was formed. It is the complex that actually catalyzes the telomerization.

As shown in Table 1, the difference between conversion and yield is mainly due to the formation of the 1 : 2 adduct 2. To improve the selectivity, we extended the reaction conditions and the results were presented in Table 2.

Reaction temperature offered the energy for the telomerization and the lower temperature sharply decreased the yield (entries 1 and 2). High pressure is needful during the formation of telomeres for raw materials were all in the gaseous state. The yield of telomeres increased with the elongation of reaction time from 20 h to 40 h.

As shown in entries 1–5, high yield usually accompanies low selectivity, which is mainly caused by high reaction temperature and long reaction time. In recent years, ultrasound has been employed in various chemical transformations with considerable enhancement in rate and yield and, in several cases, facilitates organic transformations at ambient conditions [20, 21]. So, ultrasound was introduced to continue our research.

The pronounced effect of ultrasound can be easily demonstrated from the results shown by the entries 6 and 7. It is expected that these radical generation processes are facilitated by ultrasonic irradiation. For the mild reaction, the ultrasound mediated telomerization has led to high yields in a relatively short period with high selectivity.

4. Conclusion

A breakthrough was made in the telomerization of vinyl chloride with chloroform initiated by ferrous chloride-dimethylacetamide under ultrasonic irradiation. With trace byproducts, 1,1,3,3-tetrachloropropane was gained in 51.9% yield, more than four times the one reported before. The important achievements of our work are (1) DMAC selected as both solvent and cocatalyst; (2) reduction of the reaction time and temperature by ultrasound introduction; (3) control over generation of byproduct; (4) remarkable increase in the yield of products. With the use of this new catalyst system, the telomerization of less reactive materials, such as chloroform, on a large scale may become possible.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors would like to express their thanks to Professor J. Mizukado for useful discussions and Dr. Y. Suzuki for assistance in the measurements.

References

- [1] A. M. Whaley and H. W. Davis, "Preparation of 1,1,3,3-tetrachloropropane," *Journal of the American chemical society*, vol. 73, no. 3, pp. 1382–1383, 1951.
- [2] A. Teruzo, S. Manabu, and C. C. Wu, "Telomerization of olefin with chloroform initiated by amine and metal salt," *Indian Journal of Chemistry*, vol. 72, no. 8, pp. 1818–1822, 1969 (Japanese).
- [3] B. Boutevin, Y. Pietrasanta, M. Taha, and T. El Sarraf, "Synthesis of macromers of vinylchloride and vinylidene chloride from telomers," *Polymer Bulletin*, vol. 10, no. 3–4, pp. 157–161, 1983.

- [4] B. Boutevin, Y. Pietrasanta, and M. Taha, "Télomères monofonctionnels du chlorure de vinyle—I: synthèse et caractérisation d'étalons de télomères du chlorure de vinyle," *European Polymer Journal*, vol. 18, no. 8, pp. 675–678, 1982.
- [5] M. Kotora and M. Hájek, "Selective additions of polyhalogenated compounds to chloro substituted ethenes catalyzed by a copper complex," *Reaction Kinetics & Catalysis Letters*, vol. 44, no. 2, pp. 415–419, 1991.
- [6] N. P. Zhiryukhina, A. A. Kamyshova, E. T. Chukovskaya, and R. K. Freidlina, "Synthesis of polychloroalkanes with several different chlorine-containing groups," *Bulletin of the Academy of Sciences of the USSR*, vol. 32, no. 1, pp. 129–133, 1983.
- [7] V. Mathieu and J. P. Schoebrechts, "Process for preparing halogenated hydrocarbons," U.S. Patent no. 6,500,993, 2002.
- [8] A. Lambert and V. Mathieu, "Process for preparing halo-hydrocarbons in the presence of a co-catalyst," U.S. Patent 6,452,057, 2002.
- [9] A. Teruzo, S. Manabu, and C. C. Wu, "Telomerization of vinyl chloride with carbon tetrachloride using aming-cupric chloride. Effects of amines and solvent," *Bulletin of the Chemical Society of Japan*, vol. 43, no. 4, pp. 1127–1131, 1970.
- [10] M. Asscher and D. Vofsi, "Chlorine-activation by redox-transfer. Part III. The "Abnormal" addition of chloroform to olefins," *Journal of the Chemical Society*, pp. 3921–3927, 1963.
- [11] A. Teruzo, S. Manabu, and O. Noritaka, "Telomerization of ethylene with chloroform initiated by N-chloroalkylamines," *Bulletin of the Chemical Society of Japan*, vol. 47, no. 8, pp. 2007–2010, 1974.
- [12] A. Teruzo, S. Manabu, and O. Noritaka, "Reactions of ethylene with chloroform initiated by amine-ferrous chloride system," *Bulletin of the Chemical Society of Japan*, vol. 47, no. 12, pp. 3142–3145, 1974.
- [13] J. R. Briggs, H. Hagen, S. Julka, and J. T. Patton, "Palladium-catalyzed 1,3-butadiene telomerization with methanol. Improved catalyst performance using bis-o-methoxy substituted triarylphosphines," *Journal of Organometallic Chemistry*, vol. 696, no. 8, pp. 1677–1686, 2011.
- [14] I. Chung, "Monte Carlo simulation of free radical telomerization," *Polymer*, vol. 41, no. 15, pp. 5643–5651, 2000.
- [15] I. Wlassics and V. Tortelli, "Tetrafluoroethylene telomerization using dibromohaloethanes as telogens," *Journal of Fluorine Chemistry*, vol. 127, no. 2, pp. 240–248, 2006.
- [16] N. A. Porter, R. Breyer, E. Swann et al., "Free-radical telomerization of chiral acrylamides: control of stereochemistry in additions and halogen-atom transfer," *Journal of the American Chemical Society*, vol. 113, no. 18, pp. 7002–7010, 1991.
- [17] J. P. Schoebrechts, V. Mathieu, and F. Janssens, "Method for the preparation of 1,1,1,3,3-pentachlorobutane," US Patent 6,399,840, 2002.
- [18] X. Cheng, C. P. Zhang, and L. Jian, "Advances in the catalysts for synthesis of halo-hydrocarbons by liquid-phase catalytic telomerization," *Industrial Catalysis*, vol. 15, no. 11, pp. 11–14, 2007.
- [19] M. Asscher and D. Vofsi, "Chlorine activation by redox-transfer, part I: the reaction between aliphatic amines and carbon tetrachloride," *Journal of the Chemical Society*, vol. 439, pp. 2261–2264, 1961.
- [20] Q. Hua, Y. Zhiwen, and L. Chunxu, "Ultrasonically promoted nitrolysis of DAPT to HMX in ionic liquid," *Ultrasonics Sonochemistry*, vol. 15, no. 4, pp. 326–329, 2008.
- [21] Q. Hua, L. Dabin, and L. Chunxu, "Ultrasonically-promoted synthesis of mandelic acid by phase transfer catalysis in an ionic liquid," *Ultrasonics Sonochemistry*, vol. 18, no. 5, pp. 1035–1037, 2011.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

