December, 1988] *Bull. Chem. Soc. Jpn., 61, 4393—4395 (1988)*

The Chlorination of Vinyl Compounds in Alcohols

Kiyonori SHINODA* and Kensei YASUDA
Toyama National College of Technology, 13 Hongo, Toyama 939
(Received April 25, 1988)

Upon the chlorination of vinyl compounds in alcohols, the reaction products were composed of 2-alkoxy-1-chloro compound (A), 1-alkoxy-2-chloro compound (B) and vicinal dichloride (C). Various vinyl compounds were chlorinated in alcohols at 40 °C in order to elucidate the effect of their molecular structure on the product distribution. The A/(A+B) was inversely proportional to the relative rate of ordinary chlorination in carbon tetrachloride. The A/(A+B) for the chlorination of allyl chloride in methanol was little affected by the reaction conditions: (1) reaction temperature, (2) mole ratio, and (3) elapse of time. However, the A/(A+B) increased with increasing E_s value of the alkyl group of alcohol.

It has been well-known that vicinal dichloride is accompanied by solvent-incorporated products during chlorination in common protic solvents.[1-3] The addition of bromine to olefin in methanol also produces methoxybrominated products.[4,5] The chlorination of various olefins in the protic solvent has been reviewed in detail by de la Mare and Bolton.[6] The kinetic forms, environmental effects, structural effects on the rates of chlorination and products have been described. The solvent-incorporated products for the chlorination of vinyl compound in methanol are composed of 1-methoxy-2-chloro and 2-methoxy-1-chloro compounds. These compounds represent Markownikoff and anti-Markownikoff orientations, respectively.

However, little is known concerning the formation ratio of two solvent-incorporated products. Furthermore, there has been no report on a quantitative examination of the alkoxychlorination of vinyl compounds.

The chlorination of vinyl compounds in various alcohols was carried out in order to elucidate the effect of the molecular structure on alkoxychlorination.

Results and Discussion

The solvent-incorporated products for the chlorination of vinyl compounds in methanol are composed of 1-methoxy-2-chloro and 2-methoxy-1-chloro compounds. The formation ratio of a mixture of two methoxychlorides to dichloride was gradually decreased with the elapse of time in the chlorination of vinyl compounds in methanol. This was because the concentration of methanol decreased as the reaction proceeded. The product composition of the chlorination of allyl cyanide in methanol is illustrated in Table 1.

On the other hand, the proportion of two methoxy chlorides was, roughly, kept constant throughout the reaction. Nevertheless, the formation ratio of two methoxy chlorides was widely changed with the molecular structure of the substrate. The product ratios for the chlorination of various vinyl compounds in methanol at 40 °C are shown in Table 2, together with the rate ratios for chlorination in carbon tetrachloride.[7] Symbols A, B and C represent 2-methoxy-

Table 2. The Effect of the Olefin Structure (CH_2=CH-R) on the Chlorination in Methanol and Carbon Tetrachloride

Substituent (R)	σ^*	A/(A+B) in CH_3OH	k/k_0[6] in CCl_4
-CN	3.64	—	0.00109
-COOH	2.94	—	0.00197
-Br	2.80	92.5	—
-$COOCH_3$	2.00	89.1	0.0181
-$COCH_3$	1.65	81.2	0.0352
-$CHClCH_2Cl$	1.435	81.2	—
-CH_2CN	1.300	66.6	0.215
-CH_2Cl	1.050	66.1	1.00
-CH_2Br	1.000	—	1.40
-$CHClCH_3$	0.950	46.2	2.06
-CH_2I	0.85	—	1.63
-C_6H_5	0.600	—	2.00
-CH_2OH	0.555	32.8	—
-$CH_2CH_2COCH_3$	0.215	22.9	—
-CH_3	0	20.9	—
-$CH_2CH(CH_3)_2$	−0.125	27.7	—
-$CH_2CH_2CH_2CH_3$	−0.130	26.1	26.9
-$CH(CH_3)CH_2CH_3$	−0.210	—	35.9
-$C(CH_3)_3$	−0.300	12.4	—

Table 1. Product Composition, A/(A+B) and C/(A+B+C) for the Chlorination of Allyl Cyanide in Methanol at 40 °C

Reaction time	Product composition (%)				A/(A+B)	C/(A+B+C)
min	CH_2:$CHCH_2CN$	A	B	C	(%)	(%)
5	81.5	11.1	5.5	1.9	66.9	10.3
10	62.2	20.4	12.7	4.7	61.6	12.4
15	41.6	33.4	16.8	8.7	66.5	14.0
20	19.2	44.1	23.4	13.2	65.3	16.5
25	1.8	53.7	26.9	17.6	66.6	17.9

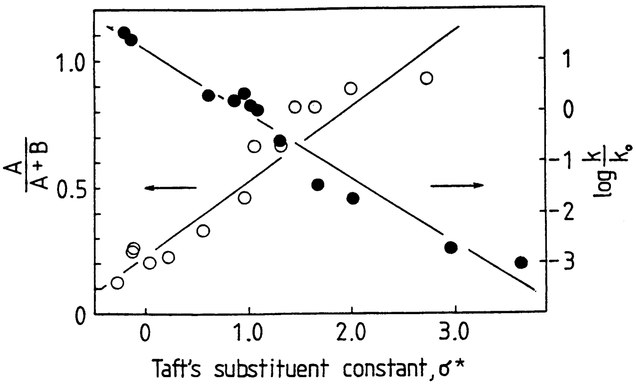


Fig. 1. The plots of A/(A+B) and k/k_0 for the chlorination of various vinyl compounds against σ^*.
○: A/(A+B), ●: k/k_0.

1-chloro, 1-methoxy-2-chloro compounds and vicinal dichloride in the product composition, respectively. Two vinyl compounds were competitively chlorinated in carbon tetrachloride in the presence of oxygen at 30 °C. The value of the relative rate constant was caluculated according to a previously described method.[8] The k/k_0 is the relative rate constant with respect to the standard reaction (allyl chloride in this case). Figure 1 shows the effect of the molecular structure of a vinyl compound upon the formation ratio of two methoxy chlorides [A/(A+B)]. The logarithms of the relative rate constant for the chlorination of a vinyl compound in the presence of oxygen in carbon tetrachloride, as well as the formation ratio of two methoxy chlorides for the chlorination in methanol, are plotted against Taft's substituent constant (σ^*).[9] The data follow two straight lines, though opposite in sign. It is essential that k/k_0 be compared with A/(A+B) in order to consider the reaction mechanism of alkoxychlorination. The general nature of the first stage of attack by chlorine on an unsaturated molecule is established by the effect of the structure on the reaction rate.

As can be seen in Fig. 1, the rate of dark chlorination of a vinyl compound in the presence of oxygen in carbon tetrachloride was increased by the electron-releasing substituent group and decreased by the electron-withdrawing group. The reaction of chlorine with the vinyl compound (Q) in methanol might proceed according to the following mechanism:[2]

$$\begin{array}{lll} Q + Cl_2 \longrightarrow QCl^{\oplus} & \xrightarrow{Cl^{\ominus}} & QCl\text{-}Cl \\ & \xrightarrow{MeOH} & QCl\text{-}OMe + H^{\oplus} \end{array} \qquad (1)$$

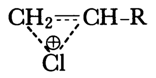
Fahey and Schubert,[1] using a stereochemical criterion, have shown that $QCl^{\oplus}$ may be either bridged or open, depending upon the stability of the open ion. It can be assumed that the intermediates formed in the rate-determining step for chlorination may alternatively be carbonium ion (**1**), carbonium ion (**2**) or bridged chloronium ion (**3**). In view of previous results,[7] the chlorine cation attacks on the carbon which carries an electron-withdrawing substituent to form the carbonium ion (**1**), whereas the substrate, having an electron-releasing group, converts into the carbonium ion (**2**). On the contrary, the bridged chloronium ion (**3**) is formed by the reaction of a chlorine cation with a vinyl compound having a moderate group, such as allyl chloride. While carbonium ion (**2**) is predominantly converted into B by a nucleophilic attack of methanol, carbonium ion (**1**) is transformed into A. It is reasonable to consider that A, B and C are produced by a competitive nucleophilic attack of methanol and a chloride ion to the bridged chloronium ion. That is to say, A/(A+B) is dependent on the carbocationic intermediate, which is controlled by the relative rate constant.

$^{\oplus}CH_2\text{-}CHCl\text{-}R$

1


$CH_2Cl\text{-}\overset{\oplus}{C}H\text{-}R$

2



3

Since allyl chloride could be considered to have a moderate group, allyl chloride was chlorinated in order to investigate the effect of the reaction condition on the A/(A+B) and C/(A+B+C). While the relative rate of chlorination to alkoxychlorination C/(A+B+C) was increased with an increase in the concentration of allyl chloride in methanol, the A/(A+B) was little affected by the concentration of allyl chloride in methanol (Fig. 2) and the reaction temperature. A/(A+B) also remained approximately constant throughout the chlorination, despite the elapse of time. Neither photochemical chlorination under irradiation nor dark chlorination in the presence of oxygen could change A/(A+B). It could be assumed that the chlorination of a vinyl compound in methanol was an ionic reaction.

Since the nucleophilicity and steric hindrance of an alkyl group in a long or bulky chain alcohol were

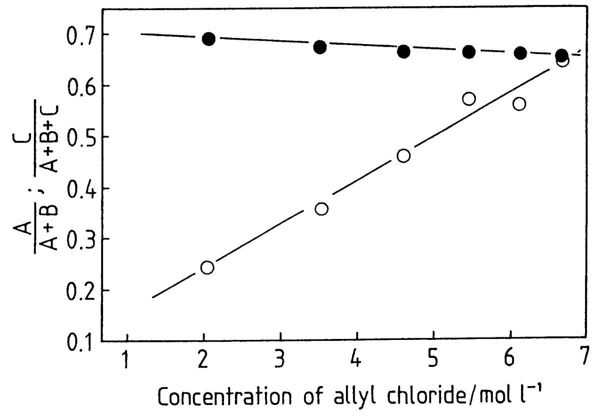


Fig. 2. The plots of A/(A+B) and C/(A+B+C) against concentration of allyl chloride for the chlorination of allyl chloride in methanol at 40 °C.
●: A/(A+B), ○: C/(A+B+C).

Table 3. Effect of E_s Value on A/(A+B) and C/(A+B+C)

Alcohol	E_s[10]	A/(A+B) (%)	C/(A+B+C) (%)
CH_3OH	0.00	66.2	14.2
C_2H_5OH	−0.07	66.5	22.3
n-$C_6H_{13}OH$	−0.34	65.3	36.8
i-$C_5H_{11}OH$	−0.35	66.4	36.5
n-C_3H_7OH	−0.36	63.5	29.7
n-C_4H_9OH	−0.39	64.8	26.8
n-$C_5H_{11}OH$	−0.40	60.1	27.7
i-C_3H_7OH	−0.47	69.0	41.6
i-C_4H_9OH	−0.93	64.4	38.6
$(CH_3)(C_2H_5)CHOH$	−1.13	58.9	50.2
t-C_4H_9OH	−1.54	54.9	82.5

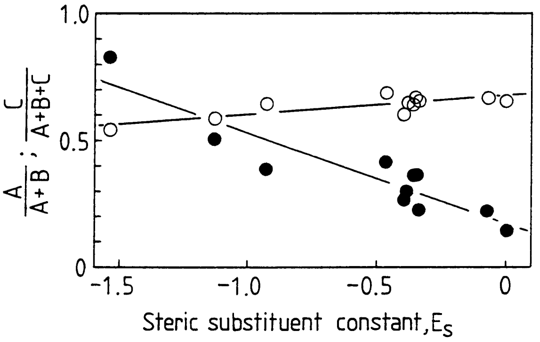


Fig. 3. The relations of A/(A+B) vs. E_s and C/(A+B+C) vs. E_s for the chlorination of allyl chloride in various alcohols at 40 °C.
○: A/(A+B), ●: C/(A+B+C).

compensated for by each other, the variation of A/(A+B) was over a narrow range, even through allyl chloride was chlorinated in several alcohols at 40 °C (Table 3).

The A/(A+B) value for the alkoxychlorination of allyl chloride in various alcohols slightly decreased in the following order:

$$i\text{-}C_3H_7OH > C_2H_5OH > i\text{-}C_5H_{11}OH > CH_3OH > n\text{-}C_6H_{13}OH > n\text{-}C_4H_9OH > i\text{-}C_4H_9OH > n\text{-}C_3H_7OH > n\text{-}C_5H_{11}OH > s\text{-}C_4H_9OH > t\text{-}C_4H_9OH.$$

The relations of A/(A+B) and E_s as well as of C/(A+B+C) and E_s are shown in Fig. 3. E_s on the abscissa indicates the steric substituent constants[10] for the alkyl group of alcohol. Since the C/(A+B+C) value increased with the elapse of time, C was obtained by extrapolating the experimental data back to the initial time. The increase in the C/(A+B+C) value with the elapse of time can be explained by using the same reason why the concentration of alcohol in a reaction solution decreases as the reaction proceeds.

It is clear that the rate of a nucleophilic attack on the intermediate was decreased with a long or bulky chain alcohol. On the other hand, the rate of the addition of chloride ion might remain unaltered. Therefore, the C/(A+B+C) value might be changed by the E_s value of the alkyl group of alcohol.

Experimental

Reagents. All the reagents used in this work were purchased from Tokyo Kasei Kogyo Co., except for the alcohols, which were obtained from Wako Pure Chemical Industries. They were not purified further. Chlorine and oxygen were fed from commercial cylinders and were passed through a sulfuric acid trap before use.

Chlorination of Vinyl Compound in Methanol. A 100 ml, flat, cylindrical semibatch Pyrex reactor thermostated at 40 °C was equipped with a Teflon magnetic stirring bar, a gas inlet tube and a reflux condenser. A mixture of 0.1 mol of vinyl compound and 50 ml of methanol was added to the reactor. Chlorine gas was fed into the reactor at the rate of 0.01 mol h^{-1}, until the reaction solution became a pale-yellow color. Chlorination products were analyzed by means of gas chromatography (Shimadzu GC-5A, SDC 550, PEG 6000).

Chlorination of Allyl Chloride in Methanol. Allyl chloride was chlorinated in methanol under various reaction conditions. The photochemical procedure and dark chlorination procedure in the presence of oxygen were similar to those used in the previous study.[7] Furthermore, 30 ml of methanol was mixed with allyl chloride at various volume ratios. The chlorination of this mixture was the same as the preceding techniques.

Chlorination of Allyl Chloride in Various Alcohols. The chlorination procedure was the same as that used in methanol. 30 ml of alcohol was mixed with 0.1 mol allyl chloride and the mixture was then placed in the reactor. The chlorination temperature was maintained at 40 °C. At regular intervals, 1 ml samples were taken from the reaction system and analyzed by gas chromatography.

References

1) R. C. Fahey and C. Schubert, *J. Am. Chem. Soc.*, **87**, 5172 (1965).
2) M. L. Poutsma and J. L. Kartch, *J. Am. Chem. Soc.*, **89**, 6595 (1967).
3) W. M. Baluzow, Ch. Duschek, G. Just, W. Pritzkow, and H. Schmidt, *J. Prakt. Chem.*, **317**, 53 (1975).
4) W. H. Puterbaugh and M. S. Newman, *J. Am. Chem. Soc.*, **79**, 3469 (1957).
5) M. M. Morsumzade, A. S. Kyazimov, A. L. Shabanov, F. G. Ismdilova, and A. A. Babaeva, *Dokl. Akad. Nauk Azerb. SSR*, **29** (5), 29 (1973); *C. A.*, **80**, 59543j (1974).
6) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier Scientific Pub. Co., Amsterdam (1982), p. 93.
7) K. Shinoda, *Bull. Chem. Soc. Jpn.*, **51**, 913 (1978).
8) K. Shinoda, *Nippon Kagaku Kaishi*, **1973**, 542.
9) M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley & Sons, Inc., New York (1956), p. 618.
10) Ref. 9, p. 598.