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Chemical transformation of PVC by phase transfer catalysis*

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SUMMARY

Suspension type PVC was reacted with sodium phenoxide in presence of different quaternary ammonium halides in THF or THF/water mixtures. The competition elimination vs. substitution of chlorine atoms depends on the homogeneity of the system, i.e. the more homogeneous the reaction mixture the less substituted the polymer.

INTRODUCTION

Chemical modification of PVC by phase transfer catalysis implies either the nucleophilic substitution of labile chlorine atoms or the elimination of hydrogen chloride (1-5). Reactions of model alkyl halides, e.g. C_4H_9X or $C_8H_{17}X$, containing a secondary chlorine or bromine atom with phenoxide or thiophenoxide catalyzed by substituted quaternary ammonium halides evidenced that the competition elimination vs. substitution depends on the polarity and/or homogeneity (i.e. phase transfer condition) of the system (6).

Recently Martinez et al. (1-3) have shown that the substitution reaction of PVC with sodium benzenethiolate at 50° catalyzed by tetrabutylammonium bromide or tetrabutylphosphonium bromide is stereoselective and free of any competitive elimination process. On the other hand, a high degree of dehydrochlorination was reported by Tetsuya et al. (4) at the same temperature under the action of certain diaza compounds.

The present paper investigates therefore the reaction of PVC with sodium phenoxide/substituted quaternary ammonium halide mixtures in THF or THF/water media.

EXPERIMENTAL

Romanian technical grade PVC (suspension type, $\bar{M}_v$=78500 determined in THF at 20°) was used without further purification. The substituted quaternary ammonium halides were sythesized in routine fashion from the appropriate amines and alkyl halides, except cetyltrimethyl ammonium chloride and cetylpyridyl bromide which were commercial products. Sodium phenoxide was prepared from the reaction of freshly distilled phenol with NaOH.

In a typical experiment 0.125g (2 mmol) PVC dissolved in 10 mL THF, 0.232g (2mmol) sodium phenoxide, 0.5 mmol substituted quaternary ammonium halide and 10 mL THF were intro-

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* Dedicated to the 60th anniversary of Prof. Otto Vogl

** To whom offprint requests should be sent duced in a glass ampoule which was flushed with nitrogen and sealed. The ampoule was thereafter shaken until a clear solution was obtained and placed in an oven thermostated at the desired temperature. After a certain period the ampoule was opened and the content was poured in HCl containing methanol. The precipitated material was separated, washed on the glass filter with large amounts of water and methanol and dried in vacuum. In separate experiments water was added to the feed mixture (1 mL or 10 mL) in order to alter both the polarity and homogeneity of the system. A clear, redish polymer solution was obtained when PVC was reacted in presence of 1 mL water. When 10mL of water were added, the initially solved PVC precipitated and the system remained inhomogeneous. However, in both cases the reacted PVC was still soluble in THF and was purified by precipitation from THF solutions. A brown material separated during the reaction from the initial homogeneous mixture when no water was added to THF solution of PVC and catalyst components.

The doped samples were prepared by keeping reacted PVC in iodine atmosphere at low pressure for 24 hr. The uncomplexed iodine was pumped off at constant weight.

IR, UV and NMR spectra were recorded using a PERKIN ELMER 577, UNICAM SP 800 and JEOL 60 MHz spectrometer, respectively.

RESULTS AND DISCUSSION

Examination of chlorine content of reacted PVC in Table 1, which is an indirect indication of the catalyst activity, reveals several interesting trends as follows.

Table 1. Reaction of PVC with sodium phenoxide in THF at 50° for 22 hr catalyzed by QX

Entry	Catalyst, QX	Chlorine content, %	Softening*** temperature, °C
1	$(CH_3)_4N^+Cl^-$	55.0	92
2	$(CH_3)_4N^+Br^-$	55.3	91
3	$(CH_3)_4N^+I^-$	55.6	91
4	$(C_4H_9)_4N^+Br^-$	32.4	110
5	$(C_4H_9)_4N^+I^-$	38.0	110
6	$(C_6H_5{-}CH_2)(CH_3)_3N^+Cl^-$	25.7	110
7*	$(C_6H_5{-}CH_2)(C_2H_5)_3N^+Cl^-$	30.5	110
8	$(C_6H_5{-}CH_2)(C_8H_{17})(CH_3)_2N^+Cl^-$	34.1	110
9	$(C_{16}H_{33})(CH_3)_3N^+Cl^-$	33.0	110
10	$(C_{16}H_{33})C_5H_5N^+Br^-$	48.2	92
11	PVC + $C_6H_5{-}ONa$	54.9	92
12	PVC	55.1(56.8)**	92

* TEBA

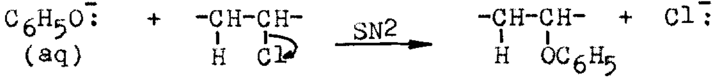
** Theoretical

*** Hot stage

Thus, it can be easily seen that (a) the benzyltrialkyl ammonium ions (e.g. entries 6 and 7) are the most effective. (b) The smallest ions, i.e. tetramethyl ammonium cations (entries 1, 2 and 3) are practically inactive. (c) The most symmetrical ions are not better than those with only one long chain. (d) The length of the alkyl rest is not a guarantee for an increased catalytic activity (entries 6, 8 and 9). (e) Pyridyl cations, even substituted with long alkyl group (entry 10) is less proficient than similarly substituted ammonium cations (entry 9). (f) No appreciable counterion effect was noted (entries 1-5). These observations do not agree entirely with the results obtained at the reaction of alkylhalides with bases under the phase transfer conditions (6,7).

In the reaction of model alkyl halides the competition between elimination and substitution shows a preference for the latter in a two-phase system, i.e. water:organic solvent (7). The same trends hold true for the reaction of PVC with bases. Thus the lesser reactivity of thiophenoxide (1) or phenoxide (present paper) under the phase transfer conditions compared to anhydrous solvents suggests that water molecules of solvation may accompany the anion into the organic phase during phase transfer:

$C_6H_5ONa + QX \longrightarrow C_6H_5O^-Q^+ + NaX$ eq. 1



$$\underset{(aq)}{C_6H_5O^-:} + -\underset{H}{CH}-\underset{Cl}{CH}- \xrightarrow{SN2} -\underset{H}{CH}-\underset{OC_6H_5}{CH}- + Cl^-:$$ eq. 2

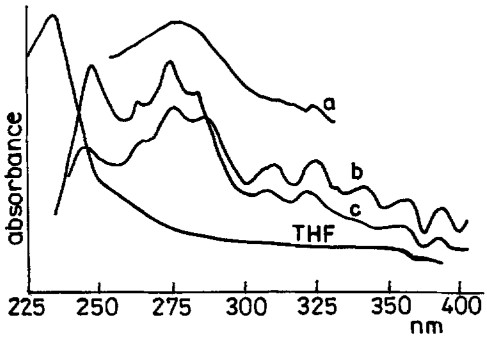


Figure 1. UV spectra recorded in THF of:
a. PVC reacted in THF
b. Idem, THF+1 mL H_2O
c. PVC reacted in THF+10 mL H_2O.
Reaction conditions as in Table 1 entry 7.

The presence of phenyl groups can be detected in UV spectra (at 245 nm, Figure 1) or NMR spectra (Figure 2) of PVC reacted in THF+H_2O but not in that of PVC reacted in anhydrous THF. In addition, the multiple absorption maxima between 275 and 450 nm which are present in the UV spectra of PVC samples reacted under the

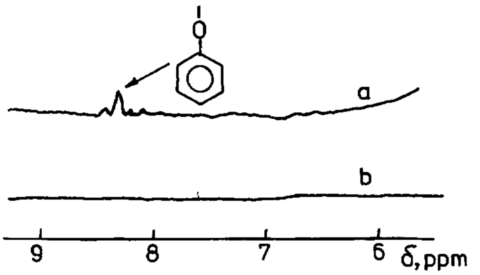


Figure 2. Aromatic region of 1-H NMR spectra of PVC
a. Reacted in THF (unprecipitated during reaction)
b. Reacted in THF+10mL H_2O.
Reaction conditions as in Table 1 entry 7.

phase transfer condition (Figures 1b and 1c) indicate that substitution of chlorine atoms is accompanied by formation of polyenic domains composed of 2-6 conjugated double bonds (8).

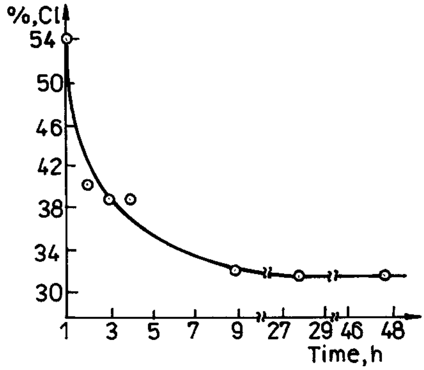
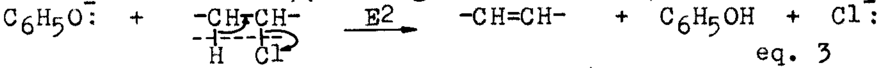


Figure 3. Reaction of PVC in THF with C_6H_5ONa at 50° catalyzed by TEBA.
Variation of chlorine content with reaction time.

However, the elimination seems to be the sole reaction when PVC is treated in anhydrous THF with strong bases such as phenoxide (no aromatic protons were observed in the NMR spectrum of the fraction unprecipitated during the treatment and the UV spectrum of the same product has no absorption band at 245 nm,(see Figures 1a and 2a):



$$C_6H_5O^{-}: \; + \; -\underset{H}{C}H-\underset{Cl}{C}H- \xrightarrow{E2} -CH{=}CH- \; + \; C_6H_5OH \; + \; Cl^{-}: \qquad \text{eq. 3}$$

The degree of transformation of PVC in anhydrous THF was dependent on the reaction time, temperature and the amount of catalyst (Figures 3 and 4). The dehydrohalogenation process is initially fast and slows down as the reaction proceeds until a limiting chlorine content is attained (Figure 3).

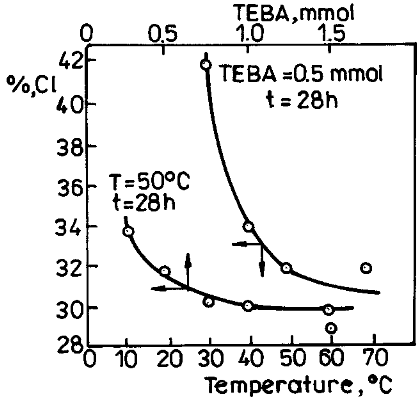
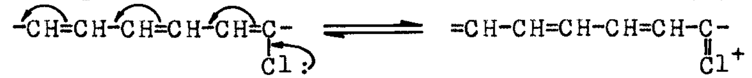


Figure 4. Reaction of PVC in THF with C_6H_5ONa catalyzed by TEBA for 28 hr.
Variation of chlorine content with temperature and catalyst concentration.

Formation of conjugated double bonds undoubtedly determines a drastic decreas of reactivity of chlorine atoms, i.e. the longer the conjugated sequences, the more enhanced the positive character of chlorine atoms, especially when these sequences result from head to head units (9):



$$-CH{=}CH-CH{=}CH-CH{=}\underset{Cl:}{C}- \rightleftharpoons {=}CH-CH{=}CH-CH{=}CH-\underset{Cl^{+}}{\overset{}{C}}{=} \qquad \text{eq. 4}$$

The conjugated polyenic sequences are long enough to be doped with iodine similarly to polyacetylene (9), as illustrated by IR spectra of both undoped and doped (17% iodine, w/w) materials (Figure 5).

CONCLUSIONS

Reaction of PVC with sodium phenoxide catalyzed by substituted quaternary ammonium halides leads only to dehydrohalogenated materials when the process is carried out in anhy-

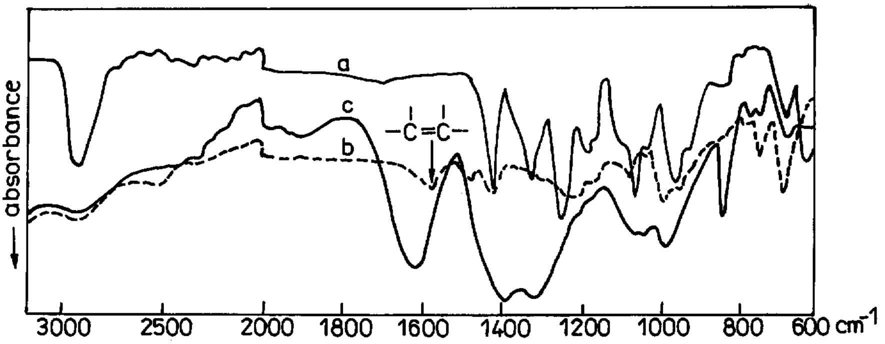


Figure 5. IR spectra of unreacted PVC (a), PVC reacted with C_6H_5ONa/TEBA in THF+10 mL H_2O at 50° for 22 hr undoped (b) and doped with iodine (c). KBr pellets.

drous THF and to unsaturated, substituted polymers if water is present in the system. The degree of dehydrohalogenation is strongly dependent on the nature of ammonium salt as well as its concentration, time and temperature of reaction.

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