THE DECAY OF 2-PHENYL-1,3-DIOXOLANE-2-YLIUM SALTS IN SOLUTION

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The decay of 2-phenyl-1,3-dioxolane-2-ylium salts in 1,2-dichloroethane solution has been studied by means of ^{1}H NMR and UV spectroscopy and conductimetry. The influence of the nature of the anion ($SbCl_6^-$, $SbCl_5Br^-$, AsF_6^-) and of the methyl substituents on the rate constants of decay is discussed.

INTRODUCTION

In the course of our studies on the stability of counter ions in cationic vinyl polymerization,[1,2] we have investigated the decay of triphenylmethylium salts ($Ph_3C^+A^-$) with complex anions $MX_nY_m^-$ (M = Sb, Al, B, As, P, Ti, Fe; X, Y = F, Cl, Br). The rate constant of the decay appeared to be strongly influenced by the nature of the central atom (M) and of the ligands (X, Y). The same kinetic treatment was used by Jones and Plesch,[3] who investigated the decay of triethyloxonium salts with various anions. The order of stabilities of triphenylmethylium and triethyloxonium salts with various anions is not the same, because the stability of the salts depends not only on the stability of the anion but also on the nature of the cation. Both factors influence the course of the polymerization initiated by stable organic cationic salts.

The importance of the stability of the anion in the polymerization of oxacyclic monomers has been illustrated by results of the polymerization of 1,3-dioxolane[4-6], trioxane[7,8] and tetrahydrofuran.[9] Studies of the polymerization of these monomers, which was initiated by substituted dioxolenium salts, have shown the interdependence between the structure and electronic behaviour of the dioxolenium cations and the stability and catalytic activity of their salts[6-10].

The aim of this work was to extend our concept of the stability of the counter ion of 2-phenyl-1,3-dioxolane-2-ylium salts ($2PhD^+A^-$, $A = SbCl_6^-$, $SbCl_5Br^-$, AsF_6^-) and to determine the influence of the nature of the anion and the structure of the cation (substituents and their configuration) on the stability of dioxolenium salts in solution, in comparison with the decay of $Ph_3C^+A^-$ and triethyloxonium salts ($Et_3O^+A^-$).

EXPERIMENTAL AND RESULTS

The dioxolenium salts were investigated by means of ^{1}H NMR spectroscopy in CD_3NO_2 and CD_2Cl_2. In both solvents the stability of the 4,5-dimethyl derivatives of the 2-phenyl-1,3-dioxolane-2-ylium hexachloroantimonates is fairly high. Decay products according to Scheme 1 cannot be monitored because of
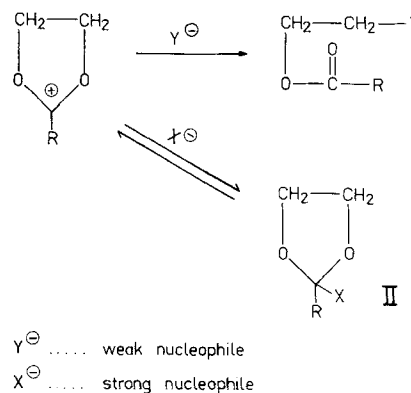
Scheme 1

the relatively low conversion (below 5%) and because signals for the ester relating to the decay cannot be separated from other peaks in the spectra. Therefore, an excess of $(C_2H_5)_4N^+Cl^-$ was added, leading to the suggested reaction and the ester appeared in form of two multiplets at 3·9 and 4·98 ppm.

Decay products according to Scheme 1 can be obtained after dissolution of 2-phenyl-1,3-dioxolane-2-ylium hexachlorantimonate. However, this salt is more stable

in CD₃NO₂ (20% conversion) than in CD₂Cl₂ (40% conversion) at similar concentrations (0·2–0.46 mol l^{-1}). The formation of the ester proceeds during the dissolution and equilibrium between the salt and ester is attained after 10 min. This equilibrium is stable for up to 24 h. The formation of the ester derived from the non-methylsubstituted derivative can be detected by the appearance of two multiplets at 4·05 and 4·41 ppm. This result suggests a decay via ion pairs, because of the higher stability in CD₃NO₂. The formation of the ester has been well established in the literature[4,5]. The mixture of products does not allow a kinetic definition of the final products obtained, which is in agreement with Penczek's statement[5] that 'a lot of ill-defined processes take place simultaneously.' However, the investigations of decay clearly show a reaction according to path I in Scheme 1. The formation of donors (esters) during the decay led to a competition with $SbCl_5$ or/and $SbCl_6^-$ in the form of complexation or ligand-exchange reactions.[4,11–13] Addition of a stronger nucleophile such as $(C_2H_5)_4N^+Cl^-$ in CD₃NO₂ or CD₂Cl₂ also results in the immediate formation of the product of decay according to path I in Scheme 1, but competition with $SbCl_5$ can be excluded in this procedure.

Hexahalogenoantimonates of triethyloxonium,[14] triphenylmethylium[15] and 2-phenyl-1,3-dioxolane-2-ylium cations show, in contrast to hexafluoroarsenate, a strong absorption ($\varepsilon \approx 10^4$ l mol⁻¹cm⁻¹) between 38 000 and 33 000 cm⁻¹. Typical spectra of 2-phenyl-1,3-dioxolane-2-ylium and triethyloxonium antimonates are shown in Figure 1.

The nature of the cation has no significant influence on the $\bar{\nu}_{max}$ values. This strong absorption band is caused by a charge-transfer transition from the ligands (Cl, Br) to the central atom (Sb) of the antimonate
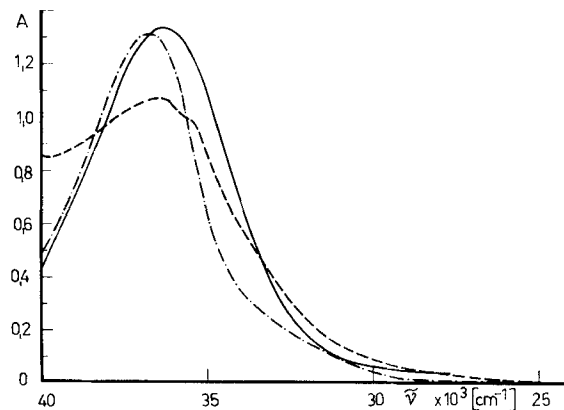

Figure 1. UV spectra of antimonates in 1,2-dichloroethane at 298 K. _____, Triethyloxonium hexachloroantimonate; ------, 2-phenyl-1,3-dioxolane-2-ylium pentachlorobromoantimonate; ·-·-·-, 2-phenyl-4,5-dimethyl *cis*-1,3-dioxolane-2-ylium hexachloroantimonate. Concentration $\approx 10^{-4}$ mol l^{-1}

anion.[16,17] An additional absorption band at 33 500 cm⁻¹ in the spectrum of 2PhD⁺SbCl₅Br⁻ is due to the charge-transfer transition Br⁻ → Sb[5+][14] The weak absorption band of the 2PhD⁺ cation at 37 740 cm⁻¹ is in the same range as that of antimonate anions.[18]

The absorption of 2PhD⁺SbXₙY₆₋ₙ solutions is not stable and gradually disappeared, as also occurred with the absorption of Ph₃C⁺SbXₙY₆₋ₙ.

The decay of 2PhD⁺SbXₙY₆₋ₙ has been considered in terms of the first-order irreversible reaction in comparison with the decay of Ph₃C⁺A⁻¹ and Et₃O⁺A⁻³ First-order plots of the decay of 2PhD⁺SbXₙY₆₋ₙ obtained by UV measurements are shown in Figure 2.
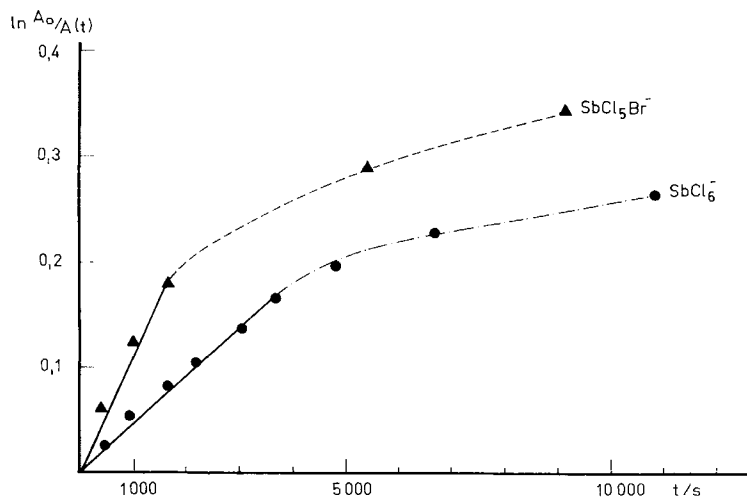

Figure 2. First-order plots of the decay of 2-phenyl-1, 3-dioxolane-2-ylium by means of UV measurements in 1,2- dichloroethane at 298 K. Concentration, $5·7 \times 10^{-5}$ mol l^{-1}

Table 1. First-order rate constants of the decay of 2-phenyl-1,3-dioxolane derivatives in 1,2-dichloroethane at 288 K

Salt	k_z/s^{-1}	
	Conductivity	Spectroscopy
2-Phenyl-1,3-dioxolane-2-ylium:		
SbCl$_6^-$	$1\cdot26 \times 10^{-5}$	$2\cdot33 \times 10^{-5}$ [a]
SbCl$_5$Br$^-$	$6\cdot7 \times 10^{-5}$ [b]	$4\cdot4 \times 10^{-5}$ [c]
	$1\cdot26 \times 10^{-5}$ [d]	
AsF$_6^-$	$1\cdot8 \times 10^{-5}$	—
2-Phenyl-4,5-dimethyl-cis-1,3-dioxolane-2-ylium SbCl$_6^-$	$3\cdot9 \times 10^{-6}$	$4\cdot5 \times 10^{-6}$
2-Phenyl-4,5-dimethyl-trans-1,3-dioxolane-2-ylium SbCl$_6^-$	$4\cdot7 \times 10^{-6}$	$5\cdot5 \times 10^{-6}$

[a] At 36 500 cm^{-1}.
[b] In the range from 0 to 900 s.
[c] At 33 500 cm^{-1}.
[d] In the range from 2100 to 7200 s.

The first-order plots deviate from a straight line after about 1500 s, and therefore a rate constant could be calculated only for the first stage of the decay, within the range of conversion below 10–15% (Table 1). In the case of 2-phenyl-4,5-dimethyl-1,3-dioxolane-2-ylium salts (PhDMD$^+$A$^-$), the absorption decreased up to 13 per cent conversion and then remained unchanged, but the position of the band shifted to the higher energy part of the UV spectrum. The shift may be caused by the fact that SbCl$_5$ or related adducts show strong absorption in the same region as SbCl$_6^-$, and so the course of the decay of antimonates determined by means of UV spectroscopy also involves the absorption of final products of the decay. The conductivity plots and the plots obtained by means of UV spectroscopy agree only in the first stage of the decay, because the decrease in absorption at 36 500 cm^{-1} due to the SbCl$_6^-$ absorption shows a molar absorptivity of $\varepsilon = 10^4$ l mol^{-1} cm^{-1}. The molar absorptivity of the SbCl$_5$ adducts is much lower than that of the strong SbCl$_6^-$ absorption, and the overall absorption was influenced after 5–10% decay.[4,11] On the other hand, rate constants determined by means of UV spectroscopy depend on the wavelength used, especially for salts with the SbCl$_5$Br$^-$ anion. Increasing rate constants of the decay were obtained when we used decreasing wavelengths. The complications involved in studying the decay of mixed bromochloroantimonates have already been discussed previously.[2,19]

The conductivities of solutions of 2PhD$^+$A$^-$ also decrease with time. First-order plots of the decay monitored by conductivity, in contrast to UV measurements, were straight lines with good correlation coefficients of about 0·99 (Figure 3). In the concentration range between 5×10^{-5} and 5×10^{-4} mol l^{-1}, the first-order rate constant of decay is independent of the starting concentration and the conductivity plots are straight lines. The reproducibility of the conductivity data is good. Every rate constant was determined by five

independent measurements. Higher starting concentrations of the salt ($>10^{-3}$ mol l^{-1}) led to an increase in the decay rate and the occurrence of numerous simultaneous processes as discussed above. The estimated second-order rate constant at a salt concentration of 0·2 mol l^{-1} is of the order of $1\cdot5 \times 10^{-3}$–5×10^{-3} l mol^{-1} s^{-1} and comparable to that reported elsewhere.[20] However, the ill-defined processes do not allow accurate data representing clean conditions as shown in Scheme 1 to be determined when high concentrations of salts are applied.

As to be seen from Figure 3, the anions SbCl$_6^-$ and AsF$_6^-$ are relatively stable, whereas SbCl$_5$Br$^-$ appears to be less stable. The decay of 2PhD$^+$SbCl$_5$Br$^-$ proceeds in two steps. We assume that the first step mainly involves the decay of the antimony—bromine bond:
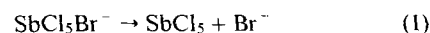
$$SbCl_5Br^- \rightarrow SbCl_5 + Br^- \qquad (1)$$

After 2500 s, the plot of the decay of SbCl$_5$Br$^-$ proceeds parallel to the plot of the decay of SbCl$_6^-$. This may be explained by the formation of the more stable SbCl$_6^-$ resulting from ligand exchange within mixed halogenoantimonates.[12] Rate constants of the decay of substituted 1,3-dioxolane-2-ylium salts calculated by means of conductivity are given in Table 1.

According to the data in Figure 3 and Table 1, the stabilities of 2-phenyl-1,3-dioxolane-2-ylium salts can be ordered in a similar manner to that proposed by Jones and Plesch[3] for triethyloxonium salts, i.e. SbCl$_6^-$ > AsF$_6^-$ > SbCl$_5$Br$^-$.

Generally, the decay of substituted dioxolenium salts is faster than that of Et$_3$O$^+$SbCl$_6^-$ determined by means of the same method: $k_z = 5 \times 10^{-6}$. The rate constants of the decay of substituted 1,3-dioxolane-2-ylium salts also depend on the cation structure.

Methyl substituents in the 4- and 5-positions on the ring lead to an increase in the stabilities of dioxolenium salts, in spite of the increased positive charge density at
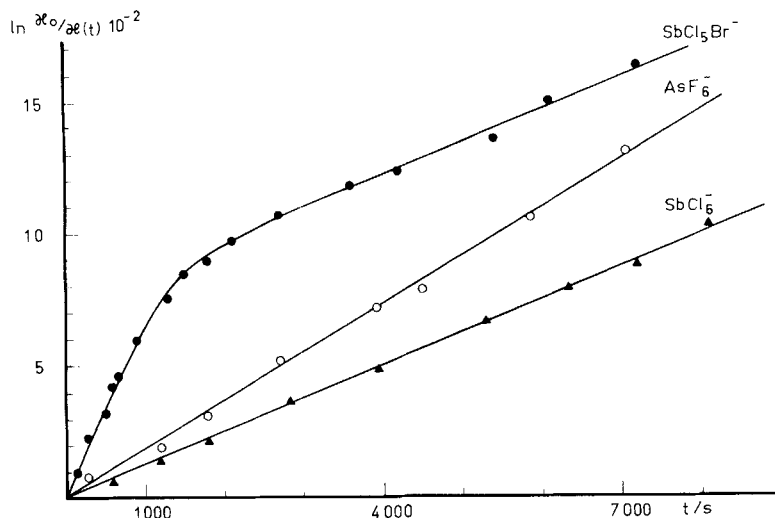
Figure 3. First-order plots of the decay of 2-phenyl-1, 3-dioxolane-2-ylium salts by means of conductivity in 1,2-dichloroethane at 298 K. Concentration, 4×10^{-4}–6×10^{-4} mol l^{-1}

C-4 and C-5.[21] A phenyl substituent in the 2-position also has a significant stabilizing effect, as can be concluded from the comparison of the decomposition of *trans* and *cis* isomers of 4,5-dimethyl-1,3-dioxolane -2- ylium hexachloroantimonates. However, these data were obtained with much more concentrated solutions, i.e. $0 \cdot 4$–$0 \cdot 8$ mol l^{-1} ($k_z = 1 \cdot 7 \times 10^{-3}$– $3 \cdot 3 \times 10^{-3}$ l mol^{-1} s^{-1}).[20] These conclusions are in agreement with the previously described relationship between the structure and catalytic activity of dioxolenium salts in the polymerization of oxacyclic monomers.[6-10,20] From the decay of PhDMD$^+$SbCl$_6^-$ determined by the conductimetric method one can conclude that the *cis* and *trans* isomers appeared to have the same stability within the range of error (Table 1).

Instruments

UV spectra were recorded with a Specord UV–visible instrument from Carl Zeiss Jena. The conductivity measurements were carried out with a Hydromat Bannewitz, LM 300 instrument. The frequency for measurement was 3000 Hz. Platinum electrodes were used in a stirring vessel under an argon atmosphere. The kinetic treatment and technique were as described elsewhere.[1]

Materials

The solvent 1,2-dichloroethane was purified by stirring with concentrated sulphuric acid and washing with distilled water. After the first redistillation over P_2O_5 the solvent was stored over CaH_2 and distilled freshly under dry argon before use.

Triethyloxonium hexachloroantimonate was synthesized from epichlorhydrin and SbCl$_5$ in diethyl ether at 198 K by the method of Meerwein.[22] It was purified by recrystallization from a dichloroethane–diethyl ether mixture.

Substituted 1,3-dioxolane-2-ylium salts were obtained from the corresponding acetals and triphenylmethylium salts by the direct reaction of a slight excess of the acetal with triphenylmethylium salts in CH_2Cl_2 solution ($0 \cdot 1$ mol l^{-1}) and subsequent precipitation with CCl$_4$ or heptane.[23] The final product was purified by dissolution and precipitation. The analytical data for the salts agreed with the theoretical elemental analysis in every case.

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