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Hydride Transfer to Some Initiators of Cationic Polymerization

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SUMMARY

The hydride transfer from xanthene to stable carbenium salts with different cation electrophilities: 2,4',4''-trichlorotriphenylmethylhexachloroantimonate, triphenylmethylhexafluoroarsenate, triphenylmethylhexachloroantimonate, 4,4',4''-trimethyltriphenylmethylhexachloroantimonate and tropylium hexachloroantimonate is investigated. The reaction is controlled by the absorption of the carbenium ions in the visible region of their electronic spectra. The formation of the product of the reaction - triphenylmethane - is detected by gas chromatography and NMR spectroscopy. The rate constants and the reaction order are determined. The acceleration of the hydride transfer on UV-irradiation of the reaction mixture is shown.

INTRODUCTION

Hydride transfer from the monomer to the initiator is one of the possible paths for initiation of cationic polymerization by stable carbenium salts (BAWN et al., 1971). This type of initiation is studied and proved only for polymerization of cyclic ethers and acetals (PENCZEK 1974, DREYFUSS 1976). No systematic

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investigations of the stable salts ability to accept hydride ion forming carbenium ion in conditions conventional for cationic polymerization are reported so far in the literature. It is known (BONTHRONE and REID 1959) that $(C_6H_5)_3CClO_4$ cleaves hydride ion from xanthene in glacial acetic acid by heating.

In order to select a convenient system for testing the stable salts ability to abstract hydride ion in medium which is typical for cationic polymerization xanthene was choosen as hydride donor. The interaction between xanthene and $(C_6H_5)_3CSbCl_6$, $(ClC_6H_4)_3CSbCl_6$, $(CH_3C_6H_4)_3CSbCl_6$, $(C_6H_5)_3CAsF_6$ and $C_7H_7SbCl_6$ in dichloromethane medium is investigated.

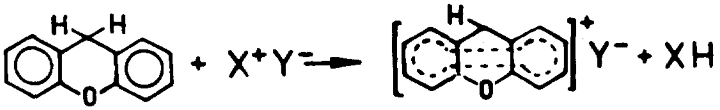
EXPERIMENTAL

$(ClC_6H_5)_3CSbCl_6$ and $C_7H_7SbCl_6$ are prepared by the method of HOLMES and PETTIT (1963). All salts used are purified by recrystalization by known method (COWELL et al. 1970). Xanthene is prepared by reduction of xanthone according to HELLER and KOSTANECKI (1908). Dichloromethane is purified as described by BOWYER et al. (1971).

The experiments are carried out in dichloromethane at 28°C in vacuo or in inert atmosphere. The concentration changes of the initial stable salts and of the xanthylium salt obtained are determined by the changes in the absorption maxima of the cations: $(C_6H_5)_3C^+$ at 412 nm, $(ClC_6H_4)_3C^+$ - 496 nm, $(CH_3C_6H_4)_3C^+$ at 456 nm and xanthylium$^+$- 380 nm. To identify $(C_6H_5)_3CH$ the product of the hydride transfer gas chromatography and NMR spectroscopy are used. The kinetic curves are analyzed by the integral and the differential methods described by LAIDLER (1966).

RESULTS AND DISCUSSION

The hydride transfer proceeds from xanthene to all salts studied according to the reaction:



where $X^+ = (ClC_6H_4)_3C^+$, $(CH_3C_6H_4)_3C^+$, $(C_6H_5)_3C^+$ or $C_7H_7^+$ and $Y^- = SbCl_6^-$, or AsF_6^-. The proceeding of the reaction is demonstrated by the changes in the visible spectrum of the reaction mixture (Figure 1) as well as by the formation of triphenylmethane.

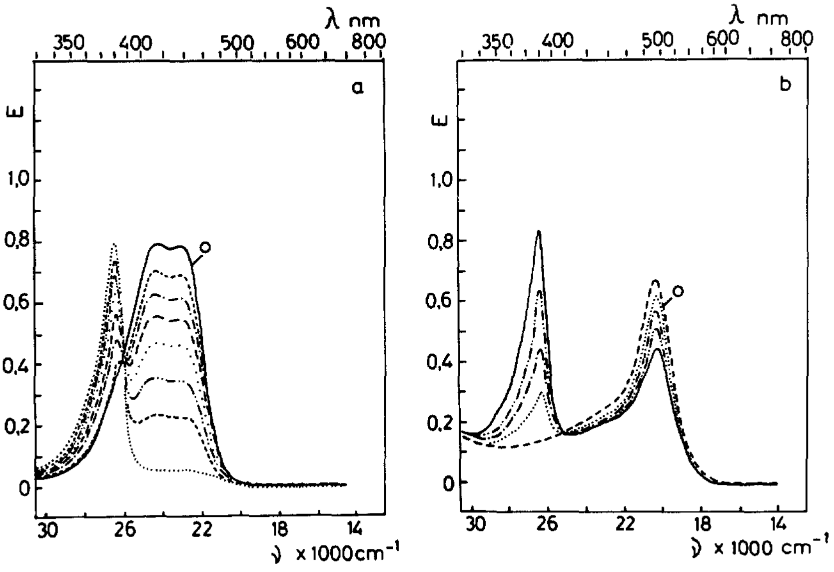


Fig. 1: Spectral monitoring of the hydride transfer from xanthene to: a) $(C_6H_5)_3CSbCl_6$;b) $(ClC_6H_4)_3CSbCl_6$.

The rate constants (Table 1) are calculated from the usual second order differential expression following the disappearance of the trityl cation k_2' and following the appearance of the xanthylium ion k_2''. The

T A B L E I

Average values of the rate constants k_2 of the hydride transfer from xanthene (XH_2) to stable salts (I) in dichloromethane at 28° C

Salt	$(I)_o.10^4$ (mole.l^{-1})	$(XH_2)_o.10^4$ (mole.l^{-1})	k_2'	k_2''	k_2^{o} a)	pK_{R+} b)	$E_{1/2}$ c) (V)
			(l.mole^{-1}.s^{-1})				
$(ClC_6H_4)_3CSbCl_6$	0,7- 5,0	1.3- 5,0	11,0	6,1	14.0	- 7,74	0,38
$C_6H_5CSbCl_6$	0,5-12,0	5.0-12,0	1,0	1.2	1,5	- 6 63	0.27
$C_6H_5CAsF_6$	0,3-10,0	0.3-15,0	1,9	1,7	2,0	- 6,63	0,27
$(CH_3C_6H_4)_3CSbCl_6$	2,5- 3,5	2,5- 3,5	10^{-8}			- 3,56	0,05
$C_7H_7SbCl_6$	15,0	15,0	$2,2.10^{-8}$				- 0,17

′) Calculated from $-\frac{d(I)}{dt}$; ″) Calculated from $\frac{d(XH^+)}{dt}$.

a) Calculated from the initial slope of the (I) vs time curves; b) DENO et al. (1955);

c) VOLZ and LOTSCH (1969).

coincidence between these constants indicates that the reaction is first order in both the stable salt and the hydride donor xanthene. The rate constants k_2^o determined from the initial slope of the salt concentration versus time plots are in good agreement with the overall rate constants. The main reaction is hydride transfer and no side reactions take place under these conditions. The hydride transfer is quantitative with all salts. The rate constants of the reaction investigated are in agreement with the rate constants of hydride transfer from bis-(N-ethylcarbazolylmethane) to $(C_6H_5)_3CSbCl_6$ and $(C_6H_5)_3CBF_4$ determined by BRUCK et al. (1970).

As expected the hyghest rate is attained with the most electrophilic cation $(ClC_6H_4)_3C^+$ and the lowest rate with $(CH_3C_6H_4)_3C^+$ (pK_{R^+} and $E_{1/2}$ values in Table 1). The very low rate of hydride transfer to $(CH_3C_6H_4)_3C^+$ is probably due to steric hindrance.

In the concentration range studied where free ions are predominately present (DREYFUSS et al. 1968, PENCZEK, 1974) the reaction rate does not depend on the type of counterion ($SbCl_6^-$ or AsF_6^-).

The rate of hydride transfer from xanthene to the salts studied decreases in the following order:

$$(ClC_6H_4)_3CSbCl_6 > (C_6H_5)_3CAsF_6 \approx (C_6H_5)_3CSbCl_6 \gg$$
$$\gg C_7H_7SbCl_6 > (CH_3C_6H_4)_3CSbCl_6$$

In order to compare kinetic parameters when experiments are carried out in vacuo or in inert atmosphere parallel runs are performed. In inert atmosphere $k_2'' < k_2'$. This fact is most likely due to the interaction of trityl salts with moisture traces. These results show that for correct investigating of the reaction kinetics use of vacuum technics is necessary.

The hydride transfer proceeds most probably via an activated complex and the hydride mobility is determined both by the electrophility of the attacking agent and the type of the hydride donor. The high yield of triphenylmethane obtained in the photolysis of trityl salts (TONCHEVA and VELICHKOVA, to be published) leads to the inference that the irradiation of the reaction mixture will favour the hydride transfer. An example of the effect of UV-irradiation of the reaction mixtures of stable salts and xanthene is shown in Figure 2.

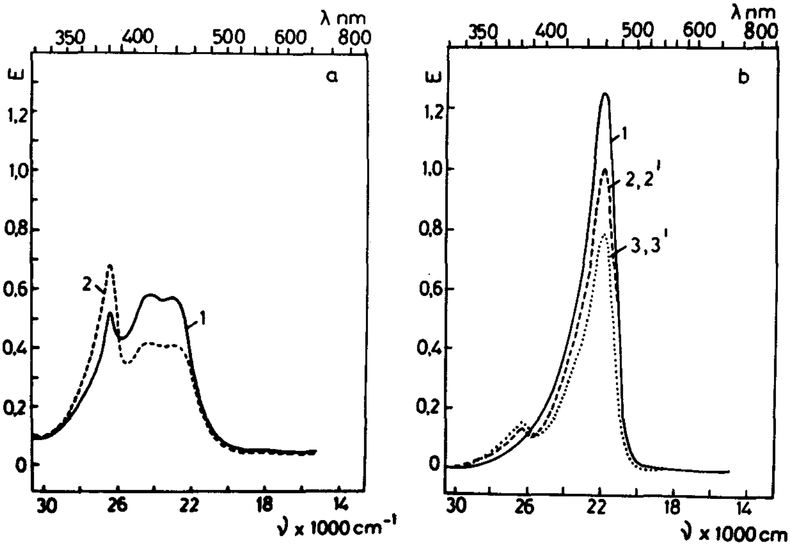


Fig.2: Influence of the UV-irradiation on the hydride transfer from xanthene to: a) $(C_6H_5)_3CSbCl_6$; reaction time: 1 - 5 min, 2 - 5 min, 1 min irradiated solution; b) $(CH_3C_6H_4)_3CSbCl_6$; reaction time: 1 - 10 min, 2 - 1 min irradiation, 15 min, 2' - 30 min, 3 - 1 min irradiation, 35 min, 3' - 50 min.

In order to eliminate the photolysis of the salts the solutions are irradiated for 30-60 s. The irradiation of the reaction mixture of tritylhexachloroantimonate and xanthene accelerates the reaction (Figure 2a). The hydride transfer to $(CH_3C_6H_4)_3CSbCl_6$ becomes appreciable on irradiation of the reaction mixture (Figure 2b). The proceeding of the reaction is observed immediately after irradiation; there is no noticeable change in the spectrum of the solution till the next irradiation. The effect of UV-light on the hydride transfer will be studied further.

CONCLUSIONS

The results obtained imply that the stable carbenium salts abstract hydride ion from xanthene via bimolecular interaction and the reaction rate depends on the electrophility of the stable salts.

The hydride transfer is accelerated by UV-irradiation.

The investigation undertaken show that the selected system is convenient for testing the stable salts ability to abstract hydride ion in conditions which are typical for cationic polymerization.

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