Kinetics of Hydride Transfer from 1,3-Dioxolan to the Free Triphenylmethyl Cation Preceding the True Initiation

By ST. SŁOMKOWSKI and ST. PENCZEK*

(*The Polymer Institute, Ministry of Education and Polish Academy of Sciences, Łódź* 40, *Poland*)

Summary The process preceding the true initiation of polymerization of 1,3-dioxolan induced by Ph_3C^+,A^- salts is hydride-transfer to the free trityl ion or ion pair.

TRIPHENYLMETHYL salts have been used in the initiation of polymerization of tetrahydrofuran[1] and cyclic acetals.[2-4] In the case of 1,3-dioxolan (diox) some of them have been reported to be completely inactive[2] while some give high reaction rates and high-molecular-weight polymers of 1,3,5-trioxan.[3,4] Attempts have been made to explain some of the observed differences in terms of the influence of the stability of the counter-ion.[3]

Our preliminary results show, however, that this cannot be the only reason.[5] In fact, $Ph_3C^+SbCl_6^-$ reacts with diox giving an unstable 1,3-dioxolenium hexachloroantimonate (dn) and Ph_3CH, following the known Meerwein reaction.[6] This latter salt decomposes, producing β-chloroethyl formate and $SbCl_5$, which reacts further with diox, forming, in a subsequent hydride-transfer reaction, dn and $HSbCl_4$ ($HCl + SbCl_3$).[5]

Although neither HCl alone nor HCl combined with $SbCl_3$ can initiate polymerization of diox, the presence of HCl is responsible for the formation of the active species (*e.g.* through formation of $H^+SbCl_6^-$.[6]

Thus, the activity of trityl salts as initiators for diox polymerizations can be related to the rate of the first hydride-transfer reaction, the stability of the dioxolenium salt produced, and the reactivity towards diox of the metal halide eventually formed.

We were unable to find any data concerning the rates of the first of these reactions—the hydride-transfer involving cyclic acetals. Recently some results on the kinetics of hydride transfer from tetrahydrofuran[7] and substituted carbazoles[8] in organic solvents have been reported. Earlier kinetic results were obtained mainly in strong acid solutions (H_2SO_4).[9]

We report on the kinetics of hydride-transfer to the free Ph_3C^+ ion obtained from trityl salts of general formula $Ph_3C^+A^-$, where $A^- = ClO_4^-$, AsF_6^-, and $SbCl_6^-$.

This reaction was studied in CH_2Cl_2 solution in the temperature range 0—30° using apparatus sealed *in vacuo*, equipped with Teflon-glass stopcocks and greaseless ground-glass joints (West-Glass, U.S.A.). 0·1 and 1·0 cm Spectrosil cuvettes were sealed directly to the mixing device. The kinetics were studied by monitoring the decrease of the absorption at 430 nm, the band characteristic for the trityl ions. Beer's law was obeyed by all the $Ph_3C^+A^-$ systems used (below 10^{-4} M). Above this concentration, the equilibrium (1) should be considered for the salts with complex anions.

A typical kinetic plot obtained for $A^- = SbCl_6^-$ is shown in Figure 1. The first experimental point at zero time was obtained for the salt solution before the introduction of diox. This absorption was unchanged after 24 h if the solution were kept in the dark in a sealed apparatus. In daylight, a slow decrease in the absorption was observed, indicating a possible slow consumption of $SbCl_5$ in the chlorination process.

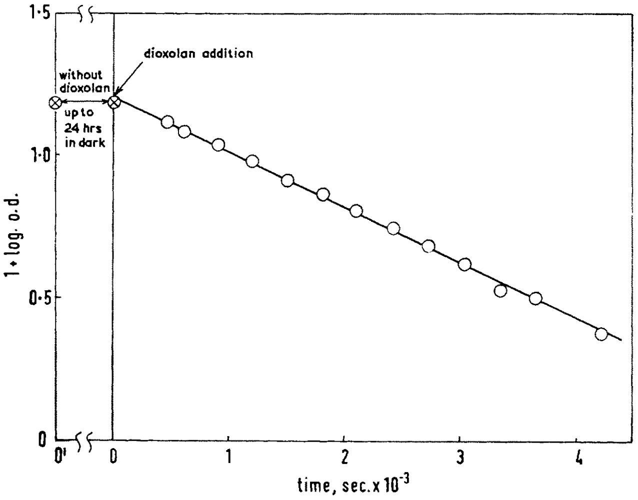


FIGURE 1. *Kinetic plot for* H^- *transfer from* 1,3-*dioxolan to* Ph_3C^+ (*from* $Ph_3C^+SbCl_6^-$) *in* CH_2Cl_2 *solution at* 22·5°. *The* 0'—0 *region corresponds to the time preceding introduction of dioxolan.* $[Ph_3C^+]_0 = 4{\cdot}41 \times 10^{-4}$ M, $[diox]_0 = 5{\cdot}17 \times 10^{-2}$ M. k_{exp} *determined from the plot equals to* $8{\cdot}3 \times 10^{-3}$ l *mole*$^{-1}$ *s*$^{-1}$.

A kinetic run, usually carried out shortly after dissolving the salt in CH_2Cl_2 and measuring its optical density at λ_{max} 430 nm, consisted of mixing diox with the salt solution and then measuring the decrease of the o.d. with time. Taking ϵ_{max} $3{\cdot}6 \times 10^4$[10] [in agreement with our independent measurements when the equilibrium (1) has been completely shifted to the ionized species side by introducing an excess of Ph_3CCl] the sum of $[Ph_3C^+A^-] + [Ph_3C^+] = C_{ions}$ has been calculated. For all the salts a plot of $-\ln(C_{ions}/C_{ions(0)})/[diox]_0$ against time is perfectly linear for different starting concentrations of the trityl salts used ($C_{ions(0)}$) and the $[diox]_0$ used (diox was always added in a large excess). $C_{ions(0)}$ was determined from the intercept and found to be in very good agreement with the value measured before addition of diox (*cf.* Figure 1). At constant temperature, experimental points for $A^- = ClO_4^-$, AsF_6^-, and $SbCl_6^-$ fall on a common line in spite of changing the value

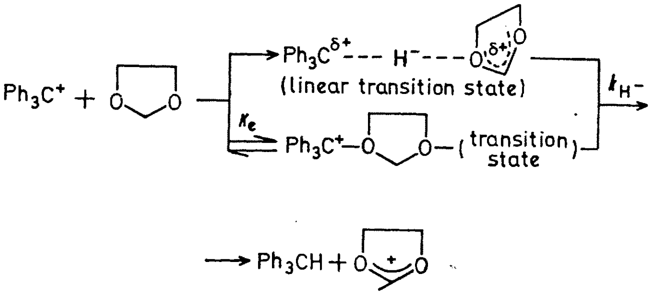
$$Ph_3C^+SbCl_6^- \underset{k_a}{\overset{k_d}{\rightleftharpoons}} Ph_3CCl + SbCl_5;\ K_1 = k_d/k_a \qquad (1)$$

$$Ph_3C^+,SbCl_6^- \underset{k'_a}{\overset{k'_d}{\rightleftharpoons}} Ph_3C^+ + SbCl_6^-;\ K_2 = k'_d/k'_a$$

of $C_{\text{ions}(0)}$ from 10^{-5} M to 10^{-4} M and $[\text{diox}]_0$ from 2×10^{-3} M to 2×10^{-1} M for different runs.

The reaction under study is of first order in both Ph_3C^+ used and diox. The rate of reaction does not depend on counter-ion structure or, more likely, predominantly free ions are involved. The latter explanation is favoured because the pseudo-first-order character of the reaction is preserved within the limits of our measurements. The slight curvature of the experimental line for perchlorate at the beginning of the reaction (*i.e.* in the region of higher salt concentration) could mean the slowing down of the reaction rate when passing from the region dominated by free ions to that dominated by ion-pairs. This transition region is located where its position could be assumed, on the basis of recent conductivity measurements reported for this salt by Lee and Treloar.[11] Thus, the reaction studied in the present work involves essentially free ions at the concentrations equal to these measured from the o.d.

The H^- transfer can proceed thus:



Further studies are needed to establish whether the reaction involves oxonium ion formation although this seems less likely than the linear transition state. The concentration of the species absorbing at 430 nm (oxonium ions probably do not absorb in this region) does not change to any measurable extent immediately after the introduction of diox (comparison of the o.d. without diox with the intercept of the kinetic curve in Figure 1). This behaviour has been a common feature in the case of diox for all the salts studied. If the reaction proceeds with a linear transition state, then the measured bimolecular rate constant $k_{\text{exp}} = k_{H^-}$; in the case of a preliminary equilibrium, followed by a unimolecular decomposition of the oxonium salt, k_{exp} would additionally involve K_e.

The dependence of k_{exp} on the reciprocal of the absolute temperature is shown in Figure 2. All the data, including those for three different salts, fit the same straight line well. From Figure 2 $k_{\text{exp}} = 8{\cdot}5 \times 10^9 \exp(-16{,}800/RT)$ l mole^{-1} s^{-1}. The experimental activation energy is very close to the enthalpy of activation reported by Bartlett for H^- transfer in H_2SO_4 solution (16·8 for $Pr^i{}_2O$ and 18·9 for Et_2O).[9]

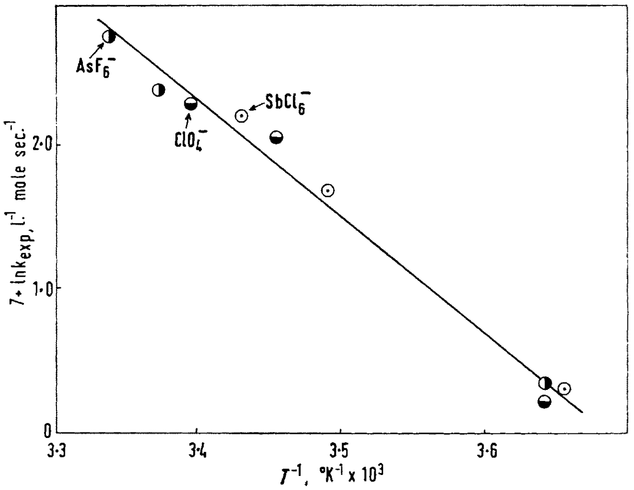


FIGURE 2. *Dependence of* k_{exp} *on reciprocal of absolute temperature for* H^- *transfer from* 1,3-*dioxolan to* Ph_3C^+ (*coming from* $Ph_3C^+A^-$) *at different starting* $[\text{diox}]_0$ *and* $[Ph_3C^+]$.

Results obtained for $Ph_3C^+SnCl_5^-$ are not included in the present report, since the large value of K_1 leads to complications in the determination of the proper k_{exp} value.

Some H^- transfer directly to $SbCl_5$ (in equilibrium with the corresponding salt) can also accompany transfer to Ph_3C^+, but the relatively low $[SbCl_5]$ in this system (less than 20% of the $[Ph_3C^+]$) does not disturb the linearity of the plots given in Figure 1.

We thank Mr. W. E. White, Director of Ozark-Mahoning Comp., Tulsa, Okla., U.S.A., for a gift of the trityl salts.

(*Received, June* 23*rd*, 1970; *Com.* 996.)

---

[1] C. E. H. Bawn, R. M. Bell, and A. Ledwith, *Polymer*, 1965, **6**, 95; I. Kuntz, *J. Polymer Sci., Part B, Polymer Letters*, 1966, **4**, 427; M. P. Dreyfuss, J. C. Westfahl, and P. Dreyfuss, *ACS Polymer Preprints*, 1966, 7 (2), 413; W. M. Pasika and J. W. Wynn, *J. Polymer Sci., Part A*-1, 1969, **7**, 1489.

[2] P. H. Plesch, "Cationic Polymerization" in "Progress in High Polymers," eds. J. Robb and W. Peaker, Iliffe, London, 1968.

[3] B. J. K Smith, J. A. Dodd, A. T. Instone, and D. B. Partridge, *J. Polymer Sci., Part B, Polymer Letters*, 1967, **5**, 625.

[4] Yu. N. Smirnov, V. P. Volkov, V. I. Irzhak, and N. S. Enikolopyan, *Doklady Akad. Nauk S.S.S.R.*, 1970, **190**, 1403.

[5] P. Kubisa and St. Penczek, *Makromol. Chem.*, to be published.

[6] H. Meerwein, V. Hederich, H. Morschel, and K. Wunderlich, *Annalen*, 1960, **635**, 1.

[7] A. Ledwith, *Adv. Chem. Ser., Amer. Chem. Soc.*, No. **91**, p. 317 (1969).

[8] P. Bruck, A. Ledwith, and A. C. White, *J. Chem. Soc.* (*B*), 1970, 205.

[9] P. D. Bartlett and J. D. McCollum, *J. Amer. Chem. Soc.*, 1956, **78**, 1441.

[10] F. Fairbrother and B. Wright, *J. Chem. Soc.*, 1949, 1058.

[11] W. Y. Lee and F. E. Treloar, *J. Phys. Chem.*, 1969, **73**, 2458.