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Stopped-Flow Investigation of Trifluoromethanesulfonic Acid Initiated Cationic Oligomerization of *trans*-1,3-Diphenyl-1-butene. 2. A Model Kinetic Study of Styrene Cationic Polymerization

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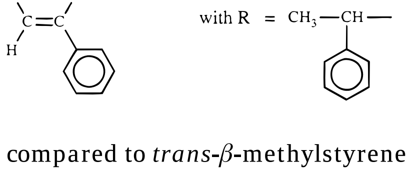
ABSTRACT: Study of the reaction of *trans*-1,3-diphenyl-1-butene (D, the trans ethylenic dimer of styrene) with triflic acid in dichloromethane has been carried out using stopped-flow technique with UV−visible spectroscopic detection. Product characterizations and cation observations have been previously described, and the present work consists of a kinetic study of the reactions which can be considered as model reactions for the behavior of the polystyryl cations in the styrene cationic polymerization, after complete conversion of the monomer. The main observed cationic species were 1,3-diphenyl-1-butylium (D^+) and oligomeric cations ($D_n{}^+$); they absorbed at 340 nm and had a transient existence. Absorbance at 340 nm first increased very fast to reach a maximum value within a few seconds, after which the peak slowly decreased. Its persistence time was shortened when either acid concentration or temperature were increased or when the D concentration was decreased. From the analysis of the rate of appearance of the 340 nm peak, kinetics of protonation of D has been studied. Reaction was first order with respect to D and 1.26 order with respect to acid. The absorbance at 340 nm reached a maximum (OD_{max}), the value of which increased when acid and D initial concentrations were increased and when temperature was lowered. Concentration of cations remained always very low as compared to the initial concentrations of reagents. As for the polymerization of styrene initiated with triflic acid, the low amount of propagating cations indicates fast deprotonation either by β-elimination or by indanic cyclization.

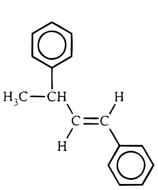
Introduction

We previously reported[1] on the reaction of *trans*-1,3-diphenyl-1-butene (D, the trans ethylenic dimer of styrene) with triflic acid which is considered a model reaction of the unsaturated chain ends appearing during the cationic polymerization of styrene either by β-proton elimination or by transfer to the monomer. This reaction was described by product characterization and real time UV−visible spectroscopic analysis of involved cations. It has been shown that D was not able to polymerize into high molecular weight chains but could oligomerize. The higher oligomers were cyclized trimers or tetramers of D and the main product was always the indanic dimer of D, whatever the initial conditions. Cyclization of D into 1-methyl-3-phenylindan (I, the indanic dimer of styrene) also occurred but in smaller proportions and was enhanced when the temperature was increased. D has the structure of trans β-substituted styrene

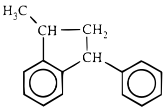


and can be compared to *trans*-β-methylstyrene for which homopolymerization is known to be limited.[2,3] From a thermodynamic point of view, polymerization is unfavorable due to repulsive interactions between substituents in the chains.

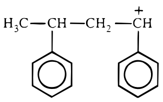
From real time UV−visible spectrophotometric observation of the reaction, various peaks have been reported and they were assigned to as follows: (i) 1,3-diphenyl-1-butylium (D^+) and oligomeric cations ($D_n{}^+$, $n = 2, 3$), absorbing at 340 nm and resulting from protonation of D and further oligomerization; (ii) an allylic cation ($D_i{}^+$, 1,3-diphenyl-1-buten-3-ylium) produced by hydride abstraction from D and absorbing at 349 and 505 nm; (iii) monoaryl and diaryl indanylium cations absorbing at 316 and 415 nm, resulting, at temperatures above −30 °C, from ionization of cyclic compounds appearing during the course of the reaction.



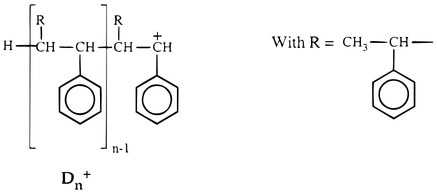
D



I



D^+



$D_n{}^+$

S0024-9297(97)00060-0 CCC: $15.00

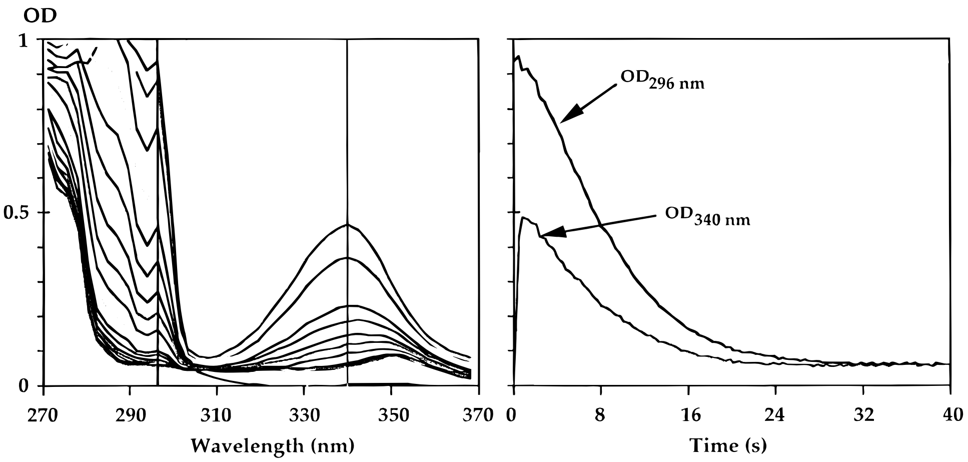


Figure 1. Typical spectra recorded during the reaction of D with triflic acid (experiment SF4, $T = -67$ °C). Consumption of D (296 nm) and simultaneous evolution of the D^+ and D_n^+ cations (340 nm).

Scheme 1

$$D + HA \xrightleftharpoons{K_1} D,HA \quad (\pi \text{ complex ?})$$
$$D,HA + HA \xrightleftharpoons{K_2} D^+A^-,HA$$
$$D^+A^-,HA + D \xrightarrow{k_c} I + D^+A^-,HA$$

Barton and Pepper[4] studied the rate of double bond consumption for reactions of D with sulfuric, chlorosulfonic, and perchloric acids in 1,2-dichloroethane solvent at temperatures higher than 0 °C. With the former two acids, the consumption rate was very fast during the first few percent of conversion but later decreased. This was explained by a decrease of active initiator concentration due to aromatic ring sulfonation. With perchloric acid, the kinetics was simple and was of second order with respect to acid and also of second order with respect to D during the whole reaction time. The proposed reaction scheme is given in Scheme 1 (with HA = perchloric acid).

Two molecules of acid are required for the protonation of D into D^+ and then cyclization (rate constant k_c) results from a transfer reaction from D^+ to D. Considering rapidly established equilibria, the consumption rate of D can be written as follows:

$$-\frac{d[D]}{dt} = k_c[D][D^+A^-,HA] = k_cK_1K_2[HA]^2[D]^2$$

In this scheme, Pepper and Barton did not take into account the oligomerization of D although they mentioned that appreciable proportions (30−50%) of low molecular weight polymer were also recovered. However, taking into account the oligomerization should result in the same type of kinetic expression where k_c would become the sum of transfer and addition rate constants. These authors supposed that ionization was occurring in two reversible steps with formation of an hypothetic intermediate π complex. An alternative explanation already proposed in our laboratory is that ionization would instead require acid aggregates, the size of which depends on temperature.[5,6]

In the present work, the study was focused on kinetic evolution of the cations absorbing at 340 nm (see typical spectra, Figure 1) in order to better understand the behavior of the polystyryl cations after complete conversion of the monomer in the styrene cationic polymerization initiated by triflic acid. The initial concentrations of reagents have been chosen in order to get the optimum optical density of the corresponding 340 nm peak. Unfortunately, such conditions were unfavorable to dimer consumption analysis (at 296 nm) due to OD saturation (see Experimental Section).

Table 1. Stopped-Flow Experiments: Experimental Conditions for the Reaction of 1,3-Diphenyl-1-butene (D) with Triflic Acid

expt no.	$[D]_0$ (mM)	$[CF_3SO_3H]_0$ (mM)	temp (°C)
SF1	16.9	4.05	−67
SF2		10.1	
SF3		23.6	
SF4	6.7	22.5	
SF5	13.5	14.0	−64
SF6		27.7	
SF7	16.3	13.1	
SF8	16.1	12.9	−53
SF9	15.8	12.6	−38

Experimental Section

Reagents synthesis and purification and also stopped-flow procedure have been previously described.[1] For the 340 nm peak, the molar absorption coefficient has been chosen equal to $\epsilon = 10^4$ L mol^{-1} cm^{-1}, a value previously proposed for polystyryl cations.[8] Therefore, with a 0.2 cm optical path (l), the product ϵl is equal to 2000 L mol^{-1}. For the dimer D, the ϵ value at 296 nm is 1160 L mol^{-1} cm^{-1} ($\epsilon l = 232$ L mol^{-1}). Because the Beer−Lambert law did not apply to the whole optical density range, calibration curves have been established respectively at 296 and 340 nm and were used every time OD exceeded 1 for the 340 nm peak and systematically for the 296 nm peak. Existence of stray light in the spectrophotometer prevented accurate measurements of $OD_{296\ nm}$ higher than 1.7 which means that D solutions more concentrated than 7 mM could not be analyzed, and this was the case for most experiments. For the 340 nm peak, the maximum measurable OD was 2.2. To determine correct optical densities, subtraction of the baseline was necessary and values were then expressed as ΔOD in the tables. Experimental conditions are reported in Table 1.

Results and Discussion

General Observations Concerning the Evolution of $OD_{340\ nm}$ vs Time. At 340 nm the absorption is due to D^+ and D_n^+ cations. After a short period of increase (duration t_{max}), $OD_{340\ nm}$ reached a maximum (OD_{max}) and then decreased more slowly (Figure 2).

At temperatures close to −64 °C, t_{max} was about 1 s and varied only slightly with the initial concentration of the reagents which is different from what was previ-

Table 2. Kinetic Characteristics of the 340 nm Peak at $T \leq -64$ °C

expt no.	$[D]_0$ (mM)	$[CF_3SO_3H]_0$ (mM)	T (°C)	initial slope (s^{-1})	t_{max} (s)	ΔOD_{max}	$\Delta OD_{max}/\epsilon l[D]_0$	initial slope/ ΔOD_{max} (s^{-1})	persistence time (t_v) (s)
SF1	16.9	4.05	−67	0.7	1.5	0.1	0.003	7.0	...
SF2		10.1		1.2	1.0	0.4	0.012	3.0	>40
SF3		23.6		5.6	1.0	1.2	0.036	4.7	25
SF4	6.7	22.5		2.2	0.8	0.5	0.036	4.4	25
SF5	13.5	14.0	−64	3.5	0.7	0.94	0.035	3.7	10
SF6		27.7		5.4	0.6	1.07	0.040	5.0	10

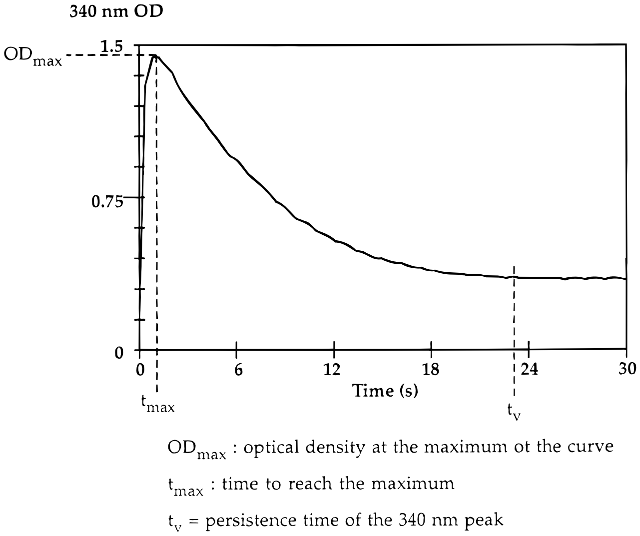


Figure 2. Optical density at 340 nm vs time for the experiment SF3 carried out at −67 °C. The final plateau results from contribution of the 349 nm peak.

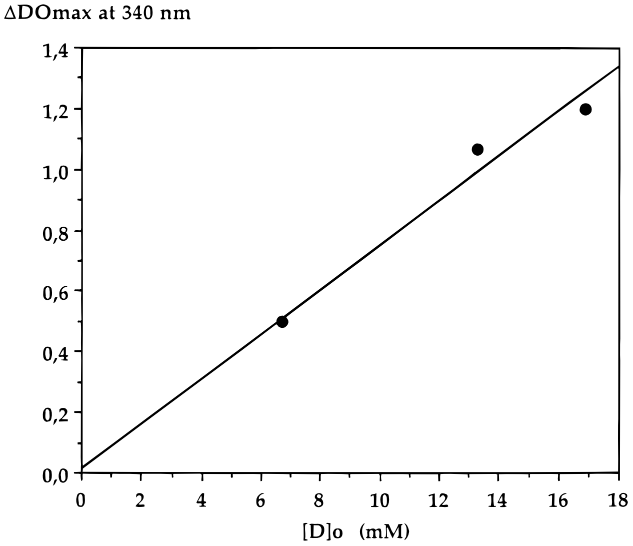


Figure 3. Influence of the initial concentration of D on OD_{max} at 340 nm for the experiments SF3, SF4, and SF6 carried out at temperatures close to −64 °C

ously observed for styrene polymerization where t_{max} significantly decreased when the acid initial concentration was increased.[5,6] When temperature was increased, t_{max} was strongly shortened (<0.1 s at −38 °C; experiment SF9, Table 1).

On the contrary, OD_{max} was strongly influenced by initial concentrations: at −64 °C, it was found to be proportional to $[D]_0$ for similar initial acid concentrations (experiments SF3, SF4, and SF6; Table 2 and Figure 3) and the ratio $OD_{max}/[D]_0$ was found to be proportional to $[CF_3SO_3H]_0{}^{1.38}$ (Figure 4). When temperature was increased, OD_{max} significantly decreased (Figure 5).

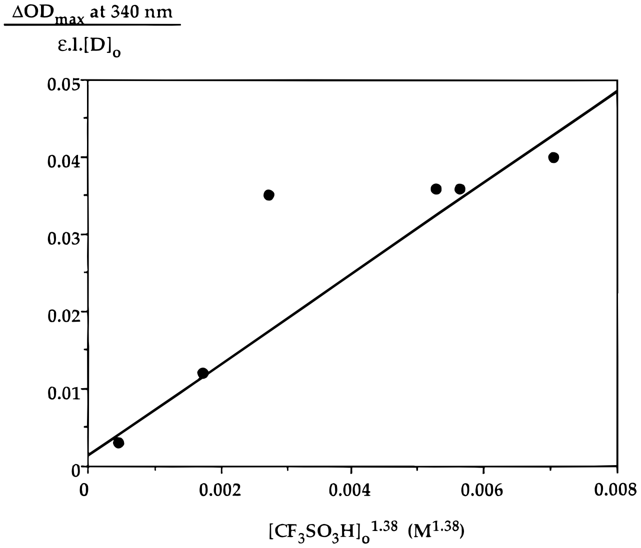


Figure 4. Influence of the initial concentration of acid on OD_{max} at 340 nm for the experiments SF1−SF6 carried out at temperatures close to −64 °C

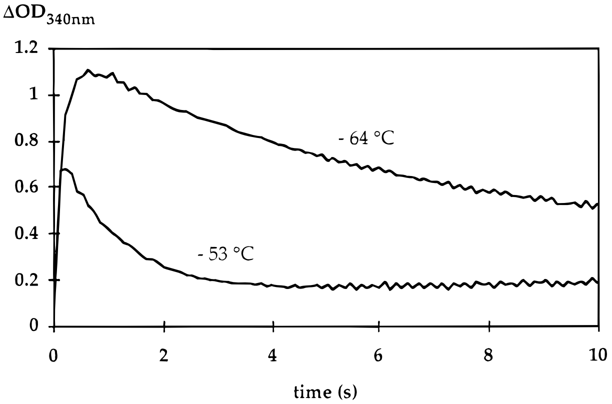


Figure 5. Influence of temperature on kinetics of $OD_{340\ nm}$. Experiments SF7 and SF8, respectively, were carried out at −64 and −53 °C (baseline was subtracted).

The persistence time (t_v) of the peak was always much longer than t_{max} (Figures 1 and 2 and Table 2) but the rate of decrease could not be accurately determined owing to a simultaneous slow appearance of the 349 nm peak[1]. At −64 °C, the persistence time was comparable to the D consumption time (Figure 1). It slightly increased when the D initial concentration was increased but decreased when acid concentration was increased. For higher temperatures and similar concentrations, t_v significantly decreased. For instance, t_v = 25 s at −64 °C (experiment SF7) and 6 s at −38 °C (experiment SF9).

Kinetic Study of the Protonation of the Ethylenic Dimer of Styrene. The appearance of the 340

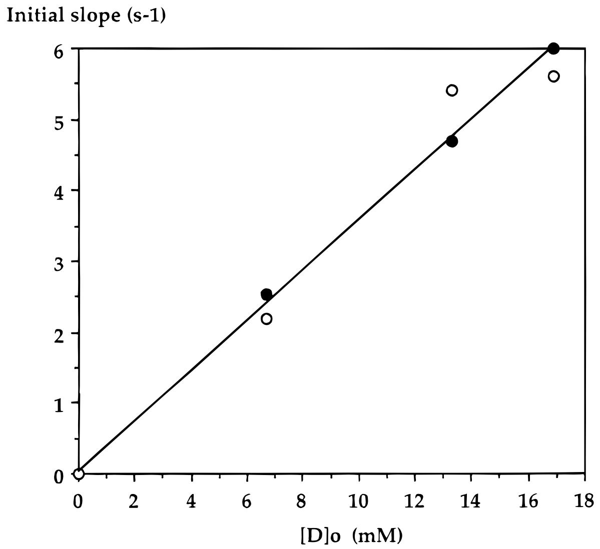


Figure 6. Initial slope of $OD_{340\ nm}$ vs $[D]_0$ for the experiments SF3, SF4, and SF6 carried out at −67 °C. Key: (○) experimental values; (●) corrected values for $[CF_3SO_3H]$ = 2.5 mM.

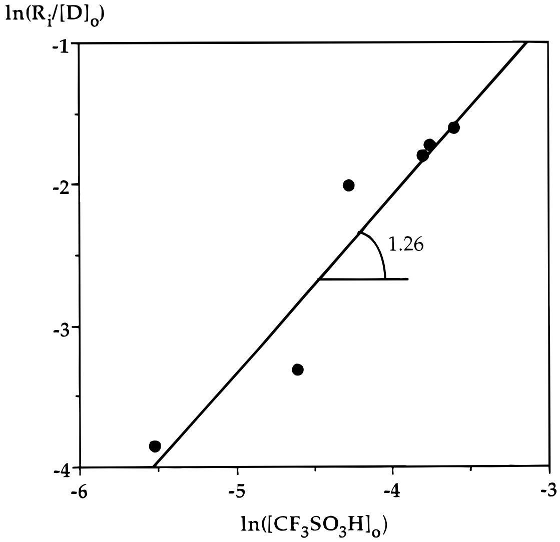


Figure 7. $\ln(R_i/[D]_0)$ vs $\ln([CF_3SO_3H]_0)$ for the experiments SF1−SF6 carried out at temperatures close to −64 °C.

nm peak corresponds mostly to the protonation of D into D^+

$$R_i = \left(\frac{d[D^+]}{dt}\right)_0 = \frac{1}{\epsilon_{340nm}l}\left(\frac{d(OD_{340nm})}{dt}\right)_0 = k_i[D]_0^{\alpha}[CF_3SO_3H]_0^{\beta}$$

with k_i = apparent protonation rate constant. The initial slopes were measured for 0.5 s total duration experiments (Δt = 5 ms between each spectrum) and results are given in Table 2 for experiments SF1−SF6. For the other experiments, the initial slope could not be accurately measured due to the disturbing influence of the simultaneously increasing 349 nm peak.

At −67 °C, from SF3, SF4, and SF6 experiments carried out with equivalent concentrations of acid, an external first order was observed with respect to D (Figure 6), which was expected from the styrene cationic polymerization results.[5,6]

From the logarithmic plot $\ln(R_i/[D]_0)$ vs $\ln([CF_3SO_3H]_0)$ (Figure 7), the value of the external order with respect to initiator was $\beta = 1.26$ (experiments SF1−6). An apparent protonation rate constant $k_i = 19.0\ M^{-1.26}\ s^{-1}$ was obtained at $T \approx -64$ °C.

Scheme 2

$$2\ CF_3SO_3H \xrightleftharpoons{K} (CF_3SO_3H)_2$$

$$D + CF_3SO_3H \xrightleftharpoons[k_{-i1}]{k_{i1}} D^+\ CF_3SO_3^-$$

$$D + (CF_3SO_3H)_2 \xrightleftharpoons[k_{-i2}]{k_{i2}} D^+\ CF_3SO_3^-,\ CF_3SO_3H$$

Such an external order between 1 and 2 can be explained by considering that protonation may result from both monomeric and dimeric forms of the acid in rapid equilibrium with each other (Scheme 2). In that case, concentration of the dimeric form should be very low (low value of K) and this form should be very reactive ($k_{i2} > k_{i1}$). The difference with cationic polymerization of styrene, for which the order with respect to acid was found to be close to 4.5 at the same temperature,[6] can be explained by the lack of activity of large aggregates of acid toward protonation of a more hindered alkene such as the dimer D.

In Scheme 2

$$K = \frac{[(CF_3SO_3H)_2]_t}{[CF_3SO_3H]_t^{\ 2}}$$

$$[CF_3SO_3H]_t + 2[(CF_3SO_3H)_2]_t = [CF_3SO_3H]_0$$

$$[CF_3SO_3H]_t + 2K[CF_3SO_3H]_t^{\ 2} = [CF_3SO_3H]_0$$

If K is small, then

$$[CF_3SO_3H]_t \approx [CF_3SO_3H]_0$$

$$[(CF_3SO_3H)_2]_t \approx K[CF_3SO_3H]_0^{\ 2}$$

In that case

$$R_i = \left(\frac{d[D^+]}{dt}\right)_0$$

$$R_i = k_{i1}[D]_0[CF_3SO_3H]_0 + k_{i2}K[D]_0[CF_3SO_3H]_0^{\ 2}$$

$$\frac{R_i}{[D]_0} = (k_{i1} + k_{i2}K[CF_3SO_3H]_0)[CF_3SO_3H]_0$$

$$= k_i[CF_3SO_3H]_0^{\ \beta}$$

where β is a value between 1 and 2 that depends on $[CF_3SO_3H]_0$, K, k_{i1} and k_{i2}.

In the case of the polymerization of styrene initiated with triflic acid,[6] the rate of appearance of the 340 nm peak could be expressed, at −64 °C, as

$$R_i = k_i[St]_0[CF_3SO_3H]_0^{\ 4.5} \quad \text{with} \quad k_i = 2.9 \times 10^{11}\ L^{4.5}\ mol^{-4.5}\ s^{-1}$$

It was determined within a range of triflic acid initial concentration of 0.77−3.17 mM.

The comparison of the values of R_i for styrene and its dimer D (R_{iSt} and R_{iD} respectively) at the same initial concentrations supports a more rapid protonation of styrene than of D for initial concentrations of acid higher than 0.72 mM as expressed by the following equations:

$$R_{iSt} = 2.9 \times 10^{11}[St]_0[CF_3SO_3H]_0^{4.5}$$

$$R_{iD} = 19[D]_0[CF_3SO_3H]_0^{1.26}$$

$$\frac{R_{iSt}/[St]_0}{R_{iD}/[D]_0} = \frac{2.9 \times 10^{11}}{19}[CF_3SO_3H]_0^{4.5-1.26} = 1.53 \times 10^{10}[CF_3SO_3H]_0^{3.24}$$

Thus

$$\frac{R_{iSt}/[St]_0}{R_{iD}/[D]_0} > 1 \quad \text{for} \quad [CF_3SO_3H]_0 > 0.72 \text{ mM}$$

Moreover, this ratio strongly increases when $[CF_3SO_3H]_0$ is increased.

As an example, the rate of protonation was found to be equal to 9×10^{-3} mol L^{-1} s^{-1} for respective initial concentrations of styrene and triflic acid of 10.7 and 3.17 mM at −62 °C.[6] This result can be compared to that of experiment SF1: $R_i = 3.5\ 10^{-4}$ mol L^{-1} s^{-1} for $[D]_0 =$ 16.9 mM and $[CF_3SO_3H]_0 = 4.05$ mM. Protonation of D is about 30 times slower than protonation of styrene despite the slightly higher alkene and acid concentrations. This can be related to the rate of hydration of *trans*-β-methylstyrene which is 3 times slower than that of styrene.[7]

For the same initial concentration of acid (higher than 0.72 mM), the respective protonation rates of styrene and of D can be compared according to the following equations. Protonation of styrene is faster than protonation of D when

$$k_{i(St)}[St][CF_3SO_3H]_0^{4.5} > k_{i(D)}[D][CF_3SO_3H]_0^{1.26}$$

i.e. when

$$\frac{[St]}{[D]} > \frac{19}{2.9 \times 10^{11}}[CF_3SO_3H]_0^{-3.24}$$

For instance, with $[CF_3SO_3H]_0 = 0.01$ mol/L, protonation of styrene is faster than protonation of D for $[St]/[D] > 2 \times 10^{-4}$. During the polymerization of styrene, the concentration of chains with an ethylenic end group is low as compared to the concentration of styrene; therefore, protonation of styrene is favored until very high conversions are reached. The unsaturated polystyrene chains are not reprotonated during the course of the polymerization, and thus, they behave as dead chains.

At temperatures higher than −64 °C, the initial slopes could not be measured with sufficient accuracy. But in fact, the effect of temperature on the rate of protonation appears rather limited as illustrated in Figure 5 by the close initial slopes observed at −53 °C and −64 °C.

Kinetic Study of the Consumption of the Cations D^+ and D_n^+ Absorbing at 340 nm. As reported in Table 2, the maximum concentration of cations (calculated by assuming $\epsilon = 10^4$ L mol^{-1} cm^{-1}) remained always very low as compared to D and acid initial concentrations, even at low temperature and for $[CF_3SO_3H]_0$ much higher than $[D]_0$. For experiments SF3−SF6 where the initial concentration of acid, $[CF_3SO_3H]_0$, was higher than the initial concentration of D, the maximum concentration of cations absorbing at 340 nm ($[\text{cations}]_{t_{max}}$) was less than 4% of $[D]_0$ (ratio expressed as $\Delta OD_{max}/(\epsilon l[D]_0)$ in Table 2).

At the maximum of $OD_{340\ nm}$ vs time plot (time t_{max}), $d[\text{cations}]/dt = 0$ which means that the rate of formation of the cations equals their rate of consumption. Since t_{max} was found to be very short with respect to the cation persistence time and to the D consumption time (Figures 1 and 2), the rate of formation at t_{max} can be expressed as the initial rate of protonation of D: $R_i = k_i[CF_3SO_3H]_0^{\beta}[D]_0$ with $\beta = 1.26$ (the initial concentration of acid was used since it does not vary significantly during the reaction as it has been mentioned that the concentrations of the cations and thus the concentrations of their corresponding counteranions always remained very low with respect to $[CF_3SO_3H]_0$). The rate of consumption of the cations can be expressed as a simple function of their concentrations: $k[\text{cations}]$, where k can be either a constant (first-order kinetics) or a value including concentrations of other reagents. Thus, at the maximum of $OD_{340\ nm}$, the following equation can be given:

$$k_i[CF_3SO_3H]_0^{\beta}[D]_0 = k[\text{cations}]_{t_{max}}$$

It can also be written as:

$$[\text{cations}]_{t_{max}} = \frac{k_i[CF_3SO_3H]_0^{\beta}[D]_0}{k} \qquad (1)$$

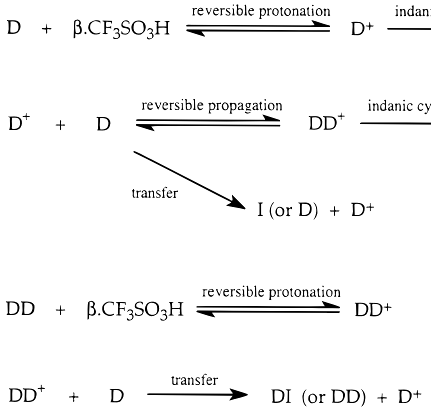
or

$$k = \frac{k_i[CF_3SO_3H]_0^{\beta}[D]_0}{[\text{cations}]_{t_{max}}} = \frac{\text{initial slope}}{OD_{max}} \qquad (2)$$

As mentioned before, the maximum concentration of cations was found to be proportional to $[D]_0$ and to $[CF_3SO_3H]_0^{1.38}$, whereas β was 1.26 for the protonation reaction. Considering that the difference between the two exponents is not significant, eq 1 implies that k is independent of $[CF_3SO_3H]_0$ and independent of $[D]_0$. The value of k could be calculated for the experiments SF1−SF6 using eq 2 which is independent from ϵ_{340}. Actually, calculated values of k do not vary significantly with initial concentrations (Table 2) and can be considered as constant, the average being 4.6 s^{-1}.

The fast first-order reactions, with apparent rate constant k, which consume the cations and prevent them from existing at high concentrations, might be irreversible cyclizations leading to indanic species (evidenced by product characterization[1]) and reversible deprotonation leading back to unsaturated molecules. It has been shown previously that reaction of D with triflic acid led to indanic oligomers, mainly to the indanic dimer of D (DI). Cyclization into 1-methyl-3-phenylindan (I) was also occurring, although in lower proportion, and was enhanced when temperature was increased. A reaction scheme applying to low-temperature conditions can be proposed (Scheme 3). It takes several possible reactions into account: D reversible protonation, reversible dimerization into DD^+, and DI formation either by spontaneous cyclization of DD^+ or by a transfer reaction to a D double bond which was postulated by Barton and Pepper.[4] Longer oligomers were not considered since they were always present in

Scheme 3. Low Temperature Reactions (= −64 °C)[a]



[a] Key: CF_3SO_3H, triflic acid; D, 1,3-diphenyl-1-butene (ethylenic dimer of styrene); I, 1-methyl-3-phenylindan (indanic dimer of styrene); DD, ethylenic dimer of D; DI, indanic dimer of D; D^+, 1,3-diphenyl-1-butylium (340 nm); DD^+, cation derived from addition of D^+ on D (340 nm).

low amounts,[1] and reversible ester formation was not included since such a triflate ester could not be observed.[9] Hydride abstraction from D, which was described in the first part of this series,[1] was considered as negligible and thus was not included in Scheme 3.

Conclusion

The reaction of trans 1,3-diphenyl-1-butene (D, the trans ethylenic dimer of styrene) with triflic acid can be considered as a model reaction of the ethylenic chain ends appearing during the cationic polymerization of styrene.

In the first part of this series,[1] we reported that D was completely consumed and mainly converted into its indanic dimer (DI); various UV−visible absorptions were observed during the course of the reaction. A transient peak at 340 nm was assigned to the distyryl cation (1,3-diphenyl-1-butylium, D^+) and higher oligomeric ones (D_n^+) which confirmed the previous attribution of this peak to the polystyryl cation.[5,6] The kinetic evolution of that peak is presented in this second part. The appearance of D^+ corresponds to the protonation of D and was compared to the protonation of styrene. A first difference concerns the order with respect to acid which was much larger in the case of styrene, 4.5 at −65 °C instead of 1.26 for D. These results indicate that protonation may result from acid aggregates in fast equilibrium with each other, the larger being the more reactive. In the case of D, which is more hindered than styrene, only the monomeric and dimeric forms of acid are active. The second difference is that protonation of styrene was found to be faster than protonation of D. Therefore, in the polymerization of styrene, protonation of the ethylenic chain ends takes place essentially at the end of the reaction, after conversion of styrene is completed. In such a case, β-proton elimination cannot be considered as a truly reversible termination. The relatively rapid dimerization of D can explain the increase of the molecular weights of polystyrene observed after the end of the polymerization.[10] As in the polymerization of styrene initiated with triflic acid, the low amount of propagating cations indicates fast deprotonation either by β-elimination or by indanic cyclization.

References and Notes

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