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Stopped-Flow Investigation of Trifluoromethanesulfonic Acid Initiated Cationic Oligomerization of *trans*-1,3-Diphenyl-1-butene. 1. Analysis of Products and UV−Visible Spectroscopic Study

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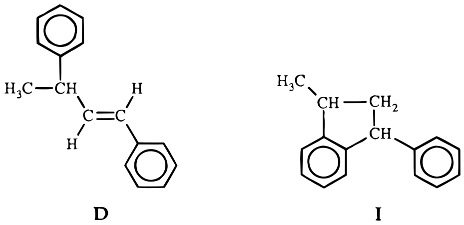
ABSTRACT: Cationic oligomerization of the trans ethylenic dimer of styrene (1,3-diphenyl-1-butene, D) initiated with trifluoromethanesulfonic acid was investigated using the high-purity stopped-flow technique coupled with UV−visible spectroscopy. This dimer was protonated into the distyryl cation (1,3-diphenyl-1-butylium, D^+) which absorbs at 340 nm, as expected from styrene polymerization results. This species appeared quickly and reached its maximum within about 1 s at low temperature (<−64 °C) and then decreased slowly during about 1 min at this temperature. The higher the temperature, the lower the intensity of this peak and the shorter the time to reach its maximum. The cation D^+ either cyclizes into 1-methyl-3-phenylindan or reacts with D to produce oligomers, and these two reactions lead to a complete consumption of the double bond evidenced by a decrease of the 296 nm optical density. It has been shown that the main final products of the reaction were always indanic styrene "tetramers" (dimers of 1,3-diphenyl-1-butene) and that the proportion of 1-methyl-3-phenylindan was higher when the temperature was increased. No styrene trimers or pentamers have been detected although they are formed at temperatures higher than +50 °C. Two other absorptions appearing immediately after mixing and increasing more slowly than the 340 nm peak were observed at 349 and 505 nm: they reached a very stable plateau at *T* lower than −30 °C, but at higher temperatures they passed through a maximum and were replaced by two other peaks at 316 and 415 nm. The 349 and 505 nm peaks were attributed to the same cationic species, plausibly an allylic cation (1,3-diphenyl-1-buten-3-ylium) produced by hydride abstraction from trans 1,3-diphenyl-1-butene. At temperatures above −30 °C, the absorptions at 316 and 415 nm were assigned to indanylium cations resulting from different cyclic species produced during the course of the reaction. The process described above can be considered as a model system for the behavior of the unsaturated chain ends in the cationic polymerization of styrene.

Introduction

With the new stopped-flow technique elaborated in our laboratory,[1,2] cationic polymerization can nowadays be investigated under a large range of temperatures and variable monomer and initiator concentrations. Moreover, the apparatus has been designed to be compatible with high-vacuum purification of the reagents and anhydrous conditions. Photodiode array detection allows the recording of successive UV−visible spectra with time intervals shorter than 5 ms. Thus, kinetic study of simultaneous evolution of the various species appearing during the course of the reaction can be performed and the corresponding rate constants can be derived.

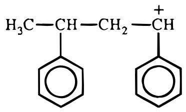
First results[1−3] concerned cationic polymerization of styrene initiated by a strong protonic acid, trifluoromethanesulfonic acid (triflic acid); they gave new information on the mechanism of the reaction and rate constant values. Nevertheless, this work needed to be completed by investigations upon the behavior of the unsaturated chains appearing as products at the very late stage of the polymerization. For example, it has been reported that the molecular weight of polystyrene prepared at −78 °C increases at nearly complete monomer conversion and doubles the theoretically predicted values.[4] The ethylenic dimer of styrene has been chosen as a model for this study because reactions of unsaturated dimer simulate behavior of the unsaturated polymer chain ends and provide information relevant to the real polymerization system. Moreover, protonation of this molecule leads to the dimeric cation which can be considered as a better model for the polystyryl one than the 1-phenylethylium cation.

Chart 1



D

I



D^+

The dimer, obtained by cationic oligomerization of styrene under conditions where transfer is faster than propagation, is the *trans*-1,3-diphenyl-1-butene[5] (D). A few studies have been previously reported on its reaction with protonic and Lewis acids, involving spectroscopic analysis of the mixture[6] and product characterization.[7−9] It has been shown that not only cyclization of D into

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1-methyl-3-phenylindan (I) was occurring but also formation of higher oligomers. Risi and Gauvin[8] studied the reaction of D with $SnCl_4$ and obtained 50% polymer and 50% I. Barton and Pepper[9] used perchloric acid (at 0 and 61 °C), sulfuric acid (at 61 and 84 °C), and chlorosulfonic acid (at 77 °C) in 1,2-dichloroethane as a solvent and obtained the same ratio of I and oligomers. Sawamoto and Higashimura[7] characterized these higher oligomers by ^{1}H NMR spectroscopy and size exclusion chromatography (SEC). They worked at high temperatures (>50 °C) under a nitrogen atmosphere with various solvents (1,2-dichloroethane, benzene, nitrobenzene) and various initiators (triflic acid, $BF_3O(C_2H_5)_2$, acetyl perchlorate). $BF_3O(C_2H_5)_2$ was found inactive for initiation (no D conversion), whereas with the other initiators, D was completely consumed and converted into I and higher oligomers ($DP_n \leq 7$ styrene units), the main fraction of which was composed of styrene tetramers. They also found some styrene oligomers with an odd number of units (3 and 5) and concluded that, simultaneously to oligomerization, depolymerization of D was also occurring, leading to the styryl cation and styrene monomer which could then be incorporated into oligomeric chains. Most of the analyzed species had an indanic structure.

For these reactions to take place, it is necessary to consider the protonation of D into 1,3-diphenyl-1-butylium (D^+). Bertoli and Plesch[6] tried to identify this cation by UV−visible spectroscopy under various experimental conditions. In 98% sulfuric acid between −20 and 0 °C, two peaks have been evidenced at 315 and 430 nm. The 315 nm peak was more intense when the amount of residual D was higher. The spectrum was identical to those obtained with either styrene or 1-phenylethanol under the same conditions. After a few days, a change occurred and two new peaks at 310 and 415 nm were observed. From these results they proposed that D^+ and higher polystyryl cations absorbed at 315 nm and that these cations were much more stable than the styryl cation (1-phenylethylium) because of the presence of an aromatic ring in the β position and "through space" interactions. The absorptions at longer wavelengths (>400 nm) were assigned to diaryl cations resulting from cyclic products, the 310 and 415 nm peaks belonging to 3-methyl-1-phenylindanylium. However, further results obtained by the stopped-flow technique led to the conclusion that polystyryl cations absorb at 340 nm as polystyryl anions do and that these cations had a very short lifetime.[1−3,10] Thus, long living species at 315 and 430 nm cannot be assigned to linear growing cations.

From the available literature, it appears that spectroscopic data about the reaction of the trans ethylenic dimer of styrene with protonic acids are insufficient and that this reaction needs to be more completely investigated, since it provides information on the fate of growing carbocations in polymerization. As for the styrene cationic polymerization study, the system 1,3-diphenyl-1-butene/triflic acid/dichloromethane was chosen and UV−visible spectroscopic studies were performed using the stopped-flow technique under subambient temperatures and various initial concentrations. Furthermore, characterization of the products was performed at temperatures lower than 0 °C to supplement earlier data[7] and to correlate with the spectroscopic observations obtained under the same conditions.

Table 1. Synthesis and Characterization of Oligomers: Experimental Conditions for the Reaction of 1,3-Diphenyl-1-butene (D) with Triflic Acid

exp no.	$[D]_0$ (mM)	$[CF_3SO_3H]_0$ (mM)	temp (°C)
1	17.1	10.0	−68
2	16.5	4.2	−73
3	17.2	24.2	−72
4	6.6	34.1	−73
5	6.3	27.1	+20

Table 2. Stopped-Flow Investigations: Experimental Conditions for the Reaction of 1,3-Diphenyl-1-butene (D) with Triflic Acid

exp no.	$[D]_0$ (mM)	$[CF_3SO_3H]_0$ (mM)	temp (°C)
SF1	16.9	4.05	−67
SF2	16.9	10.1	−67
SF3	16.9	23.6	−67
SF4	6.7	22.5	−67
SF5	6.7	33.7	−67
SF6	13.5	14.0	−64
SF7	13.5	27.7	−64
SF8	12.8	26.4	−30
SF9	12.0	24.8	+20
SF10	13.4	13.1	−64
SF11	18.2	13.1	−64
SF12	22.9	13.1	−64
SF13	27.9	13.1	−64
SF14	27.4	12.8	−48
SF15	26.7	12.5	−30
SF16	16.3	13.1	−64
SF17	16.1	12.9	−53
SF18	15.8	12.6	−38
SF19	15.6	12.5	−30
SF20	15.2	12.2	−10
SF21	14.9	11.9	0
SF22	14.6	11.7	+18

Experimental Section

Analytical Procedures. UV−visible spectroscopy was performed using a Varian CARY 219 spectrophotometer; spectra were recorded in dichloromethane solution with pure dichloromethane as a reference, using 0.50 cm optical path cells with a scanning rate of 1 nm·s^{-1}. Size exclusion chromatography (SEC) was performed using a Waters apparatus working with dichloromethane eluent at a flow rate of 1 mL·min^{-1} and equipped with four PLgel 10μ columns (100, 500, 10^3, and 10^4 Å); refractive index (RI) and UV absorption (254 nm) detectors were used and molecular weights were derived from the standard polystyrene calibration curve. NMR spectra were recorded with a FT AC200 Bruker apparatus (200 MHz for ^{1}H and 50.3 MHz for ^{13}C) in 5 mm diameter tubes, at 25 °C, with $CDCl_3$ as a deuterated solvent and tetramethylsilane as an internal standard.

Materials. Dichloromethane (CH_2Cl_2 from SDS, stabilized with amylene) was used as a solvent and purified under high-vacuum conditions according to the method usually used in the laboratory.[11] Triflic acid (CF_3SO_3H, >98% purity from Fluka, MW = 150.08, d = 1.708 g.cm^{-3}) was distilled three times under high vacuum, and only the core fractions were retained and kept in sealed phials; the anhydrous dichloromethane solutions were prepared under vacuum before use and kept in 60 mL reservoirs equipped with high-vacuum taps with Teflon plugs (from Young). *trans*-1,3-diphenyl-1-butene (D) was prepared by reaction of styrene with triflic acid in benzene at a temperature of 80 °C. After 5 min, reaction was quenched with aqueous triethylamine and washed with distilled water. The organic layer was evaporated, and D was purified by vacuum distillation (95 °C, 0.01 Torr). UV−visible spectrum was characteristic of the trans dimer of styrene: 254 nm (ϵ = 19 580 L·mol^{-1}·cm^{-1}), 284 nm (ϵ = 2100 L·mol^{-1}·cm^{-1}), and 293 nm (ϵ = 1160 L·mol^{-1}·cm^{-1}). ^{1}H NMR spectroscopy allowed characterization of an impurity, 1,1-diphenylethane (0.5 mol %), resulting from the side reaction of the styryl cation with benzene (1.63 ppm, d, 7.2 Hz, 3H; 4.13 ppm, q, 7.2 Hz, 1H; 7.0−7.5 ppm, m, 10H). ^{1}H and ^{13}C chemical shifts of D

Table 3. Reaction of 1,3-Diphenyl-1-butene (D) with Triflic Acid: UV−Vis and SEC Analysis of the Crude Products

	UV−Vis spectroscopy		SEC analysis: proportion of RI areas (wt %) at						
exp no.	characteristic peaks (nm)	chemical nature	64.8 mL (DDDI)	66.6 mL (DDI)	67.6 mL (?)	69.0 mL (DI)	70.8 mL (?)	72.2 mL (D)	73.2 mL (I)
1	260, 266 and 273 (284 and 293: weak)	indanic compounds with a low fraction of ethylene	1	10	1	78	2	2	6
2	254, 284, 293	ethylenic compounds	0	7	0	63	1	25	3
3	254, 284, 293	ethylenic compounds	0	6	0	48	2	39	5
4	260, 266, 273	indanic compounds	0	7	0	89	1	0	3
5	260, 266, 273	indanic compounds	0	3	2.5	60	8.5	0	25

Table 4. Reaction of 1,3-Diphenyl-1-butene (D) with Triflic Acid: Weight Percent of the Products (Based on SEC with RI Detection)[a]

		distribution of the products (wt %)[b]			
exp no.	residual D (wt %)	I	DI	DDI	unidentified products
1	2	6	80	11	3
2	25	4	84	10	2
3	39	7	79	10	4
4	0	3	89	7	1
5	0	26	60	3	11

[a] D: 1,3-diphenyl-1-butene. I: 1-methyl-3-phenylindan. DI: indanic dimer of D. DDI: indanic trimer of D. [b] Residual D not included.

are as follows. ^{1}H NMR (ppm): 1.45 (d, 7.3 Hz, 3H), 3.63 (m, 1H), 6.39 (m, 2H), 7.3 (m, 10 H). ^{13}C NMR (ppm): 21.22 (methyl); 42.57 (methine); 126.15, 127.04, 127.31, 128.49 (aromatic and 2-ethylenic CH); 135.21 (1-ethylenic CH); 137.57, 145.60 (aromatic C).

The SEC elution volume of D was 72.2 mL, and it was 73.2 mL for the impurity, 1,1-diphenylethane. D was dissolved in dichloromethane under high-vacuum conditions and the adventitious traces of water were eliminated by several transfers of the solvent onto a sodium mirror. Solutions were stored in the same type of reservoir as the acid solutions. Concentrations of acid and dimer solutions were calculated at room temperature and were corrected for the adequate reaction temperature using 0.001 37 K^{-1} for the CH_2Cl_2 volumic contraction coefficient.

Oligomerization Procedure. Experiments were performed at −73 and +20 °C under vacuum in a previously outgassed and sealed reactor. D solution and solvent were introduced from their reservoirs into the reactor containing a 2 mL breakable ampule filled with the triflic acid solution. After reaching the chosen temperature, the ampule was broken in the medium. At low temperatures, an orange color immediatly appeared and remained during the whole reaction time; at room temperature the color turned to yellow. After 5 min, the medium was quenched with a methanol solution of sodium methanolate and discolored instantaneously; it was then washed with distilled water, the solvent was evaporated, and the raw product was analyzed without any separation of the components. Experimental conditions are summarized in Table 1.

Stopped-Flow Procedure. A complete description of the stopped-flow apparatus has been reported previously.[1,2] In this study the reactor was equipped with a 2 mm optical path quartz cell. Two kinds of data acquisition have been used. First, for the experiments SF1 to SF5, 100 spectra of 78 points each were recorded between 271 and 448 nm for each reaction ($\Delta\lambda$ = 2.30 nm) and the time interval between spectra was varied between 4 ms (total duration of 0.4 s) and 2 s (total duration of 200 s). Second, for the experiments SF6 to SF22, 100 spectra of 122 points each were recorded between 261 and 540 nm for each reaction ($\Delta\lambda$ = 2.30 nm) and the time interval between spectra was varied between 5 ms (total duration of 0.5 s) and 12 s (total duration of 1200 s). From crude results expressed in arbitrary units of intensity, optical density (OD) was calculated using a standard spectrum which was either a triflic acid solution (experiments SF1 to SF5) or pure solvent (experiments SF6 to SF22). The first spectrum corresponded to time zero of the reaction, but the first 5 ms of reaction could not be used due to incomplete mixing. The various experimental conditions for reaction of D with triflic acid are summarized in Table 2. The D concentration was followed at a maximum absorption (293−296 nm, depending on the resolution), and cationic species were observed at higher wavelengths (from 300 to 540 nm).

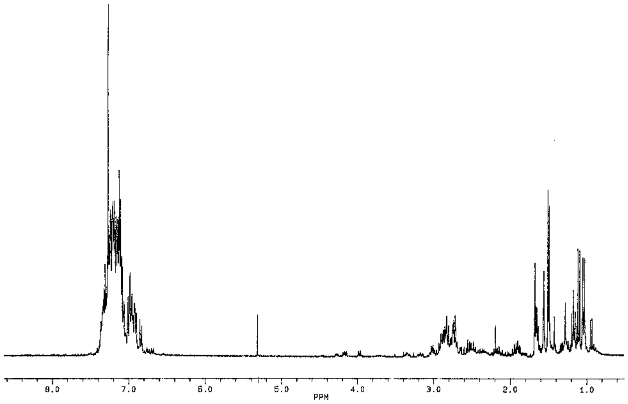
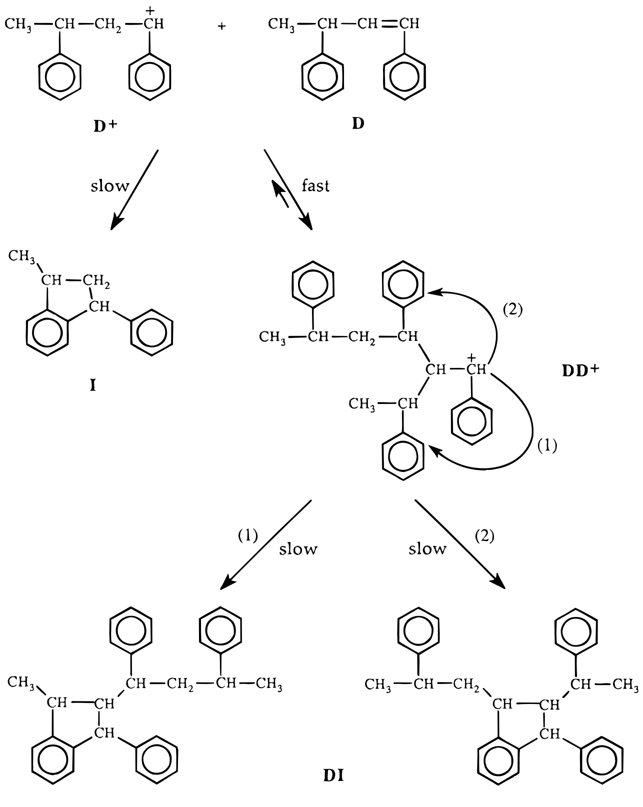


Figure 1. 200 MHz ^{1}H NMR spectrum of the crude product for experiment no. 4, mainly composed of DI, $[D]_0$ = 6.6 mM; $[CF_3SO_3H]_0$ = 34.1 mM; T = −73 °C.

Scheme 1



Results and Discussion

Products Characterization. From SEC results (Tables 3 and 4), it appears that the reaction of D with triflic acid leads to low molecular weight oligomers

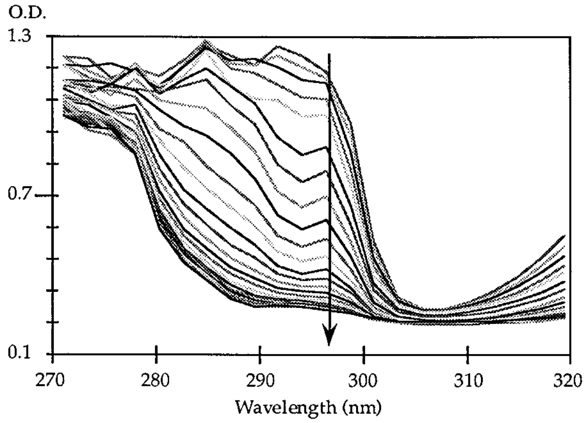


Figure 2. Consumption of dimer D during experiment SF3 (from 1.2 to 40 s, step 1.2 s), $[D]_0 = 16.9$ mM; $[CF_3SO_3H]_0 = 23.6$ mM; $T = -67$ °C.

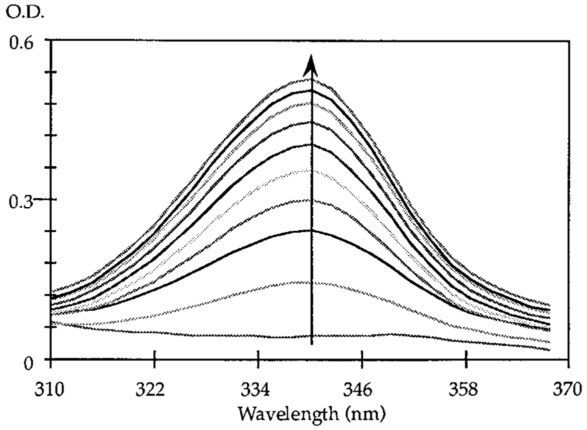


Figure 3. Appearance of the 340 nm peak during experiment SF4 (from 0 to 0.4 s, step 0.04 s), $[D]_0 = 6.7$ mM, $[CF_3SO_3H]_0 = 22.5$ mM, $T = -67$ °C.

independently of temperature. Because assignments of the SEC peaks based on the calibration curve were unsatisfactory, model oligomers from an experiment carried out under nitrogen at −73 °C were isolated by silica gel column chromatography (ethyl acetate/cyclohexane 2/98 as an eluent) and analyzed by mass spectrometry. The following results were obtained: for $V_e = 69.0$ mL, the molecular weight was 416 (2 D units) and for 66.6 mL, it was 624 (3 D units). D has been identified at 72.2 mL (see Experimental Section) and I at 73.2 mL.[12] The trimer of D was then the highest oligomer produced (amount of higher oligomers like tetramers was negligible) and the main product of the reaction was always the dimer of D (called "styrene tetramer" by Sawamoto,[7] although it has not a true polystyrene structure). The cyclic isomer of D (I) was also recovered and its amount was higher when temperature was increased. Other weak SEC peaks could be assigned to styrene oligomers with an odd number of units resulting from D depolymerization; however, this is negligible at low temperatures since they were always present at very low amounts. UV−visible analysis of crude products shows that, when D has not been completely converted after 5 min, the presence of the remaining ethylenic double bond was evidenced at 284 and 293 nm. In the other case, when no D was remaining, peaks at 260, 266, and 273 nm were observed which are typical of a disubstituted aromatic ring with indanic structure. ^{1}H NMR spectra (Figure 1) were quite difficult to interpret, because each oligomer was composed of many isomers; nevertheless, ethylenic double bonds were absent except unreacted D. Doublets around 4 ppm correspond to diaryl CH existing in indanic structure.

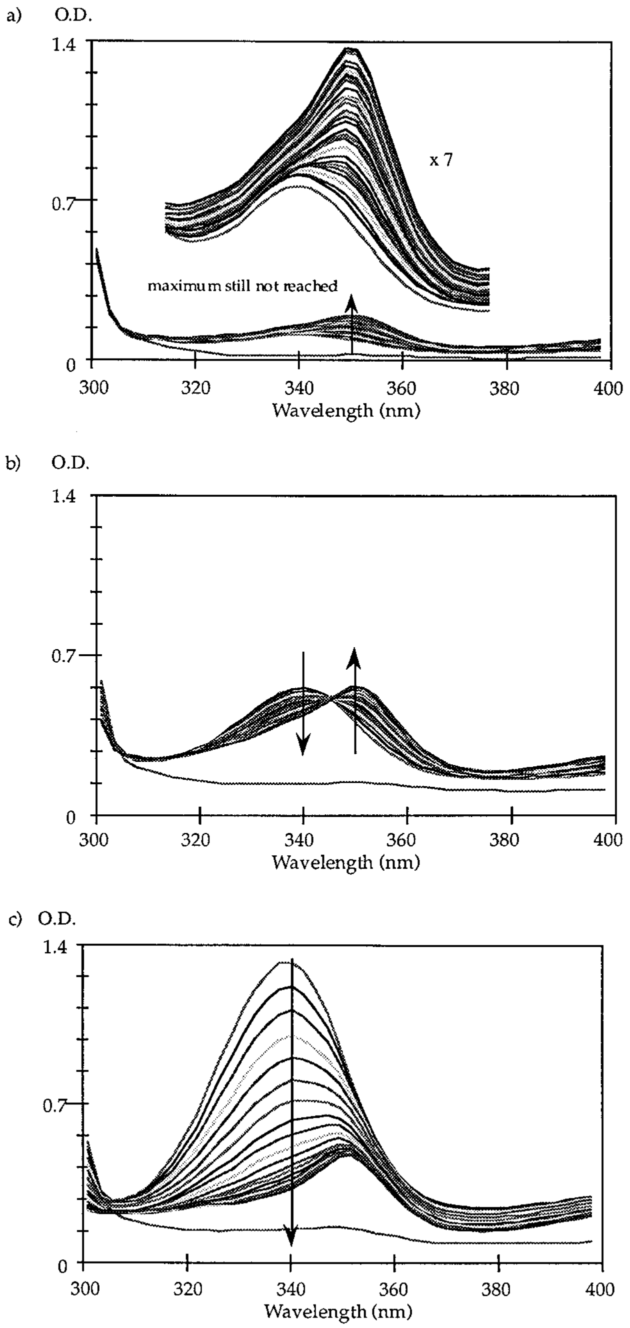


Figure 4. Decrease of the 340 nm peak and simultaneous increase of the 349 nm peak for various acid concentrations at −67 °C (from 0 to 40 s, step 1.2 s), $[D]_0 = 16.9$ mM: (a) $[CF_3SO_3H]_0 = 4.05$ mM (SF1); (b) $[CF_3SO_3H]_0 = 10.1$ mM (SF2); (c) $[CF_3SO_3H]_0 = 23.6$ mM (SF3).

Therefore, reaction of D with triflic acid resulted mainly in dimerization into a mixture of cyclized components named DI (Scheme 1). Cyclization into I was of minor importance but was significantly increased when temperature was increased. On the contrary, initial concentrations of reagents seemed to have little influence on product distribution. Incomplete consumption of D found for some experiments could not be clearly explained, and conversion seemed to be independent from initial concentrations. A probable equilibrated oligomerization is not a sufficient explanation since the occurrence of an irreversible cyclization would continuously shift this equilibrium toward D consumption.

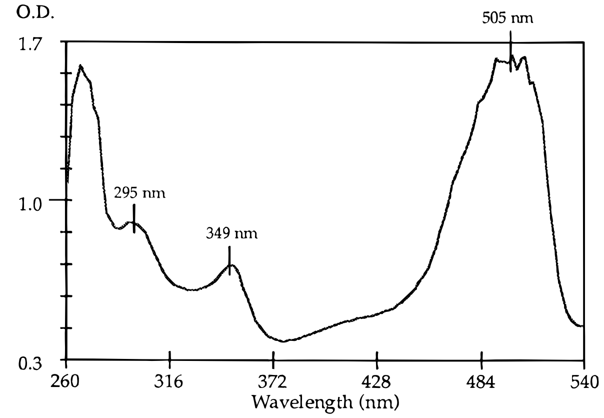
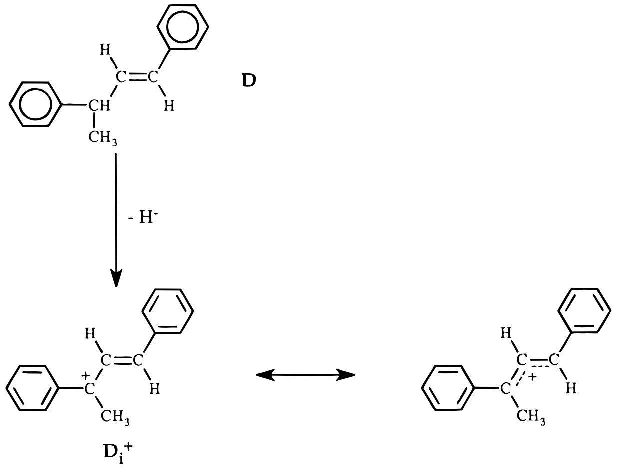


Figure 5. Complete spectrum after 600 s for experiment SF10, $[D]_0 = 13.4$ mM, $[CF_3SO_3H]_0 = 13.1$ mM, $T = -67$ °C.

Scheme 2



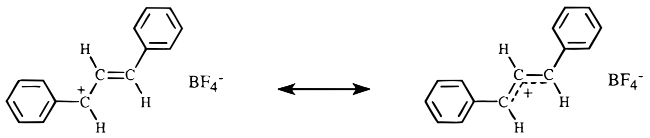
The prerequisite reaction for dimerization and cyclization is the protonation of D leading to the cation D^+. Because dimerization of D occurs preferentially to cyclization into I, even when the ratio $[CF_3SO_3H]_0/[D]_0$ is high (experiments 4 and 5), the protonation is either slow as compared to oligomerization or reversible. Since the major product is always the cyclic dimer of D (DI), the main reaction of D^+ is then addition with D resulting in the DD^+ cation which cyclizes into DI by two different possible pathways as there are two aromatic rings in the β position. Reaction of D^+ with D is then faster than D^+ cyclization, and DD^+ cyclization is faster than propagation, which is accounted for by steric factors.

Stopped-Flow Spectroscopic Study. As shown in the previous section, D is protonated by triflic acid into D^+ which is expected to absorb at 340 nm, the same wavelength as polystyryl cations observed in the styrene cationic polymerization.[1−3,10] The stopped-flow technique in connection with UV−visible spectroscopy was used to investigate this reaction.

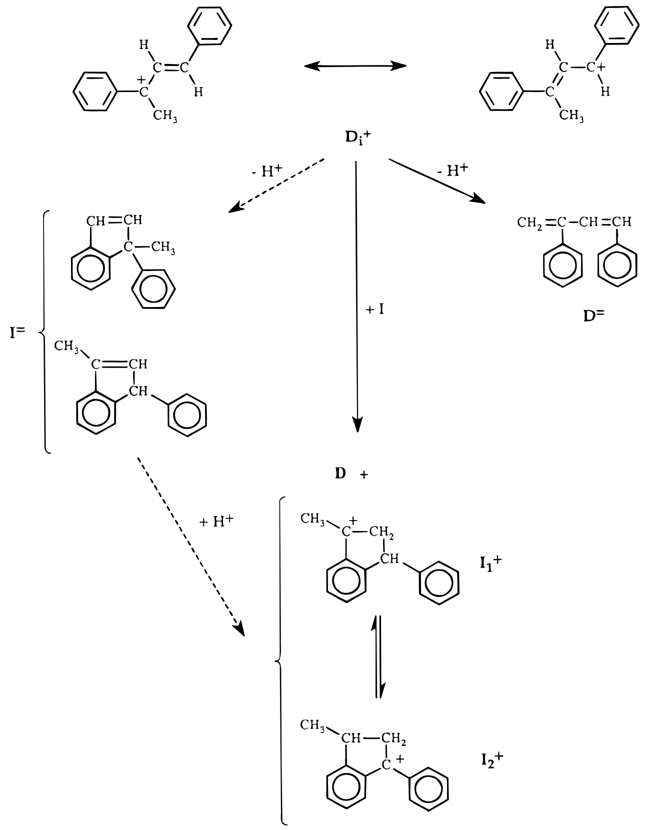
D was always completely consumed, as evidenced by the disappearance of the 296 nm peak (Figure 2). Its lifetime was dependent upon the temperature and initial concentrations: the higher the temperature and the acid concentration, the shorter the lifetime. After total D consumption, a broad absorption was still present at 295−300 nm (especially visible in Figures 5 and 6); it was assigned to unsaturated molecules.

At temperatures varying between −67 and −30 °C, a transient absorption at 340 nm was observed. It appeared quickly in about 1 s (Figure 3) and disappeared more slowly (within 50 s at lower temperatures). The intensity of the peak at 340 nm depended upon the initial conditions: the lower the temperature and the higher the acid and dimer concentrations, the higher the OD at the maximum. The time to reach the maximum (t_{max}) was fairly independent of the reagents concentrations but very temperature dependent. The value of t_{max} decreased when temperature was increased: it was close to 1 s at −67 °C and shorter than 0.1 s at −38 °C. The 340 nm absorption had a persistence time similar to that of the D double bond. This peak has been assigned to the cation D^+ which has low stability at higher temperatures.

Scheme 3



Scheme 4



In addition to absorption at 340 nm, another peak with a maximum at 349 nm appeared immediatly after mixing the reagents and increased slowly during the period of the 340 nm decrease. It reached a very stable plateau at temperatures lower than −30 °C (Figure 4). Its intensity depended on the initial concentration of D and on temperature. The corresponding species was less stable at higher temperatures.

Simultaneously, a peak at 505 nm (Figure 5) with a weak shoulder at about 420−430 nm developed with the same behavior as the 349 nm one. The 505 nm optical density was much higher than that at 349 nm and in some experiments, the former peak was too strong to be measured (Figure 5). It was determined that the ratio $\epsilon_{505nm}/\epsilon_{349nm}$ was about 5.

Knowing from product analysis that oligomerization of D occurred, i.e. that the DD^+ cation was produced,

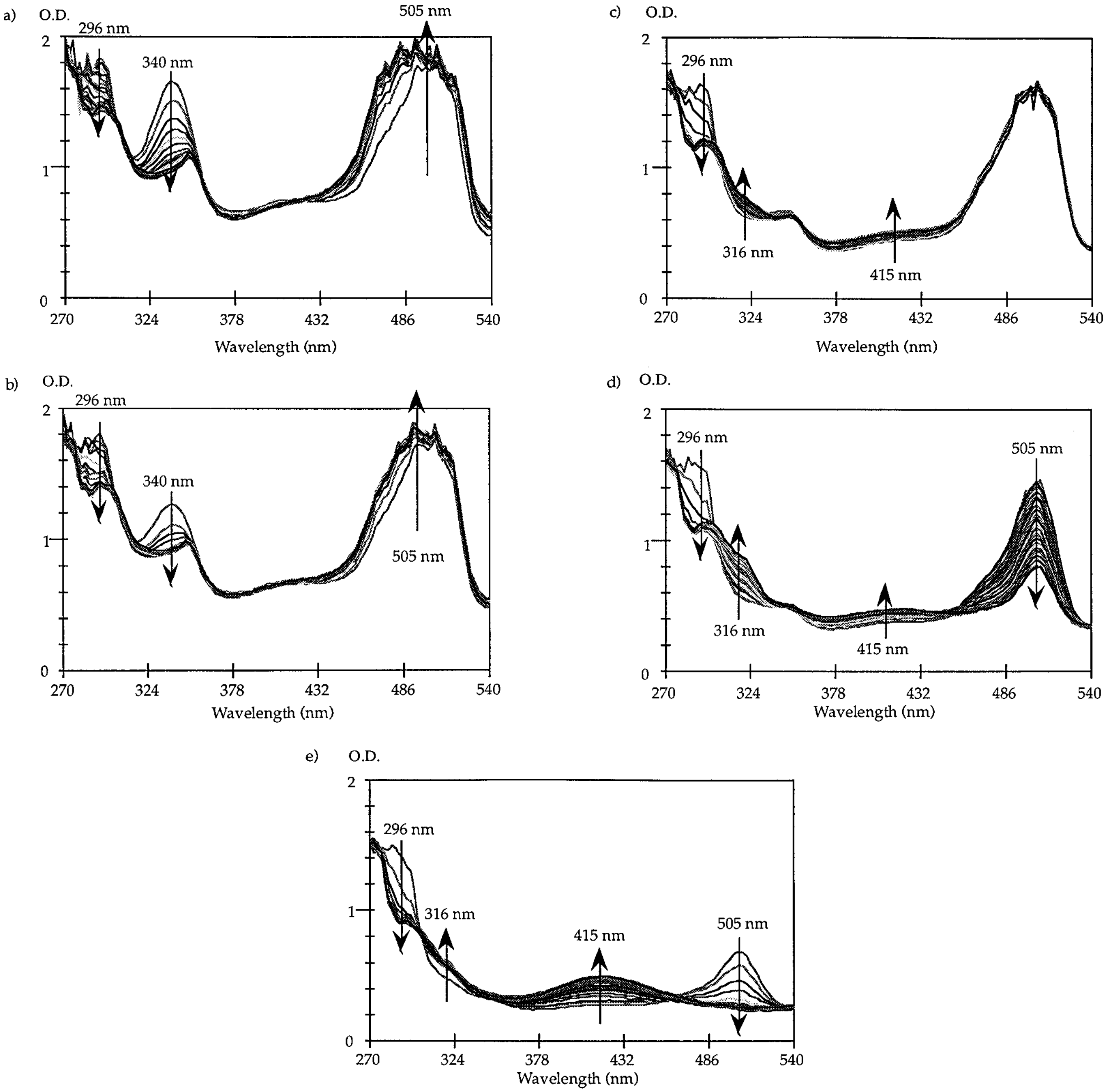


Figure 6. Evolution of spectra during 50 s for various temperatures (from 1.5 to 50 s, step 1.5 s), $[D]_0$ = 14.6 mM, $[CF_3SO_3H]_0$ = 11.7 mM (measured at room temperature): (a) SF16 (−64 °C); (b) SF17 (−53 °C); (c) SF19 (−30 °C); (d) SF20 (−10 °C); (e) SF22 (+18 °C).

then, there was a possibility that this cation could absorb at 349 nm. The bathochromic shift with respect to D^+ absorption could be assigned to structural differences since it has two aromatic rings in the β position instead of one for D^+. Although such a cation could be slightly more stable than D^+, it is difficult to explain such a large observed difference in stability: at −67 °C, the 340 nm absorption disappeared within a few seconds whereas the 349 nm one has the same intensity after more than 20 min. Moreover there is no reasonable explanation for strong absorption at 505 nm. Thus, it is more reasonable to consider that DD^+ and D^+ cations absorb at the same wavelength (340 nm) and have similar stabilities. The stability of the 349 nm peak also precludes the possibility that it could be assigned to an isomerized cation resulting from intramolecular hydride transfers of the DD^+ cation. Such isomerization would lead to cations with structures close to the poly-α-methylstyryl one which is known to absorb at 348 nm[10] but which has low stability even at low temperatures[13] and no low-energy dominating peak.

Since the two peaks at 349 and 505 nm have similar behaviors for all the temperatures studied, they could correspond to the same cationic species. This cation should have a strongly conjugated structure to agree with such high wavelengths and high stability. Thus, it might correspond to an allylic cation (1,3-diphenyl-1-buten-3-ylium, D_i^+, see Scheme 2) produced by hydride transfer from the D molecule to the D^+ cation or even to triflic acid with H_2 formation. A hydride transfer reaction would also occur for higher molecular weight unsaturated oligomers and also for the cyclic oligomers that appear in the medium, although these different products are in low concentrations at the beginning of the reaction. For instance, the previously mentioned low-intensity absorption at 420−430 nm could be assigned to diarylic cations produced by hydride abstraction from I, DI, and related compounds.

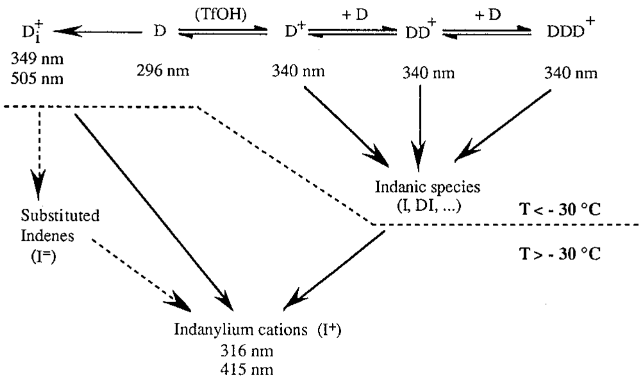
An allylic cation such as D_i^+ had been previously postulated by Gandini and Plesch[14] for styrene cationic polymerization initiated with perchloric acid at room temperature since they isolated some polyenes late after the end of the reaction. In their system, a very stable peak at 450 nm appeared within 1 h after complete consumption of styrene and was assigned to corresponding allylic cations. In light of our results it seems more reasonable to consider that this peak belonged to the final cyclic species and that allylic cations are not stable at room temperature. Moreover, they observed a transitory peak at 510 nm which disappeared in less than 50 s but for which no assignement was proposed.

The allylic cation D_i^+ is similar to that reported by Hafner and Pelster,[15] which absorbs at 485 nm (Scheme 3) and is stable at temperatures lower than −40 °C but for which no other absorption close to 350 nm has been mentioned. The existence of an eventual other absorption for the D_i^+ cation could be explained by some difference in asymmetric structure and also by a difference in media and counterions.

Such a conjugated species might be stable at low temperatures, and when temperature is increased various reactions might occur (Scheme 4): irreversible cyclization leading to substituted indene molecules ($I^=$) able to be further protonated (however, this cyclization reaction should be hindered for trans D_i^+ for steric reasons), reversible deprotonation into 1,3-diphenylbutadiene ($D^=$), and also hydride transfer from an indan species which would lead to the indanyl cation and regenerate D and eventually the ethylenic isomer of D, 2,4-diphenyl-2-butene (D′). Indeed, at temperatures higher than −30 °C, the decrease of the 349 and 505 nm peaks was observed and two other absorptions at 316 and 415 nm evolved (Figure 6). These latter peaks could correspond to those previously mentioned by Bertoli and Plesch[6] and were assigned to monoaryl (I_1^+) and diaryl (I_2^+) indanylium cations. Moreover, $D^=$ and D′ can be incorporated into oligomers and this would contribute to the complexity of the analyzed DI fraction containing various dimers of D.

Conclusion

The reaction of *trans*-1,3-diphenyl-1-butene (D), the ethylenic dimer of styrene, with triflic acid has been studied in dichloromethane at subambient temperatures with the stopped-flow technique using UV−visible spectroscopy. Products of the reaction have been characterized. The following scheme summarizes the various reactions which occur in the system, leading to various cationic species for which corresponding wavelengths have been reported.



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References and Notes

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