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THE INDANYL CATION: A REAL TIME OBSERVATION

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Abstract

A stopped-flow investigation by U. V. spectroscopy has been carried out using various reactions which yield the indanyl cation: polymerization of indene by trifluoromethane sulfonic acid (TfOH), ionization of 1-chloroindane by antimony pentafluoride and protonation of a dimer of indene (2-α-indanyl indene) by TfOH, at variable temperature. The monomer and dimer cations present a main absorption at 318-325 nm and the polyindene cation at 330 nm. A side reaction yields a derived cation, which absorbs at 519 nm. The molar absorbance of the indanyl cation has been estimated (ε = 15 500 L.mol.$^{-1}$ cm^{-1}).

INTRODUCTION

Indene is a promising monomer for controlled polymerization because it has a low transfer constant to monomer and does not undergo indanic termination. The controlled polymerization of indene has been achieved using $TiCl_4$ as activator and cumyl chloride (1,2) or methyl cumyl ether (2,3) as initiators, in the last case without additive. This suggests that the indanyl cation is relatively stable and does not undergo isomerization or destruction.

Hence it was interesting to characterize the indanyl cation involved in this polymerization and to check its stability. The characterization of the active species in cationic polymerizations of alkyl and arylalkyl monomers is fraught with difficulties, due to the reactivity of the cations, which quickly isomerize or are destroyed. In the case of indene, polymerization is often very fast, in some cases completed in a few seconds, and what can be observed might not necessarily be the propagating cation, but derived species.

The two main methods of investigation are U.V.visible spectroscopy and nuclear magnetic resonance. However, the timescale of the polymerization is generally much shorter than the time of measurement, and these methods can only be used in favourable cases in which the carbocation is sufficiently stable (4). One possibility is to use a very large excess of initiating Lewis acid with respect to the monomer in order to favour initiation with respect to

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propagation or to operate in solution in concentrated sulfuric acid or "super acids". Another possibility is to use non-polymerizable, or poorly reactive, compounds having a structure similar to that of the monomer, such as substituted indenes in the case of indene.

Olah and coll. have used "super acids" to protonate a wide range of compounds(5). For the indene series, most references in the literature refer to substituted indanyl cations. Deno et al. have investigated the protonation of 3-methylindene at room temperature by ^{1}H NMR (6) and by UV spectroscopy (7)and have reported an unexpected λ_{max} at 401nm (ε = 1148 L.mol.$^{-1}$ cm^{-1}). They also reported in the same work the chemical shifts of the 1,3,3-trimethylindanyl cation resulting from the cyclization of 1-methyl-4-phenyl-1,3-pentadiene in 96% SO_4H_2 .

A wide range of substituted indanyl cations has been investigated in our laboratory by UV spectroscopy and NMR, under high purity conditions(8,9). The main results concerning the former technique are summarized in table 1. It appears that most 1-monosubstituted indanyl cations have absorbances in the range of 312-322 nm, with exceptions for the 1,4,5,6,7-pentamethylindanyl cation (λ_{max} = 348 nm), and for the 1-phenylindanyl cation which absorbs at a still higher wavelength (λ_{max} = 412-418 nm). All these cations have molar extinction coefficients of about 30000 L.mol.$^{-1}$ cm^{-1}. The cations derived from 3-phenylindene (1-phenylindanyl cation) (10,11) and from 3-isopropyl indene (1-isopropyl cation)(12) have also been investigated using ^{13}C and ^{1}H NMR respectively.

The unsubstituted indanyl cation appears to be more elusive than its substituted counterparts, and the references are rather scarce. Most attempts at measuring the absorption maximum of this cation did not yield clear-cut results. The first mention of the spectroscopy of an indanyl cation was made by Olah and coll. (13), which reported that protonation of indene by sulfuric acid at room temperature yields a species having two main absorptions at 301 nm (ε = 14100 L.mol.$^{-1}$ cm^{-1}) and 401 nm (ε = 2200 L.mol.$^{-1}$cm^{-1}). Ledwith and col. (14) using as an initiator tropylium hexachloroantimonate for the polymerization of indene observed a transient maximum at 435-440 nm which was ascribed to a "substituted indane like carbonium ion", while a second maximum at 525 nm was supposed to be a side product involving a tropylium cation attached to the polyindene chain. In an U. V. investigation of the polymerization of indene, Prosser et al. (15) have observed a maximum at 318 nm in sulfuric acid and a "transient species" at 340 nm. Furthermore, they concluded that another maximum at 515 nm corresponds to a cation resulting from hydride abstraction from the penultimate indene unit of an unsaturated end group.

Solutions of styrene or indene in hydrocarbons in the presence of zeolites yield carbocations. For instance, styrene dimerizes and yields a 3-methyl-1-phenylindanyl cation (16) . When an activated zeolite is added to a hexane solution of indene, a strong UV absorption appears at 450-550 nm, which remains stable at room temperature(17). The authors have proposed a reaction scheme involving mainly the formation of dimers of indene.

Up to now, there is still no certainty concerning the absorption wavelength of the unsubstituted indanyl cation, the values reported varying from 301 to 340 nm.

The stopped-flow technique allows fast observation of the formation of the cations from the very beginning of the reaction, and to monitor their possible subsequent isomerizations. It is the most efficient mean of investigation in the case of fast polymerizations, such as that of indene. The first report concerning the use of a stopped-flow technique in cationic polymerization is from Pepper and coll (18) for the polymerization of styrene. This technique has been implemented to investigate the cations of styrene(19,20), pmethoxystyrene(21) and 1,1-diphenylethylene (22) . In the case of indene, Kunitake et al(23) mention a maximum at 404 nm (at 30°C) for the indanyl cation in a stopped-flow experiment. A stopped-flow apparatus allowing to operate at low temperature and under vacuum, under high purity conditions, has been built in our laboratory(24) . It has been used to investigate the polymerization of styrene(25) , as well as the reactions of the dimers of styrene(26,27) . In the present paper, this technique has been put to use to investigate the active species formed in various reactions involving the indanyl cation: the polymerization of indene by trifluoromethanesulfonic acid (TfOH), the ionization of 1-chloroindane by antimony pentafluoride and the protonation of the dimer of indene (2-α-indanyl indene) by TfOH. Triflic acid is transparent above 250 nm and can be used in relatively large concentrations, which favours protonation.

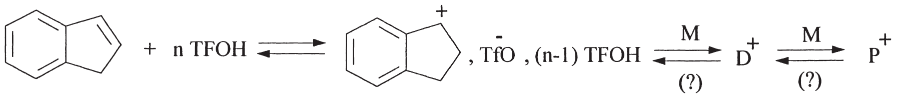
Monomer	Conditions	T (°C)	λ_{max} (nm)	ε ($M^{-1}.cm^{-1}$)
3-methyl indene	in H_2SO_4	20°C	312	27 000
3-methyl indene	$TiCl_4$ sol. in CH_2Cl_2	-70°C	318	30 000
3-isopropyl indene	in H_2SO_4	20°C	322	29 000
3-isopropyl indene	CF_3SO_3H sol. in CH_2Cl_2	-70°C	318	29 000
3-isopropyl indene	$TiCl_4$ sol. in CH_2Cl_2	-70°C	322	30 800
3-phenyl indene	H_2SO_4 sol. in CCl_4	20°C	412	32 000
3-phenyl indene	CF_3SO_3H sol. in CH_2Cl_2	-70°C	414	32 000
3-phenyl indene	$TiCl_4$ sol. in CH_2Cl_2	-70°C	418	32 000
3,4,5,6,7-pentamethyl indene	$TiCl_4$ sol. in CH_2Cl_2	-70°C	348	32 000

Table 1 : Absorbance and molar absorbance of substituted indanyl cations (ref. 8-11)

RESULTS

1) Protonation of indene by triflic acid

The polymerization of indene initiated either by Lewis acids or triflic acid is fast and completed within seconds or a few minutes. Consequently, protonation, dimerization and polymerization may take place simultaneously and the following set of reactions must be considered (scheme 1):



Scheme 1

Influence of temperature.

At 0°C, protonation of indene by TfOH ([TfOH] = 2 10^{-3} mol.L^{-1}; [Indene] = 2 10^{-3} mol.L^{-1} , R = [TfOH] / [Indene] = 1) yields in 5 milliseconds an absorbance at 330 nm which rapidly shifts to 325 nm (Figure 1) and reaches a maximum in 1 s (Figure 2). Two secondary absorbances appear at 405 nm and 519 nm. The maxima at 325 and 405 nm remain constant over 150 s, and that at 519 nm slightly increases with time. At -65°C, a single maximum at 330 nm is observed, with a low absorbance (Figure 3), which remains unchanged over 600 s.

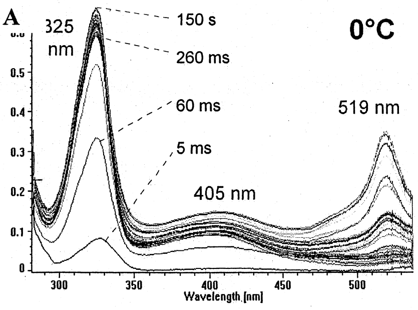


Figure 1 : Protonation of indene by triflic acid at 0°C. UV spectra of the solution. [Indene] = 2 10^{-3} mol.L^{-1} ; [TfOH] = 2 10^{-3} mol.L^{-1} ; (R=1); solvent: CH_2Cl_2

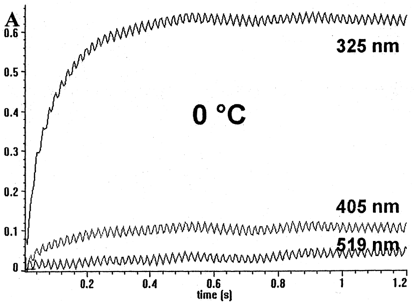


Figure 2 : Protonation of indene by triflic acid at 0°C. Evolution of the maxima with reaction time. [Indene] = 2 10^{-3} mol.L^{-1}; [TfOH] = 2 10^{-3} mol.L^{-1} ; (R=1); CH_2Cl_2

At all these temperatures, the initial absorption (10 ms) is at 330 nm. It remains stable over 600 s at -65°C, while at higher temperatures the position of the final absorption after 600 s progressively shifts towards lower wavelengths (Figure 4). The maximum absorptions of the three bands progressively decrease as the reaction temperature decreases from 0°C to -65°C (Figure 5).

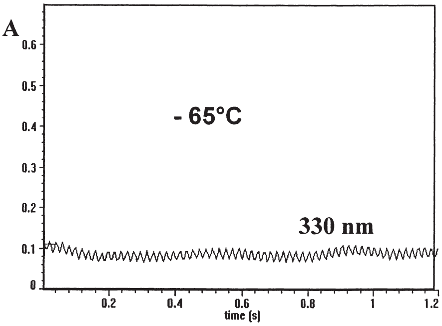


Figure 3 : Protonation of indene by triflic acid at –65°C. Evolution of the maximum with reaction time. (R=1) [Indene] = 2 10^{-3} mol.L^{-1}; [TfOH]=2 10^{-3} mol.L^{-1}

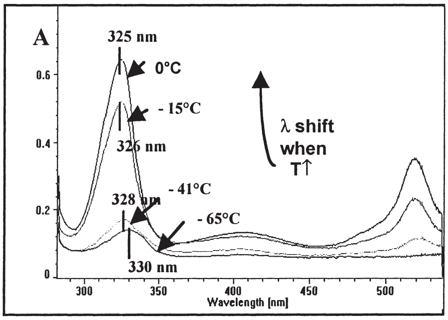


Figure 4 : Protonation of indene by triflic acid at variable temperature. UV spectra after 600 s. [Indene] = 2 10^{-3} mol.L^{-1}; [TfOH] = 2 10^{-3} mol.L^{-1}; (R=1) ; CH_2Cl_2

Influence of initiator to monomer ratio

When the ratio of TfOH to indene is increased at -65°C ([TfOH] = 4 10^{-3} M; [Indene] = 2 10^{-3} M; R = 2), a single stable maximum at 325 nm is obtained (A = 0.1 instead of 0.06 for R = 1). As expected, an increase in R increases ionization. At 0°C, the maximum at 325 nm is much higher than at -65°C, and is reached in 0.3s (A = 0.85; Figure 6). Even at 0°C, the maximum absorbance at 325 nm is relatively stable (100 s) but slowly decreases over 600 s. At this temperature, another absorption band appears at 519 nm and continuously increases up to 1.0 in 600 s (Figure 7).

In order to check the reaction products formed during the reaction, a polymerization of indene has been carried out at 0°C ([TfOH] = 3.2 10^{-3} mol.L^{-1} ; [Indene] = 2.1 10^{-3} mol.L^{-1} ; R = 1.5) for 2 minutes and quenched with a methanol / pyridine mixture. After evaporation of the solvent, the reaction products were analyzed by size exclusion chromatography. The

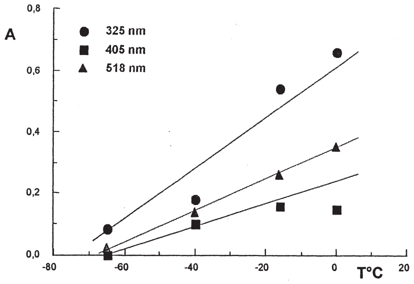


Figure 5 : Protonation of indene by triflic acid. Variation of the absorbance with temperature. [Indene] = 2 10^{-3} mol.L^{-1}; [TfOH] = 2 10^{-3} mol.L^{-1} solvent: CH_2Cl_2

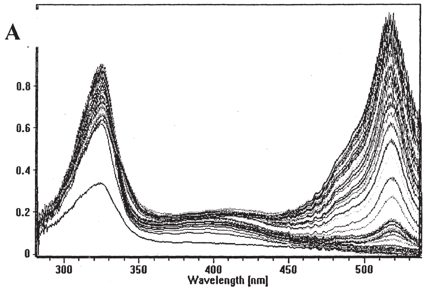


Figure 6 : Protonation of indene by triflic acid at 0°C. UV spectra of the solution. [Indene] = 2 10^{-3} mol.L^{-1} ; [TfOH] = 4 10^{-3} mol.L^{-1} ; (R=2); solvent: CH_2Cl_2

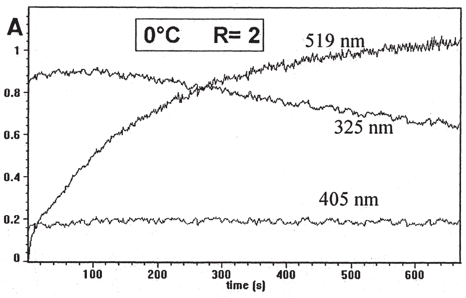


Figure 7 : Protonation of indene by triflic acid at 0°C. Evolution of the maxima with reaction time. (R=2) [Indene]= 2 10^{-3} mol.L^{-1}; [TfOH] = 4 10^{-3} mol.L^{-1}; CH_2Cl_2

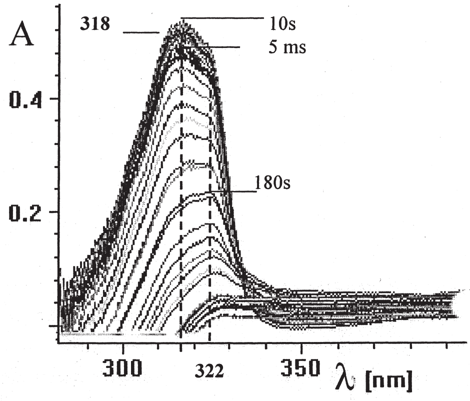
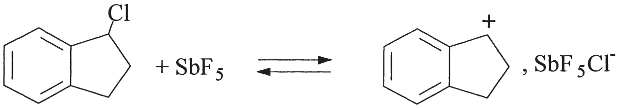


Figure 8 : Ionization of 1-chloroindane by SbF_5 at –68°C. UV spectra of the solution. [1-Chloroindane] = 1.4 10^{-4} mol.L^{-1}; [SbF_5] = 10^{-3} mol.L^{-1} (R= 7.1); CH_2Cl_2

chromatogram showed essentially oligomers of indene, but no indene monomer, which would have resulted from the monomeric cation. No trace of indene was found as well in the vapour phase analysis of the evaporate. This suggests that the maximum absorption at 325 nm, which appears at 0°C, does not correspond to the monomeric indanyl cation, but to dimeric or oligomeric species.

2) Ionization of 1-chloroindane by antimony pentafluoride.

Reaction of a Lewis acid such as antimony pentafluoride with 1-chloroindane should produce the indanyl cation (scheme 2):



Scheme 2

When SbF_5 (1.5 10^{-3} mol.L^{-1}) is reacted with 1-chloroindane (1.4 10^{-4} mol.L^{-1} ; R = 7.1) at -65°C, a large absorption band rapidly appears at 314-322 nm, which reaches a maximum in a few seconds with no other visible absorption up to 540 nm (Figure 8). Closer examination of figure 8 shows the presence of a maximum at 318 nm and of a shoulder at 322 nm. The global absorption decreases with time to half the initial value in 180 s and the main absorption shifts to 322 nm.

3) Protonation of 2-α-indanyl indene (dimer) by triflic acid

In the case of the protonation of indene, polymerization takes place concurrently with ionization, and the species observed is a mixture of oligomeric cations, particularly at high temperatures. On the other hand, protonation of the dimer of indene (2-α-indanylindene) by TfOH should yield the dimeric indanyl cation (scheme 3). 2-substituted indenes do not polymerize easily and we have found that the dimer of indene does not polymerize and that no tetramer (i. e. dimer of dimer) is formed at -60°C after 10 min, in the presence of equimolar concentrations of TfOH and dimer (2.5 10^{-2} mol.L^{-1}). In th e same conditions, but at 0°C, a protonation. For R ratios of 6 and 13, the three maxima at 325-328, 405 and observed. For higher values of this ratio (R = 26, 52, 100) there is only a main a 325 nm, a small maximum at 405 nm and practically no peak at 518 nm. The inci concentration of TfOH on the maximum absorbance of the three maxima at 325-3 519 nm is shown in figure 11. The maximum at 325 nm increases as the conc triflic acid is increased and seems to reach a plateau (A_{325} = 0.7) for R = 52. highest concentrations of TfOH, there is practically no change, which is in agreem hypothesis of an instantaneous quantitative protonation of the dimer. If one assı this case the protonation equilibrium is strongly shifted towards proto corresponding molar extinction coefficient would be 15500 L.mol^{-1}.cm^{-1}, which i value. The maximum at 405 nm also increases, but that at 518 nm decreases and visible for R = 52.

The rate of formation of the absorption at 325 nm depends on the conc TfOH. The maximum absorbance is reached in 150 s for R = 6, in 50 s for R = 13 than two seconds for highest ratios. The value of the absorbance at 325 nm aft been measured. The ratio (A_{325} / reaction time) is proportional to the protonatic corresponding plot of Ln (A_{325}/ 0.4) versus Ln ([TfOH]) shows that for the lower (from 6 to 26), the reaction order with respect to TfOH is near one (1.16, see figur

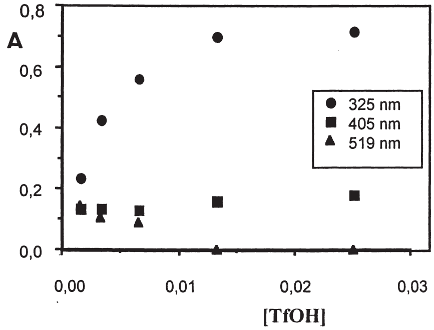


Figure 11 : Protonation of 2-indanyl indene by triflic acid at –66°C. Evolution of the maximum absorbances with TfOH concentration. [Dimer] = 2.6 10^{-4} mol.L^{-1}

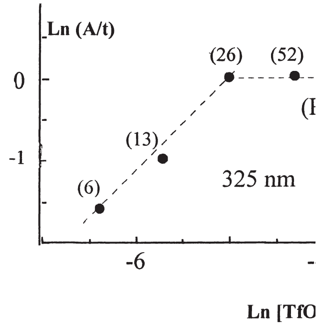


Figure 12 : Protonation of 2-indan by triflic acid at –66°C. Determina reaction order with respect to TfOI = 2.6 10^{-4} mol.L^{-1} ; solvent: CH_2Cl

protonation. For R ratios of 6 and 13, the three maxima at 325-328, 405 and 519 nm are observed. For higher values of this ratio (R = 26, 52, 100) there is only a main absorption at 325 nm, a small maximum at 405 nm and practically no peak at 518 nm. The incidence of the concentration of TfOH on the maximum absorbance of the three maxima at 325-328, 405 and 519 nm is shown in figure 11. The maximum at 325 nm increases as the concentration of triflic acid is increased and seems to reach a plateau (A_{325} = 0.7) for R = 52. For the two highest concentrations of TfOH, there is practically no change, which is in agreement with the hypothesis of an instantaneous quantitative protonation of the dimer. If one assumes that in this case the protonation equilibrium is strongly shifted towards protonation, the corresponding molar extinction coefficient would be 15500 L.mol $^{-1}$.cm^{-1}, which is a minimal value. The maximum at 405 nm also increases, but that at 518 nm decreases and is no longer visible for R = 52.

The rate of formation of the absorption at 325 nm depends on the concentration of TfOH. The maximum absorbance is reached in 150 s for R = 6, in 50 s for R = 13, and in less than two seconds for highest ratios. The value of the absorbance at 325 nm after 0.4 s has been measured. The ratio (A_{325} / reaction time) is proportional to the protonation rate. The corresponding plot of Ln (A_{325}/ 0.4) versus Ln ([TfOH]) shows that for the lower values of R (from 6 to 26), the reaction order with respect to TfOH is near one (1.16, see figure 12).

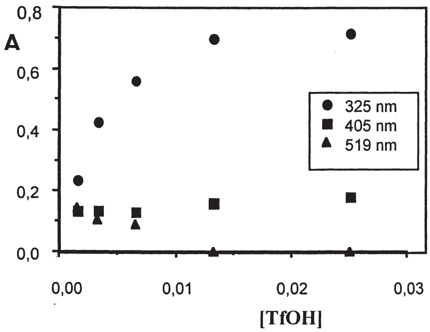


Figure 11 : Protonation of 2-indanyl indene by triflic acid at –66°C. Evolution of the maximum absorbances with TfOH concentration. [Dimer] = 2.6 10^{-4} mol.L^{-1}

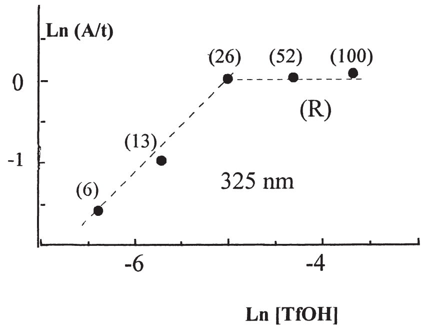


Figure 12 : Protonation of 2-indanyl indene by triflic acid at –66°C. Determination of the reaction order with respect to TfOH. [Dimer] = 2.6 10^{-4} mol.L^{-1} ; solvent: CH_2Cl_2

The influence of temperature on the three maxima is shown in figure 13. Contrarily to the case of indene, the maximum at 325 nm increases at low temperature, as well as that at 405 nm, while that at 519 nm decreases.

DISCUSSION

In all these experiments, the main absorption maximum is observed in the 318-330 nm range, but its position depends on the experimental conditions. The slight differences in wavelength in the various experiments may be due to the presence of different types of indanyl cation (provided that they are not due to experimental conditions, such as the nature of the counterion).

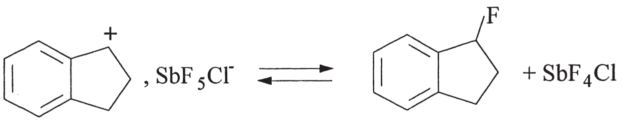
Protonation of 2-α-indanyl indene, which should give a dimeric cation, yields a maximum at 325 nm, which is stable over 600 s.

Ionization of 1-chloroindane should yield the monomeric indanyl cation, which may correspond to the maximum at 318 nm. Besides, it produces more slowly a secondary species at about 322 nm (i. e. near the λ_{max} of the dimer) which could be the dimeric cation resulting from addition of monomer units formed by deprotonation of the indanyl cation (scheme 4):

$$\begin{tikzcd}
\text{1-Cl Ind} + SbF_5 \arrow[r, shift left] & M^+ \arrow[l, shift left] \arrow[r, shift left, "(-H^+)"] \arrow[d, "(+M)"'] & M \arrow[l, shift left] \\
& D^+ \quad (+T^+ ...) &
\end{tikzcd}$$

Scheme 4

This maximum is not stable and disappears in about 200 s, contrarily to what was observed in the case of the dimer. The decrease of this maximum may result from halogen exchange which yields non-reactivable 1-fluoroindane (scheme 5).



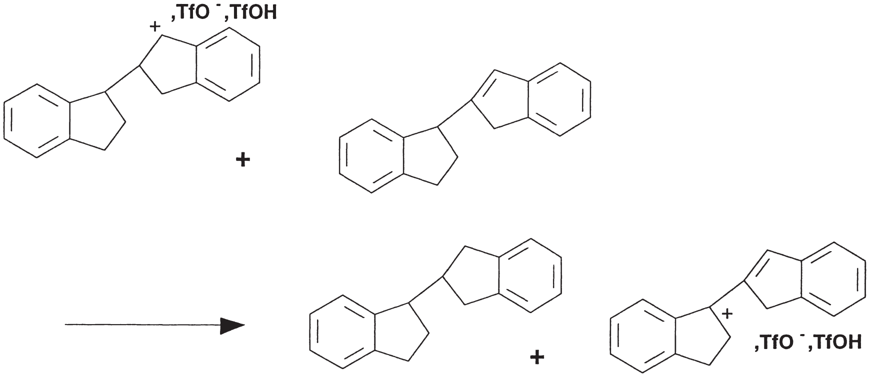
Scheme 5

The situation is more complicated in the case of the protonation of indene. In favourable conditions (low temperature, high [TfOH] / [Indene] ratios), a single stable low absorbance at 330 nm is observed. For higher temperatures, the initial maximum at 330 nm shifts to 325 nm with a much higher absorbance. A possible explanation would be that at -65°C polymerization quickly takes place, consuming a large amount of monomer and yielding few stable polymeric cations (low absorbance) and that there is no depolymerization at this temperature, while at 0°C depolymerization of indene is not negligible and eventually leads to oligomeric cations and to indene which would be cationated. The comparison of the influence of temperature on the maximum at 325-330 nm in the protonation of indene and of the dimer agrees with this hypothesis. In the case of the protonation of indene, the absorbance decreases at low temperature (Figure 5), due to fast polymerization on a small amount of stable polyindenyl cations, while in the case of the dimer it increases (Figure 13) because the dimer cation rapidly formed is more stable at low temperature (less secondary reactions).

Assuming complete protonation of the dimer for high values of the R ratio, the corresponding molar absorbance would be 15500 L.mol.$^{-1}$cm^{-1}. A comparison with substituted indanyl cations reported in the literature shows that these cations have molar absorbances in the range of 30000. However, all the cations investigated are substituted in position 1 and not in position 2 as is the dimeric cation. This might explain the difference in ε. Furthermore, the value reported here for high [TfOH] / [dimer] ratios ($\varepsilon = 15500$) is a minimum value since the concentrations of the secondary species absorbing at 405 and 519 nm are not known. They are minimal at low temperatures and at high [TfOH] / [dimer] ratios, but they nevertheless consume a fraction of the dimer.

The absorption band at 519 nm, which appears slowly at high temperature, is a derived cation.

The red colour, which is generally observed during the polymerization of indene when it is carried out under ordinary conditions, has been ascribed to this wavelength(14,15). Under high purity conditions (e. g. in polymerizations initiated with cumyl chloride and $SnCl_4$ or $TiCl_4$ under vacuum), this coloration is sometimes observed, but it develops slowly and generally after completion of the polymerization, the medium remaining pale yellow during the process, which is generally rapid (seconds or minutes depending on the conditions). Thus the species absorbing at 519 nm should correspond to the cation of a compound resulting from secondary reactions. Prosser and coll. (15) have shown that the allylic anion derived from the dimer of indene through proton abstraction by butyl lithium absorbs in the 470-520 nm range (depending on the nature of the solvent). These authors have assumed that the corresponding cation absorbs at a similar wavelength. In the case of the polymerization of indene, they have proposed for this species a cation formed by hydride abstraction by the growing chain from the penultimate indene unit of a polymer chain having an unsaturated end group (e. g. resulting from transfer). This would explain that in ordinary (non controlled) polymerizations in which transfer reactions take place, this coloration invariably appears, while it is not always visible in controlled polymerizations in which transfer is suppressed or at least reduced. In the present case, the hydride abstraction would involve a molecule of dimer, and would take place concurrently with ionization (scheme 6).



Scheme 6

This would explain the evolution of this peak with the TfOH/dimer ratio at -66°C. As mentioned before, for low values of this ratio (R = 3 and 6) initiation is slow (150 and 50 s) and the unreacted dimer present in the solution can undergo hydride abstraction to yield the species absorbing at 519 nm. For higher values of this ratio, initiation is fast, completed in two seconds, and there is no unreacted dimer available for hydride abstraction, and consequently no important absorption at 519 nm. A small amount of this compound is however formed at the very beginning of the reaction and its concentration remains constant afterwards.

It should also be noted that for high [TfOH] / [dimer] ratios, this maximum remains stable. If the case of a protonation-deprotonation equilibrium leaving a sizeable amount of unsaturated dimer, the hydride transfer would take place, shifting the equilibrium towards deprotonation to yield the species absorbing at 519 nm and this maximum would increase continuously. This apparently happens at high temperatures or at low [TfOH] / [dimer] ratios, in which cases protonation is incomplete.

Concerning the maximum at 405 nm, some authors have assumed that indanyl cations have two maxima. Pittman (28) reported two maxima at 315 nm (ε = 15700 M^{-1} cm^{-1}) and at 400 nm (ε = 6600 M^{-1} cm^{-1}) for the 1,3,3-trimethylindanyl cation and at 301 nm (ε = 14100 M^{-1} cm^{-1}) and 401 nm (ε = 2200 M^{-1} cm^{-1}) for the 1-methylindanyl cation. If the maximum at 405 nm belongs to the indanyl cation, the ratio of the absorbances at 325 and 405 nm should be independent of the reaction conditions. This is approximately verified in the case of the protonation of the dimer at variable temperature, a satisfactory correlation between these two maxima are observed during the first ten seconds of reaction (Figure 14). This would suggest that the maximum at 405 nm might also correspond to the indanyl cation.

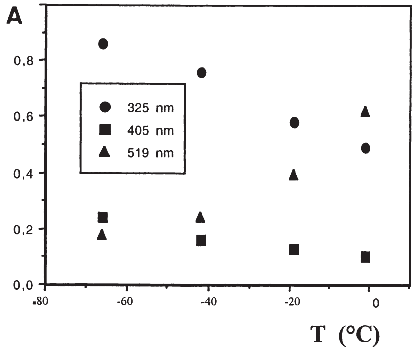


Figure 13 : Protonation of 2-indanyl indene by triflic acid at variable temperature. Evolution of the maximum absorbances with the reaction temperature. [Dimer] = 2.6 10^{-4} mol.L^{-1} ; [TfOH] =4 10^{-3} mol.L^{-1}

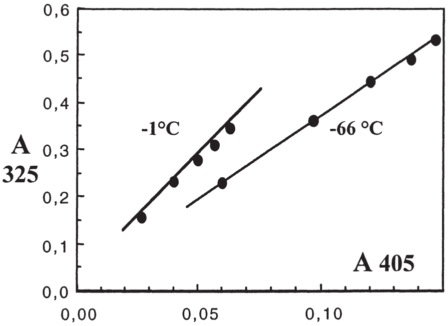


Figure 14 : Protonation of 2-indanyl indene by triflic acid at variable temperature. Evolution of the maxima at 405 nm and 325 nm during the first ten seconds of reaction. [Dimer] = 2.6 10^{-4} mol.L^{-1} ; [TfOH] = 4 10^{-3} mol.L^{-1}

Another point to be noticed is the stability of the maximum at 325 nm. This is to be compared to the protonation of styrene in similar conditions (29), in which case a transient absorption at 343 nm and a sideband at 332 nm have been observed, with shorter lifetimes

(250 ms at 0°C; 100 s at -65°C), together with a secondary band at 415 nm which has been assigned to a terminal phenylindanyl cation resulting from indanic cyclization. This reaction does not take place in the case of indene, which may explain the stability of this cation.

CONCLUSION

The experimental observations may be rationalized in the following way:

The absorption in the 318-325 nm range should belong to the indanyl cation and to the corresponding dimer cation. The cation of the growing polyindene chain would absorb at 330 nm. A secondary absorbance at 405 nm may also belong to these cations, but this is not yet clearly demonstrated. The maximum at 519 nm, which appears when unreacted dimer is present in solution, or in the case of the polymerization of indene in conditions favouring chain transfer, results from a side reaction yielding a 1-indenylindane cation.

These indanyl cations are stable at low temperature and still relatively so at -20°C and 0°C. Thus indene, which does not undergo indanic cyclization, yields stable cations and confirms the advantages of this monomer for controlled polymerization.

References

1) L. Thomas, M. Tardi, A. Polton, P. Sigwalt, Macromolecules, 1993, **26**, 4075
2) L. Thomas, A. Polton, M. Tardi, P. Sigwalt, Macromolecules, 1995, **28**, 2105
3) L. Thomas, A. Polton, M. Tardi, P. Sigwalt, Macromolecules, 1992, **25**, 5886
4) P. Sigwalt, K. Matyjaszewski, M. Moreau, Makromol. Chem., Macromol. Symp., **13/14**, 61 (1988)
5) Carbonium ions, G. A. Olah & P. von Schleyer, Interscience vol 1. Interscience, 1968
6) N. C. Deno, C. U. Pittman, J. O. Turner, J. Am. Chem. Soc. , **87**, 2153 (1965)
7) N.C. Deno, P.T. Groves, J. J. Jaruselski, M. N. Lugash, J. Am. Chem. Soc., **82**, 4719 (1960)
8) P. Sigwalt, Makromol. Chem., **175**, 1017 (1974)
9) H. Cheradame, A. H. Nguyen, P. Sigwalt, J. Polymer Sci., ACS Symposium, **56**, 335 (1976)
10) A. Leborgne, D. Souverain, G. Sauvet, P. Sigwalt, European Polymer J., **16**, 855 (1980)

11) D. Souverain, A. Leborgne, G. Sauvet, P. Sigwalt, European Polymer J., **16**, 861 (1980)

12) Nguyen Anh Hung, F. Subira, H. Cheradame, P. Sigwalt; Tetrahedron, **34**, 335 (1978)

13) See ref. 5 p. 168

14) A. D. Eckard, A. Ledwith, D. C. Sherrington, Polymer, **12**, 444 (1971)

15) H. J. Prosser and R. N. Young European Polym. J., **8**, 879 (1972)

16) Teng Xu, J. F. Haw, J. Am. Chem. Soc., **116**, 10188 (1994)

17) K. Pitchumani, V. Ramamurphy, Chem. Commun., 2763 (1996)

18) M. De Sorgo, D. C. Pepper, M. Szwarc, Chem. Commun., 419 (1973)

19) T. Kunitake, K. Takarabe, Macromolecules, **12**, 1061 (1979)

20) M. Sawamoto, T. Higashimura, A. Enokida, T. Okubo, Polym. Bull, **2**, 309 (1980)

21) M. Sawamoto, T. Higashimura, Macromolecules, **12**, 581 (1979)

22) T. Kunitake, K. Takarabe, Polymer J., **12**, 245 (1980)

23) T. Kunitake, K. Takarabe, J. Polymer Sci., ACS Symposium, **56**, 33 (1976)

24) M. Villesange, A. Rives, C. Bunel, J. -P. Vairon, M. Froyen, M. Van Beylen, A. Persoons, Makromol. Chem., Macromol. Symp., **47**, 271 (1991).

25) J. -P. Vairon, A. Rives, C. Bunel, Makromol Chem., Macromol Symp., **60**, 97 (1992)

26) B. Charleux, A. Rives, J. -P. Vairon, K. Matyjaszewski Macromolecules, **29**, 5777 (1996)

27) B. Charleux, A. Rives, J. -P. Vairon, K. Matyjaszewski, Macromolecules, **31**, 2403 (1998)

28) J. U. Pittman, Ph.D. thesis, Pennsylvania State University, 1964. University Microfilms, Inc., Ann Arbor, Mich., N° 65-6762, p. 91-98, p. 169

29) J. -P. Vairon, B. Charleux, M. Moreau, Ionic polymerization and related processes Ed. J. E. Puskas, Kluver Acad Pub., 177 (1999)