Charge-transfer complexes of pyridinium ions and methyl- and methoxy-substituted benzenes as photoinitiators for the cationic polymerization of cyclohexene oxide and related compounds

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The cationic photopolymerization of cyclohexene oxide and 4-vinylcyclohexene dioxide was achieved by using charge-transfer (CT) complexes of pyridinium salts and aromatic electron donors (hexamethylbenzene and 1,2,4-trimethoxybenzene) as initiators. Irradiation of the CT complexes with light of relatively long wavelength produces radical cations of the aromatic electron donors capable of initiating cationic polymerization. *N*-Vinylcarbazole and n-butyl vinyl ether are spontaneously polymerized in CH_2Cl_2 solution in the dark at room temperature upon addition of the CT complexes mentioned above. The molar extinction coefficients ε_{ct} and equilibrium constants K_{ct} of the CT complexes have been determined.

(Keywords: charge-transfer complexes; cationic polymerization; cyclohexene oxide)

INTRODUCTION

During the past few years it has been shown that certain pyridinium salts can act directly[1] or indirectly[2,3] as photoinitiators for the cationic polymerization of appropriate monomers such as cyclic ethers or alkyl vinyl ethers. Upon absorption of light, pyridinium salts form reactive species capable of initiating cationic polymerization. However, practical applications of some readily accessible pyridinium salts are limited because they do not absorb light at $\lambda > 320$ nm. This disadvantage was overcome by using pyridinium ions as oxidizing agents for the conversion of photolytically generated free radicals into carbocations[3].

Recently, Schuster *et al.*[4] reported that *N*-(aryloxy)-pyridinium ions are capable of forming, in the ground state, charge-transfer (CT) complexes with electron-rich donors such as methyl- and methoxy-substituted benzenes and naphthalenes. Upon light absorption, these complexes form pairs of radical cations and radical anions.

In the present work it is demonstrated that charge-transfer complexes formed by mixing *N*-ethoxy-2-methylpyridinium ions (EMP^+) or *N*-ethoxy-4-cyanopyridinium ions (ECP^+) with aromatic electron donors such as hexamethylbenzene (HMB) or 1,2,4-trimethoxybenzene (TMB) act as photoinitiators for the cationic polymerization of cyclohexene oxide (CHO) and 4-vinylcyclohexene dioxide (4-VCHO). *N*-Vinylcarbazole (NVC) and n-butyl vinyl ether (nBVE) are polymerized in a dark reaction upon the addition of these complexes.

EXPERIMENTAL

Materials

Dichloromethane (E. Merck) was treated with concentrated H_2SO_4, and washed with Na_2CO_3 solution (5%) and water. After drying with $CaCl_2$ it was refluxed and distilled from P_2O_5. Finally, it was stored over activated molecular sieve (type 4 Å). Chloroform (E. Merck) was washed with water, dried with $CaCl_2$ and distilled from CaH_2. Acetonitrile (E. Merck) was refluxed over P_2O_5 and distilled. It was stored over activated molecular sieve (type 4 Å). 2,6-Di-t-butylpyridine (Aldrich) was distilled *in vacuo* (b.p. 42°C at 1 Torr). 2-Methylpyridinium *N*-oxide (Aldrich) was used as received. *p*-Cyanopyridinium *N*-oxide (Aldrich) was recrystallized from ethanol (m.p. 221°C). Hexamethylbenzene was recrystallized three times from ethanol solution (m.p. 166°C). 1,2,4-Trimethoxybenzene (Aldrich) was purified by vacuum distillation. The middle fraction was collected (b.p. 101°C at 2 Torr). Triethyloxonium hexafluorophosphate (Aldrich) was used as received. Cyclohexene oxide (Aldrich) was refluxed over CaH_2 and distilled. The middle fraction was collected (b.p. 134°C). n-Butyl vinyl ether (Aldrich) was washed with aqueous NaOH solution. After drying with $CaCl_2$ it was distilled from CaH_2 (b.p. 94°C). *N*-Vinylcarbazole (Aldrich) was recrystallized from ethanol solution (m.p. 64°C). 4-Vinylcyclohexene dioxide (Fluka) was distilled from CaH_2. The middle fraction was collected (b.p. 108°C at 15 Torr).

Synthesis of pyridinium salts

N-Ethoxy-2-methylpyridinium hexafluorophosphate ($EMP^+PF_6^-$), *N*-ethoxy-*p*-phenylpyridinium hexafluoro-

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phosphate (EPP$^+$PF$_6^-$) and *N*-ethoxyisoquinolinium hexafluorophosphate (EIQ$^+$PF$_6^-$) were prepared according to a procedure described previously[1]. *N*-Ethoxy-*p*-cyanopyridinium hexafluorophosphate (ECP$^+$PF$_6^-$) was synthesized according to the following procedure. First, 14 g (56.4 mmol) of triethyloxonium hexafluorophosphate was added to 6 g (50 mmol) of *p*-cyanopyridinium *N*-oxide dissolved in 10 ml dry chloroform. The mixture was refluxed for a period of 6 h and then cooled down to room temperature. The precipitated product was filtered off and recrystallized twice from methanol solution. Yield, 47%; m.p. 145°C. ^{1}H n.m.r. (acetonitrile-d$_3$): $\delta = 9.10$ (d, Ar), 8.4 (d, Ar), 4.8–4.6 (4, OCH$_2$), 1.4 (t, CH$_3$). Analysis: calculated, C 32.66, H 3.08, O 5.14, N 9.53%; found, C 33.81, H 3.12, O 5.88, N 9.53%. The following instruments were used for the analysis of the pyridinium salts: a Varian instrument (model EM 390) for ^{1}H n.m.r. measurements, which were performed in acetonitrile-d$_3$ solution using tetramethylsilane as internal standard; a Shimadzu spectrophotometer (model 2101 PC) for recording u.v.-vis. spectra; and a Mettler instrument (model FP5) for the determination of melting points. Elemental analyses were performed by Mikroanalytisches Laboratorium Pascher/Remagen.

Polymerizations

Polymerization of cyclohexene oxide using the CT complex ECP$^+$/TMB. First, 0.6 ml (3.2 mmol) TMB containing 0.025 mmol ECP$^+$ was added to 4.4 ml (43.5 mmol) CHO. The solution was put into a Pyrex tube (i.d. = 11 mm) and was flushed with argon prior to irradiation with the light of a high-pressure mercury lamp (TQ 718, Original Hanau) at $\lambda_{\mathrm{inc}} > 360$ nm. Appropriate cut-off filters were placed in front of the tubes.

Polymerization of CHO using the CT complex EMP$^+$/HMB and of 4-VCHO using the CT complex ECP$^+$/TMB. First, 2.0 ml dichloromethane containing 0.025 mmol EMP$^+$PF$_6^-$ and 2.5 mmol HMB were added to 3.0 ml (30 mmol) CHO. The solution was put into a Pyrex tube (i.d. = 11 mm) and was flushed with argon prior to irradiation at $\lambda_{\mathrm{inc}} > 345$ nm in a Rayonet reactor equipped with a merry-go-round sample holder. Appropriate cut-off filters were placed in front of the tubes.

Polymerization of NVC and nBVE using the CT complex ECP$^+$/TMB. For this, 0.6 ml (3.2 mmol) TMB containing 0.025 mmol ECP$^+$PF$_6^-$ were added to 4.4 ml of a solution of NVC or nBVE in dichloromethane (total monomer concentration 1 mol l^{-1}).

Polymer characterization. The polymers were precipitation from the reaction mixture by the addition of a 50-fold excess of methanol containing a few drops of aqueous NH$_4$OH. Subsequently, they were purified by repeated reprecipitation from tetrahydrofuran/methanol.

RESULTS AND DISCUSSION

Optical absorption spectra

Optical absorption spectra of acetonitrile and dichloromethane solutions containing ECP$^+$/TMB and EMP$^+$/HMB are shown in *Figures 1* and *2*, respectively. The spectra exhibit new absorption bands at about 425 nm and about 315 nm, respectively, i.e. at wavelength ranges where the components are transparent. Therefore, these bands are assigned to CT complexes. The ECP$^+$/TMB complex absorbs light at longer wavelengths than the EMP$^+$/HMB complex, which is thought to be due to differences in the reduction and oxidation potentials of the corresponding acceptor and donor compounds, respectively. Results of studies concerning the absorption bands of CT complexes of various

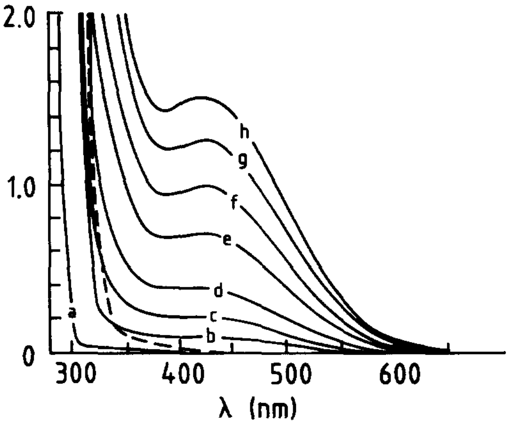


Figure 1 Absorption spectra of acetonitrile solutions containing ECP$^+$PF$_6^-$ (5×10^{-3} mol^{-1}) and TMB at different concentrations (mol l^{-1}): (a) 0, (b) 0.01, (c) 0.4, (d) 0.8, (e) 1.6, (f) 2.4, (g) 3.2, (h) 4.0; (----) TMB (3.2 mol l^{-1}) in the absence of ECP$^+$PF$_6^-$

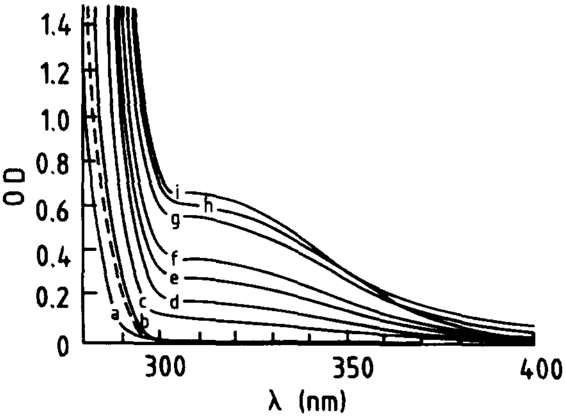


Figure 2 Absorption spectra of dichloromethane solutions containing EMP$^+$PF$_6^-$ (5×10^{-3} mol^{-1}) and HMB at different concentrations (mol l^{-1}): (a) 0, (b) 0.01, (c) 0.05, (d) 0.1, (e) 0.15, (f) 0.2, (g) 0.3, (h) 0.4, (i) 0.5; (----) HMB (0.5 mol l^{-1}) in the absence of EMP$^+$PF$_6^-$

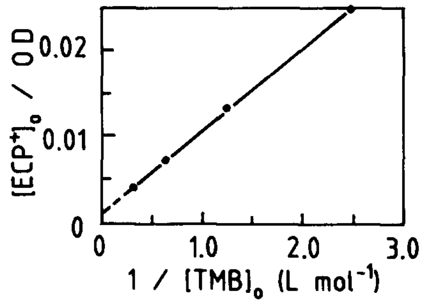


Figure 3 CT complexes of the system ECP$^+$/TMB in acetonitrile solution at room temperature. Benesi–Hildebrand plot of [ECP$^+$]$_0$/*OD* vs. 1/[TMB]$_0$ according to equation (1). [ECP$^+$PF$_6^-$]$_0 = 5 \times 10^{-3}$ mol l^{-1}; [TMB]$_0 = 0.2$ to 3.2 mol l^{-1}. The *OD* was measured at 425 nm

Table 1 Charge-transfer complexes of EMP^+, EIQ^+ and ECP^+ ions and HMB or TMB. Reduction potentials of acceptors, ionization potentials of donors and λ_{max} values of the CT absorption bands are shown

	Acceptor			Donor			Complex
	Name	Conc. ($mol\,l^{-1}$)	$E_{red}{}^{a}$ (V)	Name	Conc. ($mol\,l^{-1}$)	IP^{b} (V)	λ_{max} (nm)
1	EMP^{+c}	5×10^{-3}	−0.7	HMB	5×10^{-1}	8.18	315
2	EMP^{+c}	5×10^{-2}	−0.7	TMB	5×10^{-2}	7.36	345
3	EIQ^{+c}	5×10^{-2}	−0.48	TMB	5×10^{-2}	7.36	375
4	EPP^{+c}	5×10^{-2}	−0.46	TMB	5×10^{-2}	7.36	380
5	ECP^{+d}	5×10^{-3}		TMB	6.4×10^{-1}	7.36	425

[a] Half-wave reduction potential vs. SCE[5]
[b] Ionization potential[6]
[c] Solvent: dichloromethane
[d] Solvent: acetonitrile

pyridinium ions are shown in *Table 1*. A bathochromic shift with decreasing ionization potential (*IP*) of the aromatic donor was found for the complexes of EMP^+/HMB and EMP^+/TMP (entries 1 and 2 in *Table 1*). Likewise, a bathochromic shift with increasing reduction potential of the pyridinium ions was observed with the complexes EIQ^+/TMB and EPP^+/TMB (entries 3 and 4 in *Table 1*). A value of the reduction potential of ECP^+ ions is not available, at present. However, regarding the pronounced red shift ($\lambda_{max} = 425$ nm), a reduction potential much more positive than those of EPP^+ and EIP^+ is assumed for ECP^+.

The method of Benesi and Hildebrand[7] based on the following equation (1) was applied to obtain values of the equilibrium constant K_{ct} and the molar extinction coefficient ε_{max} at the maximum of the CT band of complexes of pyridinium ions:

$$\frac{[A]_0}{(OD)_{max}} = \frac{1}{\varepsilon_{max}} + \frac{1}{K_{ct}\varepsilon_{max}[D]_0} \qquad (1)$$

Here, $[A]_0$ and $[D]_0$ denote the initial concentrations of acceptor and donor, respectively, and $(OD)_{max}$ is the optical density at the maximum of the absorption band.

Figure 3 shows the Benesi–Hildebrand plot for the system ECP^+/TMB. Values of ε_{max} and K_{ct} were obtained from the intercept and the slope of the straight line, respectively. The results obtained for this system and for the system EMP^+/HMB are presented in *Table 2*. From the magnitude of the K_{ct} values (0.82 and $0.13\,l\,mol^{-1}$, respectively), it is inferred that the strength of the complexes is rather weak. Typical K_{ct} values of strong CT complexes are in the order of $10^3\,l\,mol^{-1}$ (e.g. $K_{ct} = 2.55\times10^3\,l\,mol^{-1}$ has been reported for the CT complex trimethylamine/SO_2 in n-heptane[8]). It should be pointed out the CT complexes mentioned above are quite stable, which was concluded from the fact that the optical densities of solutions of the complexes remained unchanged for a storage period (in the dark) of several days.

Table 2 Characterization of the CT complexes EMP^+/HMB and ECP^+/TMB

CT complex	Solvent	λ_{max} (nm)	$\varepsilon_{max}{}^{a}$ ($l\,mol^{-1}\,cm^{-1}$)	$K_{ct}{}^{b}$ ($l\,mol^{-1}$)
EMP^+/HMB	CH_2Cl_2	315	506	0.82
ECP^+/TMB	CH_3CN	425	792	0.13

[a] At λ_{max}
[b] Equilibrium constant

Table 3 Cationic photopolymerization of neat cyclohexene oxide using the CT complex ECP^+/TMB. $[ECP^+] = 5\times10^{-3}\,mol\,l^{-1}$; $[TMB] = 6.4\times10^{-1}\,mol\,l^{-1}$; $[CHO] = 8.7\,mol\,l^{-1}$; $\lambda_{inc} > 360$ nm

Run	Irradiation time (min)	Monomer conversion (mol%)	$M_w{}^{a}$ ($10^4\,g\,mol^{-1}$)
1	5	14	
2^{b}	5	16	
3	20	33	8.3
4^{c}	20	26	7.6

[a] Determined by the light scattering method
[b] The sample was irradiated for 5 min and kept in the dark for a period of 3 h prior to precipitation of the polymer
[c] The sample contained di-2,6-t-butylpyridine ($5\times10^{-3}\,mol\,l^{-1}$)

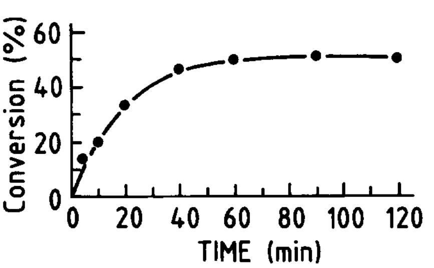


Figure 4 Photopolymerization of neat cyclohexene oxide under argon at room temperature at $\lambda_{inc} > 360$ nm. $[ECP^+PF_6^-] = 5\times10^{-3}\,mol\,l^{-1}$; $[TMB] = 6.4\times10^{-1}\,mol\,l^{-1}$. Plot of the conversion of monomer to polymer vs. the time of irradiation

Polymerization studies

Initiation by CT complexes in the ground state. The CT complex formed from ECP^+ and TMB is capable of initiating the polymerization of vinyl compounds such as NVC and nBVE in dichloromethane solution. In these cases the monomers were readily polymerized upon addition of the CT complex to the monomer solution at room temperature. Oxirane compounds are not affected.

Initiation by electronically excited CT complexes. As can be seen from *Figures 4* and *5*, CHO containing CT complexes of ECP^+/TMB or EMP^+/HMB is polymerized quite effectively upon irradiation at room temperature. Similarly, the bifunctional monomer

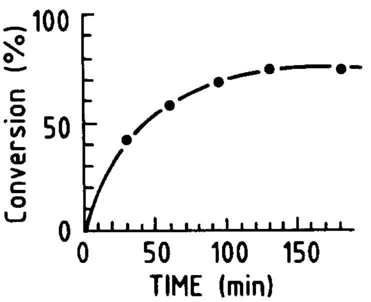
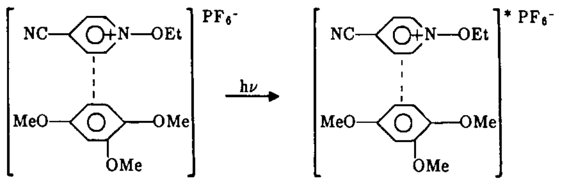
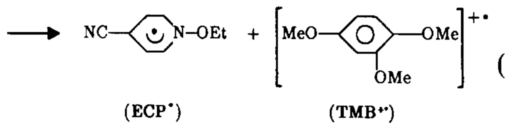


Figure 5 Photopolymerization of cyclohexene oxide in dichloromethane solution under argon at room temperature at $\lambda_{inc} > 345$ nm. $[EMP^+PF_6^-] = 5 \times 10^{-3}$ mol l^{-1}; $[HMB] = 5 \times 10^{-1}$ mol l^{-1}. Plot of the conversion of monomer to polymer vs. the time of irradiation

4-VCHO readily formed an insoluble gel. These monomers do not undergo a dark reaction with the CT complexes. Moreover, post-polymerization does not occur, as can be seen from *Table 3* (runs 1 and 2). When the irradiation was carried out in the presence of 2,6-di-t-butylpyridine, which is known to act as a proton scavenger, the rate of polymerization was not significantly reduced (see *Table 3*, run 4). On the basis of these results, the following mechanism for the initiation of the polymerization of cyclohexene oxide and related monomers is suggested (illustrated for the system ECP^+/TMB):

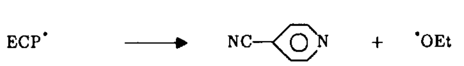


(2)



(3)

Electronically excited CT complexes undergo electron transfer resulting in the formation of aromatic radical cations ($TMB^{+\bullet}$) and pyridinyl radicals ($ECP^{\bullet}$). The latter are very short-lived and decompose according to reaction (4)[2]:



(4)

Generally, the initiation of the polymerization of a monomer M may follow various routes. Radical cations $D^{+\bullet}$ can react with the monomer, thus forming the species ${}^{\bullet}D\text{-}M^+$:

$$D^{+\bullet} + M \rightarrow {}^{\bullet}D\text{-}M^+ \xrightarrow{nM} {}^{\bullet}D\text{-}(M)_nM^+ \qquad (5)$$

Alternatively, radical cations $D^{+\bullet}$ can abstract hydrogen from solvent or monomer. The resulting intermediate HD^+ yields protons upon dissociation:

$$D^{+\bullet} + RH \rightarrow HD^+ + R^{\bullet} \qquad (6)$$

$$HD^+ \rightarrow D + H^+ \qquad (7)$$

Protons can add to monomer, thus forming species capable of initiating the cationic polymerization of M:

$$H^+ + M \rightarrow H\text{-}M^+ \xrightarrow{nM} H\text{-}(M)_nM^+ \qquad (8)$$

Because of the inefficiency of 2,6-di-t-butylpyridine to reduce the polymerization rate, the occurrence of the mechanism according to reactions (6) to (8) seems to be unlikely, and radical cations seem to be the initiating species. Further investigations concerning this aspect are in progress.

CONCLUSIONS

N-Ethoxypyridinium ions such as ECP^+ and EMP^+ readily form charge-transfer complexes with various aromatic electron donors. These CT complexes are capable of initiating, at room temperature, the spontaneous polymerization of n-butyl vinyl ether and *N*-vinylcarbazole in dichloromethane solution. Moreover, they are capable of acting as initiators of the cationic photopolymerization of oxirane compounds, which do not polymerize in a dark reaction. The complexation of pyridinium salts with aromatic electron donors causes an extension of the spectral response of pyridinium salt-based photoinitiators to longer wavelengths, because of the strong CT absorption bands of some of these CT complexes. For instance, the quite effectively acting CT complex formed by ECP^+ and TMB has an absorption band with a maximum at 425 nm ($\varepsilon_{425} = 792$ l mol^{-1} cm^{-1}, solvent CH_3CN).

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