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-methyl-pyridinium 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.

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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-