polymer communications

On the reactivity of pyridines towards carbocations

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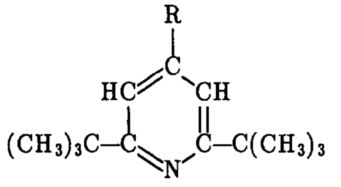
Rate constants of the reaction of tris(*p*-methoxyphenyl)vinyl cations with pyridine derivatives were measured in acetonitrile solution at room temperature using the flash photolysis technique. The lowest value ($k_2 = 3.4 \times 10^4\, \mathrm{l\, mol^{-1}\, s^{-1}}$) was found for 2,6-di-tert-butylpyridine, which is frequently used as a proton trap in cationic polymerizations. 4-tert-Butylpyridine and pyridine exhibited the highest reactivity towards the vinyl cations: $k_2 = 3.2 \times 10^7$ and $2.8 \times 10^7\, \mathrm{l\, mol^{-1}\, s^{-1}}$, respectively.

(Keywords: reactivity; pyridines; carbocations)

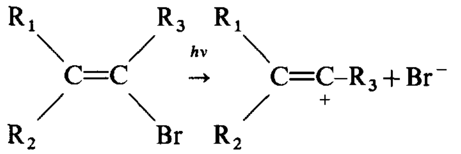
Introduction

Recently, sterically hindered pyridines (SHPs) have been employed as non-nucleophilic proton traps in order to discriminate protic from non-protic initiation mechanisms of cationic polymerizations[1]. Pyridines of the general structure



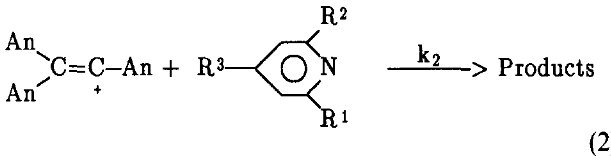
were reported by Brown and Kanner[2,3] to be reactive towards protons and to be unreactive towards Lewis acids. In numerous studies dealing with cationic polymerizations in the presence of SHPs (for a literature survey see ref. 4) it was assumed that carbocations are inert towards SHPs. The cationic polymerization initiated by certain initiator systems was reported to be either suppressed or unsuppressed by an SHP and it was concluded that suppresion is due to the proton scavenging capability of the SHP. For example, a trimodal molar mass distribution was reduced to a monomodal distribution when the polymerization of isobutene initiated by the system cumyl chloride/BCl_3 was performed in the presence of 2,6-di-tert-butylpyridine (DBP); it was concluded that the suppressed fractions arose from proton-initiation and the unsuppressed fraction from the initiation by $Ph(CH_3)_2C^+$ ions[5]. With respect to reactivity behaviour, SHPs differ from normal pyridines which rapidly react with both protons and carbocations. To date, the magnitude of the reactivity has been determined for reactions of pyridines with protons only. The rate constant $k = 3.8 \times 10^8\, \mathrm{l\, mol^{-1}\, s^{-1}}$ has been reported[6] for the reaction of protons with DBP in dioxane/water (80/20, v/v) at 25°C. This value is significantly lower than that found for the reaction of pyridine with protons in water ($k = 2.2 \times 10^{10}\, \mathrm{l\, mol^{-1}\, s^{-1}}$)[7]. The reduction of the rate constant has been attributed to a steric effect[5].

To the authors' knowledge quantitative data concerning the reactivity of SHPs towards carbocations have not yet been published. It therefore seemed of interest to carry out reactivity studies and to commence this research by investigating reactions of substituted vinyl cations with pyridines. Earlier investigations had revealed[8–10] that substituted vinyl cations can be generated by flash photolysis of corresponding vinyl bromides:



(1)

Carbocations formed in this way can be detected by their characteristic optical absorption spectrum. In this work, rate constants k_2 of reaction (2), i.e. of the reaction of various pyridines with 1,2,2-tris(*p*-methoxyphenyl)vinyl cations, were measured. The vinyl cations were generated, according to reaction (1), in acetonitrile solution at room temperature by flash photolysis of 1,2,2-tris(*p*-methoxyphenyl)vinyl bromide[9].



(2)

An: anisyl(*p*-methoxyphenyl)

Experimental

Materials. 1,2,2-Tris(*p*-methoxyphenyl)vinyl bromide was prepared as described in the literature[11,12]. The pyridines were obtained from Aldrich or E. Merck. Pyridine, 4-tert-butylpyridine, 2-methylpyridine, 2,6-dimethylpyridine and DBP were distilled *in vacuo*. 2,6-Di-tert-butyl-4-methylpyridine was recrystallized several times from ethanol solution. Acetonitrile was refluxed over P_2O_5 and distilled.

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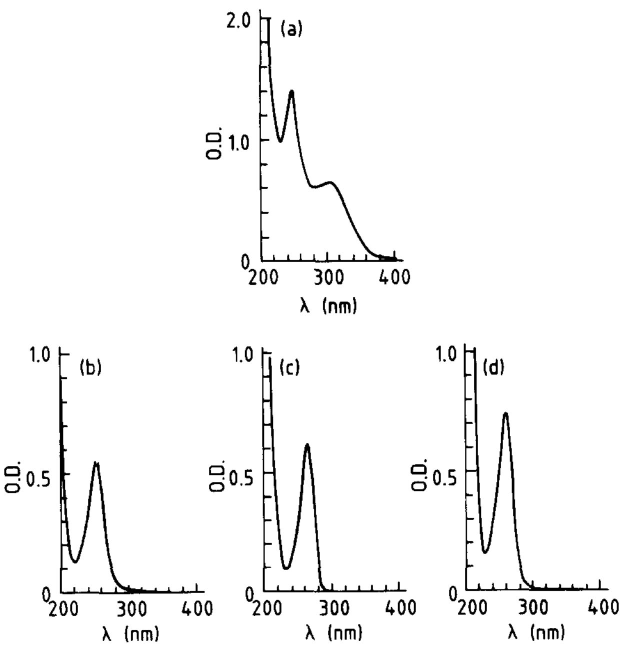

Figure 1 Optical absorption spectra of (a) 1,2,2-tris(*p*-methoxyphenyl)vinyl bromide, $c = 4.2 \times 10^{-5}$ mol l^{-1}; (b) pyridine, $c = 2.6 \times 10^{-4}$ mol l^{-1}; (c) 2,6-dimethylpyridine, $c = 1.7 \times 10^{-4}$ mol l^{-1}; (d) 2,6-di-tert-butylpyridine, $c = 1.9 \times 10^{-4}$ mol l^{-1}, recorded in acetonitrile solution at room temperature

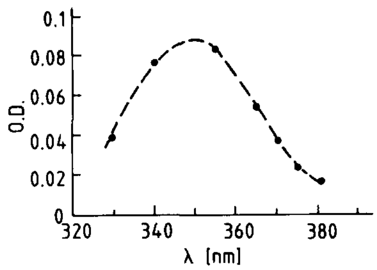

Figure 2 Irradiation of 1,2,2-tris(*p*-methoxyphenyl)vinyl bromide in acetonitrile solution at room temperature at $\lambda_{inc} = 347$ nm with a 20 ns flash. Optical absorption spectrum recorded at the end of flash

Flash photolysis. Acetonitrile solutions containing 1,2,2-tris(*p*-methoxyphenyl)vinyl bromide (2.1×10^{-5} mol l^{-1}) and a pyridine at varying concentrations were irradiated in quartz cells with 20 ns flashes of 347 nm light generated with the aid of a ruby laser (Korad K1 QS2) operated in conjunction with a frequency doubler. The optical absorption detection method was applied to detect the vinyl cations and to measure the rate of decay of the vinyl cations. It turned out that the same decay rates were found in Ar- and O_2-saturated solutions. The solutions absorbed about 20% of the laser light incident upon the cell. The light absorption was due solely to the vinyl bromides, because the pyridines are transparent at 347 nm; this can be seen from *Figure 1*, where ground-state absorption spectra of 1,2,2-tris(*p*-methoxyphenyl)vinyl bromide and of three substituted pyridines are presented.

Results

The transient optical absorption spectrum presented in *Figure 2* was formed upon irradiation of 1,2,2-tris(*p*-methoxyphenyl)vinyl bromide in acetonitrile solution. This spectrum, which was recorded at the end of the flash, is attributed to 1,2,2-tris(*p*-methoxyphenyl)vinyl cations[8]. The decay of the transient absorption followed first-order kinetics both in the absence and presence of pyridine. Second-order rate constants k_2 were obtained by plotting the experimentally measured first-order rate constants k *versus* the pyridine concentration according to equation (3), as shown in *Figure 3*:

$$k = k_0 + k_2[\text{pyridine}] \qquad (3)$$

$k_0 = (3.7 \pm 0.3) \times 10^4$ s^{-1}: first-order rate constant in the absence of pyridine.

As can be seen from *Table 1*, which contains all k_2 values, DBP exhibits the lowest and 4-tert-butylpyridine the highest reactivity. 4-tert-Butylpyridine is somewhat more reactive than the unsubstituted pyridine, indicating the action of an inductive effect (+I-effect) which leads to an increase in the electron density at the nitrogen. A similar effect may explain why 2,6-di-tert-butyl-4-methylpyridine is more reactive than DBP.

In conclusion, the results demonstrate the pronounced steric hindrance effect exerted by alkyl groups located in positions 2 and 6 on the reactivity of pyridines towards trianisyl vinyl cations. Obviously, regarding steric hindrance, tert-butyl groups are more effective than methyl groups. Notably, rate constants of the order of 10^4 l mol^{-1} s^{-1}, such as that found in the case of DBP ($k_2 = 3.4 \times 10^4$ l mol^{-1} s^{-1}), are rather low, but not low enough to be negligible under all circumstances. It should be pointed out that water possesses a reactivity definitely lower than that of DBP ($k_2 = 1.5 \times 10^4$ l mol^{-1} s^{-1}). This implies that traces of water that might have been present in the solutions did not interfere with the determination of the reactivity of the pyridines.

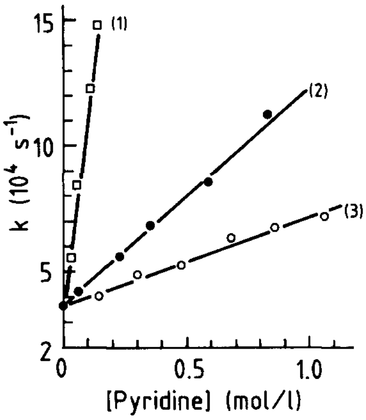

Figure 3 Typical plots of first-order rate constants of the decay of the optical absorption at 355 nm as a function of pyridine concentration: (1) 2,6-dimethylpyridine; (2) 2,6-di-tert-butyl-4-methylpyridine; (3) 2,6-di-tert-butylpyridine

Table 1 Bimolecular rate constants of the reaction of pyridines with 1,2,2-tris(*p*-methoxyphenyl)vinyl cations in acetonitrile solution at room temperature

Nucleophile	k_2 (l mol^{-1} s^{-1})
4-tert-Butylpyridine	3.2×10^7
Pyridine	2.8×10^7
2-Methyl-pyridine	1.3×10^7
2,6-Dimethylpyridine	7.7×10^5
2,6-Di-tert-butyl-4-methylpyridine	8.7×10^4
2,6-Di-tert-butylpyridine (DBP)	3.4×10^4
Water	1.5×10^4

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