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Kinetics

Kinetic Study of the Quaternization of Poly (2-Methyl-5-Vinyl Pyridine) by Hexadecyl Bromide in Dioxane-Tetramethylene Sulfone Mixtures

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Summary

We studied the kinetics of the quaternization of poly(2 methyl-5-vinyl pyridine)* by hexadecyl bromide in dioxane-tetramethylene sulfone (TMS) mixtures. The velocity of the quaternization vs the percentage of TMS presents a maximum for 75 % of TMS in the mixture corresponding (in our experimental conditions) to the limiting solubility of hexadecyl bromide. The mechanism of the quaternization was studied in two cases : 50/50 and 70/30 dioxane/TMS mixtures. In the firstcase the kinetic obeys to a second order law when in the second case we observe a first order with the reference to the polymer and a partial order (0.8) with reference to the alkylbromide. This phenomenon was explained by the possibility of participation in the quaternization of ionic species.

Introduction

The quaternization of Poly(4 vinyl pyridine) by alkyl bromides follows a second order kinetics in the first step of the reaction (1-3). In the case of the quaternization of poly(2-methyl-5 vinyl pyridine) (P2M5VP) by butyl bromide in tetramethylene sulfone (TMS) a dependence of the velocity constant with the concentration of butyl bromide was been shown (3). In order to elucidate this phenomenon we studied the kinetics of the quaternization of P2M5VP by hexadecyl bromide ($C_{16}Br$) in TMS-dioxane mixtures. We determine the influence of the solvent on the velocity of the reaction and on the order with reference to P2M5VP and $C_{16}Br$.

Experimental

P2M5VP was obtained by conventional radical polymerization using methanol as the solvent and 22'azoisobutyronitrile as the initiator. The polymer was preci-

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* IUPAC nomenclature : poly[1-(6 methyl-3-pyridyl) ethylene]

pitated in water. The molecular weight was determined from the value of the limiting viscosity number in methanol (4), we obtained $\overline{M}w$ = 290 000. The reaction temperatures were 50, 60, 70 or 80°C. These temperatures were defined at ±.02°C. The reactions were carried out in the presence of air. The reaction extent τ was determined by potentiometric titrations of Br^- using 0.05 M $AgNO_3$ solution diluted with methanol and in the presence of an excess of sulfuric acid (3,5). Radiometer equipments : pHmeter 28, Titrator 11, autoburette ABU 1C and Titrigraph SBR 2C were used. Reference electrode : glass electrode G 202C; measurement electrode : silver electrode P 4011.

The initial velocity constant v_o is given by the $t \to 0$ limiting slope of the curve $\tau = f(t)$.

Results and discussion

In a first time we studied the influence of the solvent on the velocity of the reaction in TMS/Dioxane mixtures. The results are reported in Figure 1. We show a dependence of the velocity vs the composition of TMS/Dioxane mixture. The curve exhibits a maximum for 75 % of TMS. The dielectric constant of the solvent covers the range $2.2 \leqslant \varepsilon \leqslant 42$. In the first part of the curve the increase of the dielectric constant of the solvent favors the reaction. This result is in good agreement with the literature (6,7). The maximum of the curve can be explained by the fact that $C_{16}Br$ is not completely soluble in TMS since a phase separation appeared beyond about 75 % of TMS. In consequence we study the reaction in 50/50 and 70/30 TMS/Dioxane mixtures. In these two cases two sets of experiments were made. In the first one we kept [P2M5VP] = Cte when varying [$C_{16}Br$] and we studied the inverse case in the second set. The results are reported in Tables 1 and 2.

Table 1. Rates of quaternization in a 50/50 TMS/Dioxane mixture at 70°C

A) [P2M5VP] = .0840 mole.l^{-1}

[$C_{16}Br$] mole l^{-1}	.0420	.0843	.1685	.2106
$v_o.10^6$ mole $l^{-1}mn^{-1}$	3.00	6.06	11.3	13.6

B) [$C_{16}Br$] = .0845 mole.l^{-1}

[P2M5VP] mole l^{-1}	.0474	.0843	.1246	.1741
$v_o.10^6$ mole $l^{-1}mn^{-1}$	3.38	6.09	9.79	13.02

The orders with reference to P2M5VP and $C_{16}Br$ were obtained by the slope of the straight line Log v_o vs Log [P2M5VP] or Log [$C_{16}Br$] . Figure 2 shows these variations in the case of 50/50 TMS/Dioxane mixture. We obtain n = 1 with reference to

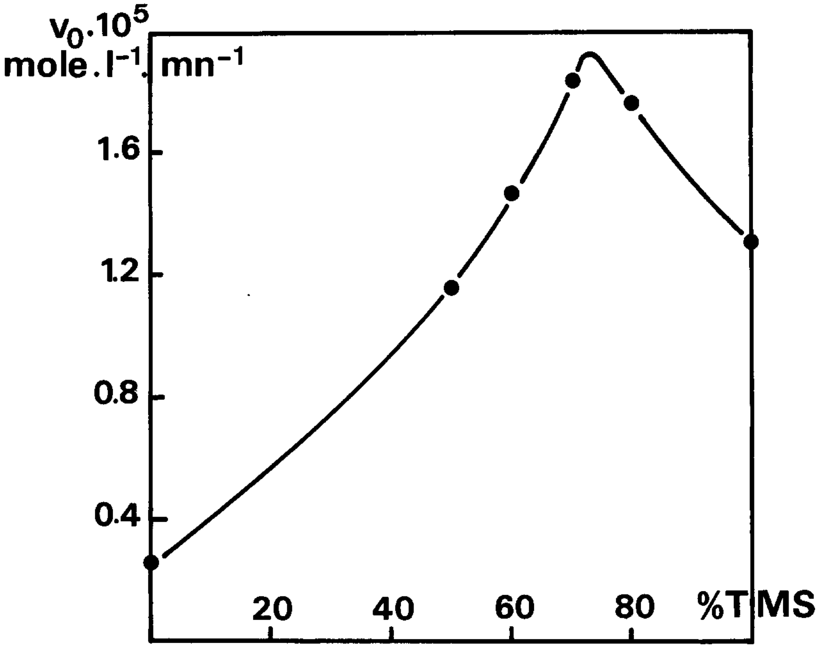


Figure 1. Rates of quaternization in TMS/Dioxane mixture $[P2M5VP]=.084$ mole l^{-1}.$[C_{16}Br]=.174$ mole l^{-1}. T = 70°C

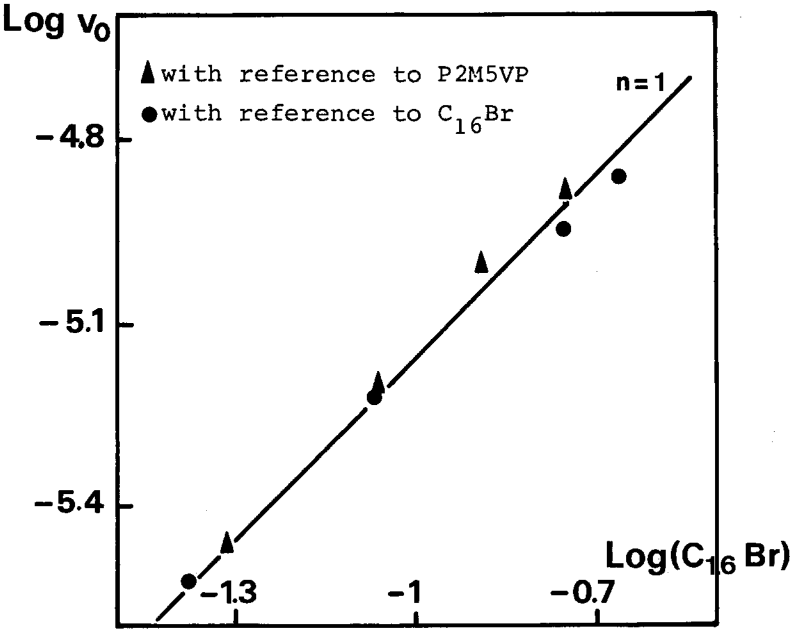


Figure 2. Quaternization in 50/50 TMS/Dioxane mixture at 70°C. Determination of the partial order.

Table 2. Rates of quaternization in a 70/30 TMS/Dioxane mixture at 70°C

A) [P2M5VP] = .0842 mole.l^{-1}

$[C_{16}Br]$ mole l^{-1}	.0473	.0877	.1246	.1741	.2503
$v_o.10^5$ mole $l^{-1}mn^{-1}$	.65	1.08	1.40	1.82	1.94

B) $[C_{16}Br]$ = .0843 mole.l^{-1}

[P2M5VP] mole l^{-1}	.0337	.0474	.0843	.1247	.1742
$v_o.10^5$ mole $l^{-1}mn^{-1}$	.45	.58	1.07	1.58	2.97

P2M5VP or $C_{16}Br$. Figure 3 shows Log v_o vs Log [P2M5VP] in the case of 70/30 TMS/Dioxane mixture, we obtain n = 1. Figure 4 shows Log v_o vs Log $[C_{16}Br]$ in the same case, we obtain n = 0.8. In a 70/30 TMS/Dioxane mixture a second order kinetics is no more followed and the velocity is given by the relation $v = k[P2M5VP][C_{16}Br]^{.8}$. The mechanism of the reaction depends on the composition of the solvent. The table 3 gives the velocity constant k in the 70/30 mixture vs the $C_{16}Br$ concentration in the two cases order = 1+1 and order = 1+.8. We can see that in the first case k is a function of the concentration of P2M5VP by butyl bromide in TMS (3) since in the second one k is constant. The mechanism of quaternization of model pyridyl species by alkyl bromides is a S_N2 mechanism and the quaternization of Poly (4 vinyl pyridine) obeys the same mechanism (1).

Table 3. Determination of the velocity constant k (order 2 or 0.8 with reference to $C_{16}Br$) vs the concentration of $C_{16}Br$. [P2M5VP] = .0842 mole l^{-1}. solvent 70/30 TMS/Dioxane Temperature 70°C

$[C_{16}Br]$		.0473	.0877	.1246	.1741	.2503
$k.10^4$	n=1	16.2	14.7	13.4	12.4	9.2
	n=.8	8.8	8.9	8.8	8.7	7.0

Table 4 gives the velocity constant of the quaternization of 2 methyl 5 ethyl pyridine (2M5EP), 4 ethyl pyridine (4EP) and P2M5VP, by $C_{16}Br$ in a 50/50 TMS/Dioxane mixture. The reaction is a little slower for the polymer than for its model molecule (6). This difference can be intepreted as a small steric hindrance effect due to the presence of the polymeric chain.

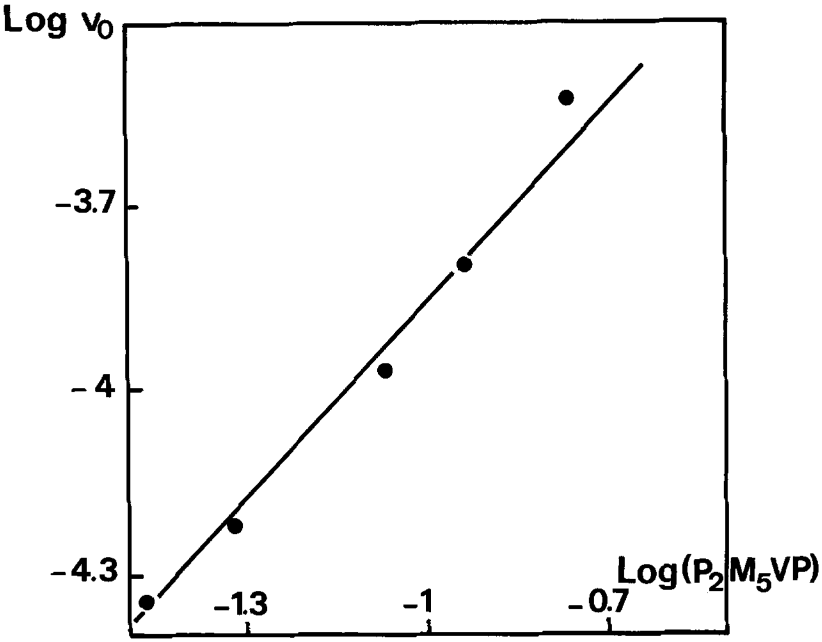


Figure 3. Quaternization in 70/30 TMS/Dioxane mixture at 70°C. Determination of the order with reference to P2M5VP.

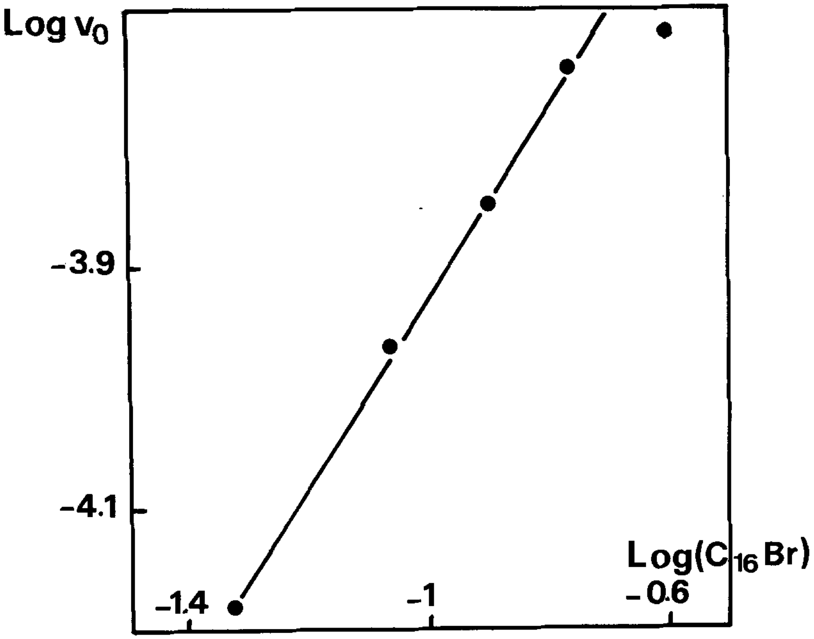
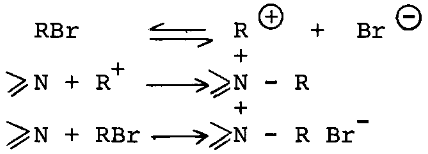


Figure 4. Quaternisation in 70/30 TMS/Dioxane mixture at 70°C. Determination of the order with reference to $C_{16}Br$.

Table 4. Determination of the velocity constant k in the case of quaternization of some pyridil group by $C_{16}Br$ in a 50/50 TMS/Dioxane mixture. Temperature = 70°C.

	2M5EP	4EP	P2M5VP
k $l.mole^{-1}mn^{-1}$	$1.1\ 10^{-3}$	$9.4\ 10^{-3}$	$8.3\ 10^{-4}$

The reactivity of 2MSEP is lower than the reactivity of 4EP probably due to the steric hindrance introduced by the methyl group in ortho position (3) in good agreement with previous results of the literature. Taking into account for the weak reactivity of this system, the fact that the global second order is no more obeyed when the dielectric constant ε increases may suggest the participation of ionic species from the alkyl bromide :



$$RBr \rightleftharpoons R^{\oplus} + Br^{\ominus}$$
$$\geqslant N + R^{+} \longrightarrow \geqslant \overset{+}{N} - R$$
$$\geqslant N + RBr \longrightarrow \geqslant \overset{+}{N} - R\ Br^{-}$$

This assumption leads to the superposition of two mechanisms. The possibility of solvatation of the ionic species is due to the high polarity of the solvent. In the same way, this participation of ionic series could be considered for the quaternization of other pyridine containing polymeric species for which some variations of the velocity constant with the alkyl bromide concentration has been observed (3).

In conclusion it seems that the second global order of this type of reaction which was generally considered as evident can yet be the object of interesting considerations.

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