

Mechanism and Kinetics of Addition of Vinyl Methyl Ketone to Protonated Poly(4 vinyl pyridine)

Taghi Taghizadeh, Claude Caze and Claude Loucheux

Laboratoire de Chimie Macromoléculaire, Université des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq, Cédex, France

Summary

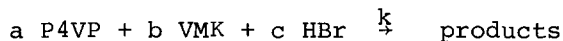
Electrophilic vinyl reagents can be reacted with a protonated tertiary amine supported by a polymeric chain. We determined the mechanism of this addition in the case of vinyl methyl ketone and poly(4 vinyl pyridinium bromide). The first step is the addition of the vinyl compound on the tertiary amine, then protonation of the intermediate species occurs. The velocity constant at 268 K is $0.087 \text{ l.mole}^{-1}.\text{mn}^{-1}$ and the activation energy is $10 \text{ kcal.mole}^{-1}$.

Introduction

It has been shown that a polymeric protonated tertiary amine can add some electrophilic compounds (GHESQUIERE et al. 1975, TAGHIZADEH et al. 1979, 1980, LUCA et al. 1980). In this paper we studied the mechanism and the kinetics of this addition in the particular case of poly(4 vinyl pyridinium bromide) and vinyl methyl ketone (VMK).

Experimental

Poly(4 vinyl pyridine) (P4VP) was prepared by conventional radical polymerization of 4 vinyl pyridine. VMK was a commercial product purified by distillation. The reactions were carried out in methanol and under nitrogen at 268 K. The rate of reaction was studied by following the VMK concentration vs time using a gas chromatography technique (internal standard : toluene). The determination of the reaction order with reference to the initial products was made by the following procedure :



$$v = k [\text{P4VP}]^\alpha [\text{VMK}]^\beta [\text{HBr}]^\gamma$$

if A_0 , B_0 and C_0 represent the initial concentration of P4VP, VMK and HBr respectively and x the concentration of P4VP which reacts at time t we have :

$$v_t = k(A_0 - x)^\alpha (B_0 - \frac{b}{a}x)^\beta (C_0 - \frac{c}{a}x)^\gamma$$

In a set of experiments we kept two concentrations constant when varying the third one. As an example, keeping $A_0 = \text{cte}$ we defined a time corresponding to the same rate v_j in all the set of experiments (This rate is determined by a differential method). If x_j is the concentration corresponding to this rate in each experiment, a plot of $\text{Log } v_j$ vs $\text{Log}(A_0 - x_j)$ should be a straight line the slope of which gives the partial order with reference to A_0 , that is to say α .

Results and discussion

Experimental concentrations used are given in table 1. Figures 1, 2 and 3 reported the determination of α , β and γ , we obtained :

$$\begin{aligned} \alpha &= \beta = 1 \\ \gamma &= 0 \text{ for } \frac{[\text{HBr}]}{[\text{P4VP}]} < 0.5 \\ \gamma &< 0 \text{ for } \frac{[\text{HBr}]}{[\text{P4VP}]} > 0.5 \end{aligned}$$

TABLE 1

Initial concentrations used (mole.l⁻¹)

Set 1	[P4VP] = 0.14				[VMK] = 0.07				
experiment	1	2	3	4	5	6	7	8	9
[HBr]. 10 ³	140,	122,	105,	86,	70,	56,	52,	43,	34
Set 2	[P4VP] = 0.14				[HBr] = 0.07				
experiment	10	11	12	13	14	15	16	17	18
[VMK]. 10 ³	140,	106,	84,	70,	51,	46,	34,	27,	17
Set 3	[VMK] = 0.07				[HBr] = 0.07				
experiment	19	20	21	22	23	24	25		
[P4VP].10 ³	280,	245,	227,	175,	140,	122,	105		

The reaction order with reference to HBr is 0 emphasizes that H⁺ plays its role in a fast step of the reaction. By analogy with MICHAËL addition of VMK (LUFT et al. 1971, LE BERRE et al. 1973) we can propose the following scheme of reaction where H⁺ represents all the species able to give a proton (free H⁺ and protonated tertiary amine).

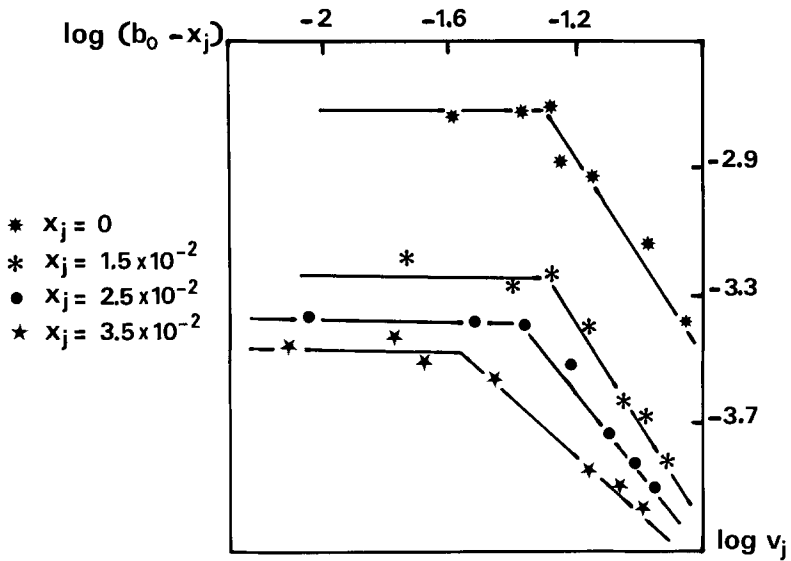


Figure 1

Determination of the order with reference to HBr

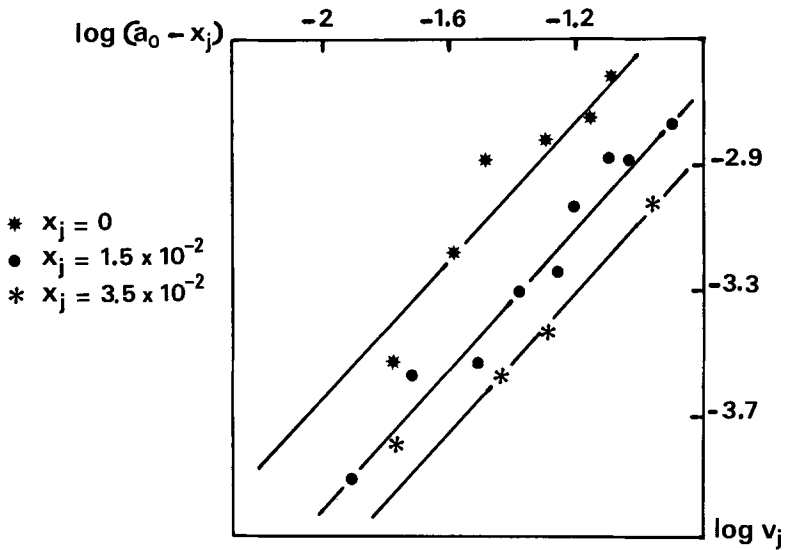


Figure 2

Determination of the order with reference to VMK

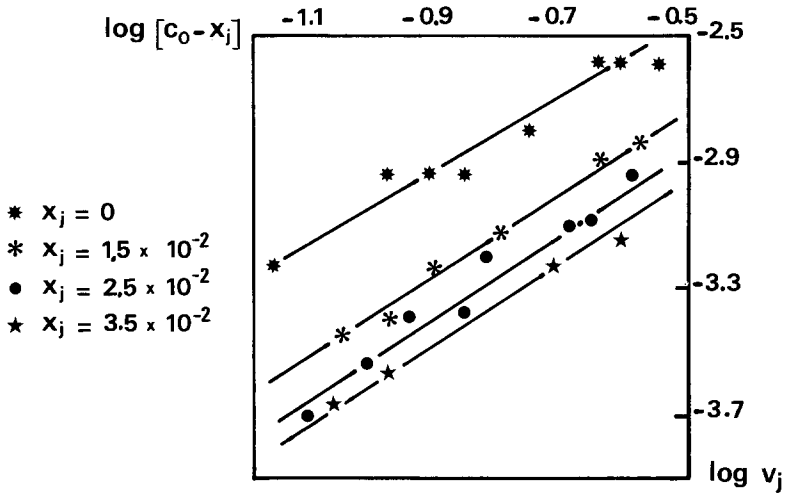


Figure 3

Determination of the order with reference to P4VP

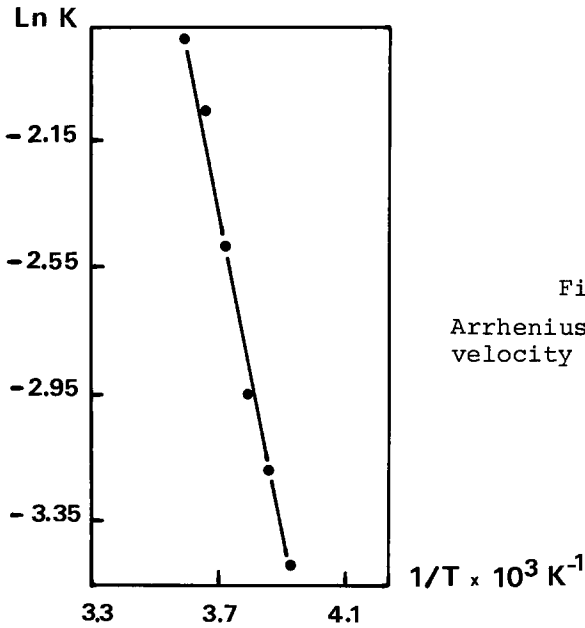
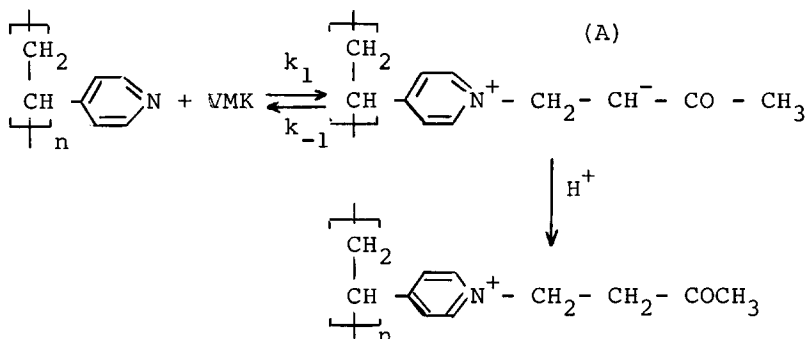


Figure 4

Arrhenius plot of the velocity constant k_1



If steady state conditions can be applied to species (A), we can write :

$$\begin{aligned}
 k_1 [\text{P4VP}] [\text{VMK}] &= k_{-1} [\text{A}] + k_2 [\text{A}] [\text{H}^+] \\
 v &= k_1 [\text{P4VP}] [\text{VMK}] \left(1 - \frac{k_{-1}}{k_{-1} + k_2 [\text{H}^+]} \right)
 \end{aligned}$$

Moreover if we suppose that the rate of protonation of species A is faster than the rate of the retrogradation step : $k_2 \gg k_{-1}$ therefore : $v = k_1 [\text{P4VP}] [\text{VMK}]$ (1) This result is consistent with experimental values of reaction order with reference to P4VP and VMK.

When $[\text{HBr}] / [\text{P4VP}] > 0.5$ each free tertiary amine have statistically two protonated adjacent units.

In these conditions the electrostatic field due to the neighbouring positive charges limits the accessibility to the unreacted pyridine units. Then the velocity of the reaction decreases when increasing $[\text{HBr}]$, explaining the experimental negative value of the reaction order.

Starting from the relation (1) we determined the velocity constant k_1 by assuming second order kinetics :

$$\frac{1}{B_0 - A_0} \ln \frac{A_0 (B_0 - x)}{B_0 (A_0 - x)} = k_1 t \quad (2)$$

if the reaction extent $\tau = \frac{x}{A_0}$ is introduced Eq (2) becomes :

$$\frac{1}{B_0 - A_0} \ln \frac{1 - \tau/B_0}{1 - \tau} = F(\tau) = k_1 t \quad (3)$$

$F(\tau)$ should be a linear function of time and the slope should give k_1 .

The results are reported in table 2.

TABLE 2

Determination of the velocity constant k_1 ($\text{l.mole}^{-1}\text{mn}^{-1}$)

experiment	5	6	7	8	9	10	11	12			
$10^3 k_1$	83	84	99	86	83	80	105	71			
experiment	13	14	15	16	17	18	19	20	21	22	23
$10^3 k_1$	82	104	80	111	80	124	89	73	86	85	83
experiment	24	25									
$10^3 k_1$	69	74									

we obtained : $k_1 = 87.10^{-3} \text{ l.mole}^{-1}\text{mn}^{-1}$ at 268 K.

The activation energy was determined from the variation of the velocity constant vs temperature. The results are reported in table 3 since the figure 4 shows the variation of $\text{Ln } K$ vs $1/T$.

We obtained $E = 10 \text{ kcal.mole}^{-1}$.

TABLE 3

Variation of the velocity constant vs temperature

$$[\text{P4VP}] = 0.14 \text{ mole.l}^{-1} \quad [\text{HBr}] = 0.07 \text{ mole.l}^{-1}$$

$$[\text{VMK}] = 0.07 \text{ mole.l}^{-1}$$

T K	254	258	263	268	273	278
$10^3 k_1$	30	41	52	87	128	158

As a conclusion, the great velocity constant measured is the result of the good electrophilic character of CO-CH_3 group of vinyl methyl ketone. This is a good example of a polymer analogous reaction.

References

- GHEsqUIERE, D., CAZE, C. and LOUCHEUX, C. : Polymer 16, 94 (1975)
 LE BERRE, A., and DELACROIX, A. : Bull. Soc. Chim. 2, 460 (1973)
 LUCA, C., BARBOIU, V., PETRARIU, I. and DIMA, M. : J. Polym. Sci. 18, 2347 (1980)

LUFT, B., DELATTE, S. and ARNAUDU, JF. : Bull. Soc. Chim. 1317 (1971)
TAGHIZADEH, T., CAZE, C. and LOUCHEUX, C. : IUPAC Symposium on macromolecular chemistry MAINZ (1979)
TAGHIZADEH, T., CAZE, C. and LOUCHEUX, C. : Polymer Bull. 3, 593 (1980).

Received March 9, 1981

Accepted March 13, 1981