Unusual Behavior of 2- and 4-Vinyl Pyridines in Polymerization Processes Initiated by Tris-π Allyl Chromium

L. A. Fedorova[a]; A. V. Yakimansky[a]; B. L. Erussalimsky[a]

[a] Institute of Macromolecular Compounds of the Russian Academy of Sciences, St. Petersburg, Russia

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UNUSUAL BEHAVIOR OF 2- AND 4-VINYL PYRIDINES IN POLYMERIZATION PROCESSES INITIATED BY TRIS-π ALLYL CHROMIUM

L.A.FEDOROVA, A.V.Yakimansky & B.L.Erussalimsky

Institute of Macromolecular Compounds of the Russian Academy of Sciences, Bolshoi Prospect 31 199004 St.Petersburg, Russia

ABSTRACT

In contrast to the data related to the BuLi–vinyl pyridine systems, 4–vinyl pyridine is distinguished by much greater activity as compared with 2–vinyl pyridine in the polymerization induced by tris–π-allyl chromium. The experimental results illustrating this difference are considered using the quantum chemical approach.

INTRODUCTION

The most data related to the anionic polymerization of 2- and 4- vinyl pyridine (2- and 4-VP) concern the difference in the microtacticity of the polymers formed[1]. The information on the kinetics of these processes is too scarce for drawing good substantiated conclusions about the relative activity of the

monomers in question. The only data which can be used for this aim are the overall effects characteristic of the polymerization of these monomers under identic conditions; they are given in Table 1.

It seems to be possible that the difference reflected by these results is caused by the lower ionization potential (IP) of 2-VP as compared with that of 4-VP. The IP values of the monomers under consideration calculated by the quantum chemical MNDO method were found to be 9.07 and 9.93 eV, respectively[3].

This difference in the IP values suggests the enhanced effectivity of the donor-acceptor interaction of 2-VP in the stage of formation of intermediate AS·M complexes, where AS is the active site (initiator or growing chain) and M is the monomer. The formation of these complexes is typical for the anionic polymerization of polar monomers[4].

Nevertheless, the difference in the IP values seems to be of no importance for the polymerization of the same monomers initiated by tris-π-allyl chromium (TPC). In this case a much higher activity of 4-VP in comparison with 2-VP was observed. This phenomenon and an attempt of its interpretation form the content of the present work.

MATERIALS

Purification of the monomers and solvents and the preparation of TPC are described in Refs.[5,6].

METHODS

Interaction of the monomers with TPC was carried out in toluene and THF. Reaction mixtures were deactivated with toluene acidified with HCl. Intrin-

TABLE 1

Polymerization of 2- and 4-VP by n-BuLi in toluene[2].
Temperature -20°C
Concentration, mole/l: monomer 0.6, BuLi 0.007

Monomer	Time needed for complete conversion of the monomer	$M_\eta \cdot 10^{-4}$
2-VP	2 min	5.0
4-VP	10 min	2.4

sic viscosity of poly-2-VP was measured in dimethyl formamide, of poly-4-VP in C_2H_5OH; in both cases at 25°C. The M_η-values were calculated according to the formulae $[\eta] = 1.47 \cdot 10^{-4} \cdot \bar{M}^{0.67}$ (for P-2-VP[7]) and $[\eta] = 1.2 \cdot 10^{-4} \cdot \bar{M}^{0.73}$ (for P-4-VP[8]).

For the quantum chemical calculations the MNDO method[9] was used. The geometry of the systems was completely optimized according to[10]. AMPAC program[11] was employed for carrying out the calculations.

RESULTS

The experimental data obtained are given in Table 2.

These results can be claimed to be caused by the structural specificity of the primary products formed during the interaction of the monomers with TPC. According to Refs.[12,13], the interaction under consideration corresponds to scheme (1), given for 2-VP as example; here All is the allyl group and cr is the equivalent of the Cr atom:
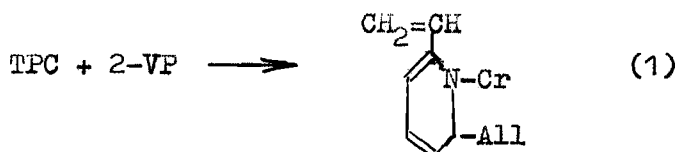
TABLE 2

Polymerization of 2- and 4-VP by TPC

Concentration, mole/l: VP 1.0,

TPC 0.007

Monomer	SOLVENT	Time	Conversion, %	$M_\eta \cdot 10^{-4}$	
2-VP	Toluene	2 h	6	0.4	13.4
	THF		7	0.4	
4-VP	Toluene	2 min	100	*)	
	THF		100	1.4**)	27.0

*) The polymer was insoluble

**) Data related to the soluble fraction; its content in the polymer was 50%

$$\text{TPC + 2-VP} \longrightarrow \quad \begin{matrix} CH_2=CH \\ \bigcirc N-Cr \\ -All \end{matrix} \qquad (1)$$

As was shown in the cited works, this reaction corresponds to the 2M/TPC stoichiometry; one of the All-groups remains bound with Cr. Because of it the following structures of the adducts in question are suggested (here Vin is the vinyl group):

Vin   All   Vin   All
  \ | / |
   N-Cr-N   Vin—   N-Cr-N   —Vin
  /   \   /   \
All   All   All   All

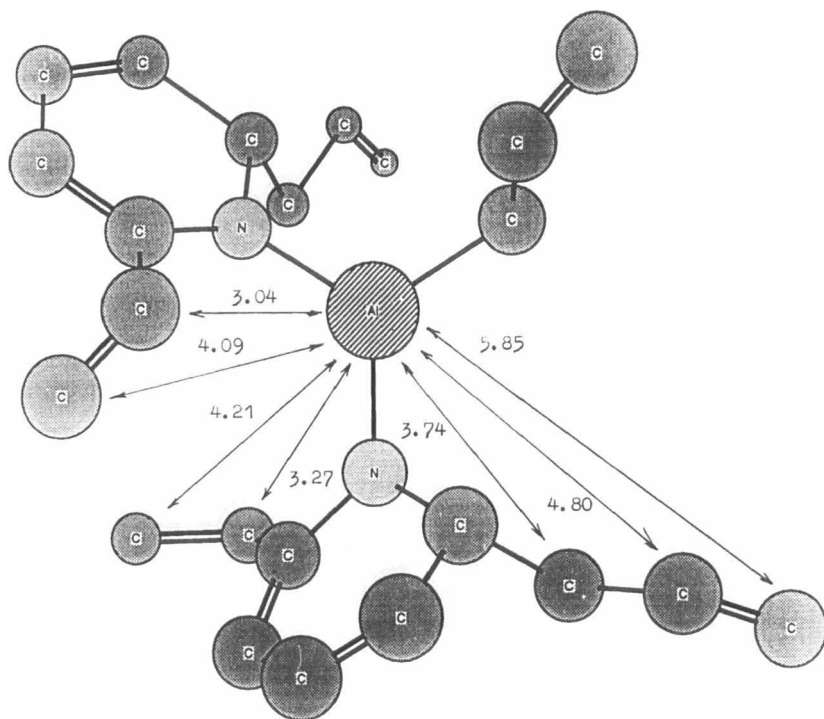   I   II
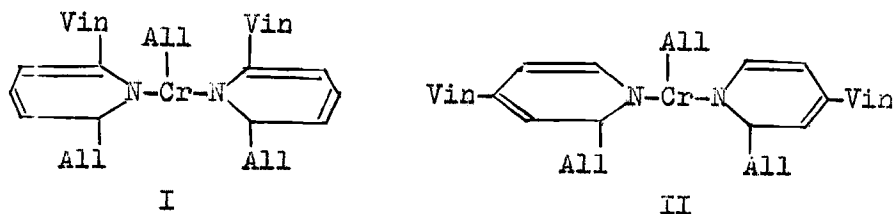
Fig.1. Optimized geometry of compound A. Distances are given in Å. H atoms are ommited.

As the Cr-All bonds do not participate in the initiation of VP-polymerization[14], the spatial accessibility of the Cr-N bonds can be responsible for the sharp difference in the reactivity of 2- and 4-VP. The comparison of the structures I and II illustrates the greater accessibility of the active bonds in the 4-VP case.

For an attempt to support this qualitative suggestion by quantitative estimation we turned to the
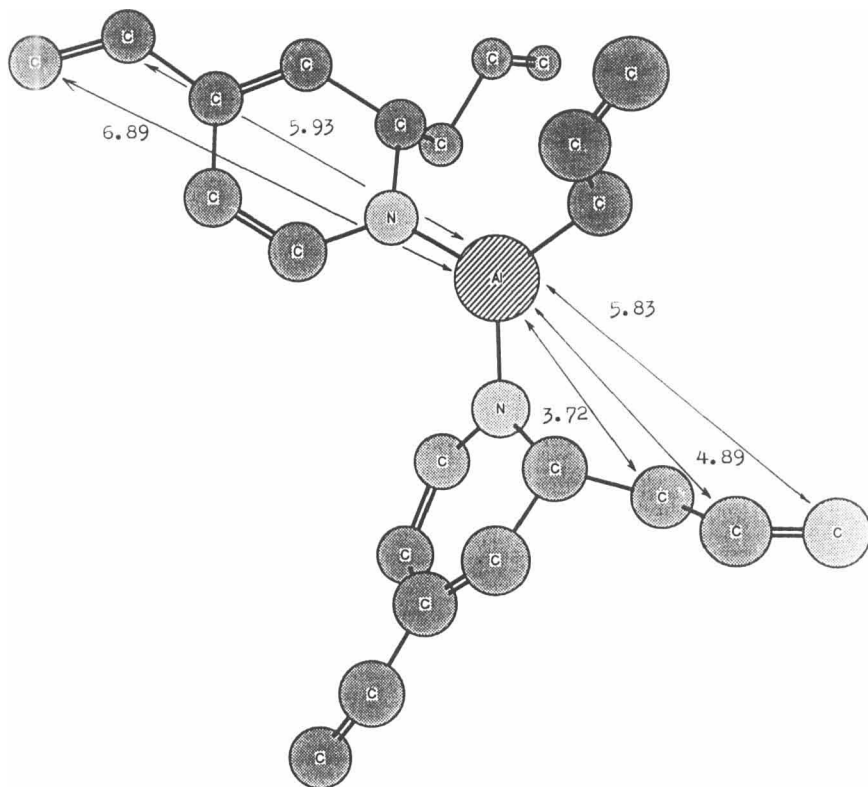
Fig.2. Optimized geometry of compound B. Distances are given in $\overset{\bullet}{\text{A}}$. H atoms are omnited.

quantum chemical approach. For this aim we were com-
pelled to choose some simplified models simulating
the structures I and II. It should be stressed that
in most quantum chemical investigations related to
the anionic polymerization various model systems
instead of the real objects were used[15].

From the general point of view the conclusions ba-
sed on the calculations of simplified models can be
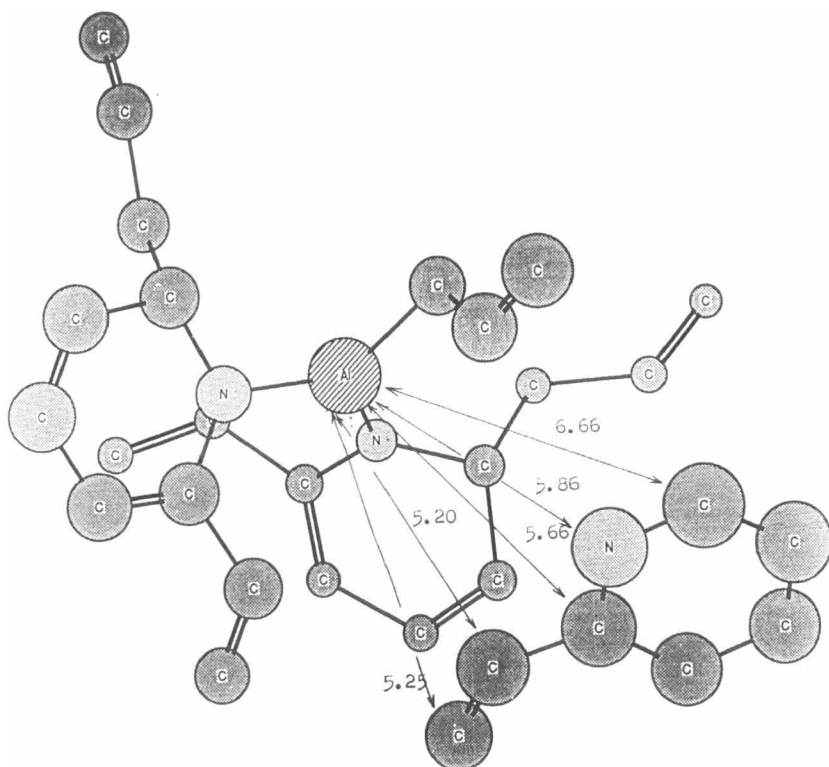
**Fig.3. Optimized geometry of intermediate complex A·2-VP.
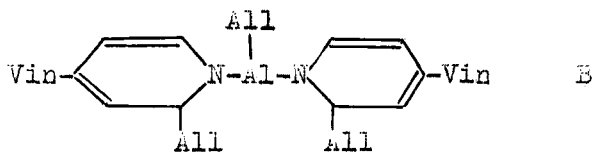Distances are given in Å. H atoms are ommited.**

considered as correct if the models chosen adequa-
tely correspond to the problem to be solved. As
emphasized above, in our case the structural speci-
ficity of the primary AS is the main (perhaps even
the only) important factor. This situation permits
us to simulate the structures I and II using the
analogues aluminium derivatives, i.e. the struct-
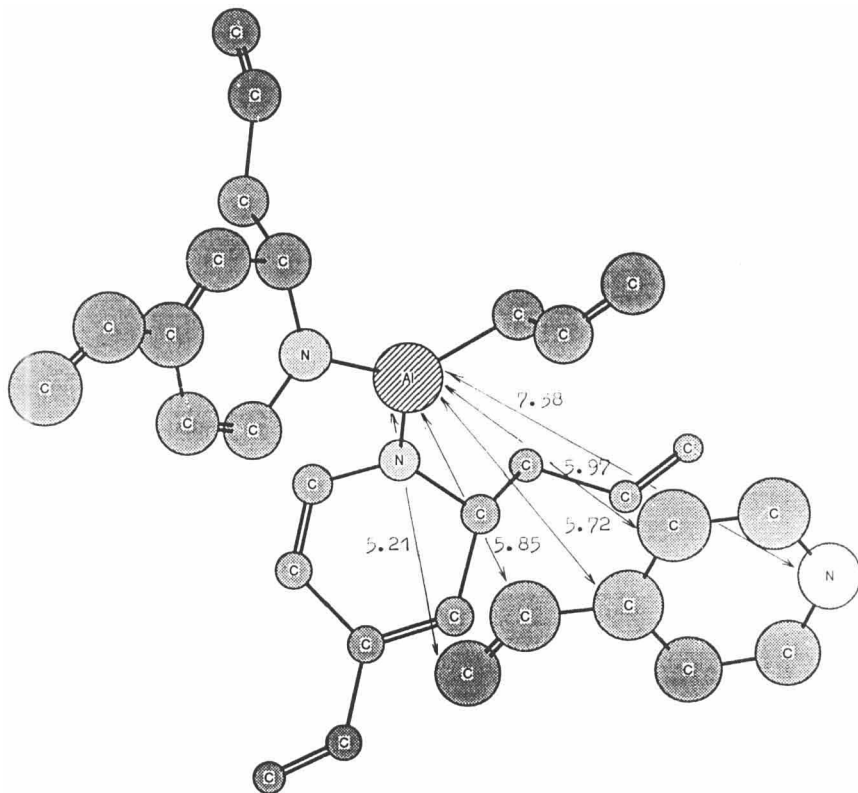
Fig. 4. Optimized geometry of intermediate complex B ·4—VP.
Distances are given in Å. H atoms are omitted.

u res A and B:
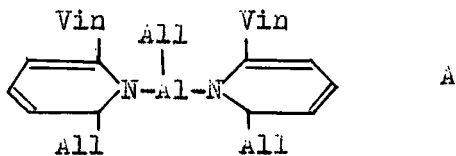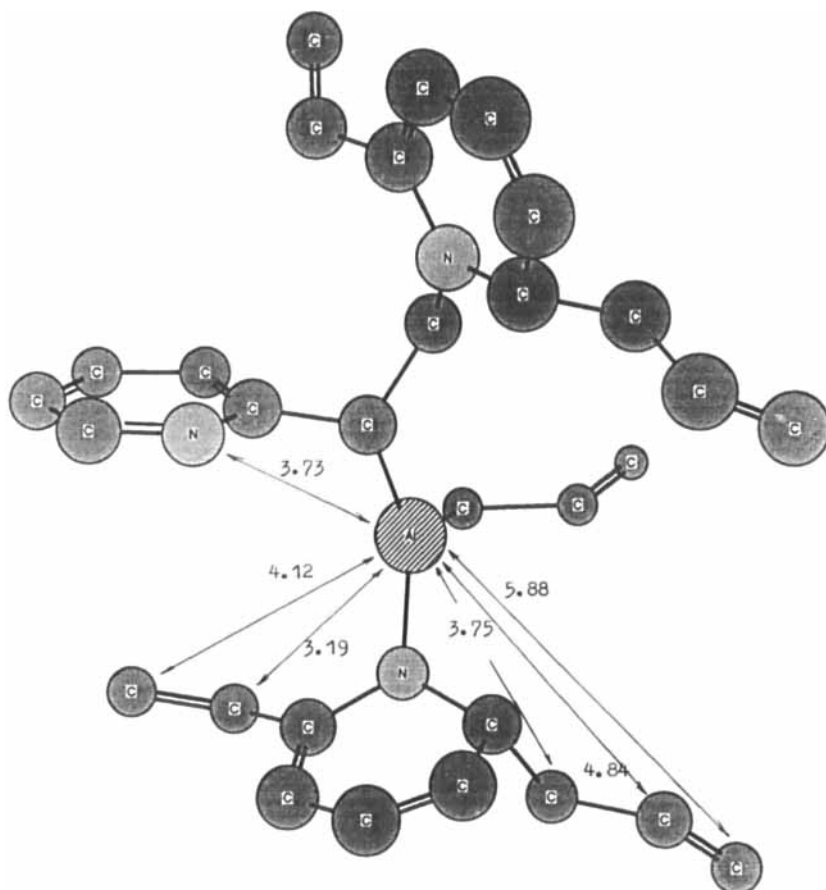
Fig. 5. Optimized geometry of adduct **B.** Distances are given in Å. H atoms are ommited.

The necessity of this simplification is due to the inability of the MNDO approach to deal with systems containing transition metals, and to the impossibility to use ab initio methods for such large systems as I and II.

Using the structures A and B as initial AS we have calculated the intermediate complexes (IC)
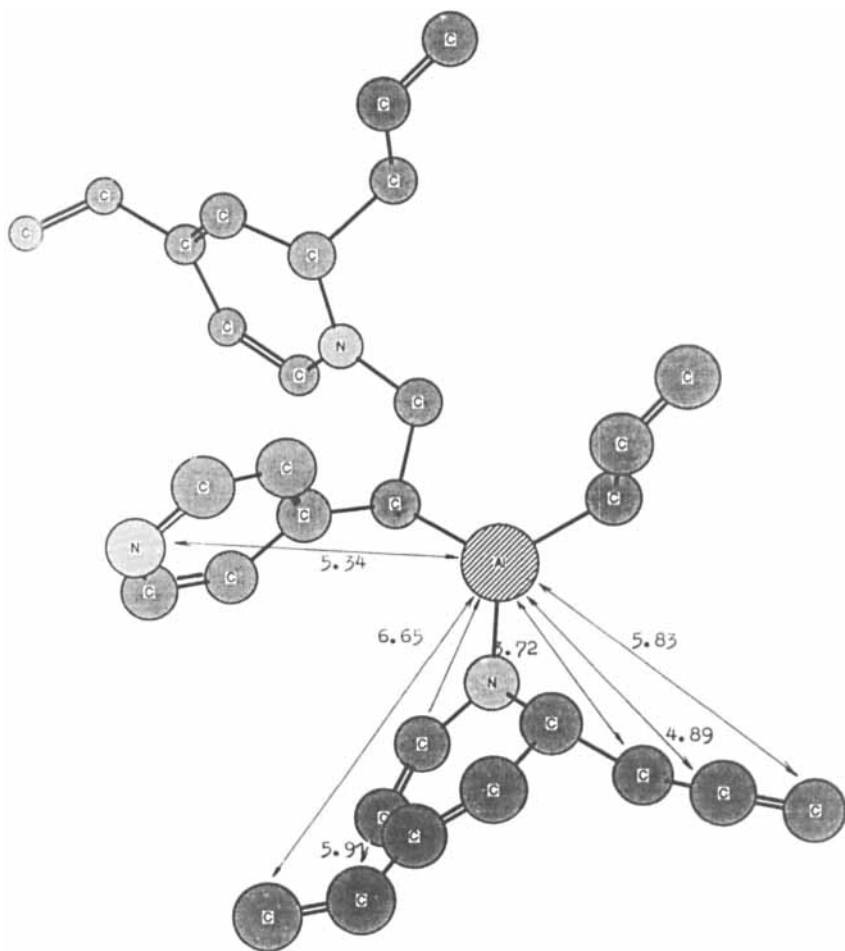
Fig. 6. Optimized geometry of adduct F. Distances are given in Å. H atoms are ommited.

TABLE 3

ΔH_f values calculated for 2- and 4-VP, active sites
A and B, complexes C and D, and adducts E and F

2-VP systems	Monomer	AS (A)	IC (C)	Adduct(E)
ΔH_f, kJ/mole	184.50	504.65	722.72	764.73

4-VP systems	Monomer	AS (B)	IC (D)	Adduct(F)
ΔH_f, kJ/mole	193.37	468.54	668.21	700.86

A·2-VP (C), B·4-VP (D) and the corresponding adducts A-2-VP (E) and B-4-VP (F). The optimized structures of these systems reflect Fig. 1-6.

Taking into account the differencies in electronic structure of Cr- and Al-derivatives, we did not consider electronic distribution characteristic of compounds studied and restricted ourselves with consideration of the ΔH_f values (heats of formation) of these compounds. They are given in Table 3.

These results permit to calculate the energy parameters related to formation of IC (E^{IC}) and adducts AS + M (E^{add}). They were found by the use of the following equations:

$$E^{IC} = \Delta H_f^{IC} - (\Delta H_f^{M} + \Delta H_f^{AS})$$
$$E^{add} = \Delta H_f^{add} - (\Delta H_f^{M} + \Delta H_f^{AS})$$

By this way the differencies between the above values characteristic of 2- and 4-VP were calculated:

$$E^{IC}_{2-VP} - E^{IC}_{4-VP} = 27.27 \text{ kJ/mole}$$
$$E^{add}_{2-VP} - E^{add}_{4-VP} = 36.63 \text{ kJ/mole}$$

As we see, both the complexation of AS with M and the
formation of adducts AS-M is more preferable for 4-VP.

The reactions of AS-M adducts formation are rather
endothermic in both cases (E_{2-VP}^{add} = 75.58 kJ/mole and
E_{4-VP}^{add} = 38.95 kJ/mole). However, the reaction of IC
formation is still quite endothermic for 2-VP (E_{2-VP}^{IC}
= 33.57 kJ/mole) and almost thermoneutral for 4-VP
(E_{4-VP}^{IC} = 6.30 kJ/mole). These results support our
suggestion formulated in the beginning of this section.

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