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Reactivity of 6-Methyl and 4,7-Dimethyl Indene in Cationic Polymerization

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SUMMARY

The reactivity ratios of 6-methyl and 4,7-dimethyl indene were determined with respect to styrene, at various temperatures, and the relative activation parameters calculated and discussed.

INTRODUCTION

Previous studies relative to the cationic polymerization of 6-methyl indene and 4,7-dimethyl indene have already been published [MARECHAL et al. (1969)], [CAILLAUD et al. (1970)]. The reactivity ratios of these two monomers were determined with respect to indene [CAILLAUD et al. (1970)], [EVRARD (1969)] : it appeared that the methyl groups increase drastically the reactivity of indene molecule.

In this work, the reactivities are determined with respect to styrene (which is the most commonly used reference monomer in cationic polymerization). The activation parameters relative to these reactivity ratios are determined and their values are compared to the theoretical reactivity indexes resulting from quantum chemistry calculations.

EXPERIMENTAL

Monomers

6-methyl indene and 4,7-dimethyl indene were prepared and

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purified by the methods already described by CAILLAUD (1970) and MARECHAL (1969).

Solvent

Methylene dichloride was purified according to N'GUYEN ANH HUNG (1970).

Initiator

Commercial titanium tetrachloride was freshly distilled before preparing the solutions in CH_2Cl_2.

Copolymerization

The copolymerization were carried out in a conic reactor fitted with a mechanical stirrer and a dry deoxygenated nitrogen inlet. When the solution of monomer has been cooled until proper temperature, initiator is added. The copolymers were analyzed by infrared spectroscopy, using a polystyrene vibration, at 700 cm^{-1}. From this analysis, the reactivity ratios were determined by both intersection and KELEN-TÜDOS (1975) methods.

RESULTS AND DISCUSSION

Determination of reactivity ratios

In the following, index 1 is related to methyl indenes, and index 2 to styrene. All the copolymerizations were carried out in methylene dichloride, under the same conditions : $\left[TiCl_4\right] = 10^{-2}$ mole x liter^{-1} ; $\left[M\right] = \left[Styrene\right] + \left[Indene\right] =$ 0.2 mole x liter^{-1} ; temperature : 4 values between - 75°C and + 20°C.

The variations of r_1 and r_2 with respect to the temperature for 6-methyl and 4,7-dimethyl indene are given in table I. The difference between the values obtained by "intersection" and "Kelen-Tüdos" methods were never above 5 %. Thus, due to the very high values of r_1, Kelen-Tüdos method was by far more easy to handle.

TABLE I : values of r_1 (methyl indenes) and r_2 (styrene) at various temperatures.

0°C	$\frac{1}{T} \times 10^3$	6-methyl indene		4,7-dimethyl indene	
		r_1	r_2	r_1	r_2
-75	5.05	8.7	0.1	4.8	0.2
-35	4.20	18.6	0.1	10.0	0.09
0	3.66	30.6	0.07	13.6	0.05
+20	3.41	35.0	0.05	15.9	0.07

Determination of activation enthalpy and entropy differences

Let $k^{\neq}_{ij}$, $\Delta S^{\neq}_{ij}$ and $\Delta H^{\neq}_{ij}$ be the rate constant, the activation entropy, and the activation enthalpy related to the reaction of the cation i with the monomer j. According to Arrhenius and to the definition $r_{ij} = k_{ii} / k_{ij}$

$$r_{ij} = \left[\exp\ (\Delta S^{\neq}_{ii} - \Delta S^{\neq}_{ij}) / R\right]\ \{\exp -(\Delta H^{\neq}_{ii} - \Delta H^{\neq}_{ij}) / RT\} \qquad (1)$$

where T is the polymerization temperature (°K).

From relation (1), it results that the plot of log r_{ij} against 1/T is a straight line whose slope is $-(\Delta H^{\neq}_{ii} - \Delta H^{\neq}_{ij}) / R$ and intercept $(\Delta S^{\neq}_{ii} - \Delta S^{\neq}_{ij}) / R$.

The variations of log r_1 and log r_2 versus $10^3/T$ for 6-methyl indene and 4,7-dimethyl indene are plotted in figures 1 and 2.

The values of $\Delta H^{\neq}_{ii} - \Delta H^{\neq}_{ij}$ and $\Delta S^{\neq}_{ii} - \Delta S^{\neq}_{ij}$ are reported in table II.

TABLE II : Activation enthalpies and entropies relative to the cationic copolymerization of 6-methyl and 4,7-dimethyl indene(index 1) with styrene (index 2).

	6-methyl indene	4,7-dimethyl indene
$\Delta H^{\neq}_{11} - \Delta H^{\neq}_{12}$ (Kcal.mole^{-1})	1.75	1.5
$\Delta H^{\neq}_{22} - \Delta H^{\neq}_{21}$ (Kcal.mole^{-1})	-0.9	-2.1
$\Delta S^{\neq}_{11} - \Delta S^{\neq}_{12}$ (cal.mole^{-1}K^{-1})	13	10.7
$\Delta S^{\neq}_{22} - \Delta S^{\neq}_{21}$ (cal.mole^{-1}K^{-1})	-8.8	-9

From the values of $\Delta H^{\neq}_{ii} - \Delta H^{\neq}_{ij}$ and $\Delta S^{\neq}_{ii} - \Delta S^{\neq}_{ij}$, the following relationships between $1/r_2$ and the absolute temperature were obtained :

6-methyl indene : $1/r_2 = 81.4 \exp(-450/T)$ (2)

4,7-dimethyl indene : $1/r_2 = 90.0 \exp(-1050/T)$ (3)

The $1/r_2$ values, reported in table I give the experimental reactivity of each monomer towards polystyryl cation (the reactivity of styrene towards its own cation being equal to 1). From these values and from the comparison of equations (2) and (3), the following classifications were obtained :

From experimental reactivity :

6-methyl indene ≃ 4,7-dimethyl indene >> styrene (4)

From preexponential term (entropic contribution to the reactivity) :

6-methyl indene ≃ 4,7-dimethyl indene >> styrene (5)

From exponential term (enthalpic contribution to the reactivity) :

styrene > 6-methyl indene > 4,7-dimethyl indene (6)

Comparison of relations (4), (5) and (6) shows an entropic control of the selection between the two monomers by the carbocation, in the range -75°C to +20°C ; this phenomenon is the most commonly observed in cationic polymerization.

Stabilization energy was then calculated, according to the new method described by BUNEL (1980) for cationic polymerization of some vinyl aromatic monomers. This method gave the three values we reported in table III, with the classic $\Delta E_{r,s}$ values calculated by MARECHAL (1969) and the superdelocalizabilities S_r on the reactive carbon of the monomer.

Table III : Stabilization energy calculated by BUNEL's method ($\Delta E_{\alpha,\beta}$), $\Delta E_{r,s}$ and S_r for styrene, 6-methyl indene and 4,7-dimethyl indene.

	Styrene	6-methyl indene	4,7-dimethyl indene
$\Delta E_{\alpha,\beta}$	2.4570	2.4468	2.4412
$\Delta E_{r,s}$	0.807	0.920	0.926
S_r	1.266	1.303	1.301

$\Delta E_{r,s}$ values do not fit ($\Delta H^{\neq}_{22} - \Delta H^{\neq}_{21}$) classification, while $\Delta E_{\alpha,\beta}$ shows a good agreement with the enthalpic terms obtained from our experiments.

The comparison of the Sr values give for the three monomers the following order :

6-methyl indene ≃ 4,7-dimethyl indene >> styrene (7)

This classification is absolutely identical to that obtained from the $1/r_2$ values (classification 4).

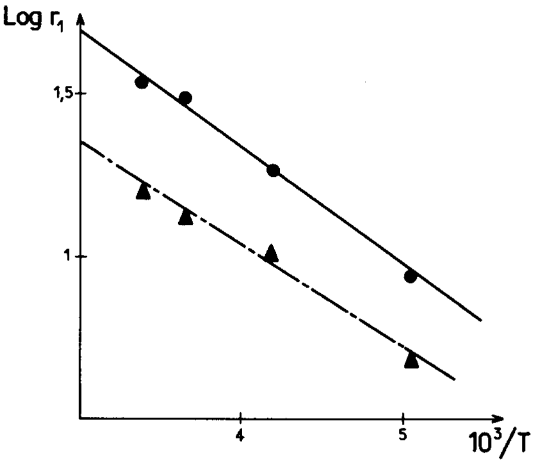

Fig. 1 : Variations of log r_1 with respect to 1/T (K) : (▲ — · —) 4,7-dimethyl indene ; (● —) 6-methyl indene.

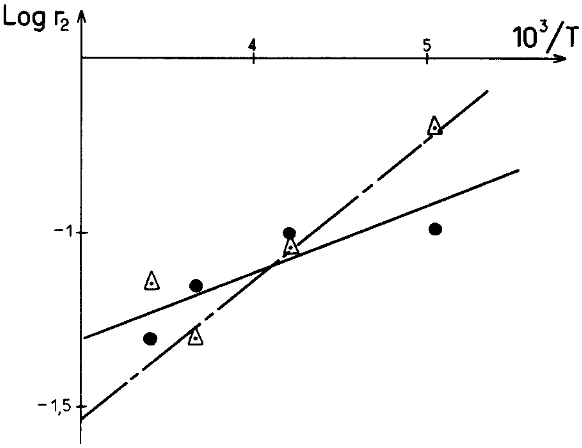

Fig. 2 : Variations of log r_2 with respect to 1/T (K) : (Δ — · —) 4,7-dimethyl indene ; (● —) 6-methyl indene.

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