CHEMISTRY LETTERS, pp. 1007-1010, 1973. Published by the Chemical Society of Japan

POLYMERIZATION OF CYCLOPENTADIENE BY ACETYL PERCHLORATE*

Shinzo KOHJIYA and Shinzo YAMASHITA

Department of Chemistry, Kyoto Institute of Technology,
Matsugasaki, Sakyo-ku, Kyoto 606

Cationic polymerization of cyclopentadiene was carried out by acetyl perchlorate. The obtained value of the propagation rate constant for this system is equal to that of perchloric acid, which agrees well with the identity of counter ions (perchlorate anion) for both systems.

We reported the kinetic features for the polymerization of cyclopentadiene (CPD) with perchloric acid.1) The values of propagation rate constant(k_p) were evaluated either in toluene or in methylene chloride, and these values were much smaller than that of CPD-$TiCl_4 \cdot CCl_3COOH$-toluene system.2)

We now describe the polymerization of CPD by acetyl perchlorate, since this catalyst has the same anionic moiety as that of perchloric acid, which would mean that both initiators induce the same propagation reaction.

Experimental

CPD and perchloric acid were synthesized and purified as reported previously.1) Toluene and methylene chloride were purified as usual, and acetyl perchlorate was synthesized by the reaction of silver perchlorate with acetyl chloride and the concentration was spectroscopically determined according to the method of Masuda.3) The concentrated initiator solution in methylene chloride was stored in a refrigerator, and was diluted on each time. The period of storage was kept not exceeding a month. The solution of acetyl perchlorate in toluene seemed not to be stable, therefore to be of limited storage life. All the manipulations were performed in a dry-box under a dry nitrogen atmosphere. Polymerizations (monomer concentration; 10 vol.%) were carried out in a binary mixture of toluene (76 vol.%) and methylene chloride (14 vol.%) because the rate of polymerization in methylene chloride was too large to be accurately traced by the present technique.

---

[*] Part III of a series of papers concerned with propagation rate constant in cationic polymerization of cyclic dienes. For the previous paper in this series, see reference 1).

Results and Discussion

Figure 1 shows the polymerization time course of CPD by acetyl perchlorate. At an initial stage the rate was extremely large but immediately the polymerization was terminated, though the monomer available for propagation existed still. Duplicate polymerizations under the same conditions (○ and ●) demonstrate the reproducibility of the present work. The good reproducibility justifies the following kinetic treatment. The relationship between the asymptotic yield (Y_∞) and the initiator concentration (C_o) is depicted in Figure 2. Y_∞ increased monotonously with increasing C_o. These kinetic behaviours were best explained by the non-stationary kinetics by Pepper$^{4)}$ as was already indicated.$^{1),2)}$ The equations derived by Pepper were as follows;

$$\ln\left(\frac{1}{1-Y_\infty}\right) = \frac{k_p}{k_t}\cdot C_o \qquad (1)$$

$$\ln\left(\frac{1}{1-Y_\infty}\right) = \frac{k_p}{k_t}\cdot C_o(\,1 - e^{-k_t\cdot t}) \qquad (2)$$

where Y_t means the yield at time t. Rate constants k_p and k_t were evaluated as shown in Table 1 and calculated curves were plotted in Figures 1 and 2.

Table 1. Propagation and Termination Rate Constants

Monomer	Initiator	Polymerization Solvent	Polymerization Temp. (°C)	k_p (l/mol sec)	k_t (sec^{-1})	References
CPD	CH_3COClO_4	Tol.-CH_2Cl_2 ^{a}	-78	0.99	0.0052	This work
"	$HClO_4$	"	"	0.93	0.0063	"
"	"	CH_2Cl_2	"	6.7	0.057	1
"	"	Tol.	"	0.83	0.0080	1
"	$TiCl_4\cdot TCA^b$	"	-75	350	0.11	2
Styrene	H_2SO_4	$(CH_2Cl)_2$	25	7.6	0.0067	4
"	$HClO_4$	CH_2Cl_2	30	17.0	———	5

a. Toluene (76 vol.%), Methylene Chloride (14 vol.%), Monomer (10 vol.%)
b. Trichloroacetic Acid.

The k_p values of acetyl perchlorate system and of perchloric acid system coincide well within experimental errors, which confirms the expectation that both initiators induce essentially the same propagation reaction since they have common anionic moieties. The present k_p for a binary mixture of toluene and methylene chloride reasonably furnishes the intermediate value between that for

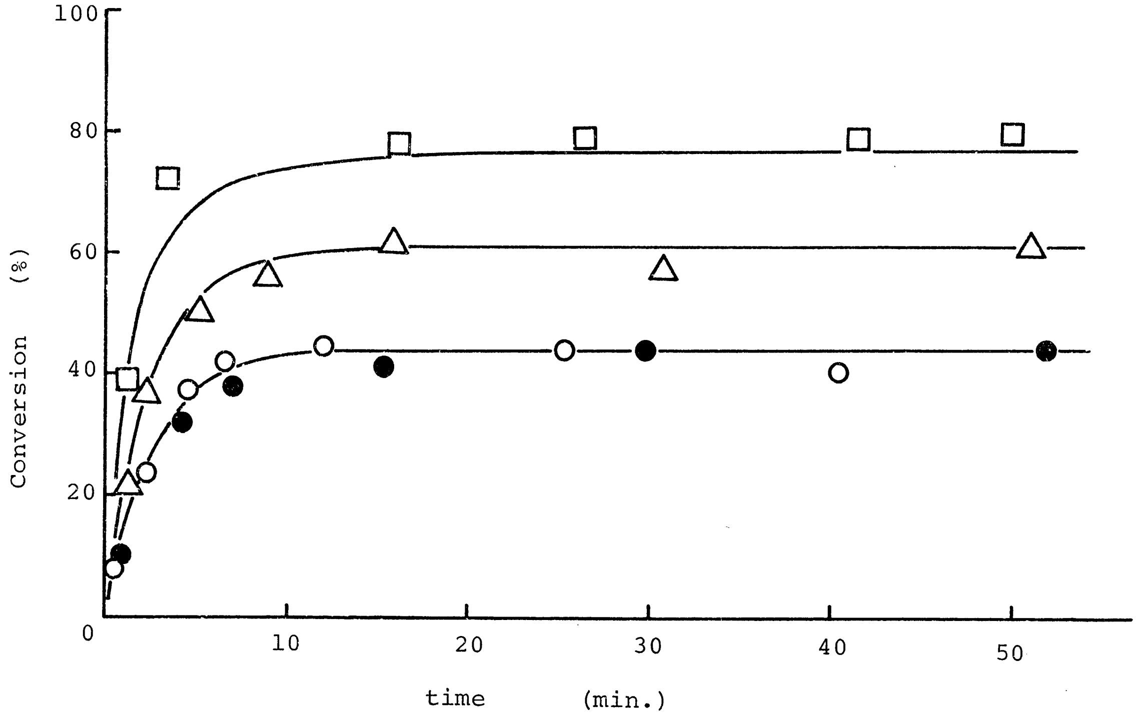

Fig. 1 Conversion-Time Curves for the Polymerization of CPD with Acetyl Perchlorate. Temp.: -78°C, M_o = 1.3 mole/l, C_o : ○ 3.0 ● 3.0 △ 4.9 □ 7.3 m mole/l

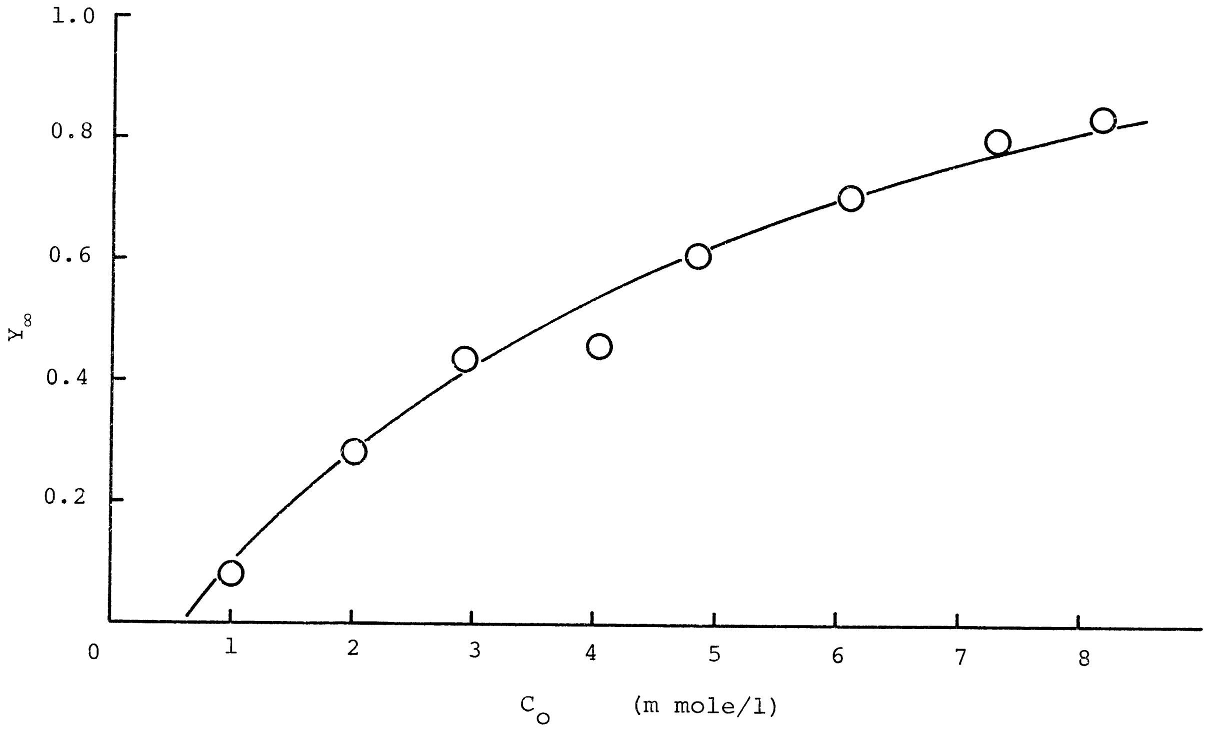

Fig. 2 Relationship between Y_∞ and C_o for the Polymerization of CPD with Acetyl Perchlorate. Temp. : -78°C, M_o = 1.3 mole/l

toluene and that for methylene chloride. The numerical values of the present work clearly show that the obtained values are the propagation rate constant of the ion pair, since it is known that a free ion or a triple ion is much more reactive than an ion pair, hence much larger k_p value (at least a hundred times larger) in anionic polymerization,6) and that the free cationic polymerization of CPD by radiation gave the k_p value of 5.8×10^8 l/mole sec.7) However, the nature of active species has not been elucidated chemically or spectroscopically in the field of cationic polymerization, and the above discussion is not a conclusive one.

It is interesting that k_p of CPD-$HClO_4$ system is smaller than that of CPD-$TiCl_4$·TCA system or of styrene-$HClO_4$ system. This may be interpreted as the distance between a carbonium ion and a gegen anion is smaller in CPD-$HClO_4$ system.

The authors gratefully acknowledge the experimental work by Mr. A. Terada.

References

1) S. Kohjiya, A. Terada, and S. Yamashita, Chemistry Lett., 1972,671 .
2) S. Kohjiya, Y. Imanishi, and T. Higashimura, J. Polymer Sci., Part A-1,9, 747 (1971).
3) T. Masuda and T. Higashimura, J. Polymer Sci., Part A-1, 9, 1563 (1971).
4) R. E. Burton and D. C. Pepper, Proc. Roy. Soc., A263, 58 (1961); M. J. Hayes and D. C. Pepper, Proc. Roy. Soc., A263, 63 (1961).
5) D. C. Pepper and P. J. Reilly, Proc. Roy. Soc., A291, 41 (1966).
6) M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Process", Interscience, New York, 1968.
7) M. A. Bonin, W. R. Busler, and Ff. Williams, J. Am. Chem. Soc., 87, 199 (1965).

(Received June 22, 1973)