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The Thermal Dimerization and Polymerization of 1,3-Cyclohexadiene

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Summary

The thermal polymerization of 1,3-cyclohexadiene to produce dimer and low molecular weight polymer is reported. The reaction initiated thermally and/or by benzoyl peroxide is kinetically of the second order, and the activation energy is 13.1 kcal/mole. The activation energy for the reaction is in quantitative agreement with that of the homopolymerization of 1,3-cyclohexadiene estimated from the kinetic study on the copolymerization with acrylonitrile. Evidently the dimerization process to give dimer as a product of typical Diels-Alder condensation is a competing type of reaction with radical polymerization to give a low molecular weight polymer. The ratio of the rate constant for two competing types of reaction at 200°C is found to be 1.21. The thermal polymerization in the presence of oxygen produces dimer in greater yield as a result of inhibition of the radical polymerization process.

In 1925, Hofmann and Damm (1) first reported that the thermal polymerization of 1,3-cyclohexadiene (1,3-CHD) gave dimer and low molecular weight polymer. Recently, several papers (2–4) showed that competing reactions of dimerization and polymerization occurred in the thermal and/or benzoyl peroxide-initiated reaction of 1,3-CHD. Shantarovich and Shlyapnikova (2,3) studied this reaction kinetically and reported that the dimerization reaction proceeds by the typical Diels-Alder condensation process. The relative ratio of these two reactions depends only on the temperature of reaction.

It is generally believed that the propagation process of thermal polymerization proceeds through a monoradical intermediate. For

the mechanism of typical Diels-Alder condensation, three types of transition states are discussed in detail: (1) the open-chain polar mechanism, (2) the open-chain diradical mechanism, and (3) the cyclic delocalized mechanism. In 1958 Walling and Peisach (5) concluded that the transition state of the Diels-Alder condensation in the thermal polymerization of isoprene proceeds by a noncyclic mechanism followed by an open-chain diradical. A similar mechanism has been reported for the thermal dimerization of acrylonitrile (6), cyclopentadiene (7), and cyclohexadiene (8).

The present paper deals with kinetic studies of the thermal polymerization of 1,3-CHD and copolymerization of 1,3-CHD with acrylonitrile, and then obtaining dimer (tricyclo[6,2,2,0]dodeca-5,9-diene) in high yield by controlling the polymerization, which is a competing reaction with dimerization.

EXPERIMENTAL

Synthesis of 1,3-Cyclohexadiene

1,3-CHD was prepared in high purity. A mixture of 52 g of benzoyl peroxide (BPO) and 1.73 kg of cyclohexene was heated to 80°C and then 3.01 kg (27.7 moles) of *t*-butyl hypochlorite was added over a period of 5 hr. The mixture was refluxed for 1 hr.

After removal of the unreacted cyclohexene, 3-chloro cyclohexene was distilled under reduced pressure (b.p. 78–80°C, 182 mm Hg). Redistillation gave 1.64 kg (51%) of 3-chloro cyclohexene. The pure 3-chloro cyclohexene was added dropwise to 6.2 liters of quinoline which was heated to 190°C under nitrogen atmosphere. Distilled crude 1,3-CHD was collected and washed with 3 *N* HCl, dried over anhydrous magnesium sulfate, and distilled under nitrogen atmosphere to give 670 g (59.5%) of 1,3-CHD (b.p. 79–80°C). Vapor-phase chromatography analysis showed that the product was 96.6% of 1,3-CHD, 2.1% of 1,4-CHD, and traces of benzene and cyclohexene.

Polymerization

Polymerizations and copolymerizations with acrylonitrile (AN) were carried out by an ordinary glass-tube method. After polymerizations, the reaction mixture was fractionally distilled in three fractions in the presence of hydroquinone: fraction 1, b.p. 68–

80°C, was monomeric product; fraction 2, b.p. 76–78°C, 45 mm Hg, was mainly dimer; and fraction 3 was polymeric residue, which was then purified by reprecipitation from benzene and methanol. Copolymers with AN were purified by reprecipitation first from benzene with methanol and then from dimethylformamide with methanol.

Analysis of the Distilled Fractions and of the Polymers

The vapor-phase chromatography analyses using diethylene glycol succinate polyester columns showed that fraction 1 consisted of 1,3-CHD, its isomer (1,4-CHD), and dimerization products, benzene and cyclohexene, which were produced in the thermal polymerization. The relative amounts of these materials were determined from vapor-phase chromatography.

Fraction 2 was identified as dimer by the determination of its chemical and physical properties (9,10). NMR and IR spectra of

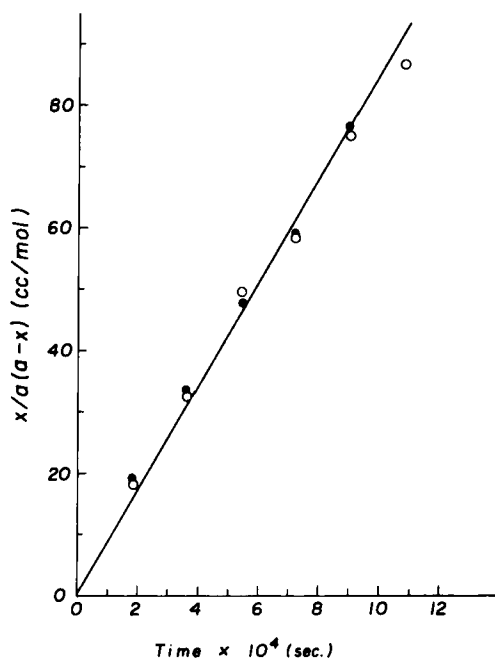


FIG. 1. Time-conversion relationship for the polymerization initiated thermally (●) and by BPO (○) at 200°C in bulk; (a) and (x) indicate the initial concentration and the conversion at time t , respectively.

TABLE I
Results of Polymerization of 1,3-CHD ([CHD] = 10.4 moles/liter)

Run	[BPO] × 10 ³ , moles/liter		Polymerization		Conversion, ^a %	Monomeric product				Dimer		Polymer	
	Temp., °C	Time, hr	Cyclohexene, %	1,3-CHD, %		1,4-CHD, %	Benzene, %	Yield, %	Endo, %	Exo, %	Yield, %	Yield, %	MW
1	0	100	0.58	70.0	5.83	7.47	10.8	—	—	—	—	2.3	1690
2	8.4	100	0.35	78.6	3.88	2.17	9.6	—	—	—	—	3.3	1150
3	16.8	100	0.16	80.0	3.17	1.67	8.9	—	—	—	—	3.6	1650
4	0	150	1.38	38.5	3.93	5.99	34.8	76.2	23.8	23.8	23.8	7.2	1490
5	8.4	150	0.87	44.5	2.44	2.19	36.9	76.2	23.8	23.8	23.8	10.1	1090
6	0	200	4.78	14.2	2.89	8.92	48.4	76.4	23.6	23.6	23.6	18.2	860
7	0	200	4.45	4.86	2.83	7.86	57.6	76.3	23.7	23.7	23.7	19.9	890
8	0	200	3.40	2.37	1.75	5.68	58.8	76.6	23.5	23.5	23.5	27.3	810
9	0	200	3.13	2.03	1.44	5.60	61.6	77.5	22.4	22.4	22.4	25.2	800
10	0	200	2.60	0.88	0.81	5.31	61.4	77.5	22.6	22.6	22.6	27.2	890
11	0	200	2.27	0.17	0.46	5.50	57.4	76.4	23.6	23.6	23.6	32.2	780
12	8.4	200	—	—	—	—	—	—	—	—	—	—	—
13	8.4	200	—	—	—	—	—	—	—	—	—	—	—
14	8.4	200	—	—	—	—	—	—	—	—	—	—	—
15	8.4	200	—	—	—	—	—	—	—	—	—	—	—
16	8.4	200	1.98	1.98	0.97	8.47	62.4	77.2	22.8	22.8	22.8	26.7	680
17	0	300	Trace	~0	~0	Trace	50.2 ^b	—	—	—	—	46.6	500

^a Determined from recovered monomeric substances.

^b Consisted of 71.5% dimer, 15.8% trimer, and 12.7% tetramer, which were determined from vapor-phase chromatography analyses.

fraction 2 were in good agreement with those reported by Valentine and co-workers (8) and also by the earlier literature (10). The ratio of endo to exo isomer in the dimer was determined by vapor-phase chromatography using Apiezon J columns.

The chemical composition of the resulting polymers and of copolymers with AN were determined from the results of their elementary analyses. Number-average molecular weights (\bar{M}_n) were determined by osmotic pressure measurement on their benzene solutions using Mechrolab Model 301-A.

RESULTS AND DISCUSSION

Polymerization Kinetics

Polymerizations initiated by thermal and/or BPO are summarized in Table 1. From Table 1, the rate of polymerization R_p initiated by BPO was found not to depend on the concentration of the radical initiator and was the same as thermal polymerization. As shown in Fig. 1, R_p was plotted as a second-order reaction for both thermal and BPO-initiated polymerization at 200°C.

The second-order rate constant k at various temperature was calculated and is shown in Table 2. From a plot of $\log k$ vs. $1/T$ based on the results of Table 2, a straight line was obtained as shown in Fig. 2, from which the following rate equation was drawn:

$$-d[\text{CHD}]/dt = k[\text{CHD}]^2$$

$$k = 8.48 \times 10^2 \exp(-13.1 \text{ kcal}/RT) \quad (1)$$

TABLE 2
Effect of Temperature on the Polymerization of 1,3-CHD

Run	Initiator	Temp., °C	$1/T \times 10^3$, °K	$k \times 10^3$, cc/mole-sec
1	Thermal	100	2.68	0.0177
2	BPO	100	2.68	0.0162
4	Thermal	150	2.36	0.0894
5	BPO	150	2.36	0.0895
10	Thermal	200	2.11	0.832
16	BPO	200	2.11	0.935
17	Thermal	300	1.74	5.46

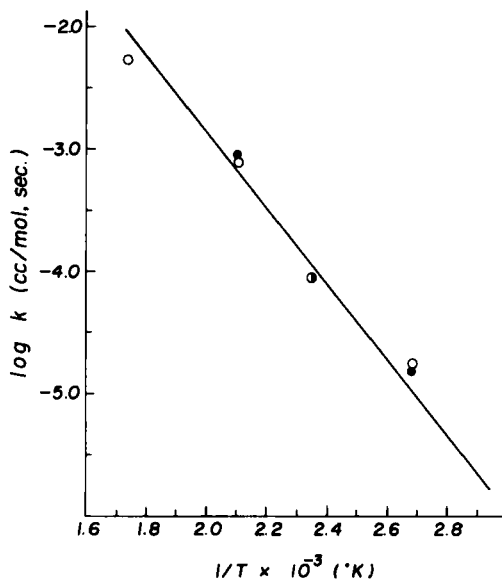


FIG. 2. Arrhenius plot for polymerization of 1,3-CHD initiated thermally (●) and by BPO (○) in bulk.

The result that the reaction is kinetically of the second order is in qualitative agreement with that of the thermal polymerization of 1,3-CHD by Shantarovich and Shlyapnikova (2) and also that of homogeneous gaseous dimerization of butadiene, isoprene (5), and cyclopentadiene (11), which are typical Diels-Alder condensations. The frequency factor A in Eq. (1), however, is quite small compared with that of literatures. Then the high reactivity of 1,3-CHD as monomer for the polymerization as well as diene or dienophile for Diels-Alder condensation arises from favorable conjugated cisoid conformation.

As can be seen from Table 1, polymers obtained in polymerizations initiated by thermal and BPO methods have low molecular weight (degree of polymerization is 8 to 21), which is reciprocal to the temperature. The result, that R_p is independent on the concentration of BPO, indicates that the radical generated from BPO is consumed by disproportionation or recombination. Accordingly, it seems probable that the reaction proceeds by a monoradical which is produced by disproportionation and/or intermolecular rearrangement of diradicals of the diallyl type arising from the bimolecular reaction of 1,3-CHD, as illustrated in Fig. 3.

Although there is now no considerable evidence on the participation of diradical in the formation of high polymer, but if diradical intermediate is formed in the polymerization, the possibility of intermolecular coupling of diradical must be considered. This process may readily account for the formation of dimer as a typical Diels-Alder condensation product in the polymerization of 1,3-CHD; however, the decision cannot be made between nonradical and diradical mechanisms for the Diels-Alder condensation.

As shown in Fig. 3, these considerations suggest that both the monoradical of 1,3-CHD and its diradical (if any) may be regarded as a reaction intermediate of polymerization and dimerization, which have different reaction orders. Hence the overall rate constants in Table 2 which were determined from the disappearance of 1,3-CHD are the rate constants, including dimerization (k_d) and polymerization (k_p). To evaluate the ratio of the specific rate constants k_d/k_p from time-conversion curves as shown in Fig. 4, the individual rate of dimerization (R_d) and polymerization (R_p) and

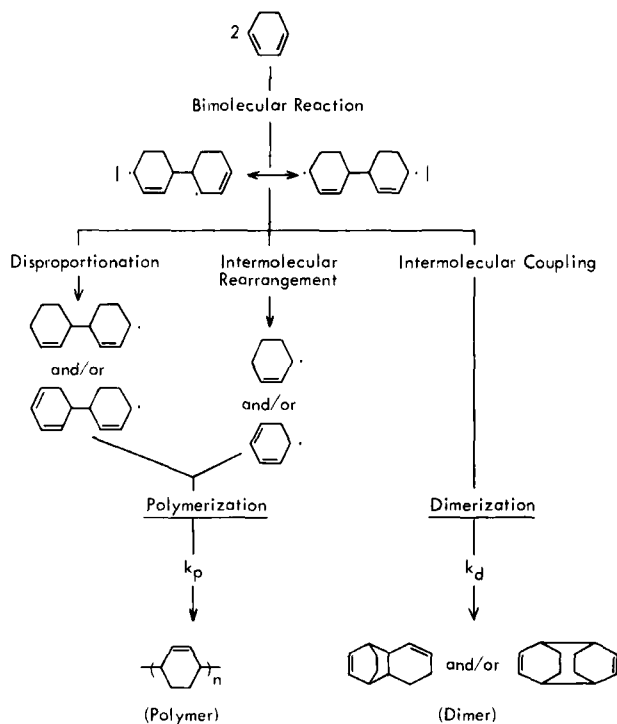


FIG. 3. Proposed mechanism for the thermal polymerization of 1,3-CHD.

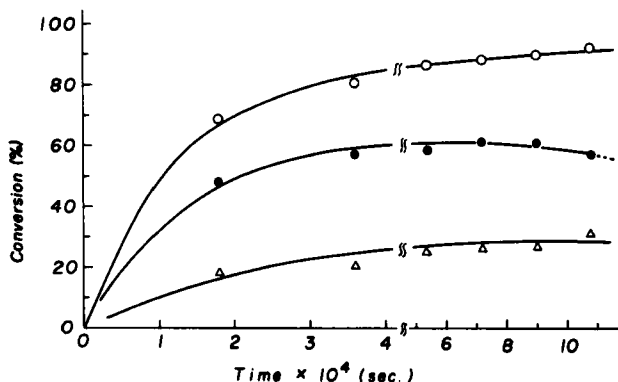


FIG. 4. Time-conversion curves for the thermal polymerization at 200°C:
○, monomer; ●, dimer; △, polymer.

the concentration of 1,3-CHD at time t were calculated and are shown in Table 3. As can be seen in Fig. 5, straight lines were obtained from a plot of $\log R$ vs. $\log [\text{CHD}]$.

TABLE 3

Results of Dimerization and Polymerization as Competing Reactions
in the Thermal Polymerization of 1,3-CHD at 200°C

$t \times 10^{-3}$, sec	Conversion			CHD, %	R_d	R_p
	Monomer, %	Dimer, %	Polymer, %		$d[\text{dimer}]/dt$	$d[\text{polymer}]/dt$
10	57	38	10	43	1.80	0.955
15	64	44	14	36	1.00	0.690
20	70	48	17	30	0.699	0.512
30	77	55	22	23	0.512	0.313
40	82	55	25	18	0.269	—

Then the following relationships were drawn, and the apparent k_d/k_p for the thermal polymerization at 200°C was found to be 1.21:

$$\begin{aligned}
 R_d &= d[\text{dimer}]/dt = k_d[\text{CHD}]^{1.96} \\
 R_p &= d[\text{polymer}]/dt = k_p[\text{CHD}]^{1.82} \\
 R &= -d[\text{monomer}]/dt = k[\text{CHD}]^2
 \end{aligned}
 \tag{2}$$

where $k = k_d + k_p$.

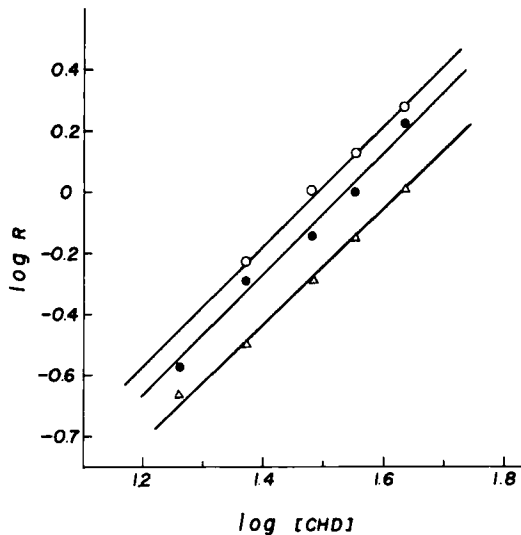


FIG. 5. Relationship between $\log R$ (%/hr) and $\log [CHD]$: \circ , monomer; \bullet , dimer; Δ , polymer.

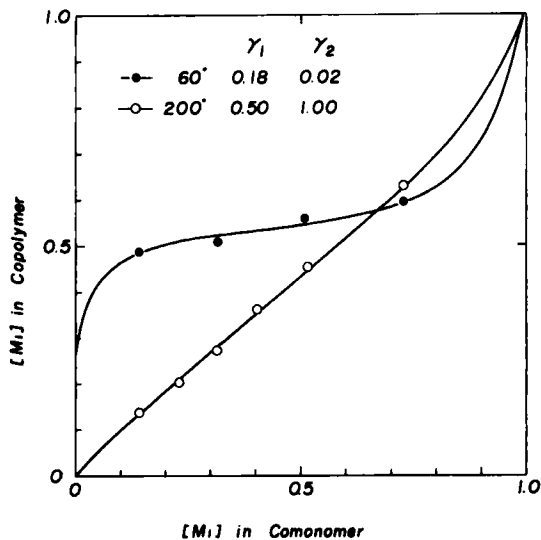


FIG. 6. Monomer-copolymer composition curves for the copolymerization of 1,3-CHD (M_1) with AN (M_2) initiated by BPO at 60 and 200°C.

Copolymerization

Recently some studies were reported on the reactivity of 1,3-CHD toward free radicals (12,13). However, all these studies were discussed on the monomer reactivity determined at 60°C. To deduce the effect of temperature on monomer reactivity ratio, the kinetic study of copolymerization of 1,3-CHD (M_1) with AN (M_2) has been made in the presence of BPO at 60 and 200°C.

The resulting monomer-copolymer composition curves were shown in Fig. 6, from which monomer reactivity ratios r_1 and r_2 were calculated by the Fineman-Ross method (14). The values $r_2 = 0.02$ and the product $r_1 \cdot r_2 = 0.004$ at 60°C are almost similar to the values obtained by Ferdinandi and co-workers (13). These values indicate the high reactivity of 1,3-CHD and a considerable degree of alternation, however, at 200°C the negative deviation of these reactivity and alternating effects was observed.

Although the temperature coefficient of r_1 is rather small, the increase of r_1 may indicate the increase of reactivity of 1,3-CHD at 200°C. From a plot of $\log r$ vs. $1/T$ based on the data in Fig. 5, the following relationships were drawn:

$$\begin{aligned} r_1 &= \exp[(\Delta S_{11}^\ddagger - \Delta S_{12}^\ddagger)/R] \exp[-(\Delta H_{11}^\ddagger - \Delta H_{12}^\ddagger)/RT] \\ &= \exp[(0.165 \text{ eu})/R] \exp[(-2.3 \text{ kcal})/RT] \\ r_2 &= \exp[(\Delta S_{22}^\ddagger - \Delta S_{21}^\ddagger)/R] \exp[-(\Delta H_{22}^\ddagger - \Delta H_{21}^\ddagger)/RT] \\ &= \exp[(0.855 \text{ eu})/R] \exp[(-8.7 \text{ kcal})/RT] \end{aligned} \quad (3)$$

where ΔS^\ddagger and ΔH^\ddagger are, respectively, the entropies and energies of activation for the reaction of the M_1 or M_2 type of radical with monomer.

The ΔS^\ddagger do not differ from each other, so that the difference in reactivity of monomers comes from energy of activation. Although the overall energy of activation of BPO-initiated polymerization of AN in homogeneous system cannot be determined, the value of E_{22} may be calculated by

$$E_{22} = \frac{1}{2}E_i + E_p - \frac{1}{2}E_t \quad (4)$$

where E_i , E_p , and E_t are, respectively, the energy of activation of initiation, propagation, and termination. E_{22} is found to be 19.8 kcal/mole, by assuming that the value of E_i for homogeneous polymerization of styrene reported by Brown-Mellish (15), and the value of $(E_p - \frac{1}{2}E_t)$ for homogeneous polymerization of AN in dimethyl-

formamide reported by Onyon (16) can apply. Thus the value of E_{11} ($=\Delta H'_{11}$) is found to be 13.2 kcal/mole from the data in Eq. (3) assuming $\Delta H'_{12} = \Delta H'_{21}$.

It is noted that the energy of activation of polymerization of 1,3-CHD derived from the kinetic study for the copolymerization is in quantitative agreement with that obtained from Eq. (1).

Thermal Polymerization of 1,3-CHD in the Presence of Oxygen

In the thermal polymerization of 1,3-CHD, the relative ratio of two competing types of reaction depends on the temperature. However, no significant change in the ratio of dimer and polymer formed was observed at up to 200°C, because each activation energy of dimerization and polymerization process was quite similar.

To obtain dimer with maximum yield, thermal polymerization was carried out in the presence of a third additive such as a radical inhibitor or oxygen. The results are shown in Table 4. From this table it was found that the oxygen gave dimer in good yield, but no noticeable increase on the ratio of dimer to polymer was observed in the case of hydroquinone, hydrogen peroxide, and diphenyl picryl hydrazyl (DPPH).

Table 5 shows the effect of the concentration of oxygen on the product distribution for the thermal polymerization. Although there is no change in the conversion, the dimer increases and the polymer conversely decreases with increasing concentration of oxygen, as can be seen from Fig. 7. Remarkably this tendency was observed

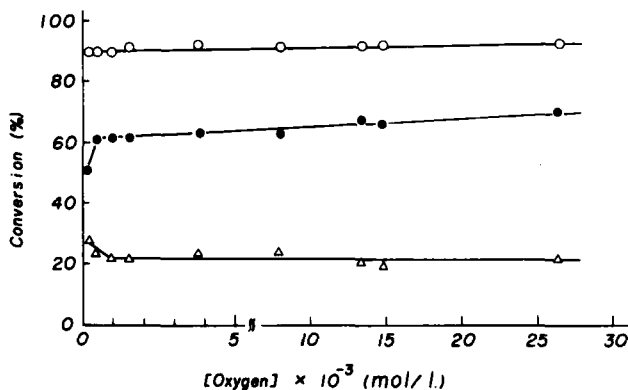


FIG. 7. Effect of oxygen on the products distribution: ○, monomer; ●, dimer; △, polymer.

at lower concentrations of oxygen, and the product consisted 70% of dimer, 20% of polymer, and 5.5% of a mixture of the remaining monomeric products.

TABLE 4

Results of the Thermal Polymerization at 200°C in the Presence of a Third Additive ([CHD] = 9.0 moles/liter in benzene; time: 20 hr)

Additives × 10 ³ , moles/liter	Conversion, %	Yield			
		Dimer, %	Polymer, %	Dimer/ polymer	
None	—	74.2	43.0	33.1	1.38
Hydroquinone	3.8	70.0	48.7	22.0	2.21
DPPH	4.0	69.5	45.8	20.0	2.29
H ₂ O ₂	9.4	54.0	33.4	19.9	1.67
Oxygen	0.11	80.5	59.4	15.8	3.76

TABLE 5

Effect of Oxygen in Thermal Polymerization at 200°C ([CHD] = 10.4 moles/liter; time: 25 hr)

Oxygen, moles/liter	Con- version, %	Monomeric product				Dimer yield, %	Polymer	
		Cyclo- hexene, %	1,3- CHD %	1,4- CHD %	Ben- zene, %		Yield, %	\overline{MW}
$\sim 3.0 \times 10^{-7}$	89.4	2.8	1.9	1.9	5.0	51.2	27.6	686
3.78×10^{-4}	90.0	2.6	1.6	1.2	4.6	60.8	23.9	705
8.70×10^{-4}	88.5	2.8	2.3	1.5	4.9	60.9	22.2	730
1.50×10^{-3}	90.8	2.2	1.6	1.2	4.2	60.6	21.8	739
3.76×10^{-3}	92.1	2.1	1.0	0.9	3.9	63.0	24.7	902
7.84×10^{-3}	91.2	2.0	1.6	1.2	4.0	63.3	24.8	813
1.33×10^{-2}	90.9	2.4	1.5	1.0	4.2	67.8	21.1	900
1.45×10^{-2}	90.3	2.6	1.4	1.1	4.5	65.4	19.7	850
2.62×10^{-2}	92.5	2.0	1.2	0.8	3.5	70.0	20.3	872

Thus the thermal polymerization of 1,3-CHD in the presence of oxygen produces dimer in better yield than that reported in the early works (1-4).

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Zusammenfassung

Es wird über die thermische Polymerisation von 1,3-Cyclohexadien zu dimeren und niedermolekularen Polymeren berichtet. Die thermisch oder durch Benzoylperoxid gestartete Reaktion ist kinetisch gesehen von zweiter Ordnung, wobei die Aktivierungsenergie 13.1 kcal/mole ist. Die Aktivierungsenergie ist in quantitativer Übereinstimmung mit jener der Homopolymerisation des 1,3-Cyclohexadiens, wobei diese Aktivierungsenergie aus einer kinetischen Untersuchung der Kopolymerisation mit Acrylnitril abgeschätzt wurde. Augenscheinlich ist der Dimerisierungsprozess, der zu einem typischen Diels-Alder Kondensat führt, in Konkurrenz mit einer Radikalpolymerisation welche zu niedermolekularen Polymeren führt. Das Verhältnis der Geschwindigkeitskonstanten der

beiden konkurrierenden Reaktionen ist 1.21 bei 200°C. Die thermische Polymerisation in Gegenwart von Sauerstoff ergibt grössere Ausbeuten an Dimerem als Folge einer Hemmung der Radikalpolymerisation.

Résumé

Les auteurs font un rapport sur la polymérisation thermique du 1,3-cyclohexadiène dans le but d'obtenir le dimère et des polymères à bas poids moléculaire. La réaction amorcée thermiquement ou à l'aide du peroxyde de benzoyle est du point de vue cinétique du second ordre, l'énergie d'activation est 13.1 kcal/mole. L'énergie d'activation de cette réaction est en accord quantitatif avec celle d'homopolymérisation, calculée, d'après une étude cinétique de la copolymérisation avec l'acrylonitrile. Le processus de dimérisation donnant un dimère comme produit d'une condensation du type Diels-Alder est donc en compétition avec la polymérisation radicalaire qui donne un polymère à bas poids moléculaire. On a trouvé que le rapport des constantes de vitesse pour deux réaction en compétition à 200°C est 1.21. Le rendement en dimère plus élevé de la polymérisation thermique en présence d'oxygène résulte de l'inhibition de la polymérisation radicalaire.

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