Chemistry

1962

SovietRxiv

Abstract

Full Text

Chemistry

Ya. M. Paushkin, A. G. Yuzvyak, and A. I. Rubinshtein

Synthesis of Dimethylcyclohexadiene and Vinylcyclohexene by Dimerization of Butadiene

(Presented by Academician A. V. Topchiev, 30 XII 1961)

In recent years, new monomers have been used to obtain high-quality polymers, such as, for example, vinylcyclohexane, which gives thermoplastic polymers with a melting point above 300°.

In our work it was shown that vinylcyclohexane can be obtained by hydrogenation of vinylcyclohexene.

Vinylcyclohexene is obtained by dimerization of butadiene (^{2}). In connection with this, the aim of the present work was to determine the optimal regime for the cyclopolymerization of butadiene in order to obtain cyclic dimers of butadiene, to study the reaction products, and to carry out a thermodynamic calculation of the process, since previously this reaction had been studied insufficiently, without taking into account the thermodynamics of the process and without investigation of the by-products. Polymerization was carried out at 350–500° in a stainless-steel reactor, and the dependence of the yield and composition of the polymer on temperature was established.

As studies show (^{3}), liquid butadiene polymer contains a large number of various hydrocarbons of an unsaturated character, which may find independent application in the high-polymer industry. In the work performed, the target products were 1,3-dimethylcyclohexadiene and vinylcyclohexene.

The cyclopolymerization reactions were carried out on a pilot installation. The polymer was fractionated on a laboratory column with the collection of narrow fractions at 5–7°; then their physicochemical constants were determined. The initial and blow-off gases were studied mainly for their content of unsaturated compounds.

Effect of temperature on the process. The effect of temperature on the process of cyclopolymerization of butadiene was studied at a constant volumetric feed rate of the raw material equal to 28 h^{-1}. The experimental results are summarized in Table 1. The experiments showed that the optimal reaction temperature is 400–420°. At the same volumetric rate, with increasing temperature the yield of liquid polymer increases, with a simultaneous increase in the specific gravity and refractive index. The presence of the target fractions

1,3-dimethylcyclohexadiene and vinylcyclohexene decreases with increasing temperature. This is seen in Fig. 1.

Table 1

Temperature, °C	Conversion to liquid polymer, %	Yield of polymer based on passed divinyl, %	Content of dimethylcyclohexadiene in the polymer, %	Yield of dimethylcyclohexadiene based on initial divinyl, %	Yield of dimethylcyclohexadiene based on reacted divinyl, %	Content of vinylcyclohexene in the polymer, %	Yield of vinylcyclohexene based on initial divinyl, %	Yield of vinylcyclohexene based on reacted divinyl, %
350	35.6	61.0	8.0	8.3	9.3	35.0	14.4	21.3
400	66.0	71.0	7.0	5.9	6.4	25.0	16.5	17.8
450	75.0	93.6	4.0	2.8	6.2	16.0	12.0	15.3
500	80.0	95.0	3.0	1.0	1.2	8.0	5.0	5.0

Effect of the space velocity of feed supply on the process. Determination of the effect of space velocity on the polymerization process showed that the yield of the target fractions increases with decreasing space velocity and falls sharply when the space velocity of feed supply is increased. The results of the experiments are summarized in Table 2 and presented in Fig. 2.

Table 2

Space velocity, hr^{-1}	Butadiene conversion, %	Polymer yield based on reacted butadiene, %	Content of oligomers in the polymer, %	Dimer yield based on the original butadiene, %	Trimer yield based on the reacted butadiene, %	Content of vinylcyclohexene in the polymer, %	Vinylcyclohexene yield based on the original butadiene, %	Vinylcyclohexene yield based on the reacted butadiene, %
11.0	61.0	91.5	11.0	10.0	14.0	49.5	45.0	68.5
12.0	60.0	86.0	10.0	9.0	13.7	45.0	43.0	62.0
18.5	40.8	80.8	7.0	7.2	13.0	30.0	16.0	65.3
37.0	32.0	75.7	5.0	3.1	5.0	30.0	10.8	69.9
28.0	40.0	78.0	6.0	4.0	6.5	29.0	13.5	68.8

Figure 1: Effect of temperature on the yield of polymer and dimer.

Figure 1: Figure 1: Effect of temperature on the yield of polymer and dimer.

The highest yield of vinylcyclohexene (45%) and 1,3-dimethylcyclohexadiene (10%) based on the original butadiene is attained at a temperature of 400° and a space velocity of 11 hr^{-1}. Based on the reacted butadiene, the yields of these products are still higher (68.5% and 14.0%, respectively). If compared with previously published data ([2]), the increase in pressure favored an increase in the yield of dimer fractions.

Investigation of the chemical composition of the polymer. As the investigations showed, in addition to 1,3-dimethylcyclohexadiene and vinylcyclohexene, the polymer contains a comparatively large amount of other valuable products. The liquid polymer was distilled on a laboratory column, with narrow fractions being collected, corresponding predominantly to individual hydrocarbons. The constants of these hydrocarbons were determined and then compared with literature data. Bromine numbers, refractive indices, and specific gravities show that the substances obtained have double bonds and a cyclic character. As the investigations showed, butadiene polymer has a complex composition, and therefore it should be assumed that not only formation of the ring occurs, but also its rupture with the formation of intermediate compounds entering into further reactions.

Fig. 1. Effect of temperature on the yield of polymer and dimer. 1 —yield of polymer based on reacted butadiene; 2 —yield of polymer based on original butadiene; 3 —content of the dimethylcyclohexadiene and vinylcyclohexene fraction in the polymer; 4 —content of the vinylcyclohexene fraction in the polymer.

The analyses showed that the polymer contains several isomers of such a valuable product as dimethylcyclohexadiene, with 1,3-dimethylcyclohexadiene being present in a considerable amount.

1,3-Dimethylcyclohexadiene

	d_4^{20}	n_D^{20}	b.p., °C	Bromine number	Hydrogen number
Literature data ([3])	0.8203	1.4636	126—128	296	411
Experimental data	0.8240	1.4633	123—128	270	406

Spectral-analysis data also confirm the presence of dimethylcyclohexadienes and vinylcyclohexene. Of the remaining hydrocarbons

one may note the presence of products of aromatic structure with a long aliphatic chain, hydrocarbons of the cyclooctadiene and cyclodecene type.

Thermodynamic calculation of the process

A thermodynamic calculation was carried out for the reaction:

$$\text{Divinyl} \overset{K_p}{\rightleftarrows} \text{Vinylcyclohexene (I)}$$

$$\text{Divinyl} \overset{K_p'}{\rightleftarrows} \text{Vinylcyclohexene (I)}$$

$$\overset{K_p^2}{\rightleftarrows} \text{Dimethylcyclohexadiene (II)}$$

It was assumed that the reactions proceed in the gas phase. The calculation was performed according to equations (4):

$$K_p = \frac{p_{\text{vin}}}{p_{\text{div}}^2} \qquad \text{for reaction I} \tag{1}$$

$$K_p^{(1)} = \frac{p_{\text{vin}}}{p_{\text{div}}^2} \tag{2}$$

$$K_p^{(2)} = \frac{p_{\text{dimethyl}}}{p_{\text{div}}^2} \qquad \} \text{ for reaction II} \tag{3}$$

where K_p, $K_p^{(1)}$, $K_p^{(2)}$ are the equilibrium constants at constant pressure for the first and second reactions, respectively, and p_{vin}, p_{div}, p_{dimethyl} are the partial pressures of vinylcyclohexene, divinyl, and dimethylcyclohexadiene, respectively, in the equilibrium state.

If we denote by $z \cdot 100$ the yield, in percent, of vinylcyclohexene by reaction I; by $x \cdot 100$ the same by reaction II; by $y \cdot 100$ the yield, in percent, of dimethylcyclohexadiene by reaction II; and by P_0 the pressure at which the reaction proceeds, then, after the corresponding transformations, we obtain:

$$K_p = \frac{\frac{1}{2}z\left(1 - \frac{1}{2}z\right)}{(1-z)^2 \cdot P_0} \tag{1''}$$

for reaction I,

$$K_p^{(1)} = \frac{x\left(1 - \frac{1}{2}x - \frac{1}{2}y\right)}{(1-x-y)^2 \cdot P_0} \tag{2''}$$

$$K_p^{(2)} = \frac{y\left(1 - \frac{1}{2}x - \frac{1}{2}y\right)}{(1 - x - y)^2 \cdot P_0} \qquad \} \tag{3”}$$

for reaction II.

At the same time:

$$-RT \ln K_p = \Delta Z^0;$$

$$\Delta Z_0 = \Delta H^0_{298.16} - T\Delta S^0_{298.16};$$

$$\Delta H^0_{298.16} = \Delta H^0_{\text{form. } 298.16\, C_8} - 2\Delta H^0_{\text{form. } 298.16\, C_4};$$

$$\Delta S^0_{298.16} = S^0_{298.16\, C_8} - 2S^0_{298.16\, C_4},$$

where ΔZ^0 is the thermodynamic potential; $\Delta H^0_{\text{form. } 298.16\, C_4}$ is the heat of formation of divinyl; $\Delta H^0_{\text{form. } 298.16\, C_8}$ is the heat of formation of the corresponding dimer; $S^0_{298.16\, C_4}$ is the entropy of divinyl; $S^0_{298.16\, C_8}$ is the entropy of the corresponding dimer.

Fig. 2. Effect of space velocity on cyclodimerization at a temperature of 400°: 1 —polymer yield based on the initial butadiene, 2 —polymer yield based on reacted butadiene, 3 —content of the dimethylcyclohexadiene and vinylcyclohexene fraction in the polymer, 4 —content of the vinylcyclohexene fraction in the polymer.

Thus, by calculating the equilibrium constants K_p, $K_p^{(1)}$, $K_p^{(2)}$ from thermodynamic quantities and substituting their values into (1″), (2″), (3″), it is possible to calculate x, y, z at different temperatures and pressures.

Since the values of the entropy and heat of formation of vinylcyclohexene and dimethylcyclohexadiene are not given in the literature, they were

Table 3

Temperature, °C	Calculation by reaction: $K_p^{(1)}$	Calculation by reaction: $K_p^{(2)}$	II: x	II: y	I: K_p	I: z
0	$2.71 \cdot 10^{19}$	$3.66 \cdot 10^{23}$	$0.73 \cdot 10^{-4}$	0.985	$2.71 \cdot 10^{19}$	~ 1.0
100	$5.87 \cdot 10^{11}$	$8.34 \cdot 10^{13}$	0.0069	0.981	–	–

Temperature, °C	Calculation by reaction: $K_p^{(1)}$	Calculation by reaction: $K_p^{(2)}$	II: x	II: y	I: K_p	I: z
300	29100	53150	0.3537	0.6455	29100	0.997
400	275.1	150.8	0.8239	0.3418	275.1	0.9899
420	127.4	57.16	0.8544	0.2935	–	–
450	43.39	14.75	0.6774	0.2302	–	–
475	18.91	5.18	0.6729	0.1845	–	–
500	8.692	1.95	0.6439	0.1444	8.894	0.833
550	0.2117	0.03298	0.1566	0.0243	–	–
600	0.06063	0.00683	0.0553	0.0062	0.06083	0.106

calculated from bond energies ([5,6]). The results of calculations for reactions I and II are summarized in Table 3, on the basis of which the graphs in Fig. 3 were constructed.

On considering Fig. 3 it becomes evident that the maximum yield of vinylcyclohexene can be obtained at 400–500°.

Fig. 3. Yield of dimer as a function of temperature at $P = 1$ atm for reaction (II). 1 –yield of vinylcyclohexene, 2 –yield of dimethylcyclohexadiene

We have found the dependence of the yield of dimer on temperature under the condition that only vinylcyclohexene is formed during dimerization. If side reactions are suppressed in some way, the temperature range in which a high yield of vinylcyclohexene can be obtained will be considerably expanded. At the same time, it is obvious that it is necessary to take into account that, as the temperature is lowered, the reaction rate also decreases. From Fig. 3 it is seen that carrying out the dimerization reaction of divinyl above 600° is not expedient.

Thus, we have studied the thermal polymerization of divinyl in a metal reactor with activated carbon as packing at various temperatures (from 350 to 500°) and space velocities. It was established that the highest yield of the dimeric fractions of 1,3-dimethylcyclohexadiene (10%) and vinylcyclohexene (45%), based on the starting divinyl, is attained at 400–420°, a space velocity of 11 hr^{-1}, and a pressure of 3 atm. With increasing pressure, the yield of dimeric fractions increases. The composition of the liquid polymer was investigated. Products of interest from the chemical point of view were found, among which 1,3-dimethylcyclohexadiene and vinylcyclohexene are of greatest interest.

Institute of the Petrochemical and Gas Industry
named after I. M. Gubkin

Received
30 XII 1961

CITED LITERATURE

1. Ya. M. Paushkin, A. G. Yuzyak, *Izv. vyssh. shkoly. Neft' i gaz*, **2**, 69 (1961).
2. Ya. M. Paushkin, A. G. Yuzyak, *Neftekhimiya*, **1**, no. 1, 60 (1961).
3. E. Gil-Av, J. Shabtal, F. Steckel, *Ind. Eng. Chem.* **52**, 139 (1960).
4. D. H. Harries, *Ber.* **35**, 1175 (1902).
5. M. Kh. Karapet' yants, *Chemical Thermodynamics*, Moscow, 1953.
6. *Physicochemical Constants of Individual Hydrocarbons*, ed. V. Ya. Tatevskii, Moscow, 1960.

Note: Figure translations are in progress. See original paper for figures.