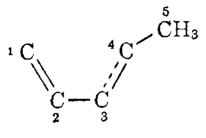
(iii) A portion of the reactants disappears to give material other than $C_5H_8$ isomers at a rate which is nearly independent of time. Evidently both *cis* and *trans* isomers participate in this reaction which presumably gives high boiling material.

(iv) Beyond the maximum in the concentration of *cis*-pentadiene, the reaction

$$cis\text{-}CH_2{=}CHCH{=}CHCH_3 + h\nu \longrightarrow trans\text{-}CH_2{=}CHCH{=}CHCH_3 \quad (10)$$

may account for the decrease in the *cis* isomer.

These results give more direct evidence for the statement made in an earlier section that the general reaction[2] is probably rapid when compared to the rates of rotation around the carbon–carbon bonds in the molecule. Reaction 8 may be pictured as proceeding through an excited state (V) which is probably the same as the state which leads to the *cis* isomer through rotation around the bond between $C_3$ and $C_4$. The latter operation has no energy barrier in the excited state up to an angle of $\pi/2$[14] and its rate may be comparable to the rate of rotation around the bond between $C_2$ and $C_3$. Since the rate of reaction 8 is observed to be faster than reaction 9, it follows that the former is favored by a suitable configuration in the ground state in the molecules which undergo the process.[15]



V

**Acknowledgment.**—The author wishes to thank Dr. Harold L. Friedman for his advice and encouragement during the course of this work. He is grateful to Drs. J. Kumamoto and J. C. Powers for many helpful discussions.

[14] J. R. Platt, "Encyclopaedia of Physics," Vol. 37, part II, Springer-Verlag, Berlin, 1961, p. 204.

[15] The inference may be drawn that excited molecules with the right configuration for ring closure may react at a much faster rate to give methylcyclobutene compared to the rate of isomerization to *cis*-pentadiene. The observed 10% difference in rate between 8 and 9 may be caused by the averaging of the rate of the former over molecules in all configurations.

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# The Use of Rhodium Salts as Catalysts for the Polymerization of Butadiene[1]

BY ROBERT E. RINEHART, HOMER P. SMITH, HARRY S. WITT AND HENDRIK ROMEYN, JR.

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The study of stereoregulating polymerization effects of inorganic salts in polar solvents revealed that certain rhodium salts catalyze polymerization of butadiene to the *trans*-1,4 structure in high steric purity. The rhodium salts behave simultaneously as efficient inhibitors for the free-radical emulsion polymerization. Rhodium salts also catalyze the isomerization of *cis*- and *trans*-polybutadiene toward an equilibrium structural composition.

Crystalline *trans*-polybutadiene is usually prepared by a Ziegler-Natta catalyst system.[2] Such catalysts are, of course, completely destroyed by traces of water or air. In contrast, solutions of rhodium salts *in water* catalyze the stereospecific polymerization of butadiene to the all *trans*-1,4 configuration.[3,4] An emulsifier may be present, but it is not necessary for polymerization, if the proper rhodium salt is selected.

In water, sodium dodecylbenzenesulfonate increases the rate with rhodium nitrate from 0.1 g./hr. to 0.4, while with rhodium chloride it increases from 0 to 2.4. A non-ionic emulsifier shows a slight rate increase for the nitrate, but is inactive with the chloride. Thus, rhodium nitrate is the more efficient catalyst in water with no emulsifier. Rhodium chloride is the more efficient catalyst in water with certain anionic emulsifiers.

Rhodium nitrate catalyzes the polymerization of butadiene in alcohol to the all *trans* polymer. Rhodium chloride, with or without sodium dodecylbenzene sulfonate, is ineffective in alcohol for the formation of high polymer. Analysis by gas chromatography has shown, however, that butadiene disappears at a faster rate for rhodium chloride in alcohol than for the nitrate. The reaction product from rhodium chloride is a complex mixture of hydrocarbons. More than twenty steam-volatile components, including butene-1 and butene-2 have been separated.

**Rate of Polymerization.**—The rate of formation of polymer under an emulsion condition using $RhCl_3$ as the catalyst is shown in Fig. 1. The rate shows no evidence of an induction period. At high conversions, there is usually a considerable amount of precipitated polymer. It might be expected that some catalyst would be removed from reaction along with the precipitated polymer. leading to a corresponding rate decrease. Despite this, the determined rates are quite linear, even at high conversion. It is then empirically correct to assume linear conversion with time.

The dependence of rate on catalyst concentration was determined for the polymerization of butadiene by rhodium nitrate in aqueous solution, with and without an emulsifier (Fig. 2). In each case, there was a leveling off of the rate when the

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[1] Presented in part at the 141st National Meeting of the American Chemical Society, Washington, March 28, 1962, and at the New York–New Jersey Regional Meeting, January 22, 1962.

[2] N. O. Gaylord and H. F. Mark, "Linear and Stereoregular Addition Polymers," Interscience Publishers, New York, N. Y., 1959, p. 368.

[3] R. E. Rinehart, H. P. Smith, H. S. Witt and H. Romeyn, Jr., *J. Am. Chem. Soc.*, **83**, 4864 (1961).

[4] After this paper had been submitted for publication, a communication[5] appeared which reported observations parallel to our first report[3] on the stereoregulating effects of $RhCl_3$ in butadiene polymerization.

[5] A. J. Canale, W. A. Hewett, T. M. Shryne and A. E. Youngman, *Chemistry & Industry*, 1054 (1962).

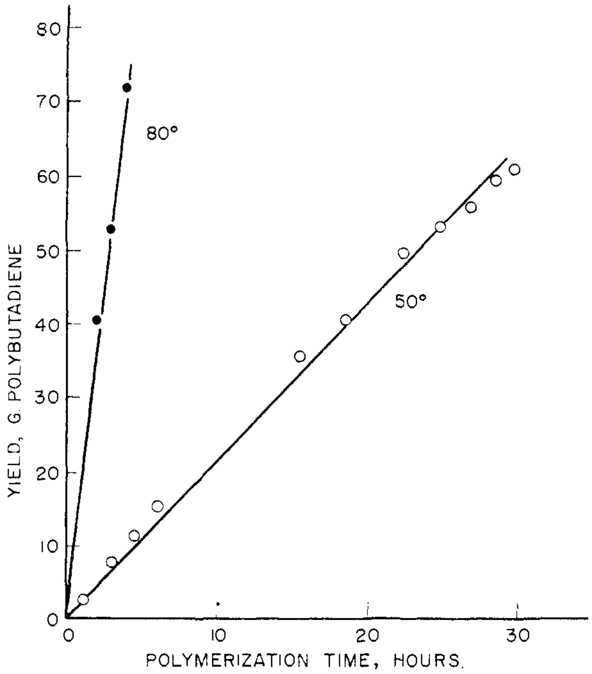

Fig. 1.—Polymerization in emulsion: (1 g. $RhCl_3{\cdot}3H_2O$, 100 g. butadiene, 5 g. sodium dodecylbenzenesulfonate, 200 ml. $H_2O$).

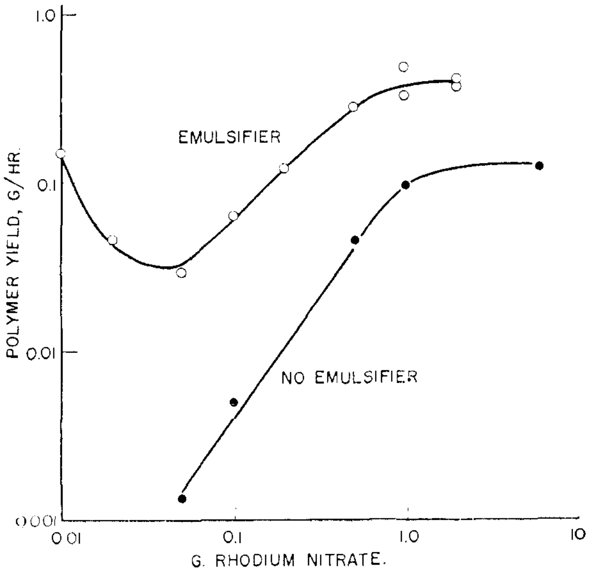

Fig. 2.—Catalyst concentration effects in the polymerization of butadiene by $Rh(NO_3)_3{\cdot}2H_2O$ (100 g. butadiene, 200 ml. $H_2O$: emulsion curve; plus 5 g. sodium dodecylbenzenesulfonate).

catalyst concentration exceeded about 1 g. of catalyst in 200 ml. of $H_2O$ (0.015 $M$). The over-all rate at every concentration was faster in the presence of emulsifier, as shown by the upper curve.

The faster rate at low catalyst concentration (below about 0.05 g.) in the emulsion polymerization is attributed to a competition of polymerization mechanisms. Rhodium salts not only are catalysts for the production of stereospecific polybutadiene, but they function also as inhibitors for the free-radical emulsion polymerization. When no rhodium salt is present, an average rate of polymerization of about 0.3 g./hr. can be expected, because of the residual presence of free-radical sources in the emulsifier. The addition of small amounts of rhodium nitrate leads to a decrease in the rate of the free-radical polymerization. At the same time, the rhodium nitrate initiates polymerization by the rhodium-catalyzed mechanism. The free-radical mechanism is unimportant at high rhodium concentration. At intermediate catalyst levels, both polymerization mechanisms are operative.

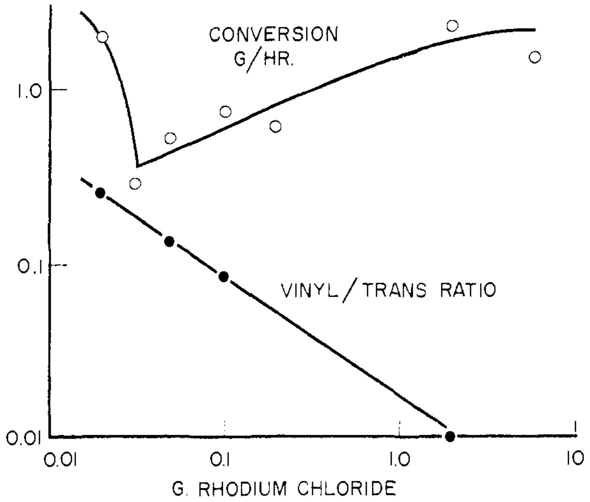

Fig. 3.—Catalyst concentration effects in the polymerization of butadiene by $RhCl_3{\cdot}3H_2O$ in the presence of a free-radical initiator (100 g. butadiene, 1 g. $\alpha,\alpha'$-azodiisobutyronitrile, 5 g. sodium dodecylbenzenesulfonate, 200 ml. $H_2O$). Vinyl/*trans* ratios were determined by infrared analysis.

The competition between free-radical polymerization and rhodium-catalyzed polymerization was studied in more detail (Fig. 3). A constant amount (1 g.) of $\alpha,\alpha'$-azodiisobutyronitrile was added to a $RhCl_3$ emulsion recipe, to insure a large, calculable supply of free radicals. The polymer produced at selected rhodium concentrations was precipitated, washed, and dried. The vinyl/*trans* ratios were determined by infrared analysis.[6] As the rhodium chloride concentration was increased, the vinyl/*trans* ratio decreased gradually from 0.24 which is about normal for free-radical polybutadiene, to 0.01, which is normal for rhodium-catalyzed polybutadiene. Thus, both from the rate, and also from the structure of the polybutadiene produced at incrementally higher rhodium salt concentrations, a transition from free-radical catalysis to rhodium salt catalysis can be observed.

These data adequately explain the observed minimum in the rate curve at low concentrations of rhodium catalyst in the presence of free-radical initiators. The decrease in catalyst efficiency at concentrations above 1 g. of $Rh^{+++}$ salt in 200 ml. of water probably is related to the complexity of aqueous solutions of rhodium salts.

Depending upon the method of preparation, as well as upon the length of time of aging, as many as

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[6] R. R. Hampton, *Anal. Chem.*, **21**, 923 (1949).

six or more ionic and neutral species have been reported for aqueous solutions of rhodium chloride alone.[7,8] The possibility of bridged forms[9] increases the complexity. Since there is an interaction between the catalyst and the monomer to produce polymer, it may be argued that at least one new equilibrium species, with butadiene as the ligand, is present. The complexity of the species in solution would suggest that complicated rate effects may be observed, governed by the equilibrium concentrations of the reactive species.[10]

**Isomerization of Polybutadiene.**—It may be reasoned that more than one type of olefin reaction is possible with different rate constants and with different equilibrium species for each of the competing reactions. A reaction, for instance, with polybutadiene was considered possible. To test this hypothesis, samples of polybutadiene prepared by various methods were treated with rhodium chloride in aqueous emulsion. There was definite evidence of a reaction between rhodium chloride and polybutadiene (Table I). In all cases, the original amount of *trans* microstructure of the polymer had been increased. The effect was particularly noticeable when high *cis*-polybutadiene was used as the standard.

TABLE I

CHANGES IN STRUCTURE OF POLYBUTADIENE TREATED WITH RHODIUM CHLORIDE IN EMULSION

| | Infrared analysis[a] | | | | | |
|---|---|---|---|---|---|---|
| | Before treatment, % | | | After treatment, % | | |
| Type of polybutadiene | *trans* | Vinyl | *cis* | *trans* | Vinyl | *cis* |
| Emulsion | 68 | 17 | 15 | 74 | 11 | 15 |
| High vinyl | 3 | 63 | 34 | 20 | 67 | 13 |
| High *cis* | 2.3 | 1.6 | 96 | 69 | 2 | 29 |

[a] Ratios are normalized to 100% total unsaturation.

The isomerization can be accomplished by rhodium salts with great ease. Although most isomerizations were conducted in emulsion at 80°, the reaction was quite rapid even at 50°.

Although there is some discrepancy in the literature[11,12,13] about the equilibrium ratio of *trans* and *cis* double bonds in polybutadiene, the value expected at the polymerization temperature can be considered to be about 75 *trans* to 25 *cis*. It would then be expected that the polybutadiene formed by the rhodium catalyst should show a considerably higher amount of *cis* than the 0.1–2% which is found, since the polybutadiene formed early remains in contact with catalyst long enough for the possibility of extensive isomerization.

This anomaly has been investigated in a model reaction using geometrically pure butenes instead of polybutadiene. The isomerization of butene by rhodium salts is quite rapid at moderate temperatures, giving essentially the equilibrium ratios of butene-1, *cis*- and *trans*-butene-2 in less than 1 day at 50°. However, small amounts of butadiene monomer have a profound effect upon the rate of isomerization of butene. The polymerization of the butadiene competes successfully, almost to the exclusion of the butene isomerization. In a typical experiment, the addition of an equimolar amount of butadiene completely suppressed the isomerization of *cis*-butene-2 for more than one week.

The detailed study of competitive polymerization-isomerization will be the subject of a future paper.

## Experimental

Matheson C.P. butadiene was distilled before use. Rhodium chloride and rhodium nitrate were used as obtained from Englehard Industries, Newark, New Jersey.

**Polymerizations.**—Most of the polymerizations were carried out in capped bottles, agitated in a thermostated bath. The recipes which would be expected to develop high pressure (*e.g.*, butadiene at elevated temperature) were run in heated, stirred autoclaves. After reaction, excess monomer was vented and the polymer was precipitated by the addition of methanol. The polybutadiene was filtered, washed several times with more methanol, and was dried in a vacuum oven at room temperature. The samples were analyzed by the methods previously reported.[3]

**Isomerizations.**—The polymer was dissolved in a suitable solvent such as benzene or xylene. A convenient aliquot was used to make an emulsion recipe, using $RhCl_3$, water, and sodium dodecylbenzenesulfonate. The emulsion was heated under nitrogen at 50° or 80° for varying lengths of time. After reaction, the polymer was precipitated with methanol, washed, dried, and analyzed by infrared.

**Acknowledgment.**—The authors are grateful to Messrs. B. C. Crowley and F. W. Grosseibl for their assistance with the experimental portions of this work, and to Mr. R. R. Hampton for the gas chromatographic and infrared analyses.

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(7) M. Lederer, *Zhur. Neorg. Khim.*, **3**, 1799 (1958).

(8) D. Cozzi and F. Pantani, *J. Inorg. Nuclear Chem.*, **8**, 385 (1958).

(9) J. S. Forrester and G. H. Ayres, *J. Phys. Chem.*, **63**, 1979 (1959).

(10) The complexity of the various equilibrium species is probably responsible for the reported[5] *p*H-dependent rate effects. We have also observed large rate effects for added acid or base, but feel that no satisfactory explanation can be offered until more is known about the species responsible for the formation of the reactive rhodium-diene complex.

(11) J. I. Cunneen, M. C. Higgins and W. F. Watson, *J. Polymer Sci.*, **40**, 1 (1959).

(12) (a) M. A. Golub, *ibid.*, **25**, 373 (1957); (b) *J. Am. Chem. Soc.*, **80**, 1794 (1958); (c) *ibid.*, **81**, 54 (1959); (d) *ibid.*, **82**, 5093 (1960).

(13) W. A. Bishop, *J. Polymer Sci.*, **55**, 827 (1961).