Our value for ΔH_{CH_2} is 1.8 kcal. This value is somewhat higher than that obtained by Meakins[8] for long-chain ethers, esters, and solid solutions of ketones (700 cal/CH$_2$) [or by Broadhurst[28] for the enthalpy of fusion of long-chain paraffins (~1 kcal/CH$_2$)]. It is important to remember, however, that those materials are crystalline and that therefore a displacement of the chain as a whole along the *C* axis is also present. In our case the higher value of ΔH_{CH_2} of 1.8 kcal is not surprising, in view of the fact that we are dealing with a noncrystalline environment and also that longitudinal displacement is impossible. Hoffman, *et al.*,[26] in their attempt to calculate ΔS_{CH_2}, theoretically obtained values of 2 to 3 eu, values which correspond to those found experimentally for long-chain paraffins by Broadhurst. Our value of 5.3 eu is in line with those of the above studies. The similarity of ΔS_{CH_2} as well as the closeness of the ΔH_{CH_2} values lend further support to our mechanistic assignment for the γ relaxation. ΔH_{1-2} and ΔS_{1-2} in our series have, of course, a completely different origin than those encountered in the other materials, so no meaningful comparison is possible.

The negative value of ΔS_{1-2} (-15 eu) cannot be taken as very significant in itself. It is the total entropy related to the motion of the pivot point *and* to the motion of the linear alkyl portion of the side chain that should be considered. In the case of MC$_5$PPO, which possesses the smallest side chain, this total entropy [$\Delta S_{1-2} + 3(\Delta S_{CH_2})$] is of the order of 0–1 eu, and the corresponding activation energy is 9 kcal/mol. Similar cases in which processes having small activation energies and very small entropies (or even negative entropies) have been reported previously. For example, the dielectric relaxation of dioctyl phtalate in polystyrene found by Levi[29] had an activation energy of 5 kcal/mol and an entropy of -2 eu. For higher activation energy processes, Levi observed a positive and higher value of the entropy, as is the case with the MC$_n$PPO's when the side chain of the secondary alkyl increases in length.

Finally, it should be pointed out that while our assignment of the δ mechanism is speculative, we are confident that its origin lies in the alkyl chain. This is confirmed by the fact that a peak of comparable intensity and position in temperature is encountered by Illers in his study of alkanes embedded in polystyrene. Since in those materials, this peak cannot arise from a motion outside the chain, we believe that this is true in our system also; furthermore, the identity of the activation energies suggests that we are dealing with the same group in our entire series.

Acknowledgment. The financial support of the National Research Council of Canada is gratefully acknowledged.

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[29] D. L. Levi, *Trans. Faraday Soc.*, **42**, 152 (1946).

Dependence of Butadiene Polymerization Rate on Monomer Concentration for Some π-Crotylnickel Iodide Catalysis

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ABSTRACT: An extensive study of the effect of monomer concentration for the title reaction indicates that the previously reported first-order dependence on monomer is only true for low monomer concentrations. The order is 0.5 at the highest experimental monomer concentration, but data indicate that it extrapolates to <0.5 at still higher monomer concentration. Since the nonideality of the butadiene–benzene system is known to be too small to account for this behavior, a kinetic origin is proposed. A mechanism involving precoordination of two monomer molecules to the inactive catalyst dimer is proposed.

In a previous report we described results of a kinetic study of the polymerization of butadiene by π-crotylnickel iodide (1).[1] At that time it was concluded that the rate exhibited a strict first-order dependence on monomer concentration in the range 0.3–3.0 *M* butadiene. A similar conclusion had been previously arrived at by Lazutkin, *et al.*, using a π-allylnickel iodide catalyst.[2] Subsequent to our original measurements, we have made several new and more detailed series of measurements, both on the pure π-crotylnickel iodide catalyst and on this catalyst partially deactivated by reaction with benzoyl peroxide.[3] These measurements have shown that there is a substantial departure from first order monomer dependence at high monomer concentrations.

Results

The influence of monomer concentration on the reduced rate for a variety of catalyst concentrations in benzene is shown in Figure 1. The reduced rate is defined as the observed rate in moles per liter per second divided by the square root of the catalyst concentration, and eliminates the influence of the latter (see ref 1). In addition to pure catalyst runs, a pair of duplicate runs using equimolar catalyst and benzoyl peroxide is also included. In the latter case the reduced rate was calculated assuming that benzoyl peroxide destroys catalyst dimer on a two to one molar basis.[3]

The data in Figure 1 give a slope at lower monomer concentrations that is close to unity. However, it is clear, from both visual inspection and from the computer plotted best line, that the slope diminishes at high monomer concentration. This effect is much more evident in Figure 2, which shows the variation of slope (reaction order) of the line in

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[1] J. F. Harrod and L. R. Wallace, *Macromolecules*, **2**, 449 (1969).

[2] A. M. Lazutkin, V. A. Vaskevitch, S. S. Medvedev, and V. N. Vasileva, *Dokl. Akad. Nauk SSSR*, **175**, 859 (1967).

[3] L. R. Wallace and J. F. Harrod, *Macromolecules*, **4**, 656 (1971).

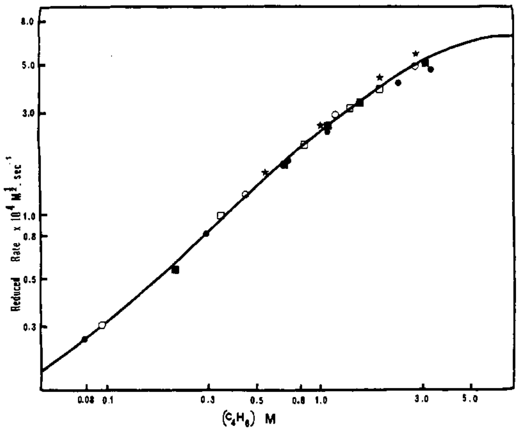


Figure 1. Dependence of reduced rate on monomer concentration: (●, ★, ○) $[C_4H_7NiI]_2$ cncentration = 0.0006, 0.0026, and 0.0049 *M*, respectively; (□ and ■) duplicate runs with an equimolar $[C_4H_7NiI]_2$ and benzoyl peroxide catalyst, both reagents 0.0051 *M*. The solid line is a computed best-fit curve to all data points. To avoid congestion only half the data points are included in the diagram. Reactions in benzene at 50°.

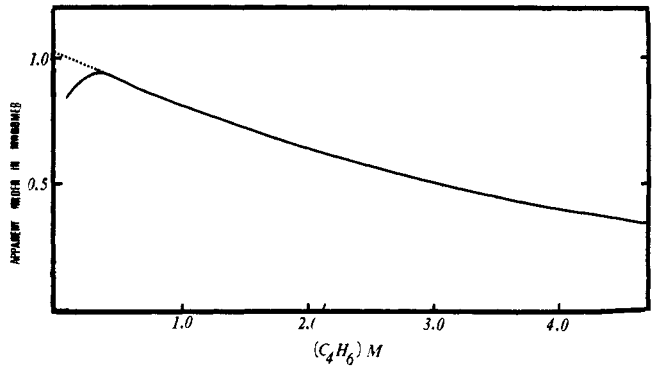


Figure 2. The variation of the slope of the best-fit line in Figure 1 with monomer concentration.

Figure 1 with monomer concentration. The apparent reaction order extrapolates very closely to unity at zero monomer concentration, descends to 0.5 at the highest experimental monomer concentration, and extrapolates to below 0.5 at higher monomer concentrations.

The possibility that the curvature in Figure 1 was due to nonideality in the butadiene–benzene system was excluded on the grounds that deviations from Henry's law were much too small. The latter was established in the course of determining the pressure–concentration curves for butadiene–benzene in preparation for our kinetic studies.

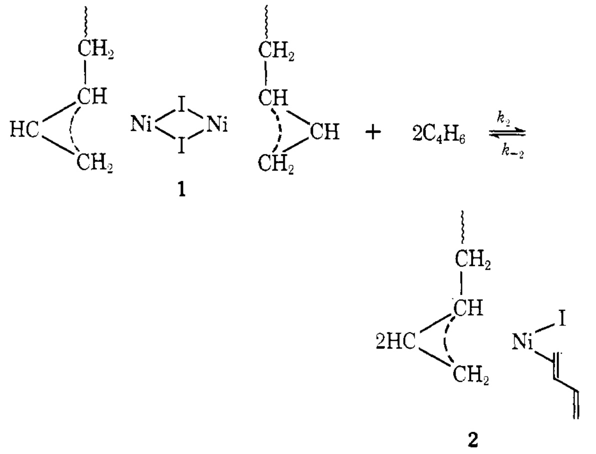
The dependence of rate on catalyst concentration has also been rechecked several times throughout the range of experimental conditions used for the data in Figure 1. The new data confirm that the reaction remains strictly one-half order in catalyst dimer in the range 0.002–0.02 *M*, as previously reported.[1]

Discussion

Assuming a rate law of the form

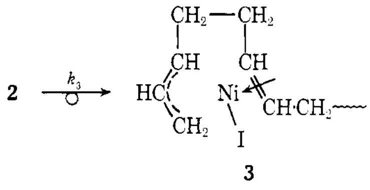
$$-\frac{d[C_4H_6]}{dt} = k[\text{catalyst}]^{1/2}[C_4H_6]$$

we previously concluded that a reasonable mechanism for the propagation process in the π-crotylnickel iodide dimer catalyzed butadiene polymerization was that represented in eq 1 and 2. After formation, **3** would either react with more



(1)

monomer to regenerate **2** or dimerize directly back to **1**.



(2)

The assumption of a strict first-order dependence on monomer concentration did not allow a distinction between the several mechanistic possibilities whereby the equilibrium (1) is established. The several possibilities are the following: (i) a slow dissociation of **1** followed by rapid equilibrium butadiene coordination to yield **2**; (ii) an equilibrium precoordination of a single butadiene to **1**, followed by slow dissociation of the adduct, followed by rapid equilibrium coordination of a second butadiene to the ligand deficient fragment resulting from dissociation; (iii) an equilibrium precoordination of two molecules of butadiene to **1** followed by equilibrium dissociation to **2**.

The kinetic features of these three cases may be summarized as follows (where C_2 = catalyst dimer and M = monomer).

case i

$$C_2 \overset{K_1}{\rightleftharpoons} 2C$$

$$C + M \overset{K_2}{\rightleftharpoons} CM$$

$$\therefore [CM] = K_2K_1^{1/2}[C_2]^{1/2}[M]$$

If $K_2K_1^{1/2}[M]$ is small, *i.e.*, equilibrium largely in direction of C_2, reaction rate ∝ $[C_2]^{1/2}[M]$.

If $K_2K_1^{1/2}[M]$ is large, reaction rate ∝ $[C_2][M]^0$.

case ii

$$C_2 + M \overset{K_3}{\rightleftharpoons} C_2M$$

$$C_2M \overset{K_4}{\rightleftharpoons} CM + C$$

$$C + M \overset{K_5}{\rightleftharpoons} CM$$

This case is not explicitly soluble, but it is readily seen that if K_3 is small enough to make the equilibrium lie in the direction of C_2, while K_5 is large enough to ensure that the monomeric nickel species are in the form of CM, the case is analogous to case i when $K_2K_1^{1/2}[M]$ was small. If K_3 is larger, to the point where most of the catalyst is in the form of C_2M, then we may approximate $[C_2M] = [C_2]$ and write

$$C_2M + M \xrightleftharpoons{K_6} 2CM$$

$$\therefore [CM] = K_6^{1/2}[M]^{1/2}[C_2]^{1/2}$$

Thus, if K_6 is small, reaction rate $\propto [C_2]^{1/2}[M]^{1/2}$. If K_6 is large, reaction rate $\propto [C_2][M]^0$.

case iii

$$C_2 + M \xrightleftharpoons{K_7} C_2M$$

$$C_2M + M \xrightleftharpoons{K_8} C_2M_2$$

$$C_2M_2 \xrightleftharpoons{K_9} 2CM$$

As in case ii, we can readily analyse these equilibria in terms of three extreme cases. Again, if K_7 is small enough to ensure that most of the catalyst is in the form of C_2 and K_9 is large enough to ensure that most of the dicoordinated catalyst is dissociated to CM, we have the analog of case i, with $K_2K_1^{1/2}[M]$ small. If the relationship of K_7 and K_8 is such that most of the catalyst exists as C_2M, we can equate $[C_2M]$ to $[C_2]_0$.

$$\therefore [CM] = (K_8K_9[C_2]_0[M])^{1/2}$$

and the reaction rate $\propto [C_2]^{1/2}[M]^{1/2}$.

If the values of K_7 and K_8, or [M], are such that most of the catalyst exists in the form of C_2M_2, we have the relationship

$$[CM] = K_9^{1/2}[C_2]_0^{1/2}[M]^0$$

It is evident that only case iii satisfies the requirements of the experimental data, namely that the order in monomer falls from unity to <0.5 at high monomer concentrations whilst the order in catalyst remains constant at 0.5.

Although we are unaware of any detailed kinetic studies on cleavage reactions of square-planar d^8 bridged dimers, it does not seem unreasonable in retrospect that such reactions should require attack at both metal atoms before complete dissociation is possible. Failure to coordinate both metal atoms before dissociation would lead to a highly unfavored three-coordinate product. On the other hand, raising the coordination of each Ni(II) to five prior to dissociation is acceptable, particularly for an organometallic species where the electron density at the metal center is high and the coordinating ligand is a π acid.[4]

Several examples of dienes coordinated to halide-bridged dimers have been reported. Winkhaus and Singer prepared (1,2:3,4-h^4-cyclohexadiene)-μ-dichlorotetracarbonyldirhodium(I).[5] Powell and Shaw prepared a rhodium(III) compound believed to be dichlorobis(1,2,3-h^3-crotyl)bis(1,2:3,4-h^4-butadiene)-μ-dichlorodirhodium(III).[6] The iridium analog of the latter was also prepared by Shaw and Singleton.[7] In all of these cases the authors favored structures in which the dienes bridged the two metal atoms. Such a form of bonding would be inconsistent with the facilitation of bridged dimer dissociation implied by the behavior of the crotylnickel iodide–butadiene system. In the latter case a monodentate association of a butadiene molecule with each nickel atom of the dimer is more likely.

Experimental Section

The experimental methods used in this study were the same as those described previously.[1] Polymerization rates were measured with a gas buret.

Catalyst solutions of known concentration were normally prepared gravimetrically. Occasionally, concentrations of active crotyl groups were checked using iodine titration. Provided the catalyst is prepared with sufficient care, we have found that gravimetric concentrations agree with those determined by iodimetry. The narrow spread of the data in Figure 1 attests to the remarkable stability and reproducibility of this catalyst system.

Acknowledgment. Financial support for this research and a Scholarship (L. R. W.) from the National Research Council of Canada are gratefully acknowledged.

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[4] For examples of five-coordinate π-crotylnickel species, see C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 6785 (1970).

[5] G. Winkhaus and H. Singer, *Chem. Ber.*, **99**, 3593 (1966).

[6] J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 597 (1968).

[7] B. L. Shaw and E. Singleton, *ibid.*, 1972 (1967).