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Contributions to the Mechanism of Isobutene Polymerization. IV. Effect of Conjugated Dienes

J. P. Kennedy[a]; R. G. Squires[ab]
[a] CENTRAL BASIC RESEARCH LABORATORY ESSO RESEARCH AND ENGINEERING COMPANY, LINDEN, NEW JERSEY [b] School of Chemical Engineering, Purdue University, W. Lafayette, Indiana

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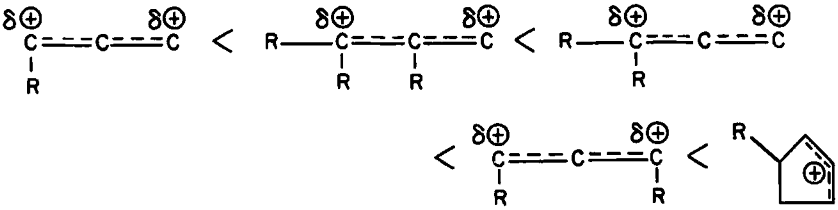
Contributions to the Mechanism of Isobutene Polymerization. IV. Effect of Conjugated Dienes

J. P. KENNEDY and R. G. SQUIRES*
CENTRAL BASIC RESEARCH LABORATORY
ESSO RESEARCH AND ENGINEERING COMPANY
LINDEN, NEW JERSEY

Summary

The effect of various conjugated dienes, e.g., butadiene, isoprene, 1,3-pentadiene, 2,3-dimethylbutadiene, 2,5-dimethyl-2,4-hexadiene, cyclopentadiene, 2-methylcyclopentadiene, and 1,3-hexadiene, on the rate of polymerization (yield) and molecular weight of polyisobutene has been investigated. The overriding effect of dienes is rate retardation (poisoning) and a lesser measure of molecular weight depression (transfer activity) (exception, 1,3-pentadiene). The effects have been expressed quantitatively with poison and transfer coefficients and their values have been discussed. The poison coefficients indicate that the order of stabilities of substituted allyl carbonium ions is



The effect of temperature on the rate poisoning with butadiene has been studied.

INTRODUCTION

The concept of allylic termination (*1*) is applicable to isobutene-conjugated diene systems. This paper concerns the effect of conjugated dienes on the cationic polymerization of isobutene and the

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[*] Present address: School of Chemical Engineering, Purdue University, W. Lafayette, Indiana.

poison and transfer coefficients P.C. and T.C. of these compounds. It is well known qualitatively that the amount of polymer formed is diminished and that the molecular weight of polyisobutene is strongly depressed if the polymerization is carried out in the presence of conjugated dienes (*2*). Empirical poison and transfer coefficients may be useful to express these phenomena quantitatively.

EXPERIMENTAL

The experimental procedure used has been described previously (*1*). The samples used in the determination of poison and transfer coefficients were analyzed chemically for unsaturation (*3*). Although the analysis was difficult to perform because of the small number of samples available, sufficient evidence was obtained to show the presence of only very small amounts of unsaturation in our samples (0.07 to 0.2 mole%). These very low unsaturation values indicate that copolymerization under our experimental conditions was neg-

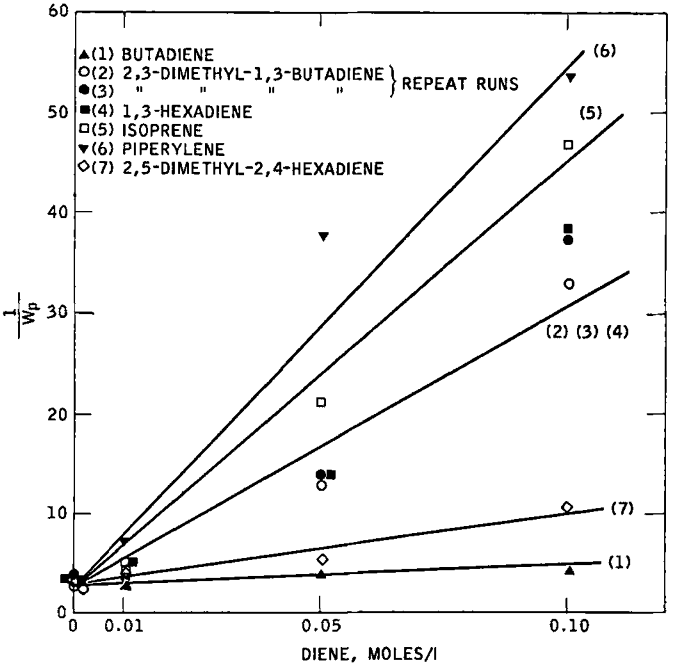


FIG. 1. Effect of dienes on reciprocal polymer yield.

ligible and perhaps the major source of unsaturation was terminal units (see below).

RESULTS

The effect of various conjugated dienes on the rate (yield) of polymerization and molecular weight of polyisobutenes is shown in Figs. 1 to 4. In particular, Figs. 1 and 2 show the effect of dienes on the reciprocal over-all yield of polyisobutene. Figure 3 shows the effect of dienes on reciprocal molecular weight and Fig. 4 summarizes the effects and shows the number of polyisobutene molecules formed as a function of increasing concentrations of various dienes. The poison and transfer coefficients have been calculated as described previously (*1*) and are given in Table 1.

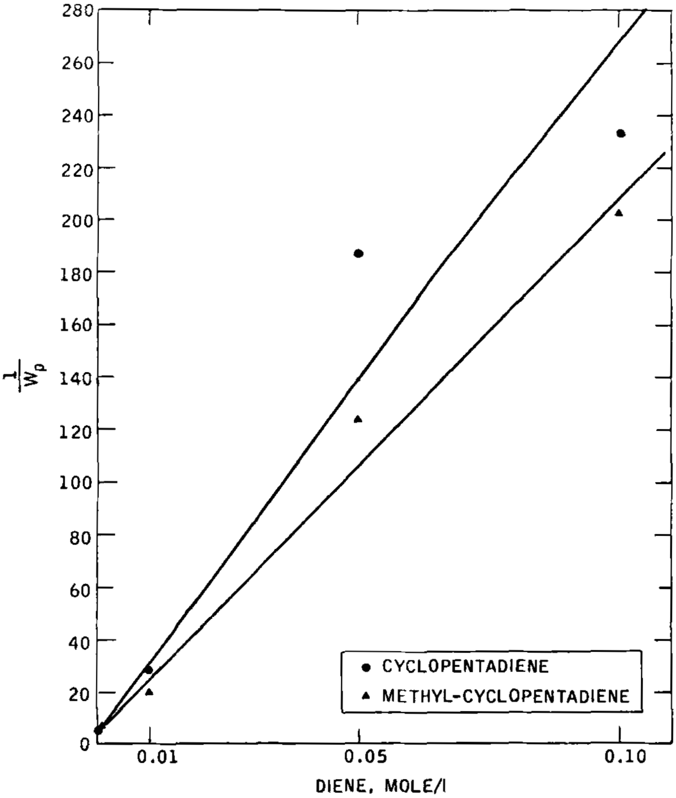


FIG. 2. Effect of cyclopentadiene and methylcyclopentadiene on reciprocal polymer yield.

TABLE 1

Experimental Poison and Transfer Coefficients of Dienes

Diene	Slope[a]	Int.[a]	P.C.	Slope[b] $\times 10^{-6}$	Int.[b] $\times 10^{-6}$	T.C.
Butadiene	23	3	7.6	2	1.0	2
Isoprene	420	3	140	60	1.0	60
1,3-Pentadiene	510	3	170	540	1.65	327
2,3-Dimethylbutadiene	280	3	107	4	1.1	3.6
1,3-Cyclohexadiene	310	3	103	48	1.0	48
2,5-Dimethyl-2,4-hexadiene	80	3	26.7	26	1.7	15.2
Cyclopentadiene	~2700	3	~900	Insufficient data		
2-Methylcyclopentadiene	~2050	3	~685	Insufficient data		

[a] Calculated from Fig. 1.

[b] Calculated from Fig. 3.

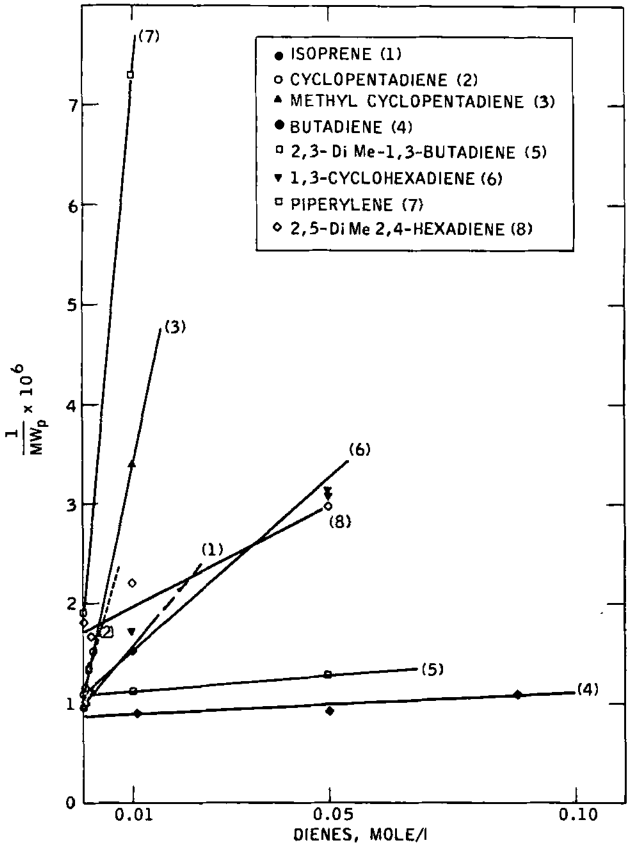


FIG. 3. Effect of dienes on reciprocal molecular weight.

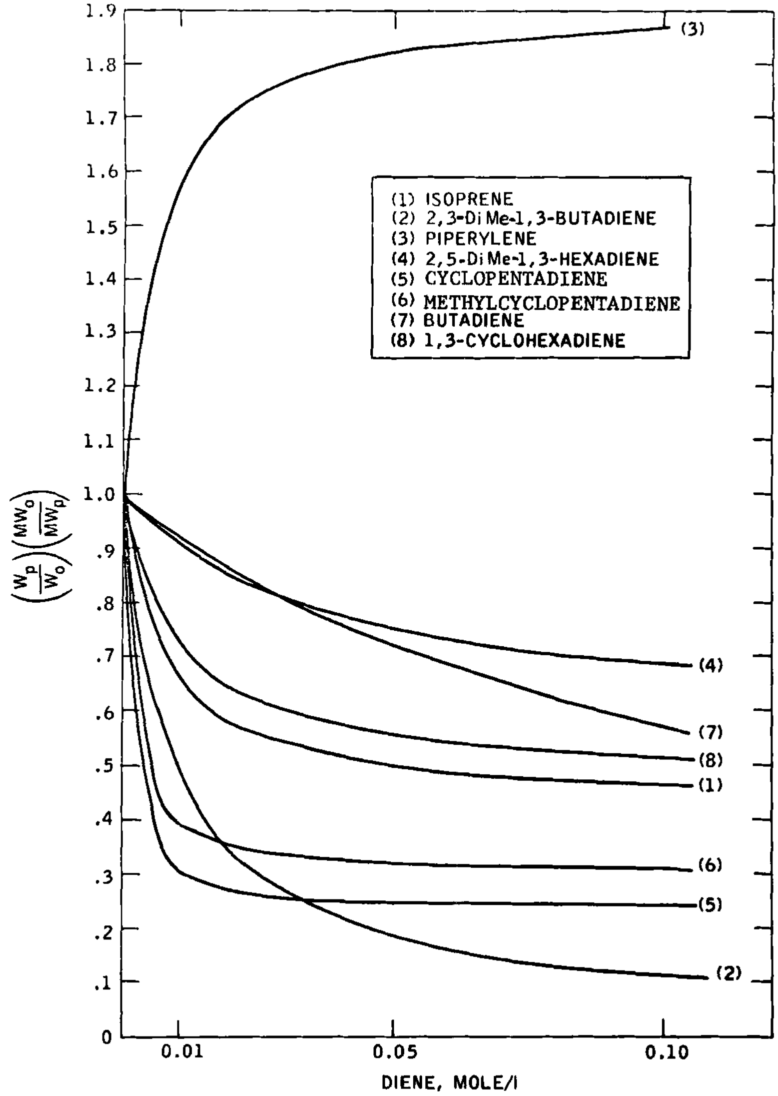


FIG. 4. Effect of dienes on relative number of molecules of polymer.

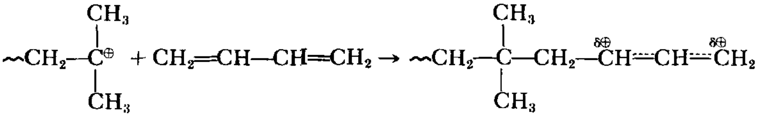
DISCUSSION

As discussed in the second section of this series of publications, when *n*-alkenes terminate the polymerization of isobutene, two kinetically independent species are formed: a saturated macromolecule and a resonance stabilized, end-substituted allylic cation.

However, in the presence of conjugated dienes only one species is formed, a macromolecular terminal allylic cation:

$$\sim C^{\oplus} + n\text{-alkene} \rightarrow \sim CH + \text{allyl}^{\oplus}$$
$$\sim C^{\oplus} + \text{diene} \rightarrow \sim C\text{—allyl}^{\oplus}$$

For example, with butadiene, the simplest diene,



$$\sim CH_2\text{—}\underset{CH_3}{\overset{CH_3}{C^{\oplus}}} + CH_2\text{=}CH\text{—}CH\text{=}CH_2 \rightarrow \sim CH_2\text{—}\underset{CH_3}{\overset{CH_3}{C}}\text{—}CH_2\text{—}\overset{\delta\oplus}{C}H\text{=}CH\text{=}\overset{\delta\oplus}{C}H_2$$

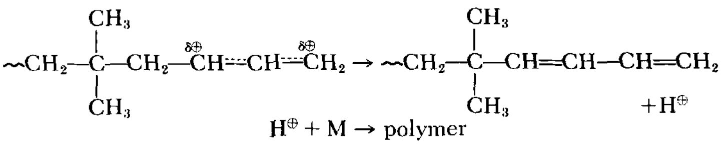
The energetics of this reaction are favorable; it goes from a tertiary carbonium ion to an end-substituted allylic carbonium ion, and a new C—C bond is formed.

That this diene incorporation reaction is an important event in the proposed mechanism is indicated by Figs. 1, 2, and 4. According to Figs. 1 and 2, dienes are efficient poisons; i.e., the over-all amount of polymer is substantially diminished in the presence of dienes. Furthermore, according to the plot in Fig. 4, the number of moles of polyisobutene obtained in the presence of dienes (except 1,3-pentadiene) has strongly decreased as compared to uninhibited control runs. The most likely explanation for these findings is that the growing polyisobutene carbonium ion incorporates a diene molecule, yielding a relatively stable substituted allylic ion which may then terminate the chain by resonance stabilization.

Decreased polymer yields in the presence of dienes may also be due to retarded initiation; i.e., the diene and catalyst interact and yield an inactive complex ("catalyst poison"). This, however, would not affect our calculated values of P.C. and T.C., since as previously derived [Ref. *1*, Eqs. (17) and (21)], P.C. and T.C. are independent of the initial effective catalyst concentration.

The fact that conjugated dienes are indeed incorporated into growing polyisobutene chains is directly indicated by the existence of isobutene-diene copolymers (butyl rubbers). Also it is well known that in the presence of dienes polyisobutenes with strongly depressed molecular weights are obtained (*2*,*4*).

Chain transfer is most likely due to protonation of a monomer molecule by an expelled proton. Proton expulsion is favored by stabilization of the terminal allyl carbonium ion and simultaneous formation of conjugation at the end of the polymer molecule:

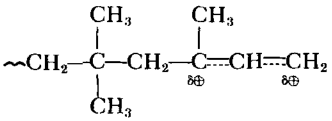


$$\sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{\delta\oplus}{C}H\text{:::}CH\text{:::}\overset{\delta\oplus}{C}H_2 \rightarrow \sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH-CH=CH_2 \quad +H^{\oplus}$$

$$H^{\oplus} + M \rightarrow \text{polymer}$$

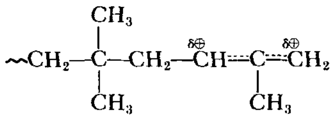
The presence of a conjugated end group has been corroborated in similar experiments (2).

Examining the dienes investigated individually, butadiene was found to be the least "poisonous" (P.C. = 7.6) and it hardly affected molecular weights (T.C. = 2). Isoprene was a much stronger poison (P.C. = 140) and transfer agent (T.C. = 60), which is conceivably due to formation of the more stable 1,1′-disubstituted (i.e., primary-tertiary) allyl carbonium ion:



$$\sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{\delta\oplus}{C}}\text{:::}CH\text{:::}\underset{\delta\oplus}{C}H_2$$

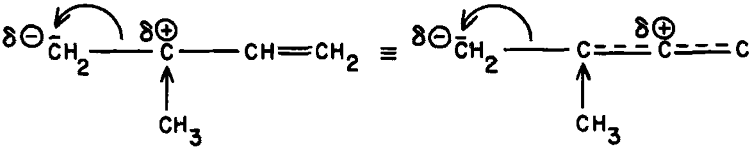
According to this theory, electrophilic attack on isoprene occurs on carbon atom 1 in preference to carbon atom 4. If the attack were to take place at carbon 4, a relatively less stable end-and-middle-substituted (i.e., primary-secondary) allyl carbonium ion would be formed:



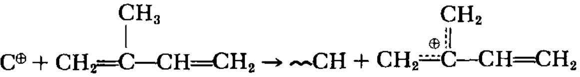
$$\sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{\delta\oplus}{C}H\text{:::}\underset{CH_3}{C}\text{:::}\overset{\delta\oplus}{C}H_2$$

Since the relative stability of this ion is conceivably below that obtainable from butadiene (middle substituent in allyl cation decreases its stability; see later), the poison and transfer coefficients of isoprene would be expected to be less than those of butadiene. This, however, is far from being the truth.

Simple electronic considerations also suggest that isoprene is attacked on carbon atom 1. The methyl substituent on carbon 2 releases electrons toward the conjugated backbone and enhances the electron density on carbon 1:

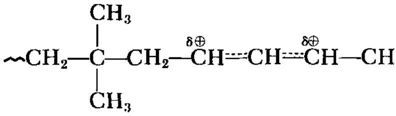


In addition to these incorporation reactions of isoprene the possibility also exists that the three primary hydrogens might also function as hydride sources:

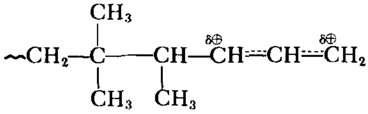

$$\sim C^{\oplus} + CH_2{=}\underset{}{\overset{CH_3}{\overset{|}{C}}}{-}CH{=}CH_2 \rightarrow \sim CH + CH_2\overset{\oplus}{\cdots}\overset{CH_2}{\overset{\|}{C}}{-}CH{=}CH_2$$

However, compared to incorporation, this reaction is probably of little importance.

1,3-Pentadiene seems to be the strongest poison (P.C. = 170) among the simple aliphatic dienes investigated. Large poisoning efficiency is probably due to the formation of highly resonance-stabilized 1,3-di-end-substituted (i.e., secondary-secondary) allyl ion:

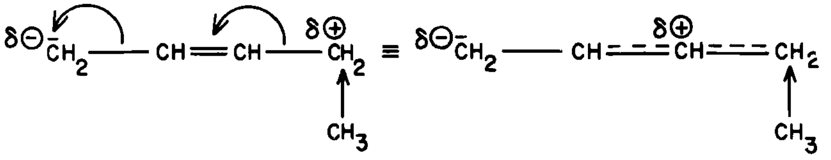

$$\sim CH_2{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}CH_2{-}\overset{\delta\oplus}{C}H\cdots CH\cdots\overset{\delta\oplus}{C}H{-}CH_3$$

This theory indicates that 1,3-pentadiene is attacked at carbon atom 1 and not at carbon atom 4 during the cationic polymerization. If 1,3-pentadiene would be attacked at carbon 4, the formation of the following relatively less stable monosubstituted (i.e., primary-secondary) allylic carbonium ion would be expected:


$$\sim CH_2{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}\underset{CH_3}{\underset{|}{CH}}{-}\overset{\delta\oplus}{C}H\cdots CH\cdots\overset{\delta\oplus}{C}H_2$$

Since the stability of this allyl ion would probably be similar to that obtainable from butadiene, the poisoning activity of 1,3-pentadiene would also be similar to that of butadiene. Since this is far from being the truth and 1,3-pentadiene is a much stronger poison than butadiene, attack on carbon atom 4 is highly unlikely.

In addition to this argument, simple steric and electronic considerations would, of course, also favor carbonium ion attack on carbon atom 1. Owing to the terminal methyl group in the diene, attack would be sterically less favorable on the 4-position than on carbon 1. And polarization induced by the terminal methyl substituent would enhance electron density, i.e., reactivity toward electrophilic attack on carbon atom 1:

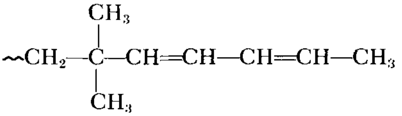


The three primary allylic hydrogens in 1,3-pentadiene might also be hydride sources. The allylic cation formed from 1,3-pentadiene after hydride transfer to the growing chain might be a very stable species:

$$\overset{\delta\oplus}{C}H_2{=}CH{=}CH{=}CH{=}\overset{\delta\oplus}{C}H_2$$

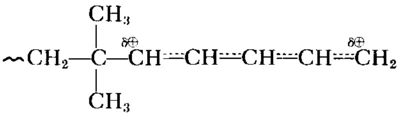
in which the electron deficiency is distributed from C_1 to C_5, giving an extremely stable highly "poisonous" structure. It could be that such a structure is at least partially responsible for the high rate-poisoning effect of 1,3-pentadiene.

The unusually high transfer coefficient of 1,3-pentadiene might be due to proton expulsion from the above-postulated 1,3-di-end-substituted allyl cation to give a disubstituted conjugated structure:



$$\sim CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH{=}CH-CH{=}CH-CH_3$$

Finally, this conjugated species could itself function as a strong poison because of its three primary allylic hydrogens, giving a high conjugated, substituted allylic cation:

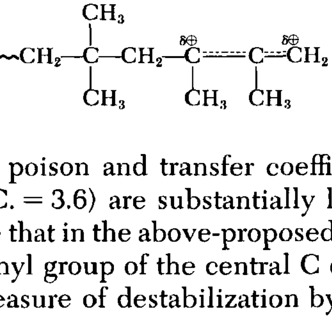


$$\sim CH_2-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\delta\oplus}{C}H{=}CH{=}CH{=}CH{=}\overset{\delta\oplus}{C}H_2$$

which might contribute to the over-all high poisoning efficiency of 1,3-pentadiene. Similar structures cannot be formed from butadiene or isopropene.

However, the contribution of these structures to the over-all poisoning effect of 1,3-pentadiene is probably not too significant. If this contribution would be important, we would expect 2,5-dimethyl-2,4-hexadiene carrying 12 primary allylic hydrogens to have an extremely high P.C. value. This, however, is contrary to the facts. Indeed, 2,5-dimethyl-2,4-hexadiene is a rather mild poison (P.C. = 26.7) and transfer agent (T.C. = 15.2). The low poison coefficient and perhaps also the small transfer coefficient of this highly substituted diene could be due to severe steric hindrance toward attack by and incorporation into the growing polyisobutene cation. Consequently, the main rate and/or molecular weight determining events in the presence of conjugated dienes probably involve diene incorporation steps.

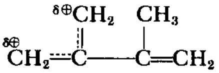
No unusual steric hindrance impedes the incorporation of 2,3-dimethylbutadiene into the growing chain, giving a 1,1,2-trisubstituted (terminal) allyl carbonium ion:



$$\sim CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{\delta\oplus}{C}}\cdots\underset{CH_3}{C}\cdots\overset{\delta\oplus}{C}H_2$$

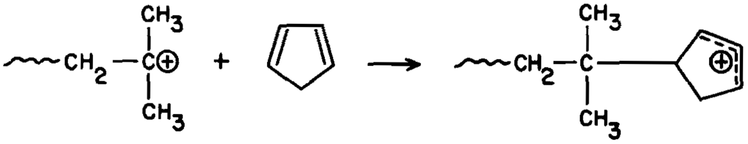
Interestingly, the poison and transfer coefficients of this diene (P.C. = 107 and T.C. = 3.6) are substantially lower than those for isoprene. It could be that in the above-proposed somewhat crowded allyl cation the methyl group of the central C of the allyl structure introduces some measure of destabilization by straining or our-of-plane puckering of the ion, which in turn manifests itself by decreased poisoning and transfer efficiency. Fisher-Briegelb atomic models seem to corroborate this proposition.

Termination by hydride transfer is possible but is considered rather unlikely with 2,3-dimethylbutadiene, because the ion formed would be a middle-substituted (relatively less stable) structure:



$$\overset{\delta\oplus}{C}H_2\cdots\overset{{}^{\delta\oplus}CH_2}{\overset{\vdots\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2$$

Cyclopentadiene and its 2-methyl derivative were found to be very strong poisons (P.C. = ~900 and ~685). Since isobutylene is known to copolymerize with cyclopentadiene (5), the existence of the following terminal ion structure is indicated:



Since this terminal allyl ion is structurally closely related to that obtainable from 1,3-pentadiene—both ions are di-end-substituted

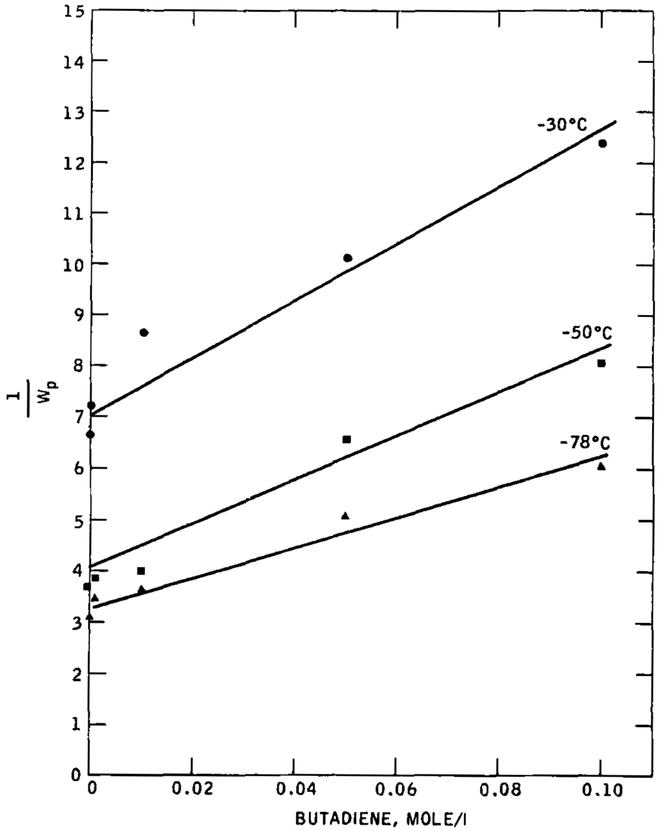
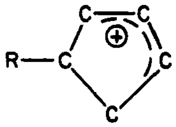
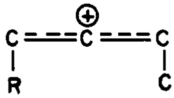


FIG. 5. Temperature dependency of poisoning effect of butadiene.

allylic species, i.e.,



and



the question arises why the bridged or cyclic ion is a more severe poison than the linear ion. Perhaps one part of the answer is that cyclopentadiene is a more strained and, consequently, more reactive monomer than 1,3-pentadiene, and therefore it requires less activation energy for incorporation into the growing chain than the latter. The P.C. of 1,3-cyclohexadiene is much lower than that of cyclopentadiene, probably because this diene exists in a relatively strainless "half-chair" configuration.

There may also be the possibility of termination by hydride

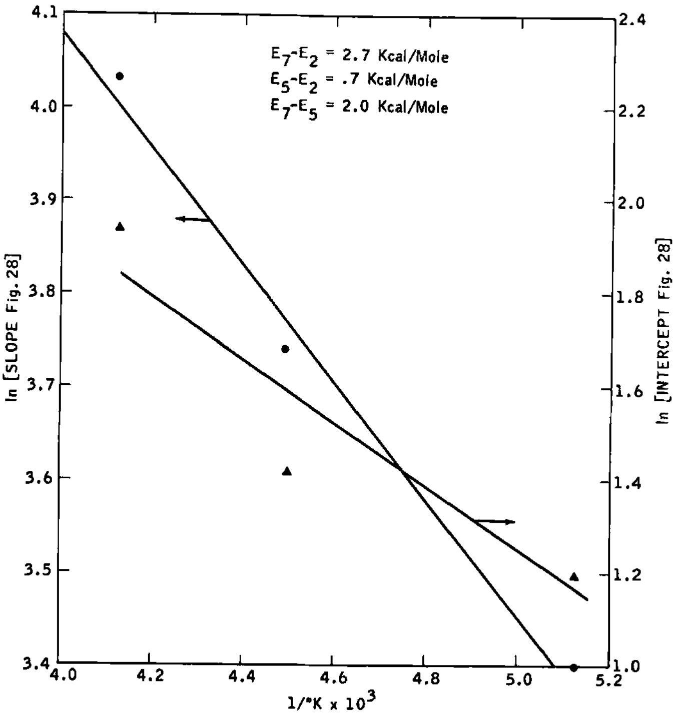
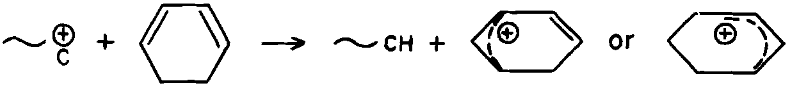


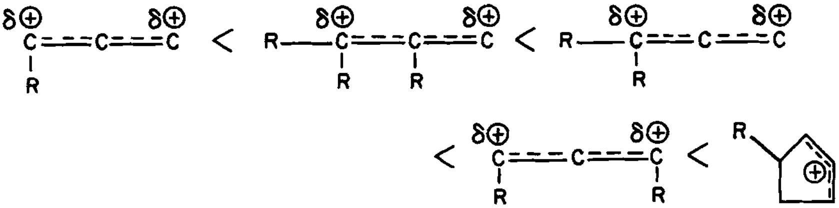
FIG. 6. Determination of activation energies for butadiene.

transfer with these cyclic dienes; i.e.,



giving rise to relatively stable resonating structures. The poison coefficients, of course, reflect the over-all situation and cannot distinguish among these possible mechanisms.

On the basis of these data the following sequence can be proposed for the over-all order of relative stabilities of substituted allyl carbonium ions (disregarding rotational isomers):



EFFECT OF TEMPERATURE ON THE POISONING WITH BUTADIENE

In an independent series of experiments, the effect of temperature poisoning activity of butadiene in isobutene polymerization was investigated in the temperature range between −30 to −78°C. Figure 5 shows the results and Fig. 6 is a plot used to calculate activation energies shown in the figure. As derived in the second paper of this series, the temperature dependency of the slope and intercept of Fig. 5 is related to the activation energies for propagation (E_2), spontaneous termination (E_5), and termination with poison (E_7) by the equations

$$\frac{d(\ln \text{slope})}{d(1/T)} = \frac{E_2 - E_7}{R}$$

$$\frac{d(\ln \text{intercept})}{d(1/T)} = \frac{E_2 - E_5}{R}$$

From these values the temperature dependence of the P.C. may be easily calculated:

$$\frac{d(\ln \text{P.C.})}{d(1/T)} = \frac{E_7 - E_5}{R}$$

From Fig. 6 we see that the P.C. for butadiene will increase with increasing temperature.

Acknowledgment

The authors are grateful to acknowledge Dr. S. Bank's valuable advice and criticism, which greatly helped to formulate the theory.

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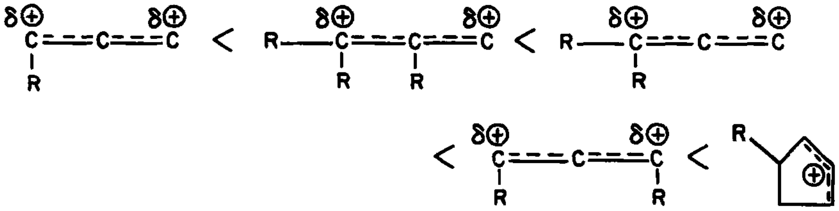
Zusammenfassung

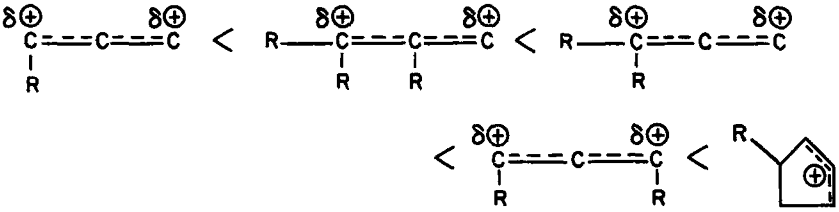
Der Einfluss verschiedener konjugierter Diene, z.B. Butadien, Isopren, 1,3-Pentadien, 2,3-Dimethylbutadien, 2,5-Dimethyl-2,4-hexadien, Cyclopentadien, 2-Methylcyclopentadien, und 1,3-Hexadien auf die Polymerisationsgeschwindigkeit (Ausbeute) und das Molekulargewicht von Polyisobutylen wurde untersucht. Der überragende Einfluss dieser Diene besteht in einer Verringerung der Geschindigkeit (Vergiftung) und zu einem geringeren Grade in einer Verringerung des Molekulargewichts (Ubertragungsaktivität) (Ausnahme: 1,3-Pentadien). Diese Effekte wurden quantitativ als Vergiftungs und Übertragungskoeffizienten ausgedrückt, deren numerische Werte diskutiert werden. Die Vergiftungskoeffizienten weisen darauf hin, dass man folgende Reihe der Stabilität für substituierte Allylcarboniumionen aufstellen kann:



Ebenfalls untersucht wurde der Einfluss der Temperatur auf die Vergiftungsgeschindigkeit von Butadien.

Résumé

On a étudié l'effet de différentes diènes conjugués, par ex. du butadiène, d'isoprène, du pentadiène-1,3, du diméthyl-2,3-butadiène, du diméthyl-2,5-hexadiène, du cyclopentadiène, du méthyl-2-cyclopentadiène, et d'hexadiène-1,3 sur la vitesse de polymérisation (rendement) et le poids moléculaire du polyisobutène. L'effet principal est le rallentissement de vitesse (empoisonnement) et une mesure plus faible de la depression du poids moléculaire (activité de transfert) (à l'exception de pentadiène-1,3). Les effets sont exprimés quantitativement avec des coëfficients empoisonnant et de transfert et leur valeurs discutées. Les coëfficients empoisonnant indiquent que l'ordre des stabilités des ions carbonium substitués est



On a étudié l'effet de température sur le retard de vitesse du butadiène.