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Contributions to the Mechanism of Isobutene Polymerization. II. Effect of *n*-Alkenes on Yields and Molecular Weights and Effect of Temperature on Poison Coefficients and Transfer Coefficients

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Summary

The effect of *n*-alkenes, i.e., propylene, 1-butene, 1-pentene, 1-hexane, and 2-octene, on the yield and molecular weight of polyisobutene obtained with $AlCl_3$ catalyst in *n*-pentane solvent at −78°C has been investigated. It has been found that the lower 1-alkenes are pure poisons; i.e., they decrease the yield (rate poisons) but do not affect product molecular weight. The rate-decreasing effect of *n*-alkenes has been treated quantitatively by poison coefficients and their numerical values correlated with relative carbonium ion stabilities using the allylic termination concept. The mild molecular weight decreasing effect of 2-octene has been attributed to moderate transfer activity. The effect of temperature on the poison coefficients of 2-octene has been investigated and some insight into the activation energies of various elementary steps has been gained.

INTRODUCTION

In the first section of this series (*1*) we presented the general concept of polymerization termination by allylic stabilization in carbonium ion polymerizations and discussed the kinetic model of the proposed mechanism used in this and subsequent publications. This section concerns the poisoning (yield decreasing) and transfer (molecular weight decreasing) effects of various simple *n*-alkenes on isobutene polymerizations in *n*-pentane solvent with $AlCl_3$ (in

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methyl chloride) catalyst solutions. A purpose of this study was to detect and analyze a possible correlation between relative carbonium ion stabilities and poison coefficients and transfer coefficients. Poison and transfer coefficients quantitatively measure the yield decreasing and molecular weight decreasing effect of materials used in conjunction with isobutylene monomer in the above system (*1*).

RESULTS

Figures 1 and 2 show the effect of various simple *n*-alkenes on the conversion of isobutene and molecular weight of polyisobutene, respectively. Figure 3 is a plot of the relative number of moles of polymer formed as a function of *n*-alkene concentrations. W_p and MW_p are product weight and molecular weight, respectively; subscripts 0 and *p* indicate the absence and presence of *n*-alkenes (poisons, in general), respectively.

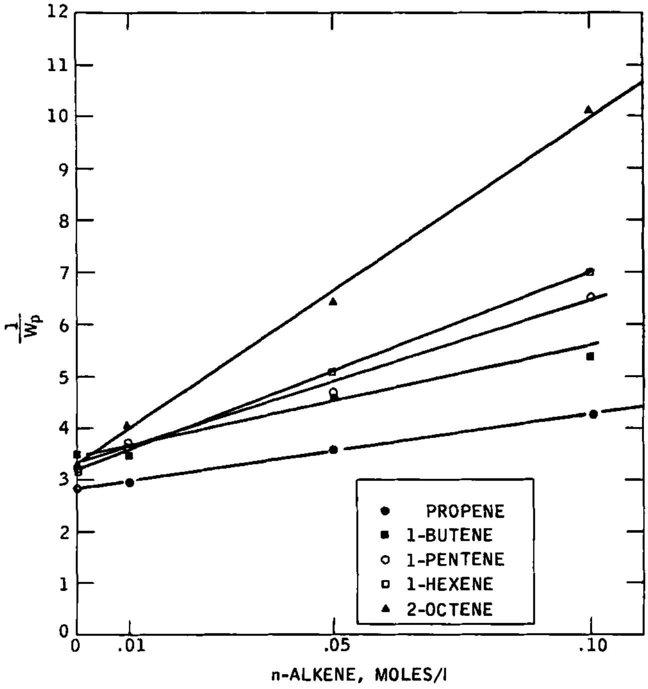


FIG. 1. Effect of *n*-alkene concentration on reciprocal polymer yield.

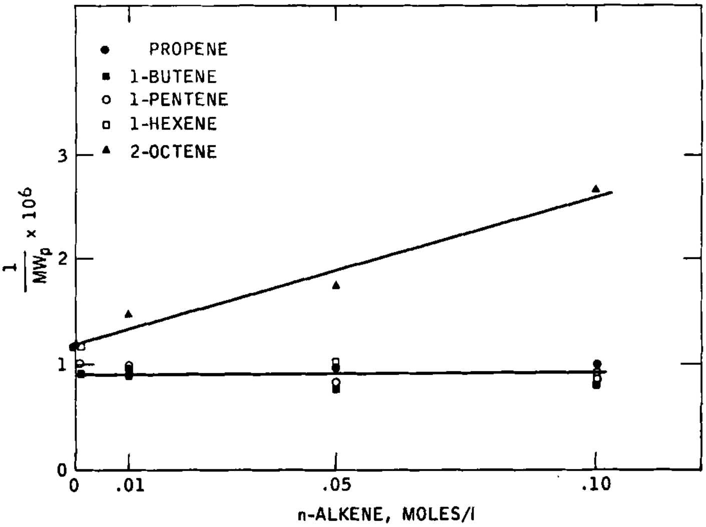


FIG. 2. Effect of *n*-alkene concentration on reciprocal molecular weight.

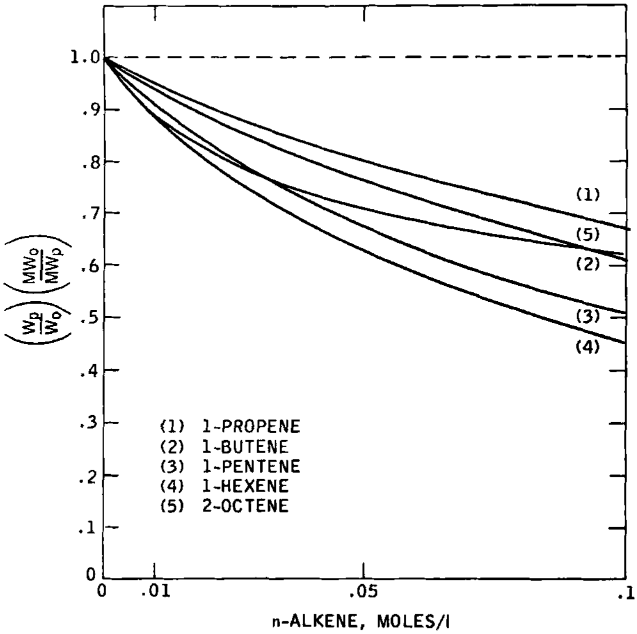


FIG. 3. Effect of various alkenes on the relative number of polymer molecules formed.

In particular, Figs. 1 and 2 show the influence of various concentrations of propene, 1-butene, 1-hexene, and 2-octene on reciprocal polymer yield and reciprocal molecular weight, respectively. As explained in the first paper of this series (*1*) the slopes of these lines divided by the corresponding intercepts give the poison coefficients, P.C., and transfer coefficients, T.C., respectively. The P.C. and T.C. of a particular compound express its effectiveness as chain terminator (poison) or molecular weight depressor (transfer agent). The data are given in Table 1.

TABLE 1

Empirical Poison Coefficients and Transfer Coefficients of *n*-Alkenes

n-Alkene	Slope[a]	Int.[a]	P.C.	Slope[b] $\times 10^{-6}$	Int.[b] $\times 10^{-6}$	T.C.
Propene	14	2.85	4.9	0	0.9	0
1-Butene	21.5	3.45	6.2	0	0.9	0
1-Pentene	32	3.3	9.7	0	0.9	0
1-Hexene	38	3.2	11.8	0	0.9	0
2-Octene	67	3.2	20.8	14	1.15	12.1

[a] Calculated from Fig. 1.
[b] Calculated from Fig. 2.

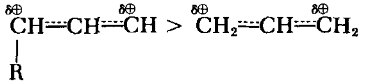
DISCUSSION

These data indicate that under our experimental conditions the lower 1-alkenes are pure poisons, i.e., only diminish the over-all rate (yield) of polymerization but do not depress molecular weights. A more subtle effect is the increasing P.C. with increasing chain length; i.e., the P.C. increases from 4.9 for propene to 11.8 for 1-hexene. These findings can be explained by the allylic termination concept.

Propene, the mildest poison of the *n*-alkene series, gives the least stable unsubstituted allylic carbonium ion on allylic termination:

$$\sim C^{\oplus} + CH_3{-}CH{=}CH_2 \xrightarrow{-H^{\oplus}} \sim CH + \overset{\delta\oplus}{C}H_2 \overset{\cdots}{=} CH \overset{\cdots}{=} \overset{\delta\oplus}{C}H_2$$

Since the driving force toward the formation of the unsubstituted allyl cation is less than that available in the case of longer-chain *n*-olefins giving substituted allylic ions, propene is the mildest poison of them all. With 1-butene, 1-pentene, 1-hexene, etc., containing two secondary allylic hydrogens, the formation of allyl carbonium ions is facilitated because the end-substituted ion is more stable than the unsubstituted one, e.g.,



$$\underset{\mathrm{R}}{\overset{\delta\oplus}{\mathrm{C}}\mathrm{H}}\text{=}\!\!\text{=}\mathrm{CH}\text{=}\!\!\text{=}\overset{\delta\oplus}{\mathrm{C}}\mathrm{H} > \overset{\delta\oplus}{\mathrm{C}}\mathrm{H_2}\text{=}\!\!\text{=}\mathrm{CH}\text{=}\!\!\text{=}\overset{\delta\oplus}{\mathrm{C}}\mathrm{H_2}$$

and because the allylic hydrogen which is transferred to the growing site is most likely a secondary one whose extraction requires less energy than that of a primary hydrogen as in the case of propene. It is interesting to note that the P.C. increase from 6.2 for 1-butene to 9.7 for 1-pentene and to 11.8 for 1-hexene. This could be due to the monotonically increasing basicity of the secondary allylic hydrogen in this series, which in turn is due to the increasing electron-donating tendency of CH_3—, CH_3CH_2—, and $CH_3CH_2CH_2$— groups in the homologs.

It was surprising to find that simple 1-olefins did not seem to affect the molecular weights under our experimental conditions. This fact might appear to contradict earlier findings by Thomas et al. (*2*), who obtained lower molecular weight polyisobutenes in the presence of increasing amounts of *n*-butenes. However, the important difference between these investigations and our experiments is that the concentrations of poisons used by the previous authors were very much higher (~10%) than those used in our work (~1%).

The molecular weight depressing effect of simple 1-olefins is very mild; they are at best weak poisons (as depicted earlier in row 3, Fig. 1, Ref. *1*). Thus, with *n*-olefins the small amount of low molecular weight material which might have formed in the presence of large quantities of "normal" molecular weight product is apparently too low to affect the average viscosity molecular weights of the over-all product. However, in the presence of larger quantities of *n*-olefins as used by the earlier workers, the amount of low molecular weight fraction increases and the over-all molecular weights start to decrease.

The fact that 2-octene is a much stronger poison, i.e., has a much higher P.C. than any of the *n*-alkenes, is probably due to the formation of the more stable doubly substituted secondary allyl carbonium ion

$$\mathrm{CH_3}\text{—}\overset{\delta\oplus}{\mathrm{C}}\mathrm{H}\text{=}\!\!\text{=}\mathrm{CH}\text{=}\!\!\text{=}\overset{\delta\oplus}{\mathrm{C}}\mathrm{H}\text{—}\mathrm{C_4H_9}$$

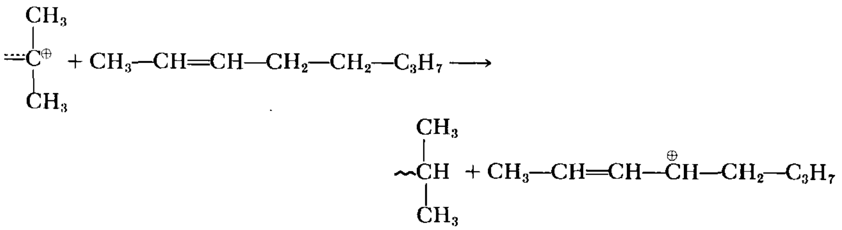
(perhaps together with some contribution from the less stable species

$$\overset{\delta\oplus}{\mathrm{C}}\mathrm{H_2}{=\!=}\mathrm{CH}{=\!=}\overset{\delta\oplus}{\mathrm{C}}\mathrm{H{-}C_5H_{11}})$$

in the termination reaction. The mild molecular weight depressing effect, i.e., appreciable T.C. value of 12.1 of 2-octene, indicates either strong poisoning (row 5, Fig. 1, Ref. *1*) or, more likely, chain-transfer activity (see below).

Figure 3 shows the effect of increasing concentrations of *n*-alkenes on the relative number of polymer molecules formed under our experimental conditions. Figure 3 (and other subsequent similar plots) are not direct plots of experimental data. They are plotted from points calculated by Eq. (23) of Ref. *1*, based on experimentally determined poison and transfer coefficients. Chain terminating, i.e., poisoning activity, is indicated by declining lines. In other words, the number of polymer molecules decreases with increasing poison concentration. As derived in Ref. *1*, the slope of the lines in Fig. 3 is given by the expression (T.C. – P.C.)/[1 + (P.C.)X]^2. And, as the poison concentration X approaches zero, the slope becomes (T.G. – P.C.). Thus for propene, 1-butene, 1-pentene, and 1-hexene, for which T.C. is zero, the initial slope of the curve in Fig. 3 is equal to the poison coefficient. Although 2-octene is a much stronger poison than the other olefins, it is also a transfer agent, as indicated by its T.C. of 12.1. Thus the initial slope of the 2-octene curve in Fig. 3 is an indication of the difference of T.C. and P.C. Note, however, that as the poison concentration increases, the slope of the 2-octene curve diminishes and, in fact, crosses the *n*-alkene curves. This relative increase in the number of moles of polymer formed in the 2-octene case emphasizes its role as a transfer agent as well as a poison.

Transfer activity of 2-octene, and conceivably of normal 2-alkenes in general, could be explained by the following mechanism:



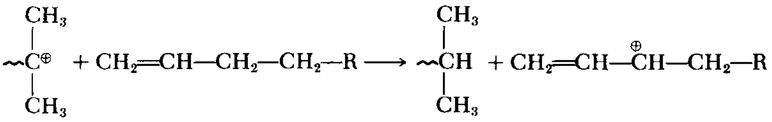
$$\sim\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}^{\oplus}}} + \mathrm{CH_3{-}CH{=}CH{-}CH_2{-}CH_2{-}C_3H_7} \longrightarrow \sim\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{CH}}} + \mathrm{CH_3{-}CH{=}CH{-}}\overset{\oplus}{\mathrm{C}}\mathrm{H{-}CH_2{-}C_3H_7}$$

$$CH_3{-}CH{=}CH{-}\overset{\oplus}{C}H{-}CH_2{-}C_3H_7 \xrightarrow{-H^\oplus} CH_3{-}CH{=}CH{-}CH{=}CH{-}C_3H_7 + H^\oplus$$

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

i.e., after termination by hydride transfer some of the allyl cations are stabilized by proton elimination and the formation of a conjugated double-substituted diene, for example, 1-methyl-4-propyl butadiene-1,3; the expelled proton may then reinitiate a chain resulting in depressed molecular weights.

At this point the question might be raised why do 2-alkenes (i.e., 2-octene) show but 1-alkenes do not show experimental transfer coefficients? As shown above for 2-octene, it would be conceivable to visualize the following reaction sequence for 1-alkenes as well:



$$\sim\overset{CH_3}{\underset{CH_3}{C^\oplus}} + CH_2{=}CH{-}CH_2{-}CH_2{-}R \longrightarrow \sim\overset{CH_3}{\underset{CH_3}{CH}} + CH_2{=}CH{-}\overset{\oplus}{C}H{-}CH_2{-}R$$

$$CH_2{=}CH{-}\overset{\oplus}{C}H{-}CH_2{-}R \xrightarrow{-H^\oplus} CH_2{=}CH{-}CH{=}CH{-}R + R^\oplus$$

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

As discussed above, the driving force for hydride transfer from 1-alkenes to the growing carbonium ion is less than that obtained during hydride transfer from 2-alkenes and the

$$\overset{\delta\oplus}{C}H_2{-}CH{-}\overset{\delta\oplus}{C}H{-}R$$

is less stable and consequently exist in lower concentrations than

$$R{-}\overset{\delta\oplus}{C}H{-}CH{-}\overset{\delta\oplus}{C}H{-}R$$

This relative difference in carbonium ion stabilities is reflected in the lower poison coefficients of 1-alkenes as compared to 2-alkenes. Significantly, however, the energetics of deprotonation of these allylic carbonium ions to the corresponding dienes are also expected to be different. Thus the stabilization energy released during deprotonation by

$$\overset{\delta\oplus}{C}H_2{-}CH{-}\overset{\delta\oplus}{C}H{-}CH_2{-}R \rightarrow CH_2{=}CH{-}CH{=}CH{=}R + H^\oplus$$

is probably substantially less than the energy released by

$$R{-}CH_2{-}\overset{\delta\oplus}{C}H{-}CH{-}\overset{\delta\oplus}{C}H{-}CH_2{-}R \rightarrow R{-}CH{=}CH{-}CH{=}CH{-}CH_2{-}R + H^{\oplus}$$

The driving force to form the di-end-substituted conjugated diene from the di-end-substituted allyl carbonium ion is larger than that available in the former reaction. Since the concentration of the less stable mono-end-substituted allylic carbonium ion is relatively small (certainly smaller than the concentration of the more stable di-end-substituted ion), its transfer activity, i.e., transfer coefficient, will be very small or might not even be noticeable, as is apparently the case under our experimental conditions.

This hypothesis is particularly attractive for 1-butene. According to this line of reasoning 1-butene would give (after hydride transfer to

$$\overset{\delta\oplus}{C}H_2 \overset{\cdots}{-} CH \overset{\cdots}{-} \overset{\delta\oplus}{C}H{-}CH_3$$

and deprotonation) 1,3-butadiene, a conjugated diene with very low (if any) resonance stabilization. Higher 1-alkenes might form more readily conjugated dienes (i.e., 1-pentene → piperylene, etc.), representing increasing amounts of resonance stabilization, but our data do not seem to indicate this tendency. However, this sequence of events, i.e., hydride transfer followed by deprotonation, is expected to be even more favorable with 2-alkenes, which in this manner would give resonance-stabilized di-end-substituted conjugated dienes.

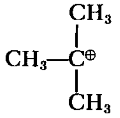
Finally, in line with this theory of resonance-stabilized conjugated diene formation from suitable 2-alkenes, we further might expect that the "in situ" formed diene will be a severe (rate) poison which in turn might contribute to and at least be partially responsible for the strongly depressed over-all rates observed in the presence of 2-alkenes. The effect of conjugated dienes on the rate of cationic isobutene polymerizations and polyisobutene molecular weights will be examined in detail later.

CARBONIUM ION STABILITIES

These results, particularly the poison coefficients, may be useful in semiquantitatively assessing over-all carbonium ion stabilities of aliphatic cations. However, at this point a fundamental question must be answered; i.e., why does propene reduce the rate of isobutene polymerization at all? One would be inclined to argue that the unsubstituted allyl ion

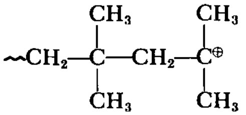
$$\overset{\delta\oplus}{C}H_2\text{=}CH\text{=}\overset{\delta\oplus}{C}H_2$$

is less stable than the *t*-butyl ion



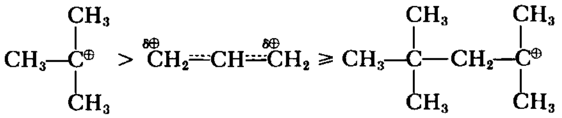
$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^{\oplus}}}$$

which is akin to the propagating species in isobutene polymerization. Consequently, one would not expect hydride transfer to occur as proposed by the basic postulate. This is the notion one would acquire from solvolisis data, displacement rates, etc. (3). However, on closer examination this argument does not hold, since the ion which must be considered in this context is not the *t*-butyl cation but the bulky



$$\sim CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^{\oplus}}}$$

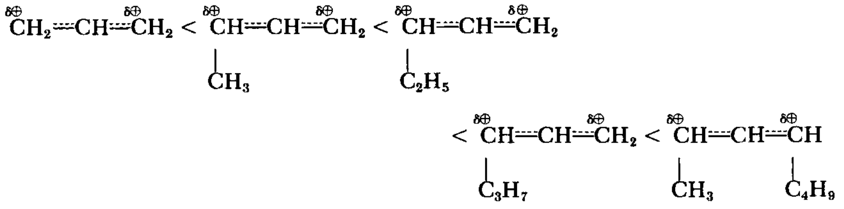
species. The latter ion is a very close relative of the 2,2,4-trimethylpentane ion and the pertinent question is how the stability of this ion compares with that of the unsubstituted allyl carbonium ion. The answer is conceivably that the stability of the 2,2,4-trimethylpentane carbonium ion is probably lower than that of the allyl ion; i.e.,



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^{\oplus}}} > \overset{\delta\oplus}{C}H_2\text{=}CH\text{=}\overset{\delta\oplus}{C}H_2 \geq CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^{\oplus}}}$$

(assuming that solvation does not substantially alter the situation). There is evidence in the literature that the 2,2,4-trimethylpentane cation is considerably less stable than the *t*-butyl ion. Thus Brown and Fletcher (*4*) found that 2,2,4-trimethyl-4-chloropentane solvolized 22 times faster than *t*-butyl chloride and Hofmann (*5*) reported that the relative rate of tritium exchange via carbonium ion formation (hydride abstraction) for 2,2,4-trimethylpentane was 0.035 in comparison to methylcyclopentane. Consequently, it is conceivable that the stability of the unsubstituted allyl carbonium ion is somewhat higher than that of the propagating ion in isobutene polymerization. Evidently, terminal substitution on the allyl carbonium ion increases its stability so that the parent olefins giving rise to such cationic species are increasingly potent terminating agents.

On the basis of empirical poison coefficients, the following qualitative sequence for the apparent stability of allyl carbonium ions can be proposed:



$$\overset{\delta\oplus}{CH_2}{=\!=}CH{=\!=}\overset{\delta\oplus}{CH_2} < \underset{CH_3}{\overset{\delta\oplus}{CH}}{=\!=}CH{=\!=}\overset{\delta\oplus}{CH_2} < \underset{C_2H_5}{\overset{\delta\oplus}{CH}}{=\!=}CH{=\!=}\overset{\delta\oplus}{CH_2}$$

$$< \underset{C_3H_7}{\overset{\delta\oplus}{CH}}{=\!=}CH{=\!=}\overset{\delta\oplus}{CH_2} < \underset{CH_3}{\overset{\delta\oplus}{CH}}{=\!=}CH{=\!=}\underset{C_4H_9}{\overset{\delta\oplus}{CH}}$$

EFFECT OF TEMPERATURE

The effect of temperature on the poison coefficient and transfer coefficients was investigated for various *n*-alkenes. Experiments have been carried out at −30, −50, and −78°C. Unfortunately, the scatter in the molecular weight data for this series of runs was too large to permit analysis of the corresponding activation energies. Analyses of the effect of temperature on yield has enabled us to gain some insight into the activation energies for propagation (E_2), spontaneous termination (E_5), and termination with poison (E_7). According to Eq. (15) derived in the first section of this series, a plot of $1/W_p$ vs. X gives a slope = $k_7/k_2M_iP_i^\oplus(MW_mV)$ and an intercept = $k_5/k_2M_iP_i^\oplus(MW_mV)$. Neglecting the effect of temperature on $M_iP_i^\oplus(MW_mV)$ as compared to the exponential effect of temperature on k_5, k_2, and k_7, and assuming that these rate constants obey the Arrhenius equation, $k = k_0e^{-E/RT}$, we may calculate the activation energies from the ln (slope) vs. $1/T$ and ln (intercept) vs. $1/T$ plots as follows:

$$\frac{d(\ln \text{slope})}{d(1/T)} = \frac{E_2 - E_7}{R} \quad \text{and} \quad \frac{d(\ln \text{intercept})}{d(1/T)} = \frac{E_2 - E_5}{R}$$

Figures 4 to 9 show $1/W_p$ vs. *n*-alkene concentrations as a func-

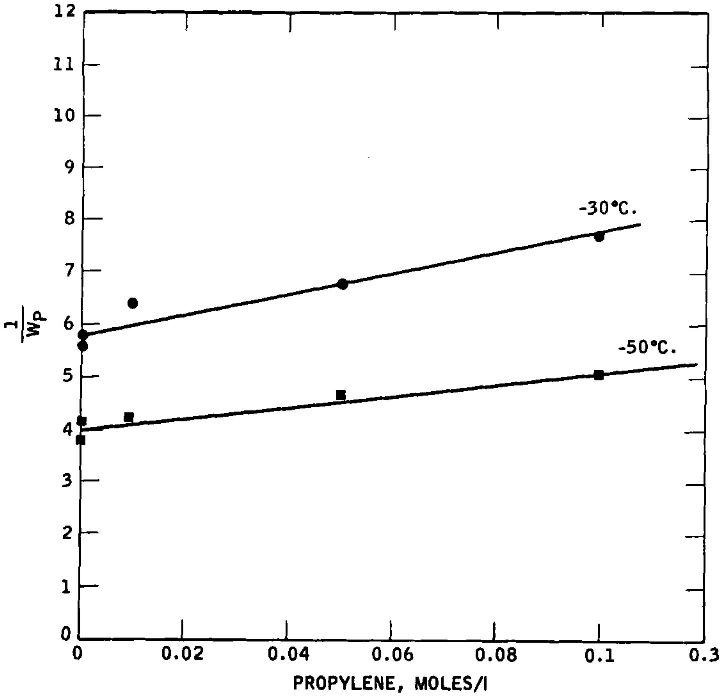


FIG. 4. Effect of temperature on the poisoning effect of propylene.

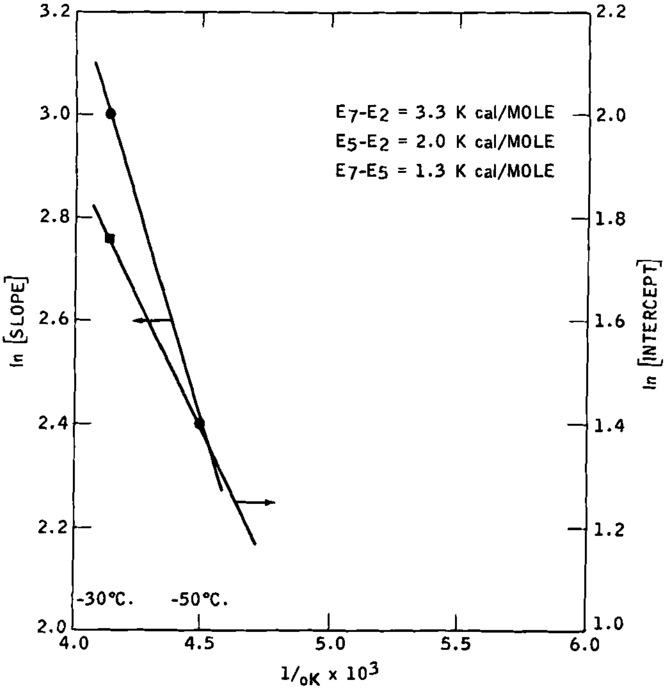


FIG. 5. Determination of activation energies for propylene.

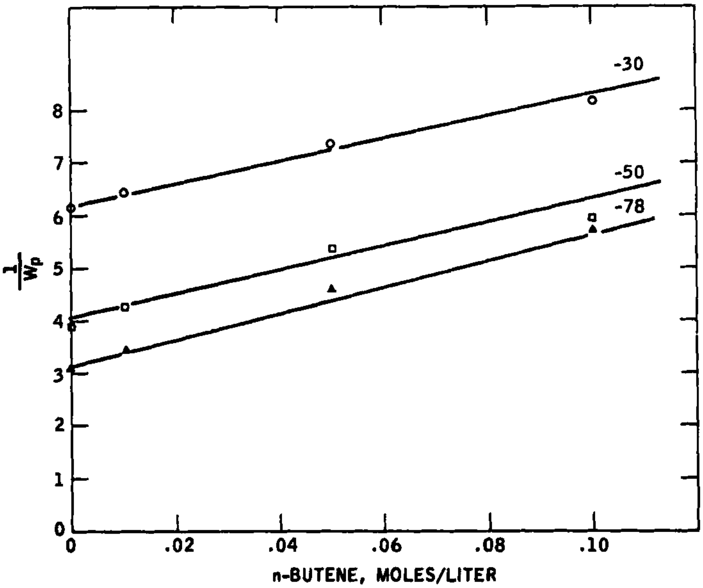


FIG. 6. Effect of temperature on the poisoning effect of butene-1.

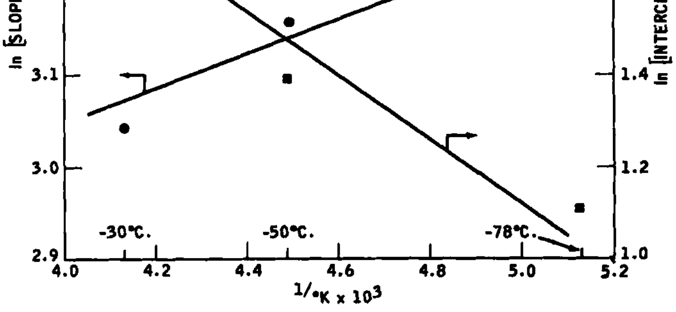


FIG. 7. Determination of activation energies for butene-1.

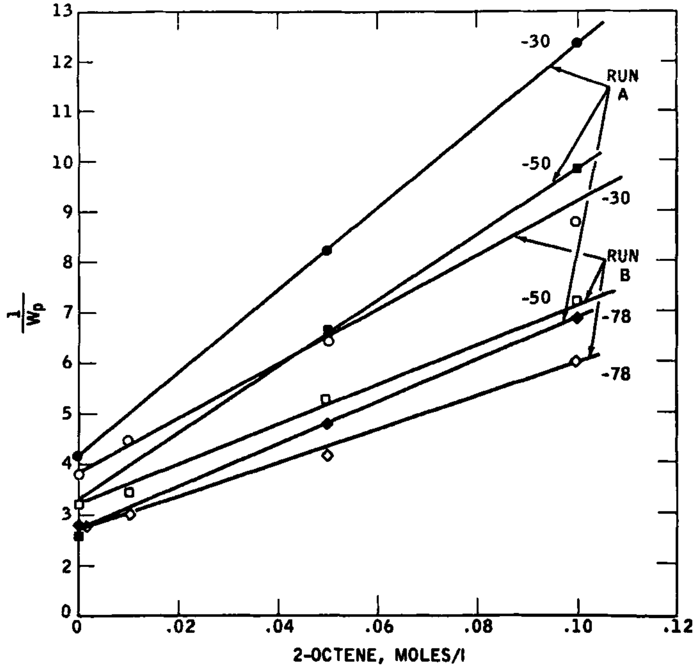


FIG. 8. Effect of temperature on the poisoning effect of 2-octene (repeat runs).

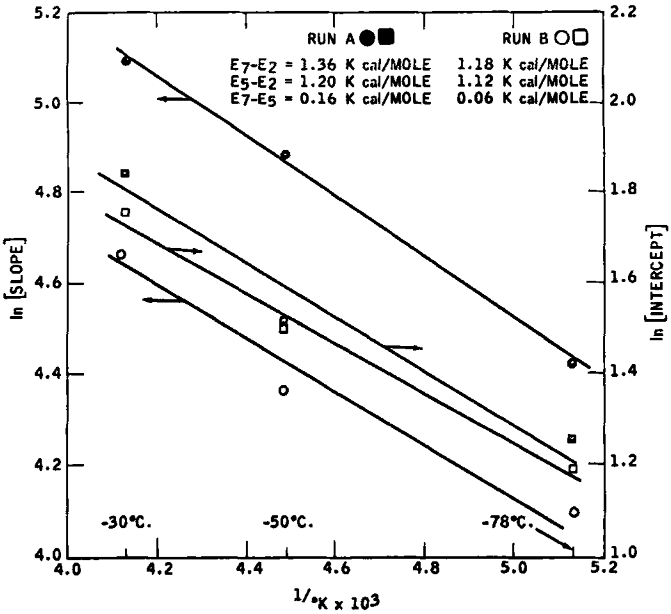


FIG. 9. Determination of activation energies for 2-octene.

tion of temperature along with the corresponding plots used for calculating the activation energies. The runs with 2-octene were repeated after an interval of 2 months. Although absolute reproducibility of individual datum points was somewhat poor, calculated activation energies were satisfactorily reproducible. Since P.C. is defined as k_7/k_5, $d \ln (\text{P.C.})/d(1/T) = -E_7 - E_5)/R$ can be calculated by taking the difference of the equations above. Thus we see that if $(E_7 - E_5)$ is positive, the P.C. increases with increasing temperature, as is the case for propylene (Fig. 5); if $(E_7 - E_5)$ is negative, P.C. increases with decreasing temperature, as is the case for pentene-1 (Fig. 7). If $(E_7 - E_5)$ is approximately zero, P.C. is relatively insensitive to temperature, as seen in Fig. 9 for 2-octene.

Acknowledgment

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Zusammenfassung

Der Einfluss von *n*-Alkanen, z.B. Propylen, 1-Buten, 1-Penten, 1-Hexen, und 2-Octen auf die Ausbeute und das Molekulargewicht von mit $AlCl_3$ als Katalysator in *n*-Pentan als Lösungsmittel bei −78° erhaltenes Polyisobutylen wurde untersucht. Es wurde gefunden, dass die niederen *n*-Alkene als reine Vergiftungsstoffe wirken, d.h. sie vermindern die Ausbeute (Reaktionsgewschwindigkeitsgifte) aber beinflussen nicht das Molekulargewicht des Produktes. Der geschwindigkeitsvermindernde Effekt der *n*-Alkene wurde quantitativ mit Hilfe von Vergiftungskoeffizienten beschrieben, wobei deren numerische Werte auf Grund des allylischen Endgruppenkonzepts mit den relativen Carboniumionenstabilitäten in Wechselbeziehung gebracht wurden. Der geringfügig erniedrigende Effekt von 2-Okten auf das Molekulargewicht wurde der nur mittleren Übertragungsaktivität zugeschrieben. Ebenfalls untersucht wurde der Einfluss der Temperatur auf die Vergiftungskoeffizienten von 2-Okten und dadurch konnte in die Aktivierungsenergien der verschiedenen Elementarprozesse Einblick gewonnen werden.

Résumé

On a étudié l'influence des *n*-alcènes c.a.d. du propylène, du butène-1, du pentène-1, d'hexane-1, et d'octène-1, sur le rendement et le poids moléculaire du polyisobutène, obtenu avec l'$AlCl_3$ comme catalyseir, dans le *n*-pentane comme solvant, à −78°C. On a trouvé que les alcenès-1 bas sont des poisons purs c.a.d. ils diminuent le rendement (Poisons de vitesse) mais n'affectent pas le poids moléculaire du produit. On a traité l'effet retardateur de ces alcenes-1 quantitativement avec des coëfficients empoisonnants et leurs valeurs numériques associées aux stabilites relatives des ions carbonium, à l'aide du concept de terminaison allylique. On a attribué l'effet moderé abaissant le poids moléculaire, d'octène-2 à l'activite moyenne de transfert. On a étudié l'influence de température sur les coëfficients empoisonnants d'octène-2 et on a acquit des connaissances plus profondes sur les énergies d'activation de différentes procedés élémentaires.