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Contributions to the Mechanism of Isobutene Polymerization. VI. Effect of Halides

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Summary

The effects of various allyl chlorides and alkyl halides on the overall yield of polymerization and molecular weight of polyisobutene have been investigated and expressed quantitatively by poison and transfer coefficients. The poison and transfer coefficients of halides have been compared with those obtained previously for corresponding hydrocarbons. The poison coefficients of halides and hydrocarbons can be treated formally in a similar manner ($1/W_p$ vs. $[X]$ plots linear for both classes); however, the appropriate transfer coefficients indicate fundamentally dissimilar transfer mechanisms in these systems ($1/MW_p$ vs. $[X]$ plots linear for hydrocarbons, whereas $1/MW_p$ vs. $[X]^{1/2}$ plots linear for halides). These results are discussed in terms of the allylic termination mechanism.

In this part of our series of publications (I) on the theory of allylic termination we will examine the effect of selected simple allylic chlorides, and various alkyl chlorides and bromides, on the rate of polymerization and molecular weight of polyisobutene obtained with $AlCl_3$ catalyst. The effect on the rate and molecular weight is quantitatively expressed by poison and transfer coefficients as developed and discussed in previous publications (I). Apparently the halogen compounds investigated are pronounced transfer agents and weak terminating agents, i.e., may reduce the molecular weight but affect only little overall yields.

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EXPERIMENTAL

The experimental procedure has been described in the first paper of this series (1).

RESULTS

The effect of some simple allylic chlorides, e.g., allyl chloride, 3-chloro-1-butene, and crotyl chloride, and alkyl chlorides and bromides, e.g., isopropyl, isobutyl, and tertiary butyl chlorides and bromides, on the overall rate of polymerization and molecular weight of polyisobutene is shown in Table I and Figs. 1 to 6. In particular Figs. 1 and 4 show the effect of increasing concentrations of allylic and alkyl halides, respectively, on the overall reciprocal yields (weights of polymers obtained). Figures 2 and 5 show the effect of these halides on reciprocal molecular weights. In contrast to similar figures discussed in our previous publications these figures are plots of $1/MW_p$ vs. the square root of allylic or alkyl halides concentration, i.e., $X^{1/2}$, and not the $1/MW_p$ vs. X plots discussed in previous sections. The reasons for presenting the data in this form are discussed below. Finally, Figs. 3 and 6 show the trends of the relative number of polymer molecules formed in the presence of increasing concentrations of allylic and alkyl halides,

TABLE I
Poison Coefficients and Transfer Coefficients of Allylic Chlorides and Alkyl Halides

Compound	Slope	Intercept	P.C.	Slope $\times 10^{-6}$	Intercept $\times 10^{-6}$	T.C.
<i>Allyl chlorides</i>						
Allyl chloride	0	2.8	0	6.5	1.0	6.2
Methallyl chloride	4.5	2.8	1.6	9.0	1.3	6.9
3-Chloro-1-butene	20	3.0	6.7	36.7	1.5	24.5
Crotyl chloride	33.5	3.0	11.1	55	2.0	27.5
<i>Alkyl halides</i>						
Isopropyl chloride	0	2.7	0	0	1.0	0
Isopropyl bromide	0	2.7	0	0	1.0	0
Isobutyl chloride	37.5	3.0	12.5	14.7	1.1	13.4
Isobutyl bromide	7.5	2.6	1.8	15.0	1.0	15.0
<i>t</i> -Butyl chloride	12.0	2.7	4.4	75.7	1.0	75.7
<i>t</i> -Butyl bromide	10.0	2.7	3.5	71.4	1.0	71.4

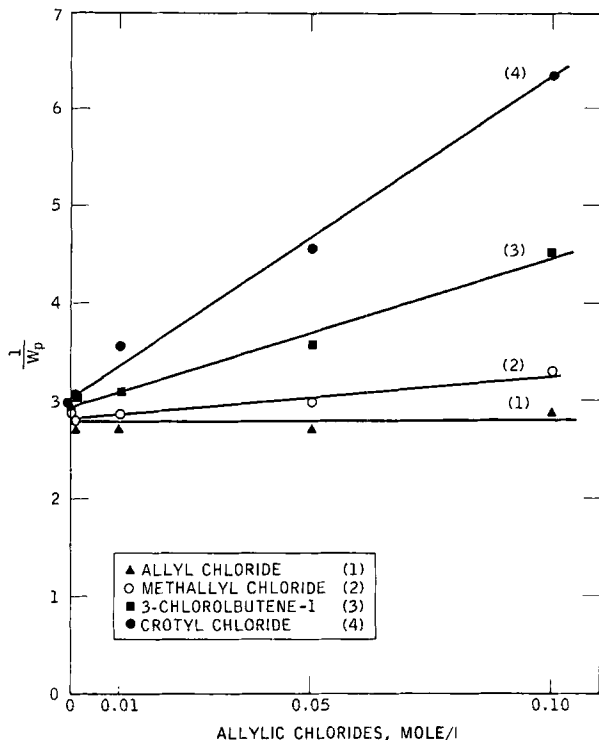


FIG. 1. Effect of allylic chlorides on reciprocal polymer yield.

respectively. Table 1 is a compilation of poison and transfer coefficients obtained from the above figures by the treatment developed in the first publication of this series (1).

Additional plots which will be discussed in connection with allylic chlorides and alkyl halides are shown in Figs. 7 and 8.

DISCUSSION

In spite of the apparent simplicity of the results shown in Figs. 1 to 6, closer examination immediately shows the complexity of the situation. Figures 1 and 4 show the effect of various allylic and alkyl halides on overall polymer yields. The data have been treated in the usual way (1) by plotting $1/W_p$ vs. poison concentration, and satisfactory straight lines were obtained. The poison coefficients calculated from these figures are shown in Table 1. These coeffi-

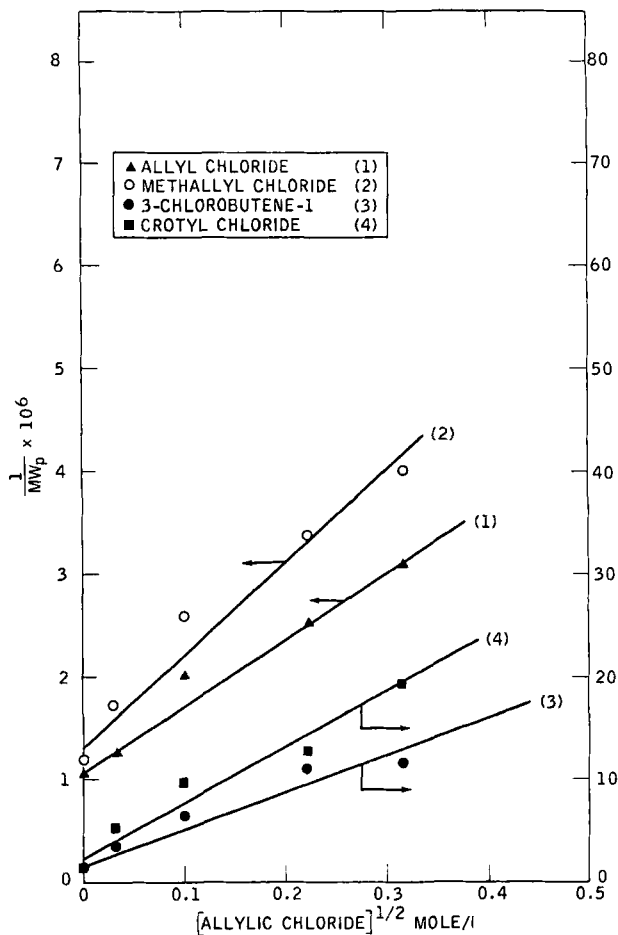


FIG. 2. Effect of allylic chlorides on reciprocal molecular weight.

cients can be directly compared and discussed together with available poison coefficients of hydrocarbons. This will be done below.

However, the situation is completely different with the transfer coefficients. In contrast to the great number of previously discussed hydrocarbon systems, where $1/MW_p$ vs. X plots gave satisfactorily defined straight lines, the present data obtained with the halides gave a family of curves in such plots. However, well-defined linear relationships were obtained with $1/MW_p$ vs. $X^{1/2}$ plots as shown in Figs. 2 and 5. This difference would indicate that the major molecu-

lar-weight-determining mechanism, i.e., chain transfer steps, operating in the presence of halides are different from those occurring in the presence of hydrocarbon olefins. This is not too surprising.

In other words, whereas the poison coefficients determined from $1/W_p$ vs. X plots are linear for all compounds investigated, i.e., hydrocarbons and halides, and might be construed as evidence that the termination mechanisms for the investigated hydrocarbons and halides are similar, this is not true for the transfer coefficients, indicating that the chain transfer mechanisms occurring in these systems are different. Consequently, the molecular weight data which yield the transfer coefficients are best treated in a different manner for hydrocarbons and halides.

The poison coefficients of the four allylic chlorides are surprisingly low (cf. Table 1) and are of the same order of magnitude

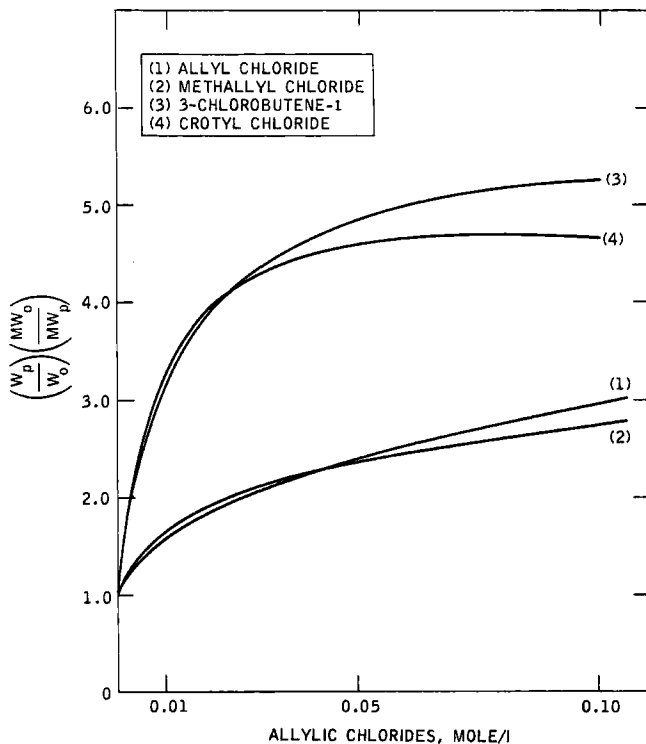


FIG. 3. Effect of allylic chlorides on relative number of polymer molecules formed.

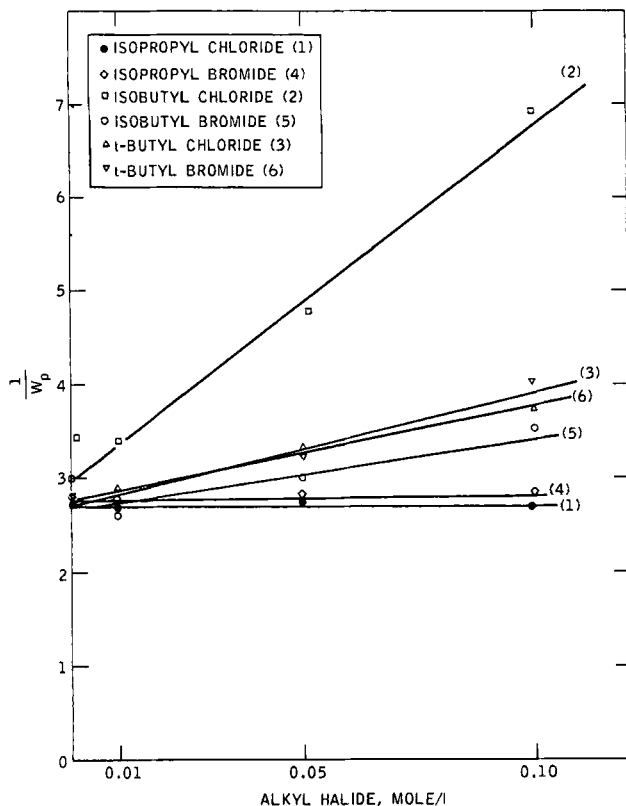


FIG. 4. Effect of alkyl halides on reciprocal polymer yield.

as those obtained with *n*-alkenes. These findings are unexpected and surprising. Organic chemical intuition would suggest that allyl chloride and even more so the higher substituted allyl chloride derivation would be much stronger poison than *n*-alkenes, since their anion(halide)-donating tendency must be stronger than the hydride-donating tendency of allyl olefins. Our results, however, indicate that propylene (P.C. = 4.9) is a stronger poison than allyl chloride (P.C. = 0), or *n*-butene-1 (P.C. = 6.2) is a stronger poison than methallyl chloride (P.C. = 1.6), etc.

If the chloride ion would be transferred from the allylic halides to the growing polymer chain, the resulting allyl cation would be identical to those obtained from corresponding olefins after hydride

transfer, i.e., propylene or allyl chloride both would give



isobutene or methallyl chloride would give

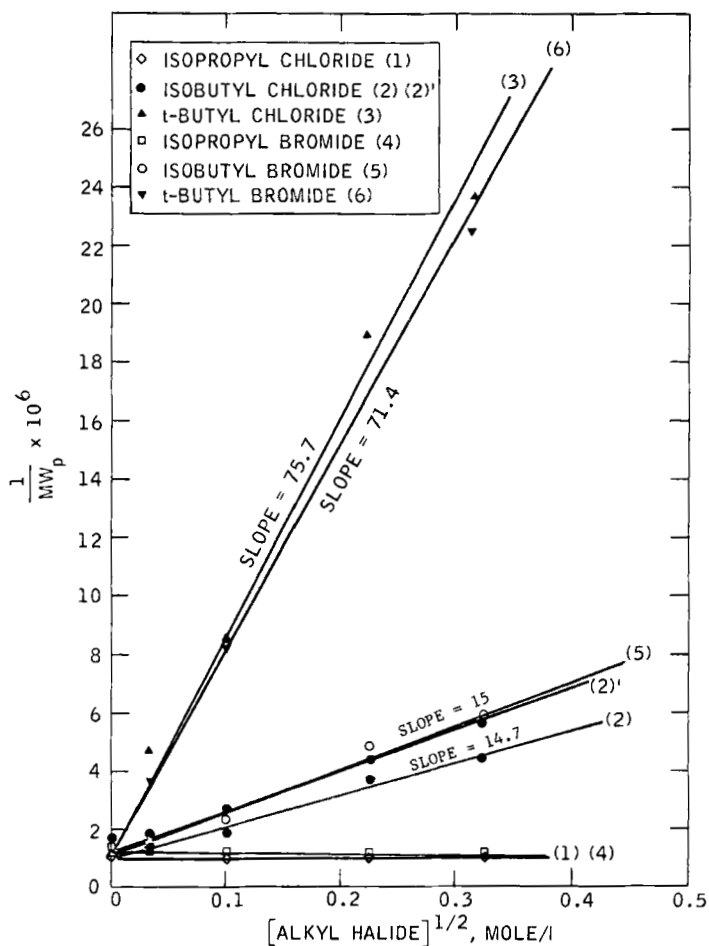
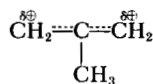


FIG. 5. Effect of alkyl halides on reciprocal molecular weight.

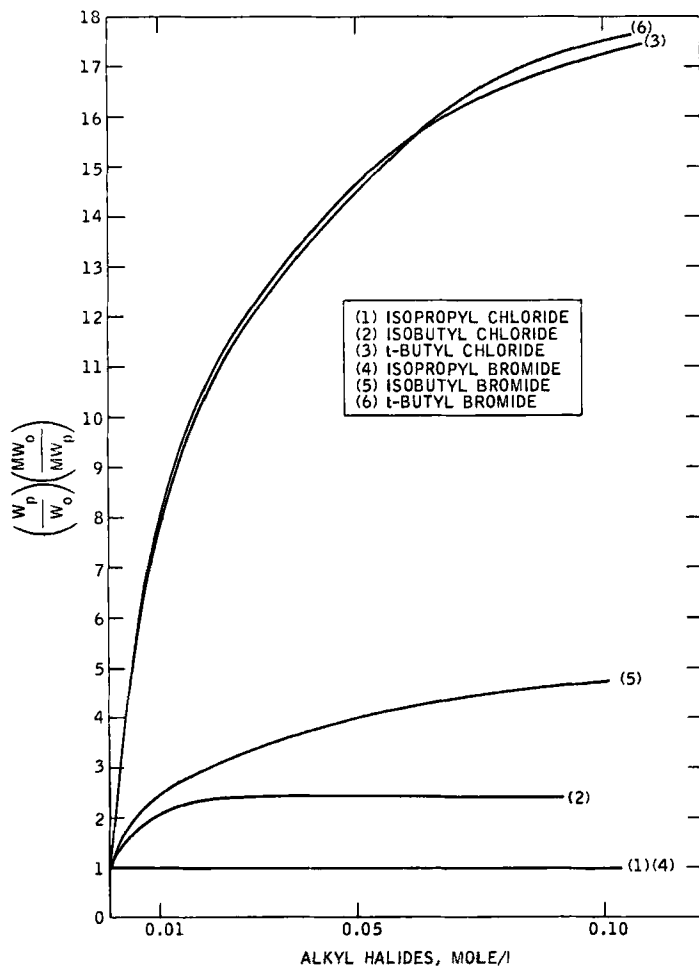
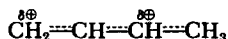


FIG. 6. Effect of alkyl chlorides on relative number of polymer molecules formed.

1-butene or 3-chloro-1-butene would give



etc. However, if the product cations, i.e., allyl ions, would be the same irrespective of whether we start from chloro olefins or from hydrocarbon olefins, we would expect similar influences of these

compounds on polymerization mechanism. Nonetheless, this is not the case and the hydrocarbon olefins are decidedly rate poisons and under our experimental conditions do not affect molecular weights, whereas the chloro olefins are very mild or not rate poisons at all but are effective chain transfer agents.

Could it be that the termination with allylic chlorides (of cationic isobutene polymerizations) does not involve the halogen but the allylic hydrogen?

Table 2 shows the structures of the possible allyl ions derivable from olefins by hydride abstraction and from allylic chlorides by either chloride or hydride abstraction together with the poison and transfer coefficients of the parent compounds. According to these coefficients, the effects of propylene and allyl chloride are opposite: Whereas propylene is a mild poison and is not a transfer agent, allyl chloride is a mild transfer agent and not a poison. Thus it

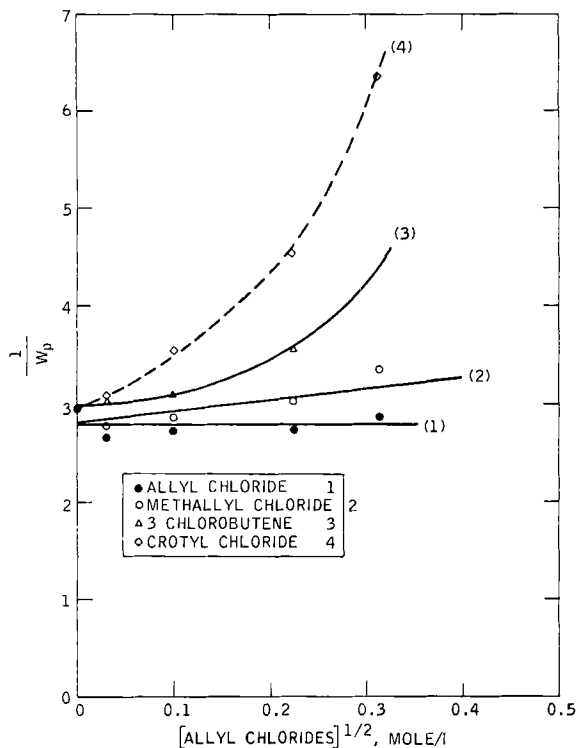


FIG. 7. $1/W_p$ versus \sqrt{X} plots for allylic chlorides.

TABLE 2
Comparison of Poison Coefficients and Transfer Coefficients of Olefins and Allylic Chlorides and the Possible Carbonium Ions Obtainable Therefrom

Olefin	Allyl ion	P.C.	T.C.	Allylic halide	H ^o transfer	C ^o transfer	P.C.	T.C. ^a
CH ₂ =CH-CH ₂	$\overset{\delta+}{\text{C}}\text{H}_2\text{---}\overset{\delta+}{\text{C}}\text{H---CH}_2$	4.9	0	$\text{CH}_2\text{---CH=CH}_2$ Cl	$\overset{\delta+}{\text{C}}\text{H}_2\text{---}\overset{\delta+}{\text{C}}\text{H---CH}_2$ Cl	$\overset{\delta+}{\text{C}}\text{H}_2\text{---}\overset{\delta+}{\text{C}}\text{H---}\overset{\delta+}{\text{C}}\text{H}_2$	0.0	6.2
CH ₃ -C=CH ₂ CH ₃	$\overset{\delta+}{\text{C}}\text{H}_2\text{---}\overset{\delta+}{\text{C}}\text{---CH}_2$ CH ₃	0	0	$\text{CH}_3\text{---C=CH}_2$ CH ₂ Cl	$\overset{\delta+}{\text{C}}\text{H}_2\text{---}\overset{\delta+}{\text{C}}\text{---CH}_2$ CH ₂ Cl or $\overset{\delta+}{\text{C}}\text{H}_2\text{---}\overset{\delta+}{\text{C}}\text{---CH}_2$ $\overset{\delta+}{\text{C}}\text{HCl}$	$\text{CH}_3\text{---}\overset{\delta+}{\text{C}}\text{---CH}_2$ $\overset{\delta+}{\text{C}}\text{H}_2$	1.3	6.9
CH ₃ -CH ₂ -CH=CH ₂	$\overset{\delta+}{\text{C}}\text{H}_2\text{---}\overset{\delta+}{\text{C}}\text{H---}\overset{\delta+}{\text{C}}\text{H}_2$ CH ₃	6.2	0	$\text{CH}_3\text{---CH---CH=CH}_2$ Cl	$\overset{\delta+}{\text{C}}\text{H}_2\text{---}\overset{\delta+}{\text{C}}\text{H---}\overset{\delta+}{\text{C}}\text{H}_2$ Cl	$\text{CH}_3\text{---}\overset{\delta+}{\text{C}}\text{H---}\overset{\delta+}{\text{C}}\text{H---}\overset{\delta+}{\text{C}}\text{H}_2$	1.5	24.5
CH ₃ -CH=CH-CH ₂ -C ₂ H ₅	$\overset{\delta+}{\text{C}}\text{H}_2\text{---}\overset{\delta+}{\text{C}}\text{H---}\overset{\delta+}{\text{C}}\text{H}$ CH ₃ C ₂ H ₅	20.8	12.1	$\text{CH}_3\text{---CH=CH---CH}_2\text{Cl}$	$\overset{\delta+}{\text{C}}\text{H}_2\text{---}\overset{\delta+}{\text{C}}\text{H---}\overset{\delta+}{\text{C}}\text{H---}\overset{\delta+}{\text{C}}\text{H}_2\text{Cl}$	$\text{CH}_3\text{---}\overset{\delta+}{\text{C}}\text{H---}\overset{\delta+}{\text{C}}\text{H---}\overset{\delta+}{\text{C}}\text{H}_2$ or $\overset{\delta+}{\text{C}}\text{H}_3\text{---}\overset{\delta+}{\text{C}}\text{H---}\overset{\delta+}{\text{C}}\text{H---}\overset{\delta+}{\text{C}}\text{H---}\overset{\delta+}{\text{C}}\text{H---}\overset{\delta+}{\text{C}}\text{H---}\overset{\delta+}{\text{C}}\text{H}_2$	2.0	27.5

^a The definition of T.C.'s of halides are different from that for hydrocarbons (see the text).

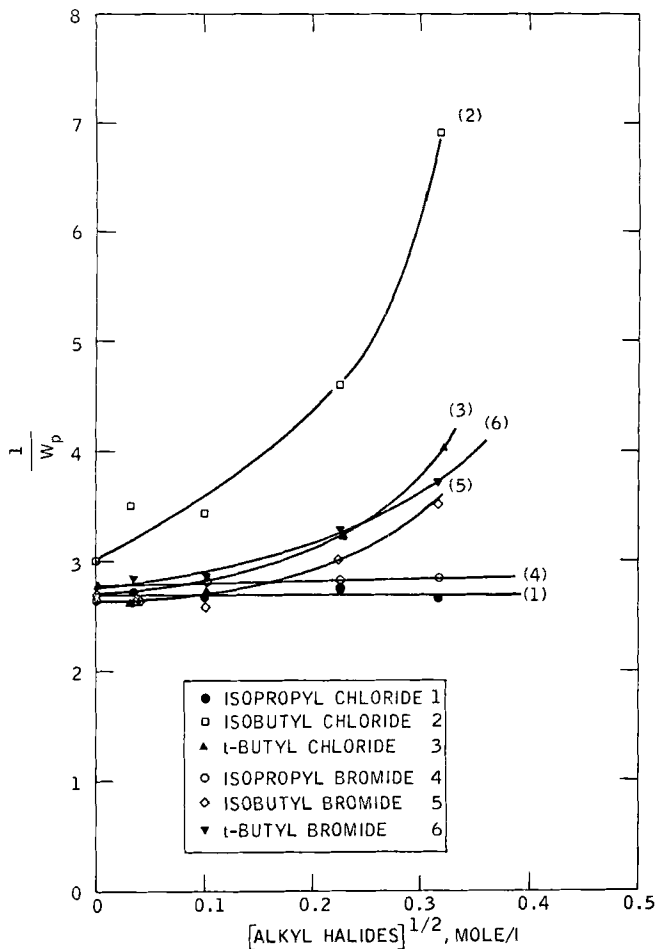
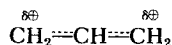


FIG. 8. $1/W_p$ versus \sqrt{X} plots for alkyl halides.

would seem highly unlikely that an identical ion, i.e., the unsubstituted allylic carbonium ion

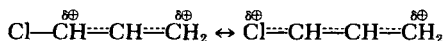


is involved during polymerization in the presence of both of these compounds. Since propylene can probably give only this one carbonium ion and the allyl halide can give two ions, we might con-

clude that allyl chloride not only yields the more probable



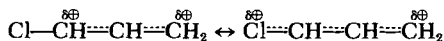
ion but also some other species, perhaps the speculative



ion. It is unlikely that allyl chloride would yield exclusively the latter ion, because this species is probably less stable than the



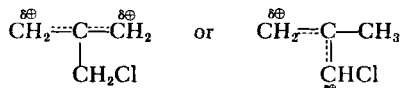
ion. It could be, then, that perhaps both ions contribute to the overall rate and molecular weight effects and that the almost negligible poisoning activity of allyl chloride is due to the



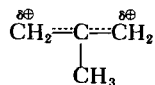
species, whereas the transfer activity is mainly derived from



Similarly, perhaps methally chloride gives



when it acts as a poison but yield the expected

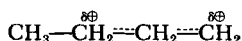


on chain transfer.

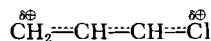
An estimate of the stability of the ions formed by hydride abstraction from the allylic chlorides was obtained by a simple Hückel molecular orbital treatment. In this treatment chlorine was considered as a heteroatom with appropriate values for the coulomb and resonance integrals. Interestingly, the calculated delocalization energy for



is 0.78β , which is larger than the value for

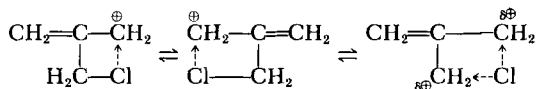


calculated as 0.69β . While these absolute magnitudes are not to be trusted, because of the crudeness of the method and assumption, the calculations clearly indicate qualitatively that the ion formed by hydride abstraction from allyl chloride is of comparable (if not greater) stability than the ion formed by hydride abstraction from the hydrocarbon. Thus according to molecular orbital calculations, the

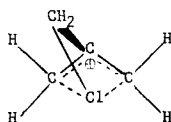


ion is quite believable.

Using a basically similar argument, at least the trend of effects of the other two compounds shown in Table 2 could be rationalized. It could be speculated that the following transition states could contribute to the stabilization of the chloro methallyl and similar cations:



particularly if the chlorine would be coplanar with the allyl cation:



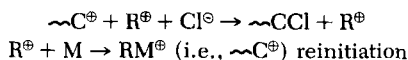
The possibility of chain termination through a mechanism which would result in a poison coefficient proportional to $X^{1/2}$ instead of X is also a possibility. Figures 7 and 8 show the $1/W_p$ vs. \sqrt{X} plots of the investigated halides. The nonlinearity of this relationship indicates, however, that this type of termination reaction, if it does occur at all, appears to be much less likely than that due to the allylic termination process.

Turning to the discussion of the transfer coefficients of these compounds, the important experimental fact is the linearity of $1/MW_p$ vs. $X^{1/2}$ plots shown in Figs. 2 and 5. This linearity immediately suggests that the transfer steps operating with hydrocarbons and with halides must be fundamentally different. An explanation for the linear $1/MW_p$ vs. $X^{1/2}$ relation for halides might be that the chlorides and bromides in the presence of AlCl_3 catalyst might exist

as partially dissociated species:



and that the dissociated species is the true chain transfer agent:



Since the dissociation of the halide is governed by

$$K = \frac{[\text{R}^\oplus][\text{Cl}^\ominus]}{[\text{RCl}]}$$

and assuming

$$\begin{aligned} [\text{R}^\oplus] + [\text{Cl}^\ominus] &\ll [\text{RCl}] = X \\ [\text{R}^\oplus] = [\text{Cl}^\ominus] &= \sqrt{KX} \end{aligned}$$

we obtain a square-root function for the molecular weight equation:

$$\frac{1}{\text{MW}_p} = \frac{k_3}{k_2} + \frac{k_5}{k_2 M_i} + \frac{k_7 X}{k_2 M_i} + \frac{k_8 X}{k_2 M_i} X^{1/2}$$

where k_8 and K have been defined above and the rest of the symbols were defined earlier (1).

If transfer predominates over termination (i.e., $k_8 K \gg k_7$)

$$\frac{1}{\text{MW}_p} = \frac{k_3 M_i + k_5}{k_2 M_i} + \frac{k_8 K}{k_2 M_i} X^{1/2}$$

and in the absence of poison,

$$\frac{1}{\text{MW}_0} = \frac{k_3 M_i + k_5}{k_2 M_i (\text{MW})_m}$$

Thus

$$\frac{\text{MW}_0}{\text{MW}_p} = 1 + \frac{k_8 K}{k_3 M_i + k_5} X^{1/2}$$

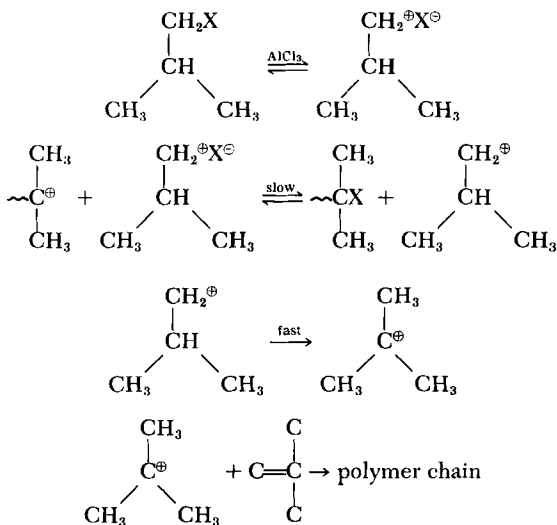
The quantity $k_8 K / k_3 M_i + k_5$ will be defined as the transfer coefficient for halides, $(\text{T.C.})_{\text{halide}}$. Thus a plot of $1/\text{MW}_p$ vs. $X^{1/2}$ would result in a straight line of intercept $(k_3 M_i + k_5) / k_2 M_i$ and a slope $k_8 K / k_2 M_i$. Dividing the slope of this curve by the intercept results in the transfer coefficient for halides.

It must be emphasized that the definition of transfer coefficients as defined earlier (1) for hydrocarbons, $(k_4 + k_7) / k_3 M_i + k_5$, is different from that derived for halides, $k_8 K / k_3 M_i + k_5$. Thus, when these coefficients are compared the difference in poison concentra-

tion, X , on molecular weight must be taken into account. Thus a hydrocarbon and a chloride with identical transfer coefficients will not, in general, have similar molecular-weight-depressing properties, since the effect of hydrocarbons on MW will be a function of $(T.C.)_{\text{hydrocarbon}}X$ while the effect of halides on MW will be a function of $(T.C.)_{\text{halide}}X^{1/2}$. If $X \ll 1$ mole/liter, the effect on molecular weight of an increase in X will be greater for the chloride than for the hydrocarbons.

The structure of the reinitiating R^{\oplus} moiety postulated in the equation above should now be considered. Obviously, materials with large K , i.e., easily dissociable halides, will be expected to be efficient transfer agents. This might explain why crotyl chloride or 3-chloro-1-butene or, among the alkyl halides, *t*-butyl chloride are the most efficient transfer agents and why allyl chloride or isopropyl chloride are much less so. In other words, transfer activity of halides is correlatable with the strength of the C—Cl bond, which in turn is determined by the stability of the corresponding carbonium ion.

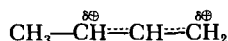
The relatively high transfer coefficient of isobutyl halides (i.e., 13.4 for isobutyl chloride and 15.0 for isobutyl bromide) may be surprising at first glance. However, these findings may be explained by the following sequence of reactions:



i.e., in the presence of AlCl_3 , isobutyl halides are probably some-

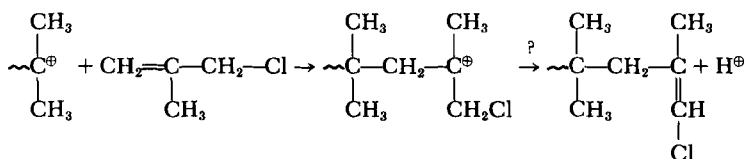
what dissociated, which results in fast rearrangement to the stable tertiary cation and halogenation of the growing end. The newly formed tertiary cation then reinitiates the chain, leading to high transfer activity.

The relatively high transfer coefficients of crotyl chloride (and 3-chloro-1-butene) are noteworthy. Since the stability of the allyl ion



derived from crotyl chloride is probably higher than the propagating polyisobutene cation (otherwise 1-butene might not be a poison; see the publication on *n*-alkenes, the second in this series), it might not be too far-fetched to speculate that this ion is stabilized by H^\oplus ejection to butadiene and that the ejected proton which immediately reinitiates a chain is, in fact, responsible for the transfer activity. This might also hold true for 3-chloro-1-butene, which yields the identical end-substituted allylic ion. Cations derived from allyl chloride and methallyl chloride via chloride transfer cannot stabilize by proton elimination. Consequently, these materials are expected to be less efficient transfer agents.

Many other complicating mechanisms could be involved in shaping the overall results. Thus telomerizations could arise in certain instances, i.e.,



In the case of methallyl chloride, incorporation is not impossible, the chlorinated carbonium ion being quite stable. The latter can either rearrange or deprotonate, giving rise to a very stable vinylic chloride, etc.

Finally, Figs. 3 and 6 show the number of polymer molecules formed in the presence of various halides as a function of halide concentration. These curves indicate that the number of moles of polyisobutene increase strongly with increasing halide concentrations, i.e., the halides are chain transfer agents. Indeed, it seems that allyl chloride and *t*-alkyl halides are almost pure transfer agents.

Our analysis of this extremely complicated situation is very ten-

tative. The answer to the questions raised is far from obvious and our understanding of this complex system is far from complete. Only further investigations can help to get closer to the answers.

Acknowledgment

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1. J. P. Kennedy and R. G. Squires, *J. Macromol. Sci.*, **A1**(5), 805, 831, 847, 861 (1967). The definitions of the poison and transfer coefficients is derived in the first section, p. 805.

Zusammenfassung

Der Einfluss verschiedener Allylchloride und Alkylchloride auf die Polymerisationsausbeute und das Molekulargewicht von Polyisobutylen wurde untersucht und quantitativ in Form von Vergiftungs- und Übertragungskoeffizienten ausgedrückt. Diese Koeffizienten der Halogenide werden mit jenen der entsprechenden Kohlenwasserstoffe verglichen. Die Vergiftungs- und Überträgerkoeffizienten der Halogenide und der Kohlenwasserstoffe können formal auf dieselbe Art behandelt werden ($1/W_p$ gegenüber $[X]$ ergibt in beiden Fällen Gerade), die entsprechenden Überträgerkoeffizienten weisen jedoch auf einen fundamental verschiedenen Übertragungsmechanismus in diesen Systemen hin ($1/MW_p$ aufgetragen als Funktion von $[X]$ ergibt eine Gerade für Kohlenwasserstoffe, dagegen wird für die Halogenide nur dann eine Gerade erhalten, wenn $1/MW_p$ gegen $[X]^{1/2}$ aufgetragen wird). Diese Ergebnisse werden in Bezug auf den Allyl-Endgruppen Mechanismus diskutiert.

Résumé

On a étudié et exprimé quantitativement par des coefficients d'empoisonnement et de transfert les effets de différents chlorures d'allyl et d'halogénures d'alkyl sur le rendement total et la masse moléculaire de polyisobutène. On a comparé les coefficients d'empoisonnement et de transfert des halogénures avec ceux obtenus précédemment. On peut traiter formellement les coefficients d'empoisonnement des halogénures et des hydrocarbures d'une manière analogue (les tracés $1/W_p$ vs. $[X]$ sont linéaires dans les deux classes), mais les coefficients de transfert correspondants indiquent un mécanisme de transfert très différent dans ces systèmes ($1/MW_p$ vs. $[X]$ est linéaire dans les cas des hydrocarbures, tandis que $1/MW_p$ vs. $[X]^{1/2}$ est linéaire pour les halogénures). On discute ces résultats du point de vue du mécanisme de terminaison allylique.

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