Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Kennedy, Joseph p. and Phillips, Robert R.(1970) 'The Influence of Aluminum-Containing Lewis Acids on Polyisobutylene, Isobutylene-lsoprene Copolymers (Butyl Rubber), and Chlorinated Isobutylene-lsoprene Copolymer (Chlorobutyl)', Journal of Macromolecular Science, Part A, 4: 8, 1759 — 1784

To link to this Article: DOI: 10.1080/00222337008059520

URL: http://dx.doi.org/10.1080/00222337008059520

J. MACROMOL. SCI.–CHEM., A4(8), pp. 1759-1784, December, 1970

The Influence of Aluminum-Containing Lewis Acids on Polyisobutylene, Isobutylene-Isoprene Copolymers (Butyl Rubber), and Chlorinated Isobutylene-Isoprene Copolymer (Chlorobutyl)

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SUMMARY

The influence of aluminum-containing Lewis acids, e.g., $AlCl_3$, $AlEtCl_2$, $AlEt_2Cl$, $AlEt_3$, and $AliBu_3$, on polyisobutylene, isobutylene-isoprene copolymer (butyl rubber), and chlorinated butyl rubber has been investigated in nonpolar and polar solvents at various Lewis acid concentrations in the temperature range -10 to -78°C. Polyisobutylene does not degrade even under the most aggressive conditions employed ($AlEtCl_2$, -10°C). Butyl rubber degrades rapidly in the presence of $AlEtCl_2$ in the range -10 to -50°C. In contrast, no degradation occurs with the milder Lewis acid $AlEt_2Cl$; however, in conjunction with small amounts of a suitable Bronsted acid (i.e., HCl) immediate and extensive degradation takes place with $AlEt_2Cl$ as well. Chlorobutyl rubber severely and very rapidly degrades in the presence of $AlCl_3$ and $AlEtCl_2$. With the less acidic $AlEt_2Cl$ and $AlEt_3$, molecular weight breakdown can be prevented only when employing milder conditions, i.e., at low Lewis acid concentrations in nonpolar solvents at lowest temperatures. A comprehensive mechanism involving carbonium ions of these degradation processes is proposed.

INTRODUCTION

The degradation of polyisobutylene and butyl rubber has previously been studied under various conditions, e.g., free radical [1], radiation [2-4], ultra sound [5], laminar flow [6], mechanical shear [7], and thermal [8] but apparently not under the influence of Lewis acids. In the course of our fundamental studies on carbonium ion reactions we became interested in the effect of Lewis acids on various polymer molecules, in particular polyisobutylene, butyl rubber (a copolymer of isobutylene with small amounts of isoprene), and chlorobutyl (chlorinated butyl rubber).

EXPERIMENTAL

Polymers

Polyisobutylenes of various origins have been used. The isobutylene-isoprene copolymer containing ~1.3 mole % unsaturation (Enjay Butyl 218) and the chlorinated copolymer containing ~1.2 wt% Cl (Butyl HT 1066) were commercial products meeting commercial specifications. The polymers were purified by reprecipitation from n-hexane/methanol and were characterized by viscosity-average molecular weights obtained from single point intrinsic viscosities in diisobutene solution at 20°C with Flory's equation [9], and by iodine numbers [10] and wt% Cl [11].

Lewis Acids

Aluminum chloride (The Matheson Co.) in ethyl chloride solution has been used. The preparation of this solution has been described [12]. Aluminum ethyl dichloride ($AlEtCl_2$), aluminum diethyl chloride ($AlEt_2Cl$), aluminum triethyl ($AlEt_3$), and aluminum triisobutyl ($AliBu_3$) (Texas Alkyls, Inc.) have been distilled under reduced pressure prior to experiment.

Solvents

All the solvents were of the highest commercially available quality and were dried and distilled before use. Their purity was ascertained by gas chromatography.

Conditions

All the experimental work was carried out in a stainless steel enclosure under nitrogen atmosphere (moisture level ~30 ppm) [13].

A typical experiment was carried out as follows: A 5 wt% chlorobutyl or butyl rubber solution was prepared in the appropriate solvent and stirred at the selected temperature level (from -10 to -78°C). The precooled Lewis acid solution was introduced into the well-stirred and thermoequilibrated solution at 0 min and aliquot samples were removed, usually at 1/2, 1, 2, 5, 20, and 30 min after catalyst introduction. The removed aliquots were introduced into vessels containing methanol and kept at the same temperature as the main reactor to decompose the Lewis acid and to precipitate the polymer. After washing with excess methanol and drying in vacuo at ~50°C the analyses were performed.

All experiments were carried out in homogeneous solutions. The solubility of chlorobutyl in ethyl chloride at -10°C was sufficient to carry out experiments in 5 wt% solutions. These ethyl chloride solutions were somewhat hazy but were readily stirrable and appeared to be homogeneous. Temperature control was within ±0.5°C.

RESULTS

Table 1 is a summary of the data obtained with chlorobutyl and butyl rubber. Polyisobutylene data are not shown because there was no change in the molecular weights of this polymer under the conditions employed (n-hexane solvent, $AlEtCl_2$, and $AlEt_2Cl$, 5.5×10^{-3} mole Lewis acid/l solution, 30 min stirring at -10 or -50°C). The molecular weight range of the polyisobutylene starting material was from 229 to 3800×10^3.

The Lewis acid column in Table 1 shows the particular Lewis acid used and its quantity expressed by the ratio mole Lewis acid/mole of function. For butyl rubber the latter becomes mole Lewis acid/"mole" unsaturation which expresses the number of moles of Lewis acid per double bonds in the butyl rubber; for chlorobutyl this ratio becomes mole Lewis acid/atom chlorine and expresses the number of moles of Lewis acid added per chlorine atom in the chlorobutyl molecule.

Table 1. The Effect of Various Lewis Acids on Butyl Rubber

Lewis acid					
Formula	Mole Lewis acid/ mole of function	Solvent	Temp (°C)	Control → final $(M_X \times 10^{-3})$	Number of calculated chain scissions
Butyl rubber	Mole Lewis acid/ "mole" unsat. in butyl				
Series I					
$AlEtCl_2$	1.57	nC_6	-10	457 → 110	3.1
	1.57	nC_6	-50	457 → 220	1.1
Series II					
$AlEt_2Cl$	1.57	nC_6	-10	457 → 457	0
	1.57	nC_6	-10	451 → 451	0
Series III					
$AlEt_2Cl$	1.57	nC_6	-10	421 → 421	0
$AlEt_2Cl$/0.1 HCl	1.57	nC_6	-10	421 → 253	0.7
$AlEt_2Cl$/0.2 HCl	1.57	nC_6	-10	253 → 74	4.7
Chlorobutyl	Moles Lewis acid/ atom Cl in ClBu				
Series I					
$AlCl_3$	1.06	EtCl	-10	374 → 15	24
	0.89	EtCl	-10	395 → 7	55
Series II					
$AlEtCl_2$	1.25	nC_6	-10	392 → 12	31
	1.21	nC_6	-10	406 → 32	12
	1.25	nC_6	-50	385 → 30	12

and Chlorobutyl under Various Experimental Conditions[a]

Severity of breakdown	Approx gel content (wt%)	Chlorine content, control → final (wt%)	Iodine number, control → final	Mole % unsat, control → final
++			8.84 → 8.80	1.30 → 1.29
++			8.61 → 8.8	1.26 → 1.29
0			8.70 → 8.70	1.28 → 1.28
0			8.74 → 8.50	1.28 → 1.25
0				
+				
+++				
+++		1.06 → 0.8	7.63 → 27	
+++		1.01 → 0.5	8.23 → 46	
+++		1.08 → 0.5	8.08 → 15	
+++		1.13 → 0.8	8.99 → 14	
+++		1.05 → 0.5	7.30 → 10	

(Continued)

Table 1. The Effect of Various Lewis Acids on Butyl Rubber

Lewis acid					
Formula	Mole Lewis acid/ mole of function	Solvent	Temp (°C)	Control → final ($M_X \times 10^{-3}$)	Number of calculated chain scissions
Chlorobutyl	Moles Lewis acid/ atom Cl in ClBu				
Series III					
$AlEt_2Cl$	0.55	CH	+20	282 → 27	9.5
	1.25	nC_6	-10	374 → 58	5.5
	1.23	nC_6	-10	346 → 66	4.2
	0.90	nC_6	-10	346 → 46	6.5
	0.63	nC_7	-10	421 → 28	14
	0.465	nC_6	-10	346 → 35	9
	0.314	nC_7	-10	421 → 21	18
	0.232	nC_6	-10	346 → 109	2.2
	0.126	nC_7	-10	421 → 305	0.4
	0.116	nC_6	-10	346 → 215	0.6
Series IV					
$AlEt_2Cl$	0.63	nC_7	-50	421 → 64	5.6
	0.314	nC_7	-50	421 → 33	11.8
	0.126	nC_7	-50	421 → 409	0.03
Series V					
$AlEt_2Cl$	1.28	nC_6	-65	400 → 160	1.5
	0.64	nC_6	-65	400 → 210	0.9
	0.128	nC_6	-65	400 → 400	0
Series VI					
$AlEt_2Cl$	1.28	nC_6	-78	383 → > 383	0
Series VII					
$AlEt_2Cl$	0.63	nC_6/EtCl	-10	421 → 15	27
	0.314	nC_6/EtCl	-10	421 → 11	37
	0.126	nC_6/EtCl	-10	421 → 179	1.3
Series VIII					
$AlEt_2Cl$	0.63	nC_6/EtCl	-50	421 → 28	14
	0.314	nC_6/EtCl	-50	421 → 21	19
	0.126	nC_6/EtCl	-50	421 → 299	0.4
Series IX					
$AlEt_2Cl$	1.25	EtCl	-10	351 → 38	8.2

and Chlorobutyl Under Various Experimental Conditions[a] (Continued)

Severity of breakdown	Approx gel content (wt%)	Chlorine content, control → final (wt%)	Iodine number, control → final	Mole % unsat, control → final
+++		1.20 → 0.2	6.06 → 11.5	
+++		1.09 → 1.09	7.62 → 8.9	
+++		1.42 → 0.6	8.01 → 9.7	
+++		1.42 → 0.35	8.01 → 9.7	
+++				
+++		1.42 →	8.01 → 9.6	
+++				
++		1.42 → 0.58	8.01 → 11.0	
+				
+		1.42 → 0.78	8.01 → 9.2	
+++		– –	– –	
+++		– –	– –	
~0		– –	– –	
++	25.0	1.07 → 0.5	7.48 → 7.6	
+	2.0	1.08 → 0.5	7.74 → 7.7	
0		1.08 → 1.1	7.74 → 7.7	
0		1.11 → 1.2	8.95 → 8.7	
+++		– –	– –	
+++		– –	– –	
++		– –	– –	
+++		– –	– –	
+++		– –	– –	
+		– –	– –	
+++		1.08 → 1.1	7.45 → 9.6	

(Continued)

Table 1. The Effect of Various Lewis Acids on Butyl Rubber

Lewis acid					
Formula	Mole Lewis acid/ mole of function	Solvent	Temp (°C)	Control → final ($M_X \times 10^{-3}$)	Number of calculated chain scissions
Series X					
$AlEt_3$	1.28	nC_6	-10	400 → 400	0
	1.24	nC_6	-10	445 → 445	0
	0.583	nC_7	-10	421 → 409	0.03
	0.292	nC_7	-10	421 → 359	0.16
	0.117	nC_7	-10	421 → 409	0.03
Series XI					
$AlEt_3$	1.28	nC_6	-50	378 → 378	0
	0.583	nC_7	-50	421 → 407	0.03
	0.292	nC_7	-50	421 → 398	0.06
	0.117	nC_7	-50	421 → 319	0.32
Series XII					
$AlEt_3$	0.583	nC_7/EtCl	-10	421 → 52	7.1
	0.292	nC_7/EtCl	-10	421 → 47	7.8
	0.117	nC_7/EtCl	-10	421 → 273	0.5
Series XIII					
$AlEt_3$	0.583	nC_7/EtCl	-50	421 → 320	0.3
	0.292	nC_7/EtCl	-50	421 → 206	1.0
	0.177	nC_7/EtCl	-50	421 → 288	0.5
Series XIV					
$AlEt_3$	0.61	MeCH/EtCl	-78	314 → > 314	0
Series XV					
$AliBu_3$	0.292	nC_7/EtCl	-10	436 → 30	13.5

[a] Abbreviations: ClBu = chlorinated isobutylene-isoprene copolymer. EtCl = ethyl chloride.

and Chlorobutyl Under Various Experimental Conditions[a] (Continued)

Severity of breakdown	Approx gel content (wt %)	Chlorine content, control → final (wt %)	Iodine number, control → final	Mole % unsat, control → final
0		1.08 → 1.1	8.06 → 8.03	
0		1.05 → 1.05	5.07 → 5.5	
~0		— —	— —	
~0		— —	— —	
~0		— —	— —	
0		— —	— —	
~0		— —	— —	
~0		— —	— —	
~0		— —	— —	
+++		— —	— —	
+++		— —	— —	
+		— —	— —	
+		— —	— —	
+		— —	— —	
+		— —	— —	
0	20.0	1.22 → 1.18	7.34 →	
+++		— —	— —	

nC_6 = n-hexane. nC_7 = n-heptane. CH = cyclohexane. MeCH = methyl cyclohexane.

The "molecular weight breakdown" column shows the experimentally determined viscosity-average molecular weights starting with the control (in the absence of catalyst) down to (→) the final molecular weight level. Degradation rates of butyl rubber and chlorobutyl were extremely fast in almost all cases. Indeed the molecular weights dropped almost immediately after catalyst introduction (i.e., < 1/4 min) and reached a final level which did not change during the later course of the experiment (usually 30 min). Thus the molecular weight breakdown column expresses the sudden drop in molecular weights between the control and the average of this final plateau.

The "number of calculated chain scissions" column is an estimate of the number of cleavages occurring during degradation and can be readily calculated from the previous molecular weight breakdown column.

The drop in molecular weights after catalyst introduction is so sudden under our conditions that no meaningful quantitative kinetic analysis is possible. To quantize the available data, the number of calculated chain scissions are grouped into four classes shown in the "severity of breakdown" column. The first group (+++), most severe degradation, comprises the cases where more than 4 chain scissions per molecule occurred; the next group (++), medium degradation, includes 1-4 chain scissions; and the next (+), minor degradations with 0-1.0 chain scissions; finally under certain conditions no chain scission occurred, and this is indicated by a 0 in both columns. A more quantitative analysis of the molecular weight data would be unwarranted since viscosity determinations at very low molecular weights (below ~50,000 viscosity average) are quite inaccurate.

In three experiments we found gel (toluene insoluble material) whose amount was determined quantitatively and is shown in the appropriate column.

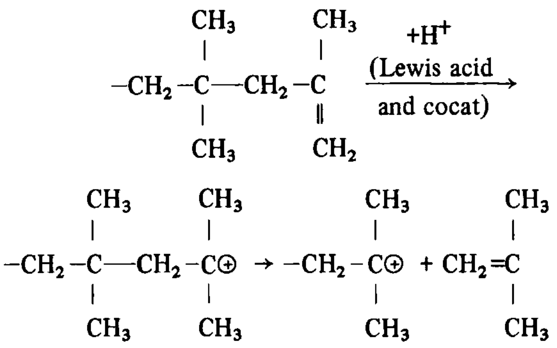
The "chlorine loss" column shows the chlorine content of the chlorobutyl starting material and the average chlorine levels reached after catalyst introduction. Similarly to molecular weights, the chlorine contents also dropped extremely rapidly to an average level immediately after catalyst introduction.

The "I_2 number" column shows the iodine number of the starting material and the final average iodine number level reached after catalyst introduction. The rates of change of the three quantities, molecular weights, chlorine contents, and iodine numbers, were extremely fast (see above). From the iodine number the mole % unsaturation (i.e., the number of double bonds per 100 isobutylene units) can be calculated for butyl rubber [12]. These data are also included in the table. In the case of chlorobutyl this calculation cannot be made [11].

The chlorobutyl and butyl rubber experiments have been grouped in series (Series I to XV) depending on the Lewis acids ($AlCl_3$, $AlEtCl_2$, $AlEt_2Cl$, $AlEt_3$, $AliBu_3$), solvents (polar, nonpolar, or mixtures of these), and temperature (from -10 to -78°C) used.

DISCUSSION

No molecular weight degradation occurred with polyisobutylene under our experimental conditions. Thus, in contrast to the relative ease of degradation of polyisobutylene under various kinds of free radical attack [1-8], polyisobutylene is stable in the presence of the Lewis acids employed. Our results indicate that unzipping by



$$-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_2}{\overset{CH_3}{\underset{\|}{C}}}\xrightarrow[\text{and cocat)}]{+H^+\ \text{(Lewis acid}}$$

$$-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}\oplus \rightarrow -CH_2-\underset{CH_3}{\overset{CH_3}{C}}\oplus + CH_2{=}\underset{CH_3}{\overset{CH_3}{C}}$$

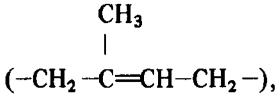
is highly unlikely. Indeed, this depolymerization reaction would be thermodynamically quite unfavorable, i.e., endothermic by about 12.8 kcal/mole [14]. Also the temperature range of these degradation studies was way below the ceiling temperature of isobutylene polymerization (~50°C) which is of importance considering the last step (monomer elimination) in the above equation. Finally it is unlikely that the Lewis acids used would be able to extract a hydride ion from the $-CH_2$ or CH_3 groups in the polymer under the mild conditions employed. Thus it is not surprising that polyisobutylene is completely resistant to degradation by Lewis acids under the conditions employed.

In contrast, the ease of degradation of butyl rubber is remarkable under essentially identical conditions. High molecular weight (457,000) butyl rubber with an unsaturation level of 1.3 mole % rapidly (in less than 1/2 min) degrades in the presence of 1.57 mole $AlEtCl_2$ per "mole" unsaturation at -10 and -50°C, i.e., about 3 and 1 chain scissions occur, respectively, with this Lewis acid.

In the presence of $AlEt_2Cl$, but otherwise under identical conditions, butyl rubber did not degrade.

These results may be explained as follows: In the presence of $AlEtCl_2$ butyl rubber which contains a fair amount of unsaturation is protonated and undergoes chain scission by the mechanism shown in Scheme 1.

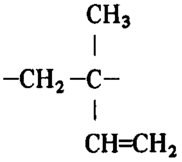
Butyl rubber, a copolymer of isobutylene and isoprene, contains two kinds of unsaturations depending on the mode of isoprene entry. The protonation of the major structure,



$$(-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-),$$

formed by a 1,4-isoprene incorporation, probably occurs readily with $AlEtCl_2$ in the presence of adventitious traces of protogenic substances (moisture?) and a relatively stable tertiary macrocarbonium ion is formed. This then may undergo β-scission [15], generating a tertiary cation and a branched terminal double bond. The over-all energetics of this not overly favorable cleavage (a tertiary carbonium ion and a C–C single bond is sacrificed to produce another tertiary ion and a double bond) is aided by favorable entropy (two species generated from one) and increased solvation (the smaller product-carbonium ion is more readily solvated than the sterically hindered initial-cation).

The other, minor structure in butyl rubber,



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

which arises by a 1,2-isoprene entry in the chain may also be protonated, although at a relatively much reduced rate, to yield a secondary carbonium ion. The latter may undergo methide shift [16] to give a more favored tertiary ion which, in turn, again may undergo β-scission to give a more stable tertiary species together with terminal unsaturation. The tertiary carbonium ions formed in both processes may subsequently decay by secondary processes.

Turning to the less acidic $AlEt_2Cl$, the results show that no degradation occurs with this Lewis acid even at relatively high temperatures, e.g., -10°C.

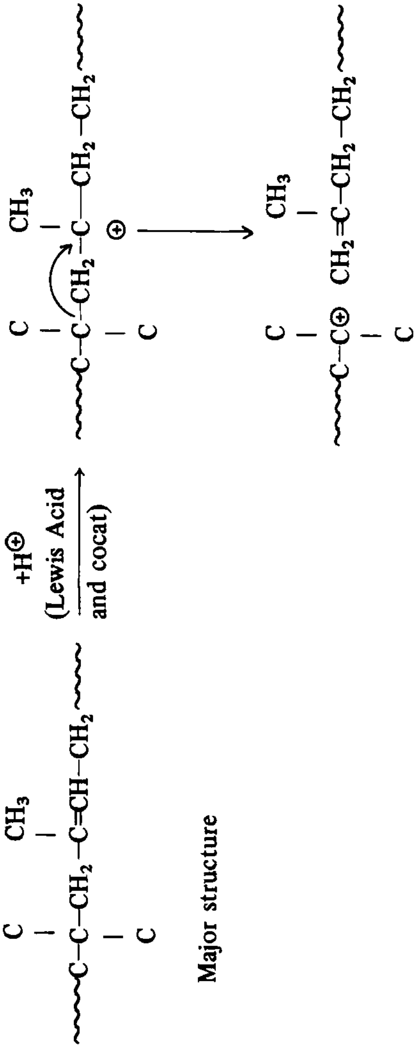
$AlEt_2Cl$ apparently needs a larger than trace amount of a "cocatalyst" for initiation and no protonation can take place with this Lewis acid in the absence of a purposely added proton or carbonium ion source. This is in agreement with the observation that $AlEt_2Cl$ does not initiate the polymerization of cationically readily attackable species, e.g., isobutylene and styrene; in the absence of a suitable cocatalyst, however, immediate polymerization commences on the introduction of a suitable proton source [17]. Thus it was anticipated that isobutylene-isoprene rubbers would be immediately degraded in the presence of $AlEt_2Cl$ by adding a small amount of HCl to the system. An experiment corroborated this expectation (Series III in Table 1). In this experiment a butyl rubber in n-hexane solution was stirred in the presence of 1.57 mole $AlEt_2Cl$ per "mole" unsaturation at -10°C. It was ascertained that the molecular weight of the rubber did not change after 5 min of stirring. Then 0.1 mole of HCl in n-hexane solution was added per mole of $AlEt_2Cl$ to the system. The viscosity of the stirred solution immediately decreased and a faint yellow color (carbonium ions) appeared. Molecular weight determination showed a drop from 421,000 in the control to 253,000 in a sample withdrawn 1.5 min after HCl introduction. Two more samples were withdrawn after 6 and 15 min but the molecular weights did not drop further. Subsequently, 16 min after the first HCl addition a second 0.1 mole HCl per mole of $AlEt_2Cl$ was added at -10°C and samples were withdrawn at 17, 22, and 30 min. According to the viscosities of these samples, the molecular weight suddenly dropped to 74,000 and remained at this level.

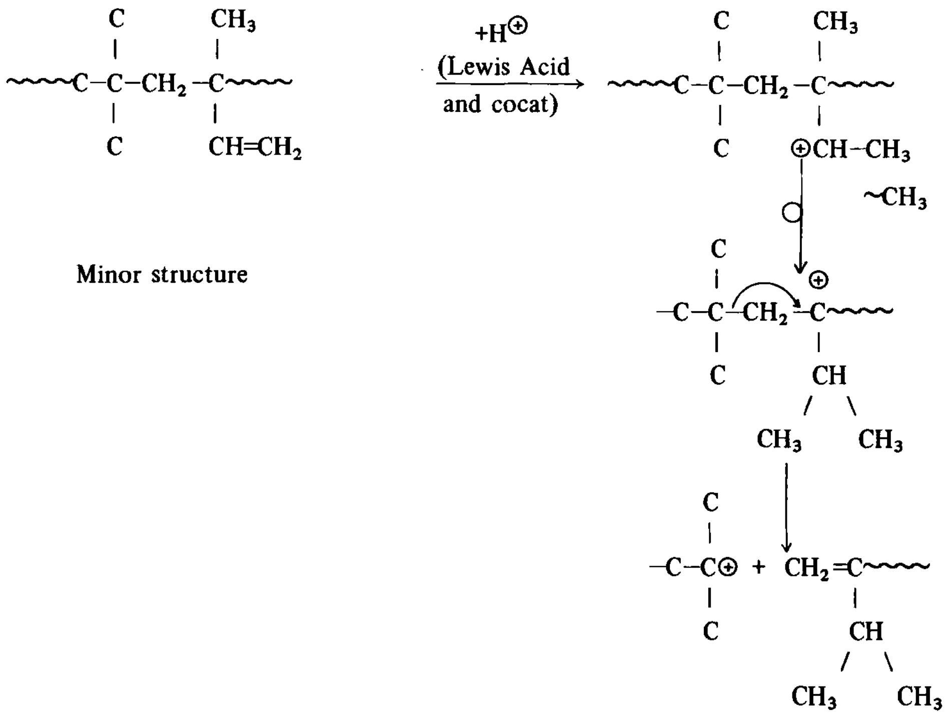
These results indicate that isobutylene-isoprene copolymers are readily degraded by carbonium ions. Evidently, hydrocarbon polymers containing unsaturation may be degraded in solution under proton or carbonium ion attack provided a favorable chain scission mechanism is available.

Chlorinated butyl rubber represents a considerably more involved picture. According to the data compiled in Table 1, chlorobutyl readily degrades in the presence of aluminum containing Lewis acids under a variety of conditions.

Looking at the results in detail, $AlCl_3$ and $AlEtCl_2$, the two most acidic agents used, severely degrade chlorobutyl under the conditions indicated in Table 1. The less acidic $AlEt_2Cl$ represents a more subtle case: This agent in nonpolar solvents degrades chlorobutyl severely at -10°C at a mole $AlEt_2Cl$/atom Cl in chlorobutyl ratio ($[AlEt_2Cl]/Cl$, for brevity) higher than about 0.25, i.e., by adding 0.25 mole of $AlEt_2Cl$ per gram atom chlorine in the polymer. Under these conditions degradation is almost instantaneous (takes less than 15 sec, the shortest time we were able to

(Scheme 1)





Scheme 1. Mechanism of chain scission of butyl rubber in the presence of certain Lewis acids.

achieve between catalyst addition, mixing, and sampling). After the initial precipitous drop, the molecular weights reach a plateau and they do not change further. Assuming 70 chlorine atoms in a representative chlorobutyl molecule ($\bar{M}_v$ = 366,000; $\bar{M}_n$ = 200,000; Cl = 1.2 wt%), the $\bar{M}_c$, the molecular weight of the chain segments between individual chlorine atoms, would be 2850 and the maximum number of chain scissions would be 70 - 1 = 69. This molecular weight wqs approximated only with $AlCl_3$ or $AlEtCl_2$ at -10°C. In contrast, with $AlEt_2Cl$ these low values have not been reached (although in two experiments unusually high, 14 and 18, chain scissions per molecule were estimated).

When the amount of Lewis acid is decreased at -10°C to a $[AlEt_2Cl]/Cl$ ratio of ~0.2 and 0.1, degradation becomes much less severe (++), and very small (+), respectively (cf. column 7 in Table 1). A similar trend can be observed at -50°C where at a $[AlEt_2Cl]/Cl$ ratio of 0.126 practically no degradation occurs.

The important, degradation impeding effect of temperature is also apparent in the -65°C series where breakdown is only medium in severity (++) even at a $[AlEt_2Cl]/Cl$ ratio of 1.28, at which chlorobutyl is still severely (+++) degraded at -50°C. Chain scission at -65°C is modest (+) at an $[AlEt_2Cl]/Cl$ ratio of 0.64 and practically absent (0) at 0.128. To complete the series in nonpolar solvents, at -78° there is no degradation of chlorobutyl even at the highest (1.23) $[AlEtCl_2]/Cl$ ratio employed.

The situation seems to be similar when using a 1:1 mixture of polar and nonpolar solvents. Both lowering the temperature and/or the amount of Lewis acid used (expressed by the $[AlEt_2Cl]/Cl$ ratio) retards the degradation of chlorobutyl.

Turning to the least acidic species in the series, $AlEt_3$, according to the data in Table 1, no molecular weight degradation occurs with this Lewis acid even at the highest temperature (-10°C) and $[AlEt_3]/Cl$ ratio (1.28) in a nonpolar solvent. In a 1:1 polar-nonpolar solvent mixture under the same or even milder conditions, severe degradation takes place and the $[AlEt_3]/Cl$ ratio must be lowered to 0.117 to avoid degradation. Similarly, breakdown is much less pronounced (+) at -50°C and there are only few chain scissions even at $[AlEt_3]/Cl$ = 0.58. Finally, no degradation occurs at -78°C even at $[AlEt_3]/Cl$ = 0.61.

Evidently, $AliBu_3$ is similar in activity to $AlEt_3$ in as much as it also immediately and severely degrades chlorobutyl in polar solvent at $[AliBu_3]/Cl$ = 0.29 at -10°C.

Chlorobutyl appears to be somewhat more vulnerable toward degradation than butyl rubber in the presence of Lewis acids. For example, butyl rubber degrades moderately (++) whereas chlorobutyl strongly (+++) in the presence of large amounts of $AlEtCl_2$ at -10° or -50°C.

To explain these results we may start by considering the structure of chlorinated butyl rubber. Although numerous workers have addressed themselves to this problem [18-20] the structure of the chlorobutyl molecule is still not known in all its details; nonetheless, it can be safely assumed that this molecule contains a variety of units as shown in Table 2.

A comprehensive mechanism of chain scissions in chlorobutyl in the presence of Lewis acids is proposed in Scheme 2a and 2b. In Scheme 2a the degradation of the chlorination products of the major 1,4-isoprene structure are considered. According to Scheme 2a, the degradation of the allylic Structures $A \rightleftharpoons A'$, $C \rightleftharpoons C'$, $D \rightleftharpoons D'$, E, F, and G starts by the Lewis acid removing an active chlorine atom from the unit and producing allylic carbonium ions, I, III, or IV:

$$\text{allyl–Cl} + AlCl_3 \rightarrow \text{allyl}^{\oplus} \cdot AlCl_4^{\ominus}$$

In case a favorable scission mechanism is available, these allyl carbonium ions might undergo chain cleavage. Thus it is conceivable that allyl ion I formed from Structures $A \rightleftharpoons A'$ or F might cleave by either of two β-scission mechanisms. Both processes give a product-mix of a tertiary ion and a branched terminal olefin. Similar cleavage mechanisms have been postulated [15]. These energetically not overly favorable reactions are promoted by a favorable entropy factor and solvation (cf. above).

Allyl ion III obtained by chlorine removal by the Lewis acid from Structures $C \rightleftharpoons C'$, or G, would most likely decay by secondary processes because no favorable direct scission mechanisms are available for these structures.

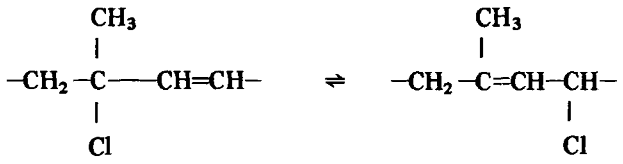
Carbonium ion IV formed from Structures $D \rightleftharpoons D'$ or E may cleave by a favorable β-scission mechanism involving a methide migration as shown in Scheme 2a. In this favored degradation a tertiary carbonium ion and a highly (5 times) substituted diolefin are formed.

Structure B contains a stable vinylic chlorine which cannot be removed by Lewis acids under relatively mild conditions. It is more likely that this species is protonated providing the tertiary ion II which then readily cleaves by a very favorable mechanism. In this species the electronegative chlorine dipole induces a partial positive charge to the neighboring hydrogen. The driving force for cleavage is then provided by the elimination of the partial positive charge α to the full positive carbonium ion site. This chain breaking also gives a tertiary carbonium ion and a branched olefin. This

Table 2. Possible Chlorinated Units in the Chlorobutyl Molecule

A. Chlorination products of the major 1,4-isoprene structure.

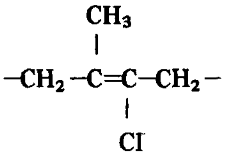
Products of ionic chlorination (more likely process)



$$-CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH{=}CH- \rightleftharpoons -CH_2-\overset{\overset{CH_3}{|}}{C}{=}CH-\underset{\underset{Cl}{|}}{CH}-$$

A A′

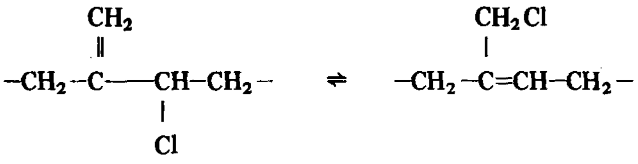
(less likely structure)



$$-CH_2-\overset{\overset{CH_3}{|}}{C}{=}\underset{\underset{Cl}{|}}{C}-CH_2-$$

B

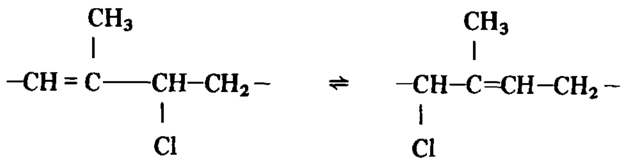
(more likely structure)



$$-CH_2-\overset{\overset{CH_2}{\|}}{C}-\underset{\underset{Cl}{|}}{CH}-CH_2- \rightleftharpoons -CH_2-\overset{\overset{CH_2Cl}{|}}{C}{=}CH-CH_2-$$

C C′

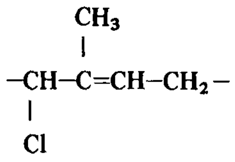
(more likely structure)



$$-CH=\overset{\overset{\displaystyle CH_3}{|}}{C}-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_2- \rightleftharpoons -\underset{\underset{\displaystyle Cl}{|}}{CH}-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-$$

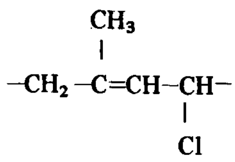
D D′ (more likely structure)

Products of radical chlorination (less likely process):



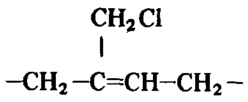
$$-\underset{\underset{\displaystyle Cl}{|}}{CH}-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-$$

E



$$-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-\underset{\underset{\displaystyle Cl}{|}}{CH}-$$

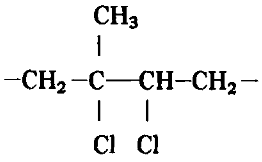
F



$$-CH_2-\overset{\overset{\displaystyle CH_2Cl}{|}}{C}=CH-CH_2-$$

G (less likely structure)

Product of chlorine addition:



$$-CH_2-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_2-$$

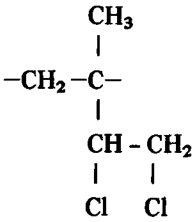
H (less likely structure)

(continued)

Table 2. (Continued)

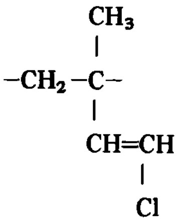
B. Chlorination products of the minor 1,2-isoprene structure.

Products of ionic chlorination:



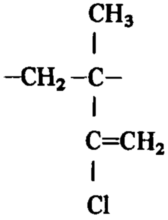
$-CH_2-C(CH_3)(CHCl-CH_2Cl)-$

I



$-CH_2-C(CH_3)(CH=CHCl)-$

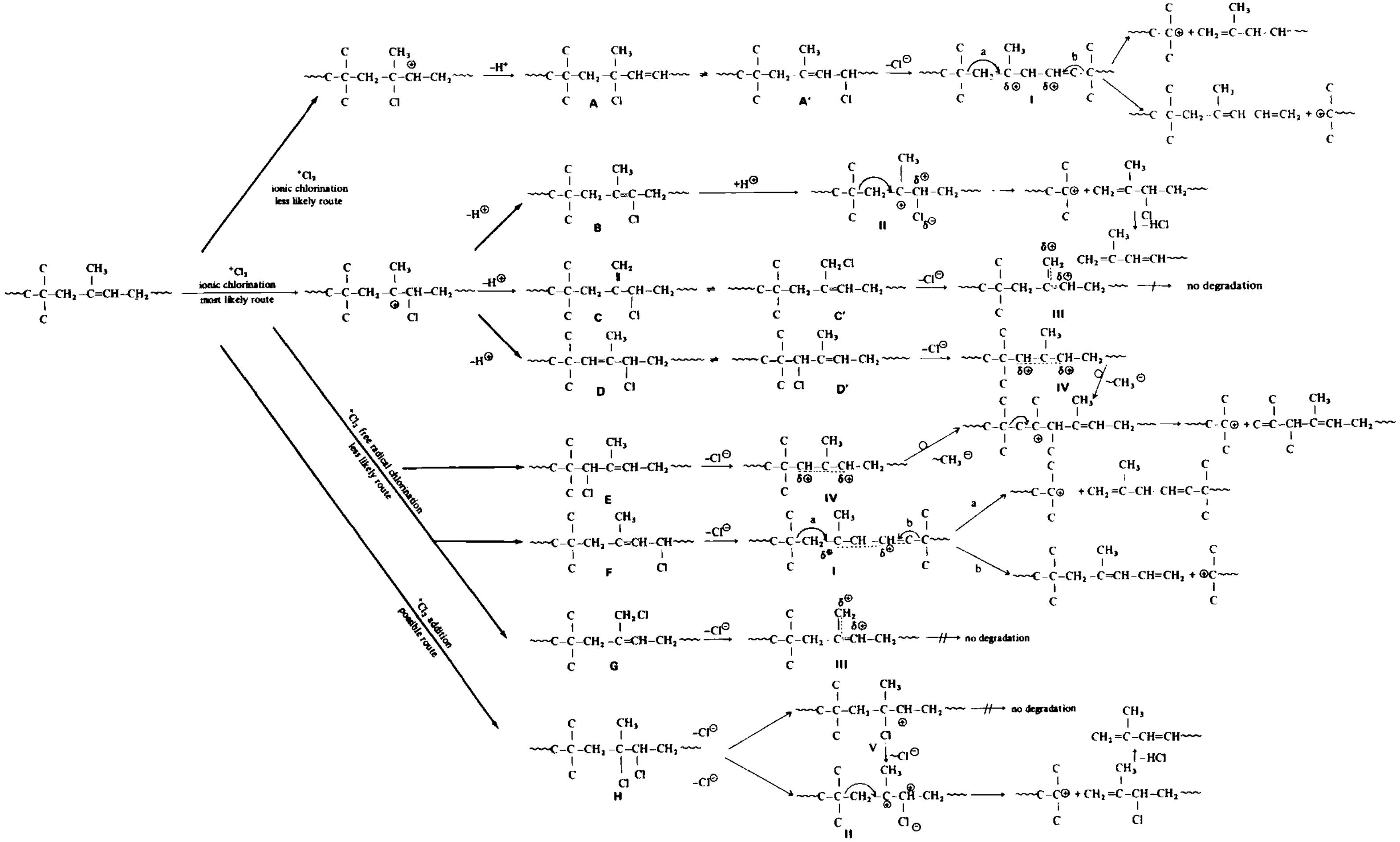
J



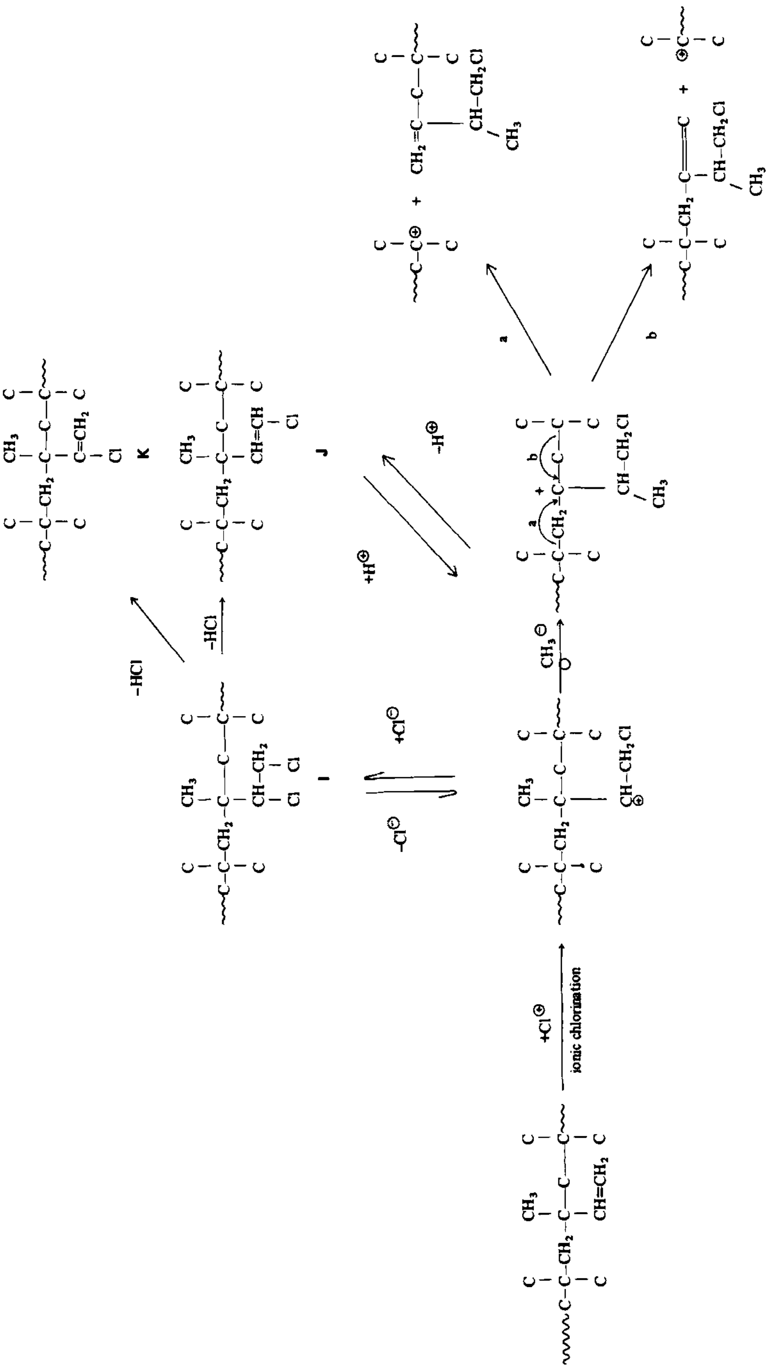
$-CH_2-C(CH_3)(CCl=CH_2)-$

K

(less likely structure)



Scheme 2a. Mechanism of chain scission of chlorobutyl in the presence of Lewis acids.

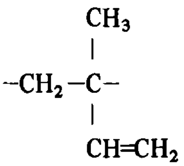


Scheme 2b. Mechanism of chain scission of chlorobutyl in the presence of Lewis acids. (minor structure)

favorable scission mechanism could be important in the over-all degradation process (the identical ion II is also obtained from Structure H, see below).

Chlorobutyl might also contain Structure H obtained by chlorine addition to the 1,4-isoprene unit in the chain. However, the iodine numbers of chlorobutyl are not much different from those of the unchlorinated butyl rubber which indicates that this saturated structure is probably not important. Structure H in the presence of Lewis acids can lose either the tertiary chlorine (more likely process) or the secondary chlorine (much less likely) giving carbonium ions II or V, respectively. Since the secondary carbonium ion V cannot degrade, it conceivably isomerizes by chloride shift to the more stable tertiary carbonium ion II which then may undergo β-scission by the favorable route discussed above. Chlorine shifts similar to this proposition have been demonstrated to occur in certain carbonium ion polymerizations [21].

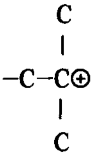
In addition to these chain scission mechanisms, there might be those originating from less important but still possible Structures I, J, and K in chlorobutyl (Table 2). These structures might arise by the chlorination of the minor



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

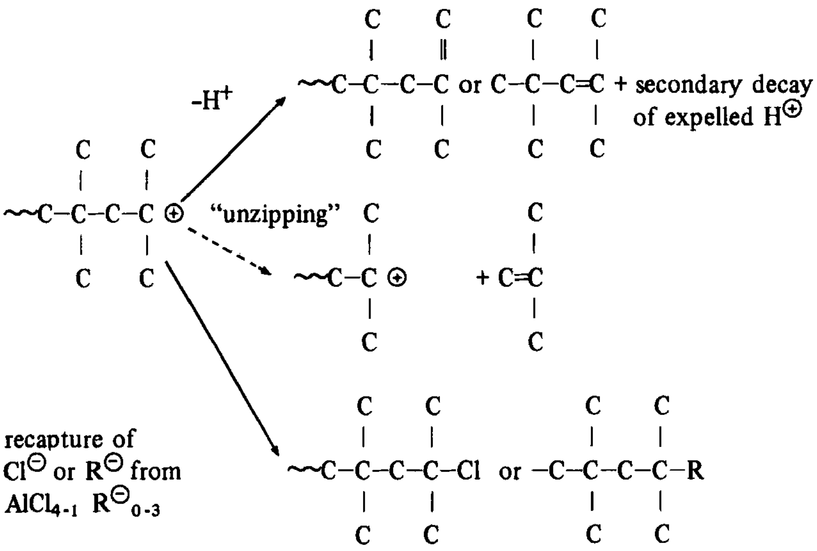
unit in butyl rubber. A possible degradation mechanism for these units is shown in Scheme 2b. Again it is interesting to note that pendant unsaturations might also lead to chain cleavage provided that a favorable rearrangement occurs which transfers the carbonium ion to the main chain.

In all these β-scissions the common reaction product postulated is a stable tertiary carbonium ion



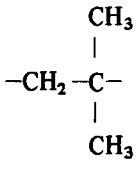
$$-C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}\oplus$$

and a (more or less) branched olefin. As discussed in connection with the polyisobutylene experiments, it is highly unlikely that the carbonium ion species would "unzip"; rather, this cation might decay by proton elimination or by the recapture of a chloride ion (or carbanion) from the counter-ion:



Also, all these cleavage reactions are more or less aided by favorable entropy and solvation considerations (cf. above).

Finally, the chlorobutyl molecule may also contain $-CHCl-$ or $-CH_2Cl$ groups generated by the chlorination of the



$$-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-$$

units in the copolymer. However, these groups are probably quite unimportant in chlorobutyl considering the mild chlorination conditions used and the low amounts (~1.2 wt%) of chlorine incorporated. Even if present, these primary and/or secondary chlorines could not have been removed by the Lewis acids used under the mild conditions employed and consequently have been ignored in this discussion.

Chlorobutyl is somewhat more vulnerable toward degradation than butyl rubber (cf. above). This could be explained by assuming that the removal of active allylic chlorines from chlorobutyl is faster than the protonation of internal unsaturations by Lewis acids.

Evidently the iodine numbers (or mole % unsaturation) of butyl rubber do not change appreciably during degradation (columns 10 and 11 in Table 1). This is in agreement with the proposed mechanisms. With chlorobutyl in certain cases the iodine numbers increase with degradation. This is particularly evident in experiments with $AlCl_3$ and $AlEtCl_2$. Some of the favorable scission routes in Scheme 2a give two moles of unsaturation (terminal dienes) per one mole of initial unsaturation which might explain these increased iodine numbers.

The chlorine levels decrease during degradation. This again is in agreement with the proposed mechanism according to which the first step of the degradation is the removal of chlorine atoms by the Lewis acids.

CONCLUSION

Polymers and copolymers in solution will readily degrade under the influence of Lewis acids (or Bronsted acids) if a carbonium ion can be generated on their backbone and if a favorable degradation mechanism can take place. The carbonium ion may be produced by protonating a double bond or by removing a halogen and presumably by any other suitable processes, e.g., hydride abstraction. The subsequent cleavage of the chain requires a favorable cracking mechanism. Chain degradation can occur even when the first carbonium ion generated is in a pendant group outside of the main backbone provided a favorable isomerization mechanism transfers the charge to the main chain. The over-all rate of catalytic degradation reactions may be extremely fast even at very low temperatures; this is not too surprising considering the carbonium ion nature of these processes.

In particular, the molecular weight breakdown of butyl rubber or chlorbutyl is determined by the relative rates of numerous partly competitive cationic mechanisms. In the presence of the highly acidic $AlCl_3$ and/or $AlEtCl_2$, protonation or chlorine removal is fast and virtually complete, and very severe degradation occurs under otherwise mild conditions, e.g., low temperatures. With the less acidic $AlEt_2Cl$ or $AlEt_3$ the experimental conditions have to be more vigorous (e.g., working in polar solvents or at higher temperatures) to achieve severe degradation.

The proposed mechanisms derived from accepted carbonium ion reactions satisfactorily explain the experimentally observed molecular weight, iodine number, and chlorine data.

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Accepted by editor May 22, 1970
Received for publication June 3, 1970