Nuclear magnetic resonance study of the hydrobromination reaction and the microstructure of hydrobrominated natural rubber

J. H. Bradbury, J. A. Elix and M. C. S. Perera*
Chemistry Department, Australian National University, Canberra, ACT 2601, Australia
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The hydrobromination of natural rubber was studied by ^1H and ^{13}C nuclear magnetic resonance spectroscopy and resonances of partially hydrobrominated rubber were assigned on the basis of triads and dyads. Reaction of natural rubber with HBr in a non-polar solvent to low conversions did not hydrobrominate adjacent double bonds and caused an appreciable amount of *cis–trans* isomerization due to steric hindrance. Reaction in the presence of a Lewis acid ($AlBr_3$) occurred more rapidly and caused cyclization rather than isomerization. In dichloromethane hydrobrominated rubber underwent E2 elimination to produce exomethylene groups. Contrary to expectations, addition of peroxides did not cause substitution by bromine at tertiary carbon atoms but produced the normal substitution at the quaternary position.

(Keywords: ^1H and ^{13}C nuclear magnetic resonance; natural rubber; hydrobromination; reaction mechanism; microstructure; isomerization)

INTRODUCTION

During the last 40 years, hydrohalogenation of natural rubber and gutta-percha have been extensively studied[1–8]. Both polymers readily add hydrogen chloride according to Markovnikov's rule, the chlorine atoms substituting the tertiary carbon atom, as proved by X-ray analysis[1]. It was shown by ^1H n.m.r. studies[6] that some cyclization occurred during hydrochlorination but little or no *cis–trans* isomerization. Similar conclusions were reached[9] for the reaction of *cis-* and *trans*-1,4-polyisoprene with hydrogen bromide and hydrogen iodide and of natural rubber with hydrogen fluoride[10]. In contrast to results of earlier workers[6], a recent study of the microstructure of hydrochlorinated 1,4-polyisoprene, by ^1H and ^{13}C n.m.r. and by physical property measurements, established that practically no cyclization occurred[7], and that hydrogen chloride added randomly along the polymer chain. Polybutadiene[11] and polypentenamer[12] have also been hydrobrominated and the products used as substrates for further reactions including alkylation[13,14] and conversion to a nitrile[12]. Hydrobromides of both *cis-* and *trans*-polyisoprenes have been prepared but their structures do not appear to have been elucidated[15]. In this paper we report a ^1H and ^{13}C n.m.r. study of the microstructure of hydrobrominated natural rubber and of the products obtained using different methods of hydrobromination of natural rubber.

EXPERIMENTAL

Materials

Solid natural rubber and natural rubber latex were obtained from Sri Lanka. Solid natural rubber was purified by dissolution in benzene, precipitation from acetone, followed by lyophilization from benzene[16]. Analytical-grade toluene, tetrahydrofuran, dichloromethane, aluminium bromide, ferric chloride, benzoyl peroxide, quaternary ammonium bromide and 48% hydrogen bromide solution were obtained from Aldrich Chemicals. Anhydrous hydrogen bromide gas was obtained from Matheson. Spectral-grade deuterated chloroform was used for n.m.r. spectroscopy.

Nuclear magnetic resonance spectroscopy and viscosity determination

^1H n.m.r. spectra at 200 MHz and ^{13}C n.m.r. spectra at 50.1 MHz were obtained using a JEOL FX 200 n.m.r. spectrometer using instrumental conditions described elsewhere[17]. Spectra were determined at 298 K and tetramethylsilane (TMS) was used as an internal standard. Spectral intensities were measured by cutting out and weighing each peak area. A modified[18] INEPT pulse sequence was used to separate methyl and methine carbon resonances, which remained in phase, from methylene resonances, which were inverted, and from quaternary carbon resonances, which disappeared[19]. Relative ^{13}C n.m.r. intensities could be used for quantitative sequence analysis provided that a repetition time of $>5T_1$ was used and also gated decoupling[20], which effectively removed any variability in the nuclear Overhauser effect (NOE)[21]. The intrinsic viscosity ($dl\,g^{-1}$) was measured using a suspended-level Ubbelohde dilution viscometer at 25°C in toluene[19,22].

Hydrobromination of natural rubber

Solution method using hydrogen bromide gas. The hydrobromination reaction was carried out at different temperatures on a 5% (w/v) solution of purified natural rubber in toluene, dichloromethane or tetrahydrofuran in

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* Work performed while on leave from the Rubber Research Institute of Sri Lanka, Thelewala Road, Ratmalana, Sri Lanka

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a vessel covered with aluminium foil to prevent entry of light. The solution was first purged with dry nitrogen to remove molecular oxygen, after which dry hydrogen bromide was bubbled through the reaction mixture at a rate of 5 ml min^{-1}. The effect of various additives (per cent on weight of rubber) such as aluminium bromide (2%), ferric chloride (2%) and benzoyl peroxide (1%) were also tested. Aliquots of the reaction mixture were withdrawn from the system at intervals from 1 to 24 h. The aliquots were purged with nitrogen, washed with distilled water to remove unreacted hydrogen bromide, and precipitated by pouring into methanol. The products were dried at 34°C.

Solution method using hydrogen bromide solution. To a solution of purified natural rubber (5% w/v in toluene or tetrahydrofuran) a catalytic amount of t-butylammonium bromide or cetyltrimethylammonium bromide was added. To these solutions held at a constant temperature, 80, 90, 100°C or boiling temperature) a predetermined amount of 48% hydrogen bromide in water or acetic acid was added dropwise. The product was isolated as above.

Latex method. Latex (2 ml) of 20% dry rubber content was stabilized with a non-ionic surfactant. One millilitre of 40% hydrogen bromide in acetic acid was added dropwise at room temperature. Samples were coagulated by pouring into methanol and were washed with water.

Determination of the extent of hydrobromination

The ^1H n.m.r. spectrum of the partially hydrobrominated natural rubber given in *Figure 1* shows a resonance at 5.08 ppm due to $-C{=}\underline{CH}$[19]. This resonance was used to determine the amount of residual unsaturation by comparing its area with the area of the 5.08 ppm peak from natural rubber. Both samples (0.1 g) were dissolved in the same volume of $CDCl_3$ containing TMS at a fixed concentration and the areas were normalized for instrumental variability using the heights of the TMS peaks at 0 ppm.

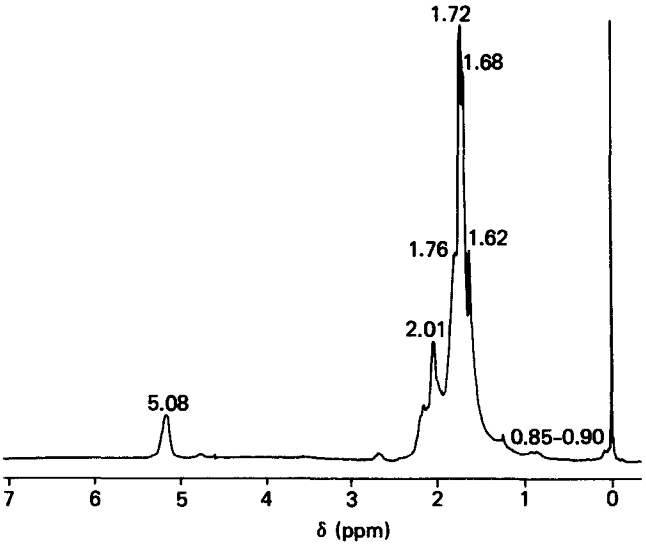


Figure 1 ^1H n.m.r. spectrum at 200 MHz of partially hydrobrominated natural rubber

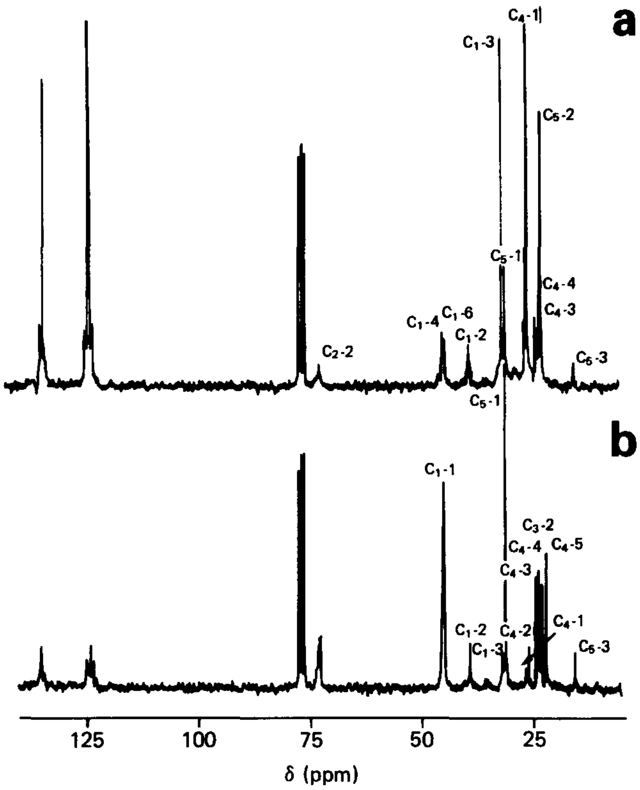


Figure 2 ^{13}C n.m.r. spectra at 50.1 MHz of (a) 30% and (b) 65% hydrobrominated natural rubber

RESULTS AND DISCUSSION

Assignment of ^{13}C nuclear magnetic resonances of partially hydrobrominated natural rubber

The assignments of the peaks of the ^{13}C n.m.r. spectra of partially hydrobrominated natural rubber shown in *Figure 2* were made by considering triad sequences of unreacted isoprene units (C) and reacted isoprene units (B) (*Figure 3*). The five carbon atoms in the centre unit in a triad are denoted as explained previously[19]. An INEPT spectrum of the product (not shown) separated the resonances into those from methyl (C_5), methylene (C_1 and C_4), methine (C_3) and quaternary (C_2) carbon atoms. Thus all the peaks designated C_1 and C_4 in *Figure 2* arose from methylene carbons and those labelled C_5 were due to methyl carbons, except for C_5-1 which may be a mixture of methyl and methylene peaks, as shown by the INEPT spectrum and off-resonance decoupling.

Methyl and methylene resonances. The assignments corresponding to unreacted natural rubber[19] and fully hydrobrominated[8] natural rubber were made according to previous work. Thus the assignments of C_1-3, C_4-1, C_5-2, C_1-1, C_5-1 and C_4-5 followed as C^1CC^1, CC^4C, CC^5C, (B^1BB/BB^3B), B^5BB and BB^4B respectively. Most of the remaining peaks in this region were assigned by using substitution factors as discussed in a previous publication[17]. Bromine substitution factors due to Wiberg *et al.*[23] are given in *Table 1* and chemical shifts in the triads calculated using these substitution factors are in *Table 2*. The assignments were made by matching the calculated and observed chemical shifts as shown in *Table 2*. Some carbons were sensitive only to dyad arrangements, e.g. resonance C_1-3 was assigned to both C^1CB and C^1CC. Carbon atoms within each of the pairs B^1BB, BB^3B and B^1BC, CB^3B had the same chemical

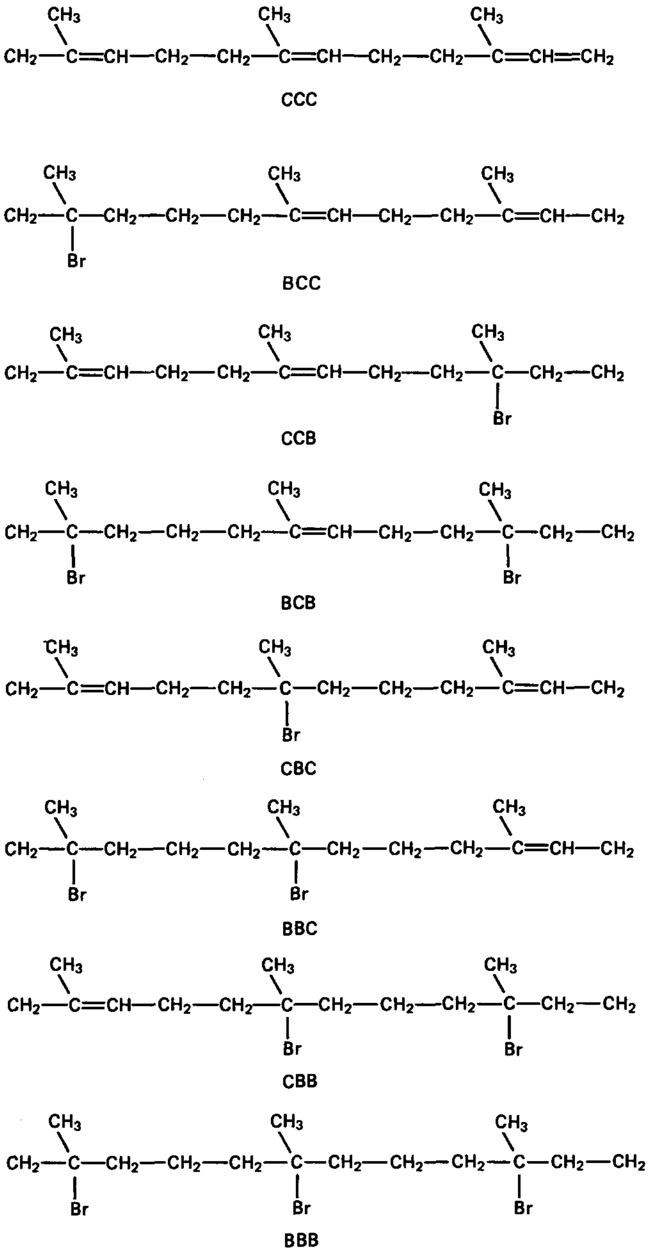


Figure 3 Structures of the possible triad arrangements of unreacted (C) and hydrobrominated (B) isoprene units

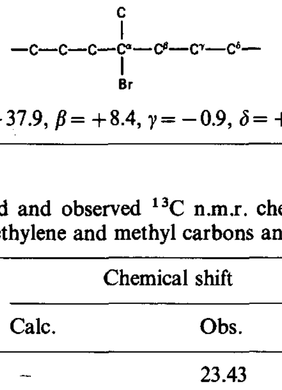
environment (see *Figure 3*) and were all assigned to resonance C_1-1 (*Figure 2*). At low levels of bromination, several resonances were observed in this region, as shown in *Figure 4*. The calculated chemical shifts showed that BB^3C should be slightly upfield of BB^3B, and thus resonance C_1-6 was assigned to BB^3C. At low levels of modification C_1-4 was the first peak to appear (*Figure 4a*) and was assigned to C^1BC/CB^3C; C_1-5 appeared later and was assigned to C^1BB. Assignments of the C_4 resonances followed directly from calculated values.

The above assignments of this region left C_1-2, C_4-2 and C_5-3 unassigned. The chemical shifts of these three small peaks were comparable to the chemical shifts of methyl and methylene carbons atoms of *trans*-1,4-polyisoprene[24]. The existence of *trans* units in the product was further confirmed by the presence of a resonance at 1.62 ppm in the ^1H n.m.r. spectrum (*Figure 1*) of the product[25,26]. The *trans* unit was denoted by T and the chemical shifts of carbon atoms in the triads containing *trans* units were calculated using bromine substitution factors and matched with observed values to make the assignments as given in *Table 3*. The *cis* or *trans* nature of the double bond was only felt by the α-carbon atom attached to the double bond[27]. Therefore, for example, it would be expected that C^1BB and T^1BB would resonate at the same position. In the final assignments given in *Table 3* this fact was taken into account and in such cases the double bond was denoted by I, where I denotes either the *cis* or *trans* double bond. The assignments in *Table 3* indicated the presence of BT and TB dyads but not TT.

Assignments of quaternary brominated carbon atoms. The resonance C_2-4 (*Figure 4*) was assigned to B^2BB previously[8]. The first resonance that occurred at 30% hydrobromination (C_2-2, *Figure 4b*) was assigned to the quaternary carbon atom attached to the bromine atom of a singly brominated triad (C^2BC). The peaks C_2-1 and C_2-3 appeared at higher levels of hydrobromination and hence were assigned to doubly brominated triads. Comparison of these triads (C^2BB and B^2BC) in *Figure 3* indicated a small difference between the structures which was simulated by comparing the chemical shift (14.06 ppm) of C-6 of 2-methyl-1-hexene (similar to B^2BC) with the chemical shift (13.85 ppm) of C-6 of 2-hexene (similar to C^2BB). It was expected that B^2BC would be found downfield of C^2BB, hence allowing the assignments of C_2-1 and C_2-3 in *Table 4*.

Assignments in the olefinic region. The resonances in this region were also assigned on the basis of known

Table 1 Effect of bromine substitution on ^{13}C n.m.r. chemical shifts[23] (ppm)



$$—C—C—C—\underset{Br}{\overset{C}{C^{\alpha}}}—C^{\beta}—C^{\gamma}—C^{\delta}—$$

$\alpha = +37.9$, $\beta = +8.4$, $\gamma = -0.9$, $\delta = +0.1$

Table 2 Calculated and observed ^{13}C n.m.r. chemical shifts (ppm) of resonances of methylene and methyl carbons and assignments

Carbon atom	Chemical shift		Peak
	Calc.	Obs.	
CC^5C	–	23.43	C_5-2[a]
B^1CC, BB^5C	32.33	31.41	C_5-1
B^1CB	32.33	31.41	C_5-1
C^1CC	–	32.23	C_1-3[a]
C^1CB	–	32.23	C_1-3[a]
C^1BC	45.87	45.57	C_1-4
C^1BB	45.87	45.36	C_1-5
B^1BC	45.97	45.28	C_1-1
B^1BB	–	45.28	C_1-1
CC^4B	25.46	24.49	C_4-3
BC^4B	25.46	24.49	C_4-3
CC^4C	–	26.36	C_4-1[a]
BC^4C	26.36	26.36	C_4-1
CB^4C	23.61	24.00	C_4-4
BB^4C	23.61	24.00	C_4-4
CB^4B	22.71	22.30	C_4-5
BB^4B	–	22.30	C_4-5[b]
CB^3C	45.87	45.57	C_1-4
CB^3B	45.97	45.28	C_1-1
BB^3C	45.87	45.20	C_1-6
BB^3B	–	45.28	C_1-1[b]

[a] Assignments by Bradbury and Perera[19]
[b] Assignments by Lacas *et al.*[8]

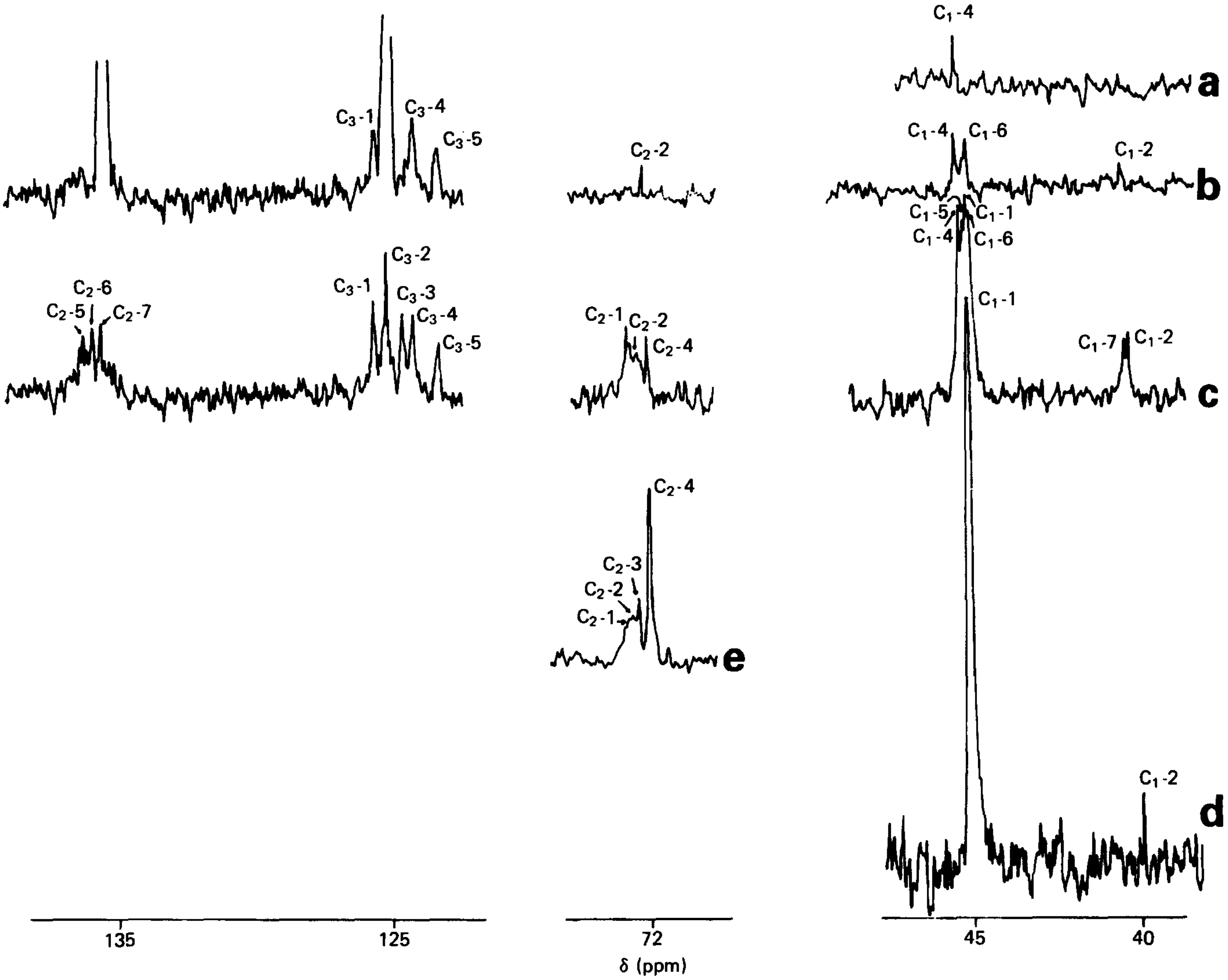


Figure 4 Expansions of the ^{13}C n.m.r. spectra at 50.1 MHz of (a) 15%, (b) 30%, (c) 54%, (d) 63% and (e) 68% hydrobrominated natural rubber

Table 3 Calculated and observed chemical shifts of methylene and methyl carbons in triads containing *trans* units

Carbon atom[a]	Chemical shift Calc.	Chemical shift Obs.	Signal
IT^5I	–	15.91	C_5-3
T^1BI	45.87	45.57	C_1-4
T^1BB	45.87	45.36	C_1-5
B^1TB	39.84	39.82	C_1-2
B^1TI	39.84	39.82	C_1-2
T^1TB	39.74	–	–
T^1TI	39.74	–	–
BT^4T	26.69	–	–
IT^4T	26.69	–	–
BT^4B	25.79	25.91	C_4-2
IT^4B	25.79	25.91	C_4-2
BB^4T	23.61	24.00	C_4-4
IB^4T	23.61	24.00	C_4-4
BB^3T	45.87	45.20	C_1-6
IB^3T	45.87	45.28	C_1-1

[a] I denotes either *cis* or *trans*

Table 4 Assignments of downfield resonances to bromine-substituted quaternary carbon atom and olefinic carbons

Signal	Chemical shift (ppm)	Assignment
C_2-1	73.37	B^2BC
C_2-2	73.17	C^2BC
C_2-3	73.02	C^2BB
C_2-4	72.71	B^2BB
C_2-5	135.83	B^2CC[a]
C_2-6	135.51	B^2CB[a]
C_2-7	135.23	C^2CC, C^2CB
C_3-1	125.49	BC^3C[b]
C_3-2	125.07	CC^3C
C_3-3	124.47	BC^3B
C_3-4	124.09	CC^3B[b]
C_3-5	123.27	IT^3B

[a,b] Assignments may be interchanged

chemical shifts of C^2CC and CC^3C[19] and on the order of disappearance of resonances with increasing extents of hydrobromination (*Figure 4*). Assignments given in *Table 4* show further evidence for the presence of a *trans* unit in resonance C_3-5.

Microstructure of partially hydrobrominated natural rubber and rate of the reaction

The resonances due to the C-4 carbon atom were well separated without any overlap with other peaks (*Figure 2*) and were used for quantitative analysis using the n.m.r. precautions given above to allow quantitative intensity measurements. As shown in *Tables 2* and *3*, the C_4

resonances were sensitive only to dyad arrangements. The percentage existence of each dyad obtained experimentally (for hydrobrominated rubbers obtained by the gaseous method in toluene at 25°C) and calculated values assuming random hydrobromination (no isomerization) are given in *Table 5*. At low levels of modification (30%) as shown in *Figure 2*, the peak C_4-5 was absent, hence there were no adjacent hydrobrominated units; this was also evident in the 72 ppm region (*Figure 4*). This result contrasted with the observation on epoxidized natural rubber where, even at 30% epoxidation, triads EEE appeared[28]. As the reaction proceeded, the dyad BB appeared but the experimental value was always lower than the calculated value; however, the difference throughout was approximately equal to the amount of *trans*-isoprene units (TB) in the product.

Similar *cis–trans* isomerization had been observed[29] when low molecular weight olefins were treated with hydrogen bromide, and a free radical mechanism was proposed. However, such isomerizations occurred even in the presence of free radical trappers, so that they may be due to ionic intermediates[30]. As attempts to extend photosensitized bromine radical isomerization of polybutadiene[31] to polyisoprene were unsuccessful[32], it was unlikely that isomerization occurred in the above reaction (since oxygen and light were carefully excluded) by a free radical mechanism. The formation of *trans* units may be a result of steric restriction imposed by a bromine atom of an adjoining reacted unit. A ^{13}C n.m.r. study[33] of substituted squalene indicated that a hetero-atom such as bromine had a steric interaction with the adjacent double bond, but a group such as an epoxide had an insignificant effect. As the mode of hydrogen bromide addition to olefins in non-polar solvents with low dielectric constants was inconsistent with that predicted by a free radical mechanism, a 2:1 complex was proposed as a possible transition state[30,34]. The bulkiness of the cyclic structure restricted its formation with a double bond adjoining a hydrobrominated group though the double bond is cleaved. It would therefore revert to the thermodynamically more favourable *trans* unit. This on–off type reaction would continue as the reaction proceeded and, once the restriction was overcome, the hydrobrominated product was quite stable (>24 h at 50°C) compared with the conditions (2 h at 25°C) used for hydrobromination. This provided further proof of the on–off type reaction (to form the double bond) rather than elimination of hydrogen bromide from a product (hydrobrominated) unit. Further evidence for such steric restriction was the fact that towards completion of the reaction it was obvious that the *cis* units disappeared faster than *trans* units, though it has been shown that in hydrochlorination *cis* and *trans* units reacted at similar rates[7]. This means that the *trans* units in the present system were more sterically hindered and this would only be possible if *trans* units were formed as explained above. A very low degree of cyclization was observed in this product as indicated by ^{1}H n.m.r. peaks at 0.85–0.90 ppm.

Effect of temperature, additives and solvent on reaction

An increase in the rate of reaction was observed with an increase in temperature, as shown in *Table 6*. An increase in temperature had no significant effect on the microstructure of the product obtained but the decreased intrinsic viscosity of the product indicated that scission of the rubber backbone had occurred at 60°C. The

Table 5 Percentage of different dyads experimentally observed by ^{13}C n.m.r. and calculated assuming random hydrobromination

		Amount of hydrobromination calculated by ^{1}H n.m.r.									
		15%		30%		54%		63%		74%	
Dyad	Peak	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
TB	C_4-2	5	0	9	0	13	0	9	0	8	0
CC	C_4-1	74	72	50	49	22	21	13	14	0	7
CB	C_4-3	10	12	21	21	24	25	25	23	17	19
BC/BT	C_4-4	11	12	19	21	26	25	25	23	17	19
BB	C_4-5	0	3	0	9	15	29	29	42	58	55

Table 6 Effect of solvent, temperature and other additives on rate of hydrobromination using HBr gas

Solvent[a]	Temperature (°C)	Additives	Time (min) for conversion 25%	Time (min) for conversion 100%	Intrinsic viscosity [η] (dl g^{-1}) of 70% converted product
Toluene (2.43)	0	None	45	150	2.91[b]
	25	None	30	120	–
	50	None	25	100	–
	60	None	25	100	0.7
THF (2.95)	25	None	150	–	–
Dichloromethane (9.08)	25	None	40	–	–
Toluene	25	$AlBr_3$	–	90	2.92
	25	$FeCl_3$	–	60	2.01
	25	Acetic acid	45	150	Very low
	50	Benzoyl peroxide	–	100	Very low
	100	Benzoyl peroxide	–	90	Very low
	25	Silica gel	120	–	–

[a] Values in parentheses are dielectric constants of the solvents

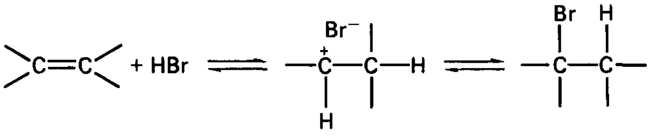
[b] [η] of unreacted natural rubber is 4.44 dl g^{-1}

reduction in $[\eta]$ from 4.44 dl g^{-1} (natural rubber, unreacted) to 2.91 dl g^{-1} (70% modified at 0°C) may be due to the effect of chemical modification on the flexibility of the polymer chain, although $[\eta]$ for partially epoxidized natural rubber fell only to 3.95[19], and hence the low value of 2.91 probably indicates some chain scission.

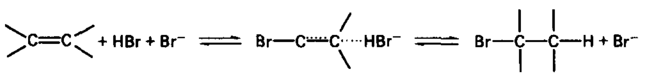
Addition of $FeCl_3$ and $AlBr_3$ increased the rate of the addition reaction, as has been previously observed for simple olefins (*Table 6*)[35]. $FeCl_3$ is known to promote ionic addition[36] and this would be expected to be much faster than molecular addition. Both $FeCl_3$ and $AlBr_3$ increased the degree of cyclization occurring during the reaction, as was expected, since Lewis acids have been used to cyclize natural rubber[37]. *Cis–trans* isomerization was not observed when $FeCl_3$ and $AlBr_3$ were used as additives. This may be due to the ionic nature of the reaction, in which case the steric effect of bromine in the δ position may not be sufficient to block the approach of the single Br^- ion. Apparently cyclization does not occur as a result of steric restrictions because, if so, the formation of BB units would not be possible, as once the units were cyclized, no further reaction would be possible. Therefore in this case, cyclization and hydrogen bromide addition appear to be independent of each other. Calculations taking into account the amount of cyclization and random reaction of the remainder of the molecule showed that the calculated and experimental values (for $AlBr_3$ added in toluene) agreed (*Table 7*); hence hydrogen bromide addition was random. In contrast, hydrobromination of polybutadiene in the presence of $AlBr_3$ showed reaction of individual double bonds with no formation of preferentially hydrobrominated blocks and no evidence of cyclization[14]. This difference would be expected because, in polyisoprene, a quaternary carbonium would be formed which would favour cyclization, whereas with polybutadiene no quaternary carbonium would be formed.

The addition of hydrogen bromide to simple olefins in the presence of an organic peroxide catalyst is known to proceed via a radical mechanism giving the so-called anti-Markovnikov product[38,39]. However, when the reaction was carried out with natural rubber in the presence of benzoyl peroxide at 50 and 100°C, no anti-Markovnikov product was observed, its intrinsic viscosity was very low and the microstructure of the product was similar to that obtained in the absence of benzoyl peroxide. The reason for this was not clear, but an attempt to ring-open epoxidized natural rubber to given an hydroxyl group in the anti-Markonikov position failed[17,28].

When the reaction was carried out in a solvent of higher dielectric constant, dichloromethane, it was expected that the hydrogen bromide addition would occur by an ionic mechanism[30], with an increased reaction rate as had been observed with $AlBr_3$ (*Table 6*). But the reaction in dichloromethane was found to be slower than in toluene, particularly at high conversion. The ^{13}C n.m.r. spectrum of the partially hydrobrominated product showed resonances at 108 ppm assigned to exomethylene groups[21,40]. The low rate of the reaction and the presence of exomethylene groups showed that the elimination occurred concurrently with addition. This probably explains the lack of agreement between experimentally observed and calculated values of the relative amounts of brominated dyads of the product in *Table 7*. A mechanism involving a reaction via a carbonium ion intermediate (ADE_2), formed as an ion pair in ion-pairing solvents, has been proposed for the ionic addition of hydrogen halide to olefins[41,42]. This is the reverse of an El elimination process[43].



The reversion of the intermediate carbonium ion to alkene may result in the formation of the double bonds in all orientations but in practice only the exomethylene group was detected[21]. A different mechanism (AD3) was proposed[21] for hydrogen halide addition in acetic acid, which is the reverse of an E2 elimination process[44].



In such an E2 elimination, Br^- is more likely to attack a hydrogen on the methyl group than a hydrogen on a methylene group due to increased steric hindrance to the approach of methylene groups on the main chain. Furthermore, it was reported[45,46] that the E2 elimination process was promoted by halide ion and other weak bases; bromide ion could well be present in dichloromethane. Thus, in dichloromethane E2 elimination would be expected rather than El elimination and so account for the formation of exomethylene groups in the product.

Other methods of hydrobromination

The rate of reaction of rubber in toluene with 48% aqueous hydrogen bromide increased with increasing temperature, and was not affected by the nature of the quaternary ammonium ion provided that this salt was not

Table 7 Percentage existence of different dyads in products obtained by gaseous hydrobromination with different additives and in different solvents, and for different extents of reaction

	$AlBr_3$/toluene		Dichloromethane					
	37%		24%		58%		68%	
Dyad	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
TB	–	–	10	0	9	0	8	0
CC	16	14	58	58	23	18	0	10
CB	12	14	13	18	30	24	19	22
BC/BT	12	14	13	18	31	24	23	22
BB	16	14	4	6	8	34	49	46

soluble in water. Thus tetrabutylammonium bromide showed very low activity. The microstructure of the product was very similar to that obtained by the gaseous method without any additives. Exomethylene groups were absent from the product, which was surprising as the presence of quaternary ammonium bromide was expected to promote E2 elimination[45]. Perhaps the bromide ion remained in the aqueous phase and was unable to participate in the reaction in the organic phase (toluene). No peroxide effect was observed.

The reaction in latex using hydrogen bromide in acetic acid produced only very small levels of reaction. The product contained numerous exomethylene groups indicating that this reaction was occurring by the AD3 mechanism, as expected[44].

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