^{13}C NMR Chemical Shifts and Cationic Reactivity of Linear Conjugated Dienes

Kan-ichi HASEGAWA, Ryuzo ASAMI, and Kensuke TAKAHASHI

Department of Synthetic Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466

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The chemical shifts of the C_1 and C_2 of *trans*-1-alkyl-1,3-butadienes were correlated with Taft's σ^*, the proportionality constants being -35.9 and 12.3 ppm/σ^*, respectively. The values 6.2 and -43.6 ppm/σ^* were obtained for the C_1 and C_2 of 2-alkyl-1,3-butadienes, respectively. The observed chemical shifts of disubstituted butadienes roughly agreed with the values estimated from those of monosubstituted butadienes by means of additivity relationship. The cationic reactivity of linear conjugated dienes should be determined by the magnitude of the steric restriction of substituents and that of the stability of the resulting cation.

The cationic polymerizability of linear conjugated dienes has been discussed in preceding papers,[1-8] with particular attention given to the relation between the structure and the reactivity of the monomers. The relative reactivity of the monomers toward a styryl cation has been explained in terms of the magnitude of both the stability of the resulting cation and the steric hindrance between substituents.[4-8]

In general, an electrophilic reagent attacks on the carbon in butadienyl framework in the mode of forming the most stable cation. Its position is considered to be that of the carbon of the highest electron density in the conjugated double bonds. Thus, knowledge of electron distribution in the ground state of the dienes is helpful for understanding the chemical reactivities of conjugated dienes.

This paper deals with the polarization of conjugated dienes in relation to their reactivity. ^{13}C NMR measurements have been made for both alkyl-1,3-butadienes and phenyl-1,3-butadienes. A discussion is given on whether ^{13}C NMR chemical shifts of the dienes, accepted as an index of the electronic distribution of monomers in the ground state, are correlative to the relative reactivity of the dienes.

Experimental

1- and 2-phenyl-1,3-butadienes,[1,2] methyl and phenyl-substituted 1,3-butadienes,[6] 1- and 2-alkyl-1,3-butadienes,[7] and dimethyl-1,3-butadienes[8] were prepared as described previously.

^{13}C NMR spectrum was measured at 10 MHz on a Hitachi R-26 spectrometer. ^{13}C chemical shifts were determined for neat liquids by using benzene as an internal reference (10% by volume) and then converted into δ_c values (TMS reference) by using $\delta(C_6H_6)=128.7$ ppm.

Theoretical Calculation

Quantum chemical calculations were carried out by the CNDO/2 method[9] and parametrization without further modification. Convergence was judged from the energy level criterion of 1.0×10^{-3} eV in all the orbital energies. The atomic coordinates of the butadienes were determined from the following bond distances and bond angles: –C=C–, 1.34 Å; =C–C=, 1.48 Å; =C–H, 1.08 Å; –C–H, 1.09 Å; =C–C–, 1.51 Å; –C–C–, 1.54 Å; C=C (aromatics), 1.39 Å; C–C_6H_5, 1.51 Å; ∠C–C–C, ∠C–C–H, 109°28′; ∠C=C–C, ∠C=C–H, 120°. Computations were made on a FACOM 230—75 Computer at the Data Processing Center of Kyoto University.

Results

^{13}C NMR Chemical Shifts of Alkyl-1,3-butadienes. The signals for alkyl-1,3-butadienes in the ^{13}C NMR spectra were assigned by means of off-resonance proton-decoupling and additivity relationship.[10,11] The chemical shifts obtained for alkyl-1,3-butadienes are given in Table 1. The signals for butadiene skeleton appeared over a span of 50 ppm in the range 107—157 ppm. Introduction of an alkyl group on C_1 of butadiene caused the signal for C_4 in the highest field among the four butadiene carbon signals.

In the case of *trans*-isomers, the chemical shift of the substituted carbon moved toward lower field by 16—30 ppm and its neighbor carbon absorption toward higher field by 6—10 ppm. Although the magnitude for the γ effect was small, the signal for the C_3 nucleus showed an upfield shift of 0.6—1.0 ppm. The signal for the C_4 was shifted to higher field by 2 ppm regardless of the kind of alkyl substituent. Alkyl substituents such as methyl, ethyl, and *t*-butyl groups deshielded the C_1 nuclei by 16.6, 19.7, and 29.2 ppm, and shielded the C_2 nuclei by 7.7, 6.3, and 10.4 ppm, respectively.

The alkyl substitution of the corresponding ethylenes also produced consistent changes such as 10.3, 17.4, and 25.6 ppm for the C_α shielding in downfield shift and 7.8, 10.0, and 14.4 ppm for the C_β shielding in upfield shift, respectively.[12,13] The deshielding effect of the alkyl group on the C_α is greater in 1-alkyl-1,3-butadienes than in 1-alkenes, the reverse being true for the shielding effect of the alkyl group on the C_β. The signals for the butadienyl carbons of the *cis* isomers appeared at higher field than those of their *trans* isomers except for the C_4 nucleus.

In the ^{13}C NMR spectra of 2-alkyl-1,3-butadienes, the signal for the C_1 appeared at the highest field. The signals for the C_1 and C_4 nuclei moved to higher field in comparison with those of butadiene. The reverse was true for both the C_2 and C_3 nuclei. The difference between C_1 and C_2 chemical shifts increased with an increase in the bulkiness of alkyl group. Introduction of an alkyl group such as methyl, ethyl, isopropyl, and *t*-butyl groups on the C_2 of butadiene gives rise to the deshielding of the C_2 nuclei by 5.7, 11.1, 16.0, and 20.0 ppm and the shielding of the C_1 nuclei by 3.2, 3.7,

Table 1. ^{13}C Shieldings of alkyl-1,3-butadienes[a]

Compound	Chemical shift (ppm)[b]					
	C_1	C_2	C_3	C_4	C_5	C_6
Butadiene (BD)[c]	116.6	137.2	137.2	116.6		
trans-1-Methyl-BD	133.2	129.5	137.8	114.4	17.2	
cis-1-Methyl-BD	130.9	126.4	132.5	116.5	12.8	
trans-1-Ethyl-BD	136.3	130.9	137.7	114.5	25.9	13.4
cis-1-Ethyl-BD	134.0	129.5	132.7	116.6	21.2	14.1
trans-1-Isopropyl-BD	142.0	128.7	137.9	114.8	31.2	22.2
cis-1-Isopropyl-BD	139.9	127.9	132.9	116.8	27.0	22.9
trans-1-*t*-Butyl-BD	145.8	126.8	138.2	114.9	43.4	29.9
Isoprene	113.4	142.9	140.3	116.4	17.6	
2-Ethyl-BD	112.9	148.3	139.6	114.7	24.6	12.6
2-Isopropyl-BD	112.4	153.2	139.1	112.7	29.1	22.1
2-*t*-Butyl-BD	107.6	157.2	137.6	114.9	35.2	29.8
1,2-Dimethyl-BD[d]	127.1	135.5	142.1	110.3	11.1	13.6
1,3-Dimethyl-BD[e]	125.1	135.1	142.2	114.5	18.8	18.3
1,4-Dimethyl-BD	126.2	132.8	132.8	126.2	17.5	
2,3-Dimethyl-BD	113.0	143.8	143.8	113.0	20.3	

a) $\overset{6}{C}-\overset{5}{C}-\overset{1}{C}=\overset{2}{C}-\overset{3}{C}=\overset{4}{C}$, $\overset{1}{C}=\overset{2}{C}-\overset{3}{C}=\overset{4}{C}$ (C-C at 5, 6) neat sample, room temperature. b) Downfield from TMS. c) See Ref. 10.

d) $\overset{1}{C}=\overset{2}{C}-\overset{3}{C}=\overset{4}{C}$ (C at 5, 6) e) $\overset{1}{C}=\overset{2}{C}-\overset{3}{C}=\overset{4}{C}$ (C at 5, 6)

4.2, and 9.0 ppm, respectively, in comparison with those of butadiene. These changes of the chemical shifts of the C_1 and C_2 of 2-alkyl-1,3-butadiene were smaller than those of either 1-alkyl-1,3-butadienes or 1-alkenes.

The signal due to the central carbon of the alkyl group in the neighborhood of butadiene skeleton moved to lower field by 4—12 ppm for the substitution of an α-hydrogen by methyl group, *i.e.*, $-C-H \rightarrow -C-CH_3$. This deshielding effect was larger in 1-alkyl-1,3-butadiene than in 2-alkyl-1,3-butadiene.

The chemical shifts of dimethyl-1,3-butadienes roughly agreed with the values estimated from the data of both 1,3-pentadiene and isoprene by means of the additivity relationship. The difference between the observed and the estimated values was the largest for the chemical shift of 1,2-dimethyl-1,3-butadiene. The chemical shifts of the C_4 nuclei in dimethyl-1,3-butadienes moved to higher field in the order 2,4-hexadiene < 1,3-dimethyl-1,3-butadiene < 2,3-dimethyl-1,3-butadiene < 1,2-dimethyl-1,3-butadiene.

^{13}C NMR Chemical Shifts of Phenyl-1,3-butadienes. The ^{13}C chemical shifts of phenyl-1,3-butadienes are summarized in Table 2. A certain uncertainty is inevitable in the assignment of closely spaced signals within *ca.* 1 ppm. Introduction of a phenyl group on either the C_1 or C_2 of butadiene gives rise to a deshielding of the C_4 nucleus by 1 ppm. The chemical shifts of the C_1 and C_2 of 1-phenyl-1,3-butadiene moved 16.5 ppm to downfield and 7.5 ppm to upfield relative to those of butadiene, respectively. In the case of styrene, these values have been reported to be 13.9 ppm and 9.6 ppm, respectively.[14] The chemical shift of the C_3 was not affected by introduction of 1-phenyl group. On comparing the data for 2-phenyl-1,3-butadiene with butadiene, we find a change of 11.6 ppm for the C_2 and 0.7—1.5 ppm for the C_1, C_3, and C_4. The chemical shifts of the C_1 and C_4 of 2-phenyl-1,3-butadiene were the same as that of the C_4 of 1-phenyl-1,3-butadiene.

Table 2. ^{13}C Shieldings of phenyl-1,3-butadienes[a]

Compound	Chemical shift (ppm)[b]				
	C_1	C_2	C_3	C_4	C_5
1-PB[c]	133.1	129.7	137.4	117.6	
1-Methyl-1-PB	143.2	117.1	133.7	113.7	16.2
2-Methyl-1-PB	130.7	135.6	142.4	115.8	20.5
3-Methyl-1-PB	131.8	129.2	142.0	117.5	17.9
trans-4-Methyl-1-PB	129.7	129.7	132.5	130.3	17.9
cis-4-Methyl-1-PB	132.5	124.3	125.1	130.3	13.2
2-PB[c]	117.3	148.8	138.7	117.7	
1-Methyl-2-PB	131.9	142.1	127.2	117.7	13.8
3-Methyl-2-PB	117.8	144.3	151.8	114.1	21.7

a) Neat sample, room temperature. b) Downfield from TMS. c) 1-PB=1-phenyl-1,3-butadiene, 2-PB=2-phenyl-1,3-butadiene.

The substituent effect on the shieldings of the butadienyl skeleton of methyl and phenyl-substituted 1,3-butadienes can also be estimated by means of the additivity relationship. An application of the additivity relationship for the chemical shift of methyl and phenyl-substituted 1,3-butadiene was shown to be more relevant than that of dimethyl-1,3-butadienes. Methyl substitution on the C_1 position of 1-phenyl-1,3-butadiene

Table 3. Electron densities of 1,3-butadienes calculated by using CNDO/2 method

Substituent	Total electron density[a]				π-Electron density[a]			
	C_1	C_2	C_3	C_4	C_1	C_2	C_3	C_4
H	4.0431	3.9853	3.9853	4.0431	1.0179	0.9821	0.9821	1.0179
trans-1-Methyl-	3.9930	4.0116	3.9848	4.0498	0.9858	1.0239	0.9765	1.0302
cis-1-Methyl-	3.9911	4.0111	3.9852	4.0484	0.9851	1.0252	0.9787	1.0272
2-Methyl-[b]	4.0631	3.9475	3.9922	4.0431	1.0529	0.9584	0.9862	1.0156
trans-1-Ethyl-	3.9908	4.0201	3.9831	4.0524	0.9782	1.0376	0.9748	1.0346
1,2-Dimethyl-	4.0120	3.9729	3.9926	4.0474	1.0181	0.9990	0.9842	1.0231
1-Phenyl-	4.0072	4.0032	3.9873	4.0447	0.9993	1.0001	0.9794	1.0221

a) Electron unit. b) Transoid.

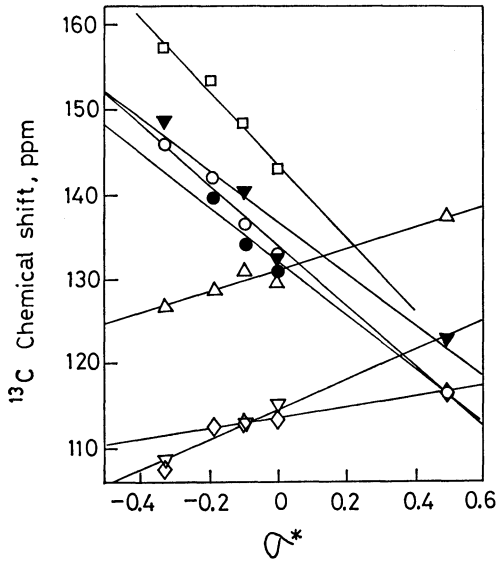

Fig. 1. Hammett plots of the ^{13}C chemical shifts of alkyl-1,3-butadienes and 1-alkenes against Taft's σ*: *trans*-1-alkyl-1,3-butadienes; ○, C_1 ($\rho^* = -35.9 \pm 1.7$ ppm/σ*); △, C_2, ($\rho^* = 12.3 \pm 1.7$ ppm/σ*); *cis*-1-alkyl-1,3-butadienes; ●, C_1, ($\rho^* = -32.3 \pm 3.3$ ppm/σ*); 2-alkyl-1,3-butadienes; ◇, C_1 ($\rho^* = 6.2 \pm 0.3$ ppm/σ*) □, C_2 ($\rho^* = -43.6 \pm 5.0$ ppm/σ*), 1-alkenes; ▽, C_1 ($\rho^* = 17.4 \pm 0.8$ ppm/σ*); ▼, C_2 ($\rho^* = -30.7 \pm 4.9$ ppm/σ*).

gives rise to the upfield shift of the C_2 as known for its β-effect. The signal for the C_4 also shifted to higher field than that estimated by means of the additivity relationship. The chemical shift of the C_4 of 1-phenyl-1,3-butadiene was not affected by introduction of a methyl group on the C_3. In 1-phenyl-1,3-pentadiene, the C_4 was no longer the most electron-rich carbon in the butadienyl framework. The signal for the C_4 of 1-methyl-1-phenyl-1,3-butadiene appeared at the highest field among the butadienyl groups of these nine phenyl-1,3-butadienes.

Discussion

Sensitivity Constants for the ^{13}C Chemical Shifts of Alkyl-1,3-butadienes. Figure 1 shows the Hammett plots of the chemical shifts of both alkyl-1,3-butadienes and 1-alkenes against Taft's σ*. A slope of −35.9 ppm/σ* was obtained from the correlation of the C_1 chemical shifts of *trans*-1-alkyl-1,3-butadienes with σ*. The value is slightly more negative than that for the C_2 chemical shifts of 1-alkenes whereas the reverse is true for the C_2 chemical shifts. No linear correlation with σ* was found for the C_3 and C_4 shieldings of 1-alkyl-1,3-butadienes; the signals for the C_3 and C_4 showed a downfield shift of 0.5—1.0 ppm and an upfield shift of 2 ppm, respectively, regardless of the kind of alkyl group.

Thus, the 1-alkyl group caused the shielding of both the C_2 and C_4 and the deshielding of both the C_1 and C_3 in the butadiene framework. The results suggest that the substituent effect is transmitted on the conjugated framework by alternation in a mode of decaying. On the ^{13}C chemical shifts along the conjugated framework of *trans*-1-substituted-1,3-butadiene, Kajimoto and Fueno[15] also concluded that the substituent effect in conjugated dienes is transmitted mainly through its π-framework by successive polarization of the –CH=CH– groups involved. However, the polarization of conjugated double bonds by the alkyl group was so small that the chemical shifts of the C_3 and C_4 were not correlated with Taft's σ*. The rearrangement of a charge caused by the introduction of an alkyl group was mainly the polarization between the C_1 and C_2 rather than a net transfer of charge from the alkyl group to the butadienyl framework, as shown in the results of CNDO/2 calculation of 1,3-pentadiene (Table 3).

In 2-alkyl-1,3-butadienes, linear correlations with σ* were found for both the C_1 chemical shifts excluding that of 2-*t*-butyl-1,3-butadiene and the C_2 chemical shifts. The ρ* value obtained for the C_1 shielding, 6.2 ppm/σ*, was smaller than that for the C_1 of the corresponding 1-alkenes. The ρ* value of −43.6 ppm/σ* obtained for the C_2 chemical shifts is 1.4 times as negative as that for the C_2 of the 1-alkenes. No correlation is found between the C_4 and σ*.

Hyperconjugation, polarization through π- and σ-bonds, and a field effect directly operative through space are seen in transmitting the substituent effect of alkyl group in 2-alkyl-1,3-butadienes. The results showing that the shielding of the C_4 approaches that of the C_1 in the order methyl<ethyl<isopropyl might be explained in terms of the field effect of the alkyl group. Unexpected values of the C_1 and C_4 chemical shifts of 2-*t*-alkyl-1,3-butadiene were observed since this compound cannot take a coplanar transoid form owing

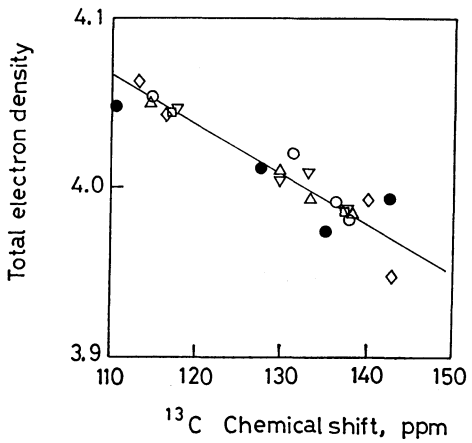

Fig. 2. Correlation of the ^{13}C chemical shifts of 1,3-butadienes with the total electron densities calculated by using the CNDO/2 method: ○, *trans*-1,3-hexadiene; △, *trans*-1,3-pentadiene; □, 1,3-butadiene; ▽, *trans*-1-phenyl-1,3-butadiene; ◇, isoprene; ●, 1,2-dimethyl-1,3-butadiene.

to the steric hindrance.[16]

Correlation of ^{13}C Chemical Shift with Total Electron Density. Figure 2 shows a correlation of ^{13}C chemical shift of 1,3-butadienes with the total electron density of carbon. Proportionality constant 340 ppm/e was obtained; this is about twice as large as the generally accepted value of 160 ppm/e for the π-electron densities in aromatics. The electron density of the butadienyl carbon can be estimated by means of its ^{13}C chemical shift.

Position Attacked by a Carbonium Ion. In general, propagating ends attack on the C_4 of 1-alkyl-1,3-butadienes and mainly the C_1 of 2-alkyl-1,3-butadienes.[6] These selective positions are due to both the carbon of the greatest electron density in the butadienyl framework and the highest stability of the resulting cation. These factors can be applied to the determination of the attacked position of dimethyl-1,3-butadienes. An attack of styryl cation on the most electron-rich carbon in the conjugated double bonds results in the highest stable cation. In nine phenyl-1,3-butadienes (Table 2), however, the positions of *trans*/*cis*-4-methyl-1-phenyl-1,3-butadienes and 1-methyl-2-phenyl-1,3-butadiene attacked by a styryl cation coincide not with that of the carbon of the highest electron density in the conjugated double bonds but the position forming the highest stable cation. Thus, the latter is the predominant factor in determining the position attacked by a carbonium ion.

Reactivity of Linear Conjugated Dienes. The relative reactivity of linear conjugated dienes toward a styryl cation is given in Table 4. The reactivities of 1- and 2-alkyl-1,3-butadienes decrease with an increase of the bulkiness of alkyl group.[7] The chemical shift of the C_4 of 1-alkyl-1,3-butadienes is unaffected whereas that of the C_1 of 2-alkyl-1,3-butadienes moves to higher field with an increase of the inductive effect of alkyl group. Thus, the order of reactivity of the alkyl-1,3-butadienes is related not to the electron density of the carbon in the ground state but to the magnitude of the steric hindrance between the monomer and an attacking cation.

Table 4. Reactivity of conjugated dienes toward a styryl cation[a]

Substituents	$1/r_1$[b]	Relative reactivity[c]	Chemical shift[d] (ppm)
1-Methyl-	0.97	0.58	114.4
1-Ethyl-	0.66	0.40	114.5
1-Isopropyl-	0.58	0.35	114.8
1-*t*-Butyl-	0.41	0.25	114.9
2-Methyl-	0.88	0.53	113.4
2-Ethyl-	0.57	0.34	112.9
2-Isopropyl-	0.54	0.32	112.4
2-*t*-Butyl-	0.50	0.30	107.6
1,2-Dimethyl-	1.64	0.98	110.3
1,3-Dimethyl-	1.82	1.09	114.5
1,4-Dimethyl-	0.85	0.51	126.2
2,3-Dimethyl-	1.30	0.78	113.0
1-Phenyl-	1.67	1.00	117.6
1-Methyl-1-phenyl-	33	19.8	113.7
2-Methyl-1-phenyl-	1.49	0.89	115.8
3-Methyl-1-phenyl-	40	24.0	117.5
4-Methyl-1-phenyl-	1.15	0.69	130.3
2-Phenyl-	0.59	0.35	117.3
1-Methyl-2-phenyl-	0.95	0.57	131.9
3-Methyl-2-phenyl-	0.63	0.38	117.8

a) Using $SnCl_4$·TCA in methylene chloride at −78 °C. b) Styrene (M_1)-diene (M_2). c) Relative reactivity for 1-phenyl-1,3-butadiene. d) ^{13}C shielding of the butadienyl carbon, attacked by a styryl cation, downfield from TMS.

The reactivity of dimethyl-1,3-butadiene can be explained not in terms of the electron density of either the C_4 or the C_1 in the ground state but the stability of the resulting allylic cation. In the case of dimethyl-1,3-butadienes, no steric hindrance in transition state on the electrophilic reaction needs to be taken into consideration except for 2,4-hexadiene.

When steric hindrance in the propagation of phenyl-1,3-butadiene series toward a styryl cation is of minor importantance or almost the same, the reactivity of the monomer increases with an increase in the stability of the resulting cation rather than in the electron density of the carbon attacked by cation. The methyl group introduced on either the β- or the δ-carbon, numbered from the terminal carbon attacked by the cation, enhances the reactivity to the extent of about 15—20, whereas methyl substitution on the γ-carbon produces a small increase or decrease in the reactivity up to the extent of 1.1.

The relative reactivity of linear conjugated dienes toward an electrophilic reagent can be determined by both the magnitude of the steric restriction of substituents and that of the stability of the resulting cation. Thus, for a detailed discussion on the reactivity of the butadienes, the above factors should be taken into consideration in addition to the information on ^{13}C NMR spectra.

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