Vibrational Circular Dichroism as a Criterion for Local-Mode versus Normal-Mode Behavior. Near-Infrared Circular Dichroism Spectra of Some Monoterpenes†

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Abstract: Vibrational circular dichroism (VCD) spectra are presented for (*S*)-(−)-limonene, (*R*)-(+)-limonene, (*S*)-(−)-perillyl alcohol, (*S*)-(−)-perillaldehyde, (*R*)-(+)-*p*-menth-1-ene, and (*R*,*R*)-(+)-*p*-menth-1-en-9-ol in the region 1300–800 nm. Bisignate couplets are observed for all six compounds; these are ascribed to overtones associated with CH stretching vibrations. The ordering of the signs in the couplets correlates with the known absolute configuration in all cases. The presence of such couplets for the terpenes just mentioned, and the absence of such couplets for closely related cyclic compounds, is interpreted in terms of normal-mode versus local-mode behavior.

I. Introduction

The question of local-mode versus normal-mode behavior is the subject of much current interest. Most of the experimental data bearing on this subject have come from various forms of absorption spectroscopy.[5,6] In this paper we report the near-infrared circular dichrosim (NIRCD) spectra in the region 1300–800 nm of a series of terpenes and related compounds. These data suggest that VCD overtone spectra at times may also provide a useful experimental criterion for distinguishing between local-mode and normal-mode behavior.

It has been pointed out, both for electronic[7] and vibrational transitions,[8] that strong circular dichroism (CD) signals are to be expected for transitions involving the rather delocalized molecular wave functions of an extended chiral chromophore, the so-called "inherently dissymmetric chromophore".[8] Laux et al.[8] have identified inherently dissymmetric chromophores of this sort for the fundamental CH stretching region in a number of different types of compounds, including cyclic terpenes. They interpreted the VCD observed for the fundamental transitions in the 3000-cm^{-1} region in terms of locally achiral CH oscillators, dissymmetrically disposed on multiple centers, that couple to exhibit normal-mode behavior. Freedman et al.[9] have invoked different, although analogous, couplings for (*R*)-(+)-3-methylcyclohexanone.

In the present work we now examine by NIRCD a number of the compounds studied by Laux et al.[8] Our motivation is to see whether or not the type of coupling among CH oscillators found for the fundamentals persists for the higher overtones.

II. Experimental Section

(*R*)-(+)-Limonene and (*S*)-(−)-limonene were purchased from Aldrich (of both "purum" and "purissimum" grade) and not further purified. In Figure 1 the absorption spectra in the regions corresponding to the second, third, and fourth CH stretching overtones are reported. The spectra were recorded on a Cary 2300 spectrometer for neat samples contained in a 1-cm cell (second overtone) and in a 10-cm cell (third and fourth overtones). The experiments were run with 1-s (second overtone) and 3-s (third and fourth overtones) time constants. The scanning speeds were 1 nm/s (second overtone) and 0.5 nm/s (third and fourth overtones). The resolution was about 1 nm.

In Figure 2 the NIRCD spectra of the two enantiomers of limonene in the region 1300–1150 nm, corresponding to the second CH stretching overtones, are given. The spectra were recorded on a Jasco Model J200D spectrometer equipped with a HgCdTe detector. The neat samples (purissimum grade) were contained in a 1-cm cuvette. The spectra shown are averages over eight scans; they were run at a 10 nm/min scanning speed, with a time constant of 8 s. The slit width was kept constant at ≃1 mm (≃8-nm resolution). The ordinate axis is the ellipticity in millidegrees (m°). In Figure 3, the analogous data for the third overtone region (1000–880 nm) are presented. The spectra were obtained with a Hamamatsu R316 photomultiplier tube in place of the HgCdTe detector. Neat samples (purum grade) in 10-cm cells were used. The scanning speed was 2 nm/min; the remaining experimental conditions were the same as for the second overtone experiment.

Despite the faintness of the signals, the spectra for the two enantiomers of limonene are virtually mirror images in both regions; this fact lends credibility to the measurements.

Similar couplets are observed in other cyclic terpenes. In Figures 4 and 5 the CD spectra of (*S*)-(−)-perillyl alcohol, (*S*)-(−)-perillaldehyde, (*R*)-(+)-*p*-menth-1-ene, and (*R*,*R*)-(+)-*p*-menth-1-en-9-ol are given for the third overtone region (1000–880 nm), together with the spectra for the limonenes. The analogous data for the second overtone region for the (*R*) enantiomers are shown in Figure 6. All the compounds were bought from either Fluka or Aldrich and used without further purification. The spectra were run with the same settings as given above for the limonenes, except that the scanning speed of 10 nm/min was used in all instances.

Except for (*S*)-(−)-perillaldehyde, the VCD spectra for *fundamentals* of all the compounds mentioned have been measured previously.[8,10-12]

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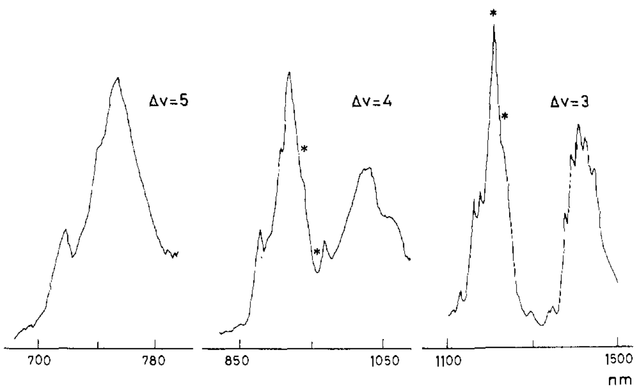

Figure 1. Absorption spectra of (*R*)-(+)-limonene in the regions of the second overtone of the CH stretchings (right), of the third overtone (center), and of the fourth overtone (left). For experimental conditions, see text. The absorption coefficients for the center and left-hand spectra are, respectively, 20 and 200 times smaller than those for the right-hand one. Asterisks indicate positions of CD peaks.

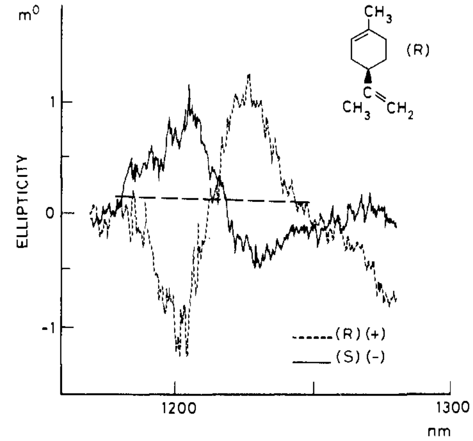

Figure 2. NIRCD spectra of (*R*)-(+)-limonene (dashed curve) and (*S*)-(−)-limonene (solid curve) in the range 1300–1150 nm. The base line used in the integration procedure for computing rotational strengths is shown.

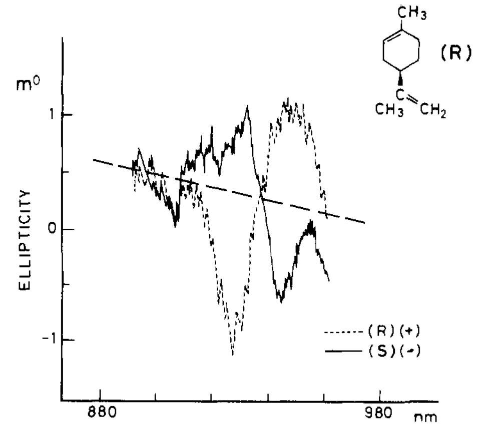

Figure 3. NIRCD spectra of (*R*)-(+)-limonene (dashed curve) and (*S*)-(−)-limonene (solid curve) in the range 1000–880 nm. The base line used in the integration procedure for computing rotational strengths is shown.

The spectrum for (*R*)-(+)-limonene is typical of such spectra, and for ease of comparison we show it in Figure 7. The spectrum was run on a 0.076 M solution in CCl_4, with the apparatus described elsewhere.[13] The ordinate axis is in units of $\Delta\epsilon = \epsilon_L - \epsilon_R$ (difference betweens molar absorption coefficients for left and right circularly polarized light in units of liter per mole centimeter).

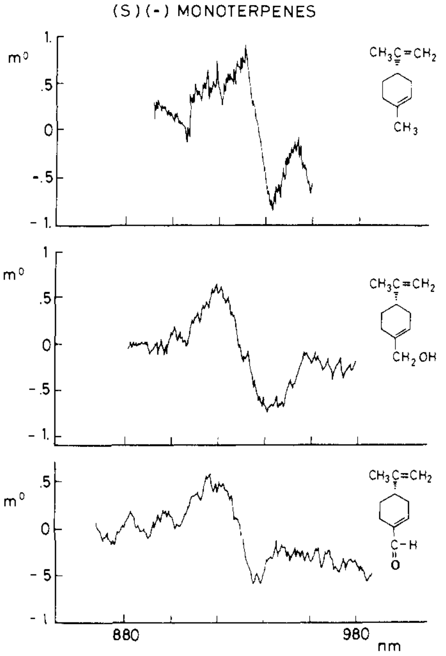

Figure 4. NIRCD spectra in the region 1000–880 nm of neat (*S*)-(−)-limonene (top), of neat (*S*)-(−)-perillyl alcohol (center), and of neat (*S*)-(−)-perillaldehyde (bottom).

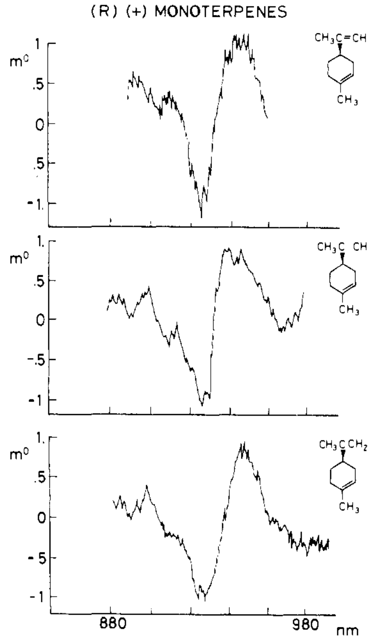

Figure 5. NIRCD spectra in the region 1000–880 nm of neat (*R*)-(+)-limonene (top), of neat (*R*)-(+)-*p*-menth-1-ene (center), and of neat (*R*,*R*)-(+)-*p*-menth-1-en-9-ol (bottom).

III. Discussion of the Results

In order to assign the bisignate NIRCD couplet that we observed in the cyclic monoterpenes, it is useful first to consider some results from absorption spectroscopy. In the first column of Table I, the frequencies of the bands observed in absorption for limonene are reported; NIRCD frequencies are given in the second and third columns. In the last two columns, the "empirical" CH stretching frequencies for propylene and cyclohexene are given.[14,15] These

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Table I. Comparison of the Frequency Values (cm^{-1}) for the Overtones Observed in the Absorption and CD Spectra of (*R*)-(+)- and (*S*)-(−)-Limonene with the Frequency Values for the Corresponding Overtones Observed in the Absorption Spectra of Propylene and Cyclohexene

limonene[a]				
abs spectrum	CD (*R*)	CD (*S*)	propylene[b]	cyclohexene[c]
			$\Delta\nu = 3$	
7939				
8244	8150	8130		8267.1 (CH_2)
8309	8313	8313	8379	
8543			8454 (CH_3)	
8664				8623.2 ($=CH$)
			8733	
8905			8772 ($=CH_2$)	
			$\Delta\nu = 4$	
	10549	10582		10782.4 (CH_2)
10845	10776	10718		
			10936	
11037			11050 (CH_3)	
~11236				11260.8 ($=CH$)
11390			11420	
			11488 ($=CH_2$)	
			$\Delta\nu = 5$	
13280				13177 (CH_2)
			13375	
13532			13535 (CH_3)	
13717				13780 ($=CH$)
13928			13995	
			14100 ($=CH_2$)	

[a] Our data. [b] Reference 14. [c] Reference 15.

frequency values were obtained through the Birge–Sponer relation, with the mechanical frequencies ω_e and anharmonicity constants χ that Fang and Swofford[14] and Henry et al.[15] have given for these two molecules. Comparison of the data for limonene, propylene, and cyclohexene in Table I leads to the following conclusions:

(i) The vibrational frequencies of the olefinic CH oscillators in the isopropylene group external to the ring in limonene are the highest in each of the three overtone spectra. They correspond to the humps observed at ≃8900 cm^{-1} (≃1120 nm), ≃11400 cm^{-1} (≃880 nm), and ≃13900 cm^{-1} (≃720 nm), respectively (see Figure 1).

(ii) The overtone stretching frequencies for the ring olefinic CH oscillator in limonene are assigned to the shoulders observed in two out of the three spectra at 11236 cm^{-1} (890 nm) and 13717 cm^{-1} (729 nm). In the 1100–1500-nm range, such a shoulder is not observed.

(iii) The methyl group modes, in both the methyl and isopropylene groups external to the ring in limonene, contribute to the high-frequency side of the major band observed in the three overtone regions. In particular, the two shoulders observed for limonene at 11037 cm^{-1} (906 nm) and 13532 cm^{-1} (739 nm) are at frequencies quite close to the corresponding ones of the methyl group in propylene.

(iv) The aliphatic CH's of the limonene ring, analogues of the aliphatic CH_2 groups in cyclohexene, contribute to the low-frequency side of the major absorption band in the three spectra shown in Figure 1.

The average frequencies for the extrema of the NIRCD couplets for limonene occur around 8130 and 8300 cm^{-1} (second overtone) and around 106000 and 10780 cm^{-1} (third overtone). These band positions are indicated by asterisks in Figure 1. These are roughly at the frequencies assigned in point iv to the aliphatic CH stretching modes in limonene. Hence, we conclude that these NIRCD couplets are to be associated with the $CH_2CH_2C^*H$ fragment and/or the CH_2C^*H fragment. Further, comparison of our NIRCD data with the data and analysis of Laux et al.[8] for VCD fundamentals (see point c below) leads us to prefer the $CH_2CH_2C^*H$ fragment.

In support of the conclusions just given, we note the following observations:

(a) Instead of using a neat sample of (+)- or (−)-limonene, we used a 1 M CCl_4 solution and measured the NIRCD spectra. We found that the couplets persist with the same sign patterns, although reduced in intensity by 1 order of magnitude. Such data indicate that the bands are of *intra*molecular origin.

(b) We were able to detect NIRCD couplets at roughly the same frequencies in the four other substituted monoterpenes mentioned earlier. These coupounds also contain the two fragments $CH_2CH_2C^*H$ and CH_2C^*H. (See Figures 4–6 and Table II.) In all cases, the sign patterns correlate with the absolute configuration of the asymmetric carbon atom in the ring; namely, in going from low to high frequencies, we have (+, −) for (*R*) compounds and (−, +) for (*S*) compounds. The addition of a second asymmetric carbon atom external to the ring in (*R*,*R*)-(+)-*p*-menth-1-en-9-ol does not alter this pattern.

(c) Between 3000 and 2800 cm^{-1} the known VCD spectra at low resolution of cyclic monoterpenes show four bands alternating in sign. Laux et al.[8] associated the three bands of highest frequency with coupled (normal) modes of the $CH_2CH_2C^*H$ fragment. These three bands exhibit the sign pattern (+, −, +) or (−, +, −) depending on the sense of chirality of the $CH_2CH_2C^*H$ fragment. The couplets observed in our NIRCD experiments correlate in sign with the second and third highest frequency fundamental bands, and these are in general the most intense VCD fundamentals (see Figures 4–7 and ref 8 and 10–12).

We note also that Laux et al.[8] found that this sign pattern persists even when the series of compounds is extended beyond the cyclic monoterpenes to include cyclic ketones, amines, and alcohols that contain the $CH_2CH_2C^*H$ fragment. We tried to measure NIRCD spectra for some of these compounds, e.g. (−)-menthone and β-pinene. However, we were not able to detect any signals of the sort measured for the cyclic monoterpenes that

Table II. Comparison of Frequencies (cm^{-1}) and Signs of Observed Bands in IRCD and NIRCD Spectra

(*R*)-(+)-limonene	(*R*)-(+)-*p*-menth-1-ene	(*R*,*R*)-(+)-*p*-menth-1-en-9-ol	(*S*)-(−)-limonene	(*S*)-(−)-perillyl alcohol	(*S*)-(−)-perillaldehyde
		IRCD ($\Delta\nu = 1$)			
2860 (−)	2866 (−)				
2893 (+)	2895 (+)	2893 (+)		2892 (−)	
2915 (−)	2925 (−)	2923 (−)		2921 (+)	
2939 (+)	2942 (+)	2960 (+)		2941 (−)	
	2971 (+)				
		NIRCD ($\Delta\nu = 3$)			
8150 (+)	8130 (+)	8110 (+)	8130 (−)	*a*	*a*
8313 (−)	8319 (−)	8262 (−)	8313 (+)	*a*	*a*
		NIRCD ($\Delta\nu = 4$)			
10549 (+)	10582 (+)	10582 (+)	10582 (−)	10582 (−)	10672 (−)
10776 (−)	10811 (−)	10811 (−)	10718 (+)	10893 (+)	10929 (+)
		11037 (−, sh)			

[a] Signals not reported, due to detector's low sensitivity in this region and insufficient optical purity of these two (*S*) compounds. (See Section II.)

Table III. Observed Values for Vibrational Rotational Strengths (esu^2·cm^2; in Order of Increasing Wavenumber)

(R)-(+)-limonene	(R)-(+)-p-menth-1-ene	(R,R)-(+)-p-menth-1-en-9-ol	(S)-(−)-limonene	(S)-(−)-perillyl alcohol	(S)-(−)-perillaldehyde
IRCD [$\Delta\nu$ = 1 (×10^{44})][a]					
−2.7	−3.3	−2.4		+3.2	
+10.8	+10.4	+8.8		−8.4	
−7.2	−8.8	−3.6		+3.8	
+1.7	+7.5	+2.5		−3.4	
NIRCD [$\Delta\nu$ = 3 (×10^{46})]					
+1.4	+1.4	+2.2	−1.2	*b*	*b*
−1.8	−1.1	−1.6	+1.5	*b*	*b*
NIRCD [$\Delta\nu$ = 4 (×10^{47})]					
+1.7	+1.4	+2.0	−1.1	−0.9	−0.4
−1.9	−2.2	−1.7	+1.5	+2.1	+1.3

[a] Evaluated from integration of the bands in the spectra reported in ref 12. [b] Signals not reported, due to detector's low sensitivity in this region and insufficient optical purity of these two (S) compounds. (See Section II.)

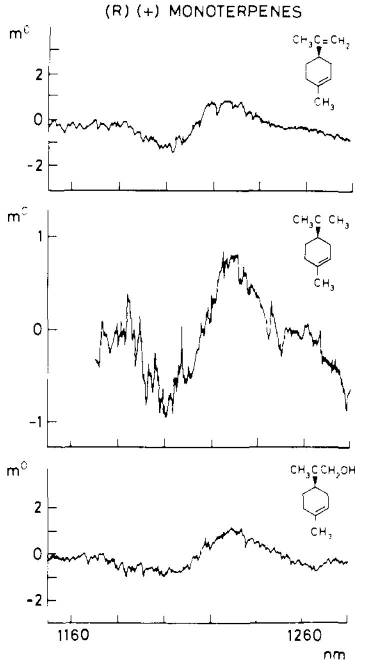

Figure 6. NIRCD spectra in the region 1300–1150 nm of neat (R)-(+)-limonene (top), of neat (R)-(+)-p-menth-1-ene (center), and of neat (R,R)-(+)-p-menth-1-en-9-ol (bottom).

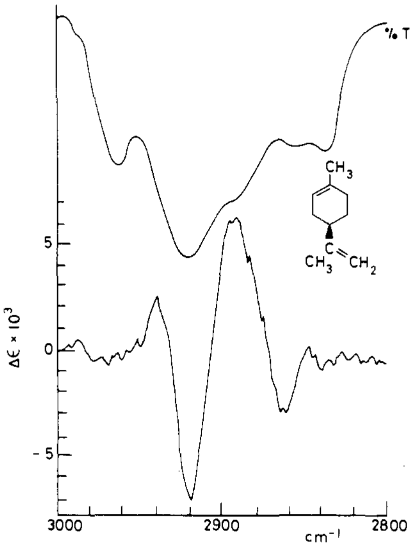

Figure 7. IRCD and transmittance spectra of (R)-(+)-limonene in CCl_4 (0.076 M) in the region 2800–3000 cm^{-1}.

contain a double bond as part of the ring. This is particularly noteworthy in the case of (−)-menthone, since this compound gives some of the strongest VCD signals in the fundamental CH stretching region.

(d) The experimental values for the rotational strengths are given in Table III. Comparison of the rotational strengths for the fundamentals and overtones shows that the overtone rotational strengths are down in magnitude (relative to those of the fundamentals) by roughly the same factor as are usually found for overtone absorption intensities.[2] Such behavior is consonant with coupled oscillator behavior.

To summarize, the analysis just given suggests that the NIRCD couplets we have observed for some of the cyclic monoterpenes are most probably associated with coupled (normal) mode behavior of the $CH_2CH_2C^*H$ fragment. This is noteworthy, since it indicates a persistence of normal-mode behavior for these compounds in spectral regions of overtones, which are generally thought of in terms of local modes.

IV. Final Remarks

The data we have presented here are for a somewhat limited set of compounds. Nevertheless, one might conjecture as to why among the compounds we have examined it is only the cyclic monoterpenes, which have a double bond as part of the ring, that exhibit NIRCD spectra, while related compounds like β-pinene and (−)-menthone do not. It is our current working hypothesis that the presence of a double bond in the perimeter of a six-membered ring molecule permits large-amplitude ring modes that are not possible when the ring is saturated. (Dreiding models indicate that a cyclohexene ring is much more floppy than is a cyclohexane ring, and molecular mechanics calculations support this assertion.) These modes involve the torsion about the C–C bond opposite to the ring double bond and lead to a coupling of CH oscillators dissysmmetrically disposed on different centers to form an inherently dissymmetric chromophore, which can exhibit NIRCD spectra.

We have made some preliminary classical trajectory calculations for the nonlinear H–C–C–H fragment in which the torsional mode is coupled kinetically to anharmonic CH stretching modes. For this model system we find that, under certain conditions, it is possible for the individual CH oscillators to interact via the torsion and exhibit coupled (normal) mode behavior. These calculations are currently being pursued further.

In conclusion we emphasize the utility of NIRCD as an *experimental* tool for distinguishing between local-mode and normal-mode behavior, especially as regards the coupling of achiral (e.g. CH) oscillators on different centers. Uncoupled, or weakly coupled, achiral oscillators, unlike coupled ones, even when dissymmetrically disposed on different centers will not exhibit measurably strong CD signals. Of course the absence of a NIRCD signal can happen for many reasons. However, it is our opinion that, in situations such as that encountered in this study for limonene versus menthone, the data are best interpreted in terms of coupled oscillator behavior in the overtones of the former and local oscillator behavior for the overtones of the latter.

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Registry No. (*R*)-(+)-Limonene, 5989-27-5; (*S*)-(−)-limonene, 5989-54-8; (*S*)-(−)-perillyl alcohol, 100692-55-5; (*S*)-(−)-perillaldehyde, 23963-70-4; (*R*)-(+)-*p*-menth-1-ene, 1195-31-9; (*R*,*R*)-(+)-*p*-menth-7-en-9-ol, 13835-30-8.

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^{13}C NMR Identification of Intermediates Formed by 2-Methyl-2-propanol Adsorption in H–ZSM-5[†]

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Abstract: ^{13}C NMR spectroscopy has been used to characterize intermediates formed by the adsorption of 2-methyl-2-propanol, $(CH_3)_3{}^{13}COH$, on a H–ZSM-5 zeolite. Previous adsorption studies had shown that, upon exposure of H–ZSM-5 to this alcohol and subsequent evacuation at 295 K, an adsorption complex could be formed, which had a coverage of 1 alcohol molecule/Al atom in the zeolite and had carbenium-ion-like properties. In the present NMR studies, it is shown that the adsorbed species can best be described as a silyl ether, with the alkyl group covalently bonded to the zeolite framework oxygen. Furthermore, the adsorption and evacuation conditions used for preparing the samples are found to be very important since these silyl ether intermediates are highly reactive. The ^{13}C NMR spectrum obtained following adsorption shows two prominant features, one at 77 ppm from TMS, which is assigned to carbon that is bonded to the oxygen, and a second at 29 ppm, which is due to aliphatic carbons formed in secondary reactions. ^{13}C NMR spectra were taken of samples at 10 K and after heating to 373 K to verify these assignments, as well as search for additional features that could be masked by dynamics at room temperature. No spectral features were observed in the region expected for carbenium ions, even though the chemistry observed for the adsorption intermediate was consistent with this chemistry and similar to that observed following olefin adsorption on H–ZSM-5. This implies that the steady-state concentration of carbenium ions in H–ZSM-5 is low or that the lifetime of these species is short.

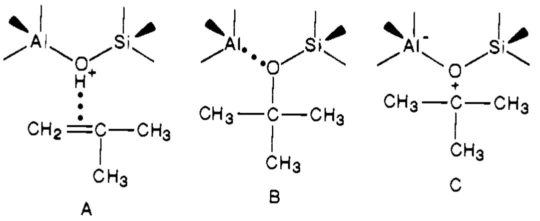
In recent studies of the acid sites in high-silica zeolites, it has been demonstrated that most of the simple alcohols form a well-defined adsorption complex in H–ZSM-5 with a stoichiometry of 1 molecule/Al site following adsorption and evacuation.[1-4] The reactivities of the different alcohols in this 1:1 adsorption complex appear to correlate with the relative stabilities of their respective carbenium ions, implying that proton transfer from the hydroxyls at the Al sites plays a major role in adsorption and reaction at these sites.[3] Furthermore, since the observed reactivity of the 1:1 adsorption complexes is found to be independent of SiO_2/Al_2O_3 ratios in the range from 38 to 520, it follows that H–ZSM-5 contains discrete sites associated with each Al atom, all having the same acid strength.[5]

The results for 2-methyl-2-propanol adsorption are particularly interesting because this molecule dehydrates at room temperature to form a bound intermediate with reaction properties that are very similar to those of a carbenium ion. The results, which suggest the presence of carbenium-ion-like intermediates, are the following:

(1) Following the adsorption and subsequent evacuation of 2-methyl-2-propanol, thermogravimetric analysis (TGA) shows that a coverage corresponding to approximately 1 molecule/Al site is retained on the zeolite.[3]

(2) Adsorption of the alcohol leads to the disappearance of the sharp zeolite hydroxyl stretch at 3605 cm^{-1} in the IR spectrum at a coverage of 1 molecule/Al site. Furthermore, the IR spectral features of the adsorbed species are significantly different from the unreacted alcohol.[4]

Chart I



(3) The adsorbed species undergoes rapid H/D exchange at 295 K when exposed to D_2O vapor, resulting in the formation of C–D bonds at the expense of C–H bonds.[4]

(4) No unreacted alcohol and only a small amount of water are observed in temperature-programmed desorption (TPD), and most of the desorbing product leaves the zeolite as octene and other olefin products.[3]

(5) The adsorbate complex will react with other gas-phase species. For example, exposure to ethanol at 295 K, followed by TPD, gives a complex product distribution that clearly implies some chemical reaction.[6]

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