Bull. Chem. Soc. Jpn. Vol. 79, No. 3, 451–453 (2006) 451

A Spectroscopic Index for Estimating the Age of Amber

Hideaki Kimura,[1] Yoshimi Tsukada,[1]
Hajime Mita,[1] Yasuhiko Yamamoto,*[1]
Riichiro Chujo,[2] and Tomohisa Yukawa[3]

[1]Department of Chemistry, University of Tsukuba,
Tsukuba 305-8571

[2]Beijing Office, Tokyo Institute of Technology,
Tsinghua University, Beijing 100084, P. R. China

[3]Tsukuba Botanical Garden, The Natural Science Museum,
Tsukuba 305-0005

Received August 19, 2005; E-mail: yamamoto@chem.tsukuba.ac.jp

Solid-state ^{13}C NMR characterization of cross-linkage formation between the exocyclic methylene groups of labdane polymers in amber demonstrated that the process is an apparent first-order reaction with a half-life of ≈13 million years.

Amber is the fossilized resin of chiefly coniferous and/or leguminous trees, and belongs to class I resinites of the five classes of Anderson et al.[1] The primary constituent of class I resinites is known to be labdanoid diterpene (structure shown in the inset of Fig. 1).[1a] Amberization, i.e., the formation of amber from resin, is proposed to occur through cross-linkage between the exocyclic methylene groups of labdane polymers.[2] ^{13}C Cross-polarization magic angle sample spinning (CP-MAS) NMR has been used extensively to characterize amber at the atomic level.[2–4] A comparative study of the spectra of various ambers demonstrated that the intensities of exocyclic methylene carbon (C_8 and C_{17} (see inset of Fig. 1)) signals resolved at ≈108 and ≈148 ppm decrease with increasing degree of amberization, possibly due to the intermolecular cross-linkage of exocyclic methylene groups.[2,3] In this study, the kinetics of the intermolecular cross-linkage of exocyclic methylene groups, upon the formation of amber from resin, is analyzed by means of a comparative study of the ^{13}C CP-MAS NMR spectra of ambers exhibiting various degrees of amberization.

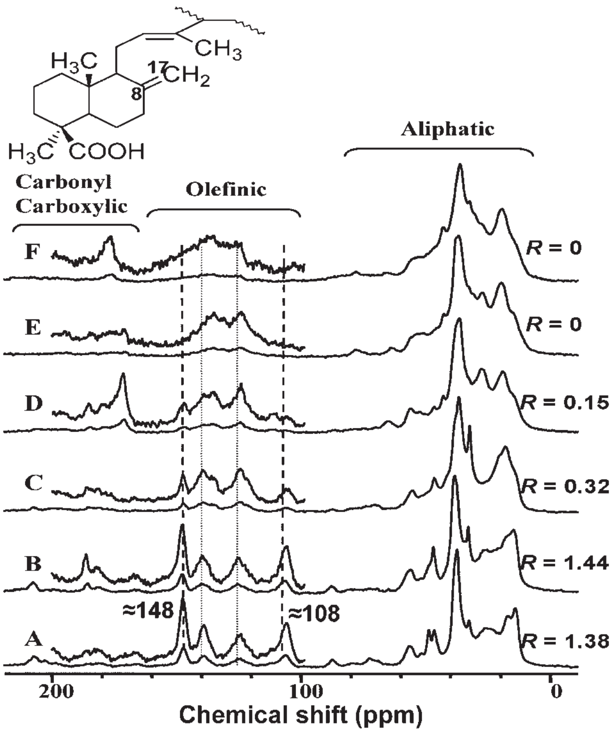
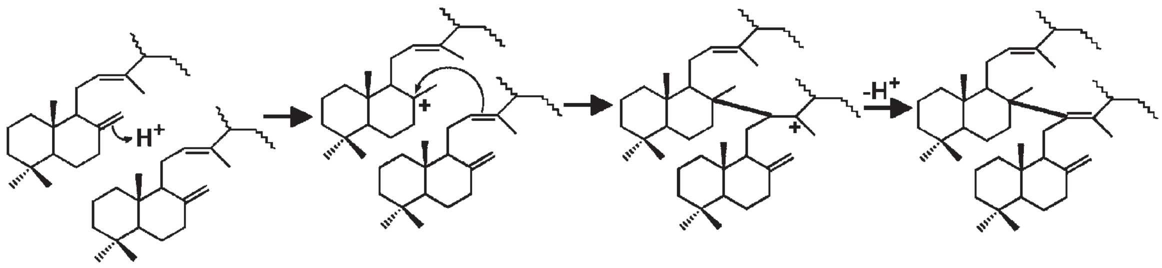


Fig. 1. 150.9 MHz ^{13}C CP-MAS NMR spectra of Madagascan copal (A, 50–60 years), Colombian copal (B, 400–600 years), Dominican amber (C, 12–20 million years), Baltic amber (D, 35–55 million years), Kuji amber (E, 83–89 million years), and Choshi amber (F, 112–125 million years). The structure of the polymer of communic acid, which is a major constituent of amber produced from Araucarian trees, is shown.[1] Exocyclic methylene carbon atoms are numbered according to the systematic IUPAC nomenclature. The *R* values of the spectra are shown.

Figure 1 shows the ^{13}C CP-MAS NMR spectra of various ambers and sub-fossilized copals, which are arranged in chronological order. In all the spectra, ^{13}C NMR signals are resolved in three distinctly different chemical shift regions corresponding to aliphatic (10–90 ppm), olefinic (100–160 ppm), and carbonyl and carboxylic acid (>165 ppm) carbons.[2–4] The aliphatic carbon signals appear to become broad with increasing age of the amber, on the other hand, the spectral pattern of the carbonyl and carboxylic acid carbon region exhibits no clear correlation with the age of the amber. In the olefinic carbon region, four main signals are resolved and the intensities of the exocyclic methylene carbon signals at ≈108 and ≈148 ppm decrease with the age of amber. The other olefinic carbon signals at ≈127 and ≈141 ppm become broad with increasing age of the amber, but their intensities are almost independent of the age, as reflected in their unaltered signal intensities relative to the aliphatic carbon signal intensities at ≈35 ppm throughout the spectra in Fig. 1. As an index for characterizing the time-evolution of the cross-linkage reaction, the *R* value was defined as the ratio between the sum of the exocyclic methylene carbons signal intensities at ≈108 and ≈148 ppm, and that of the other olefinic carbons signal intensities at ≈127 and ≈141 ppm. Each signal intensity was determined by a signal deconvolution program.

The *R* values calculated from the spectra in Fig. 1 are plotted against the age of the amber in Fig. 2. The *R* value exponentially decreased with increasing age of the amber and the fitting of the plots to exponential decay yielded an empirical equation, $R = (1.16 \pm 0.2)\mathrm{e}^{-(0.052\pm0.015)t}$, where t represents the age of the amber in millions of years. The *R* values for New Zealand,[2a] Australia,[2a] and Dominican ambers[3b] were calculated from the spectra previously reported and their plots are included in Fig. 2. The obtained empirical equation also fits well to the plots for those ambers, demonstrating the validity of the equation for evaluating the time-evolution of amber.

Published on the web March 8, 2006; DOI 10.1246/bcsj.79.451



Scheme 1.

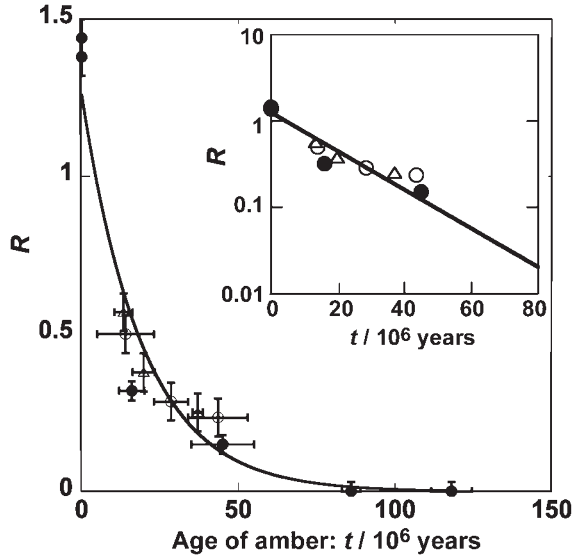


Fig. 2. Plots of the R values, that is, the ratio of the sum of signal intensities at $\approx$108 and $\approx$148 ppm to that of those at $\approx$127 and $\approx$141 ppm, versus the age of amber, t, in millions of years. The R values determined in the present study (●), and those by Lambert et al.[3b] (○) and Clifford et al.[2a] (△) are presented. A semi-logarithmic plots of the R values versus t is also shown in the inset.

The exponential decrease in the R value with increasing age of the amber shows that the cross-linkage formation proceeds as an apparent first-order reaction with an extremely slow rate, i.e., half-life = $\approx$13 million years. This finding indicates that the cross-linkage formation does not occur through a rapid chain reaction. A plausible reaction pathway for the cross-linkage formation is shown in Scheme 1. An exocyclic methylene group reacts with a surrounding olefine group to form another olefine group. Therefore, the concentration of olefine groups, other than the exocyclic methylene one, within amber does not change upon the cross-linkage formation, while that of exocyclic methylene groups decreases as the reaction proceeds. Since an exocyclic methylene group is likely to be surrounded by several olefine groups, the rate of the cross-linkage formation depends solely on the concentration of exocyclic methylene groups and is essentially independent of the concentration of olefine groups.

In general, the rate of a chemical reaction in sediments is determined by the time after sedimentation and the thermal history of the sample, especially the maximum temperature to which the sample was exposed and the elapsed time.[5] However, the cross-linkage formation appeared to be determined only by the age and not by the thermal history of the amber. This could be due to: 1) The reaction rate is not determined by a temporary high temperature that amber may experience, but by the average temperature, because of the extremely slow cross-linkage formation. When amber experiences a high temperature for a long period, cracking occurs and the amber disintegrates. 2) The glass-transition temperature of amber is reported to be higher than 350 K and it increases with increasing age of the amber.[6] The mobility of exocyclic methylene and surrounding olefine groups in the solid phase is restricted below the glass-transition temperature. In such restrictive conditions, the collision frequency of the two reacting groups would be almost ostensibly temperature-independent. 3) A radical generated due to radiation from radioisotopes in sediments can also initiate the cross-linkage formation. The radiation from radioisotopes is essentially temperature-independent. Furthermore, the concentrations of radioisotopes are an important factor. Since ambers are formed in organic rich sediments, the concentrations of radioisotopes would be similar to each other.

In conclusion, we found that the cross-linkage formation in amber is an apparent first-order reaction with a half-life of $\approx$13 million years. The time-evolution of the cross-linkage formation in amber can be characterized by the analysis of olefinic ^{13}C NMR signals, providing a spectroscopic index for estimating the age of amber.

Experimental

NMR measurements were performed on a Bruker AVANCE DRX-600 NMR spectrometer operating at 150.9 MHz. The CP contact time was 2 ms. The spectral width was 60.6 kHz and data points were 2k. The MAS rate was set to 9 kHz. The ^{13}C chemical shifts were calibrated indirectly using adamantane (29.5 ppm relative to tetramethylsilane) as an external reference. The amber and copal samples were ground to a powder for insertion into a 4 mm NMR rotor.

We thank Mr. K. Sasaki, the Kuji Amber Museum, for the Japanese ambers, and Ms. B. Pruski and Dr. M. Pruski, Iowa State University, for the Baltic amber. NMR spectra were recorded on a Bruker AVANCE DRX-600 spectrometer at the Chemical Analysis Center, University of Tsukuba.

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