in chlorophyll b, both carbonyl and aldehyde oxygen are implicated in aggregate formation.[5,7] Such aggregates should have a geometry different from chlorophyll a, where only ketone oxygen is available for aggregation.

The interpretation of solid-state spectra, however, is not as straightforward as for solution spectra. For example, particle size effects may cause serious discrepancies in solid-state spectra.[24] Furthermore, spectral variation arising from the interaction of lattice modes with molecular vibrations are particularly relevant in the far-infrared. The difference between the solid-state spectra of chlorophylls a and b may then arise because of differences in aggregate structure, lattice structure, or from differences in particle size.

Aggregated Chlorophyll in Wet and Dry Benzene. Chlorophylls a and b, methyl chlorophyllides a and b, and deuteriochlorophylls a and b in benzene solution show only a strong broad absorption peak at the typical aggregation peak position, with a vestigial shoulder at the first magnesium–nitrogen absorption position; the second magnesium–nitrogen band is also greatly reduced in intensity. The band shape is not concentration dependent over a fourfold variation in pigment concentration. The differences between cyclohexane and benzene solution spectra may be due to a solvent effect,[25] or may reflect a real difference in the structure of the aggregates in the two solvents.

The effect of water on the state of aggregation of chlorophyll in benzene solution also appears to have some anomalous aspects. The far-infrared spectra of chlorophyll are the same in dry benzene as in benzene saturated with water.[26] Although the bases methanol and pyridine dissociate chlorophyll aggregates in benzene, water does not appear to do so. This is rather surprising, since water is reported to coordinate strongly to chlorophyll.[27,28] It appears that the extent to which water acts as a disaggregating base depends on the nonpolar solvent to which it is added. While a water–chloroform mixture is disaggregating, a water–carbon tetrachloride mixture is not.[5,7] The rate at which disaggregation occurs may be an important factor here. Both methanol and pyridine disaggregate chlorophyll in benzene very rapidly. Either water reacts very much more slowly, or the solvation properties of the bulk solvent are a decisive factor. It will be important to establish whether these differences are a consequence of differences in rate processes, or whether the chlorophyll aggregates have considerably different structures in different solvents.

Acknowledgment. We are deeply indebted to Dr. A. J. Perkins of the University of Illinois (College of Pharmacy) for his advice and instruction in the experimental procedures of far-infrared spectroscopy.

[24] C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press Inc., New York, N. Y., 1963, p 587 ff.

[25] C. N. R. Rao, ref 24, p 577 ff.

[26] Infrared measurements in the carbonyl region indicate that the chlorophylls are aggregated in both wet and dry benzene.

[27] E. Rabinowitch, "Photosynthesis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, p 450.

[28] E. E. Jacobs and A. S. Holt, *J. Chem. Phys.*, 20, 1326 (1952).

Bromine Atom Catalyzed Isomerization of Terminal Olefins

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Abstract: The mechanism of isomerization of terminal olefins to the corresponding olefins with nonterminal double bonds, catalyzed by photolyzed hydrogen bromide in the gas phase, has been shown to proceed by abstraction of an allylic hydrogen from the olefin by a bromine atom, with subsequent replacement of a hydrogen on the terminal carbon. Propene, 1-butene, and 1-pentene have been examined and shown to behave in the same way. The *cis–trans* ratios of the 2-butenes and 2-pentenes resulting from this isomerization have been measured, and ΔH, ΔG, and ΔS values for these geometrical isomerizations are reported.

Two recent papers have been concerned with equilibration of 1-butene with *cis*- and *trans*-2-butene. Benson and co-workers[1,2] report that iodine is a fairly efficient equilibrating agent, while Maccoll and Ross[3] show that hydrogen bromide plus heat is an effective way of accomplishing the same thing. It had already been shown[4] that 1-butene was very rapidly converted to *cis*- and *trans*-2-butene while attempting to add gaseous hydrogen bromide, using ultraviolet light to dissociate the HBr. We had already started a further examination of the mechanism of this isomerization when the papers by Benson and Maccoll appeared. We now wish to report the results, which supplement and reinforce the work of those investigators.

Our concern was largely mechanistic rather than for thermodynamic information. It appeared likely that the course of the isomerization was *via* hydrogen abstraction, with replacement of the hydrogen largely at the terminal carbon

$$\mathrm{CH_3CH_2CH{=}CH_2 + Br\cdot \longrightarrow CH_3\dot{C}HCH{=}CH_2 + HBr} \tag{1}$$

$$\mathrm{CH_3\dot{C}HCH{=}CH_2 \rightleftarrows CH_3CH{=}CH\dot{C}H_2} \tag{2}$$

$$\mathrm{CH_3CH{=}CH\dot{C}H_2 + HBr \longrightarrow CH_3CH{=}CHCH_3 + Br\cdot} \tag{3}$$

[1] D. M. Golden, K. W. Egger, and S. W. Benson, *J. Am. Chem. Soc.*, 86, 5416 (1964).

[2] K. W. Egger, D. M. Golden, and S. W. Benson, *ibid.*, 86, 5420 (1964).

[3] A. Maccoll and R. A. Ross, *ibid.*, 87, 1169 (1965).

[4] P. I. Abell, *Trans. Faraday Soc.*, 60, 2214 (1964).

The most readily available experimental route was to use deuterium bromide in the reaction mixture, and to observe the position and extent of deuteration in the isomerized olefins by following the disappearance of the proton in question (corresponding to the substitution by deuterium) in the nmr spectrum. Thus, the mixed *cis-* and *trans-*2-butenes formed from 1-butene plus DBr would be expected to be largely 2-butene-1-*d*, and the integrated nmr spectrum of the compound would show that one of the six equivalent protons had "disappeared" compared to a standard sample of 2-butene. The equilibration of these olefins is easy to follow by gas chromatography, so that it was decided to look also at the values of the *cis–trans* ratios of 2-butene and 2-pentene while involved with these compounds.

Experimental Section

Materials. The hydrogen bromide, propene, 1-butene, and 2-butene were CP grades from Matheson Co. The 1-pentene and 2-pentene were from J. T. Baker Chemical Co. The D_2O was 99.5% purity from Bio-Rad Laboratories. All olefins were thoroughly dried and degassed before use.

Analysis. The olefin products were separated by gas chromatography on a 25-ft column containing a mixture of 20% di-2-ethylhexyl sebacate and 80% bis(2-methoxyethyl) adipate, both coated at 20% on Johns-Manville 60–80 mesh Chromosorb P, according to the method of Golden, Egger, and Benson.[1] The 2-butene isomers were chromatographed at 25°, the 2-pentene isomers at 0°. In all cases the hydrogen bromide was removed by a 3-ft column of 20% triethanolamine on Chromosorb P following the ester column. Corrections for tailing were applied. Integration of peak areas was by an Electromethods Ltd. low inertia dc integrator which gave reproducibility to about 0.5%. Samples for nmr analyses were taken from the outlet of the gas chromatograph by condensing in liquid nitrogen directly into the nmr sample tube. Nmr spectra were run on a Varian Associates A-60 spectrometer.

Apparatus. The isomerizations were carried out in a 160-ml cylindrical quartz reaction vessel, irradiated by a 75-w medium pressure quartz mercury arc. The handling of the olefins and HBr or DBr was in a conventional gas kinetics apparatus,[4] with pressures measured by a quartz spiral Bourdon gauge.

Procedure. DBr was prepared from D_2O by treatment with CP phosphorus tribromide, followed by extensive tube-to-tube distillation, drying, and degassing.

The olefin and DBr were mixed in equal pressures (about 125 mm each) in the reaction vessel, irradiated for 1 hr at 150° in the thermostated oven, and pumped into the freeze-out tube, and from there directly into the gas chromatograph. About four such runs gave adequate material for an nmr analysis.

The isomerization experiments generally employed a 2:1 mixture of olefin:HBr, at about 40 mm total pressure in the quartz reaction vessel. The proportions were not critical but were dictated only by convenience of sample size and speed of isomerization. Under these conditions 2 hr of irradiation brought the mixture quite close to the equilibrium values reported by Maccoll and Ross.[3] Gas chromatography was employed on aliquot samples of the product, and duplicate aliquots gave the same isomer ratio within about 2%. Duplicate runs gave about the same limits of reproducibility.

Results

The expectations with regard to the nmr spectra were verified quite satisfactorily, although the technique was rather a blunt tool for the job at hand. Starting with a 1:1 mixture of DBr and 1-butene and equilibrating for several hours by exposure to a medium pressure quartz mercury arc, the mixed 2-butene isomers, as separated by gas chromatography, showed a substantial reduction in the integrated area of the methyl group absorption in the nmr spectrum, using the vinyl hydrogens of the 2-butene as an internal standard. In the case of 1-butene, there are of course six equivalent methyl protons in the 2-butene produced, and since, as the reaction proceeds, the DBr is replaced by HBr, the maximum deuteration possible is one-twelfth of the methyl protons. No correction was made for isotope effects nor for the small percentage of 1-butene-3-*d* formed in the equilibration, nor for the polydeuteration that would begin to be substantial at long equilibration times. Accordingly, the 85% of the one-twelfth deuteration possible represents only an approximation of what had happened in the isomerization process.

The same experiment was carried out for 1-pentene and propene, where 1:1 reaction mixtures of DBr and olefin would be expected to give one-sixth of the maximum deuteration in the methyl protons. The results are presented in Table I.

Table I. Quantitative Nmr Data on Deuteration

	Area of CH_3 signal relative to total integrated nmr spectrum			
	Theoretical, %			
Olefin	Undeuterated	50% monodeuterated	Exptl, %	Deuteration in CH_3 group, %
Propene	50	45.5	46.7	73 ± 10
2-Butene	75	73.3	73.7	85 ± 15
2-Pentene	50[a]	47.4[a]	47.8[a]	85 ± 10

[a] Both methyl and methylene adjacent to double bond included in integration because of poor resolution of two signals.

The fact that the allylic radicals end up quite highly deuterated in the methyl groups shows that the vast bulk of the hydrogen abstraction by these radicals is from hydrogen (or deuterium) bromide and not the allylic hydrogen from another olefin molecule. If the latter had been the case (and it is what would be expected on the basis of bond dissociation energies), then a chain isomerization reaction would have occurred, and deuteration would be negligible. It is therefore the activation energy for the hydrogen abstraction that controls the hydrogen atom donor. The activation energy for hydrogen abstraction from HBr is probably 2.5–3.0 kcal/mole on the basis of the estimate for the bromoethyl radical,[5] while abstraction from the 3-position of 1-butene is likely to be about 7.5 kcal/mole.[6] Accordingly the hydrogen bromide is preferred as the source of hydrogen atoms.

The *cis–trans* ratios of isomerized olefins were obtained by gas chromatography on a mixed ester column of the type described by Golden, Egger, and Benson,[1] and are in only fair agreement with the values reported by those workers and the values reported by Maccoll and Ross.[3] The precision of measurement seems to be about the same as that of the former workers, although not over such an extended temperature range, and is considerably better than the data reported by the latter. The results are reported in Tables II and III, and shown graphically in Figure 1, along with the similar data from Benson[1] and Maccoll.[3]

A known mixture of *cis-* and *trans-*2-butene isomers, mixed with HBr and subjected to the same treatment as an isomerization experiment, but without irradiation by

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(5) P. I. Abell and R. S. Anderson, *Tetrahedron Letters*, 3727 (1964).

(6) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, 19, 169 (1951).

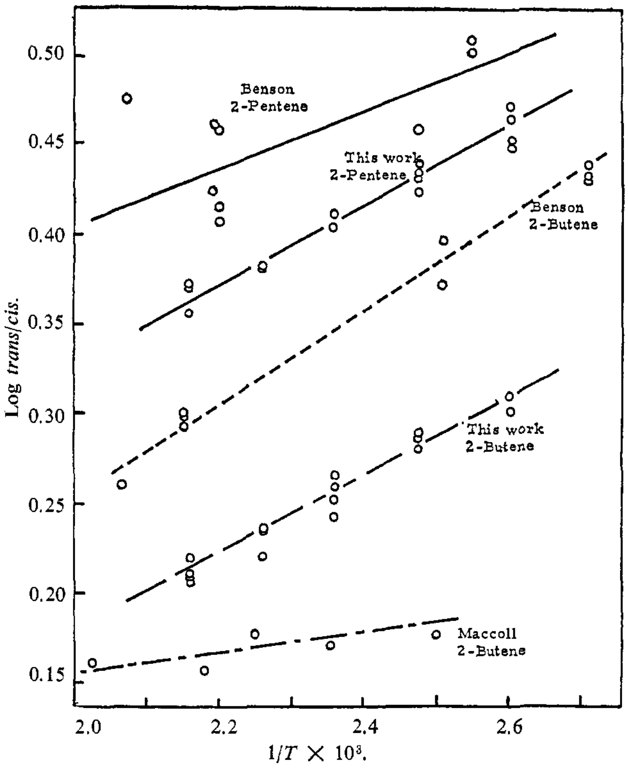

Figure 1. Arrhenius plot for the *cis–trans* equilibrium constant for 2-butene and 2-pentene isomerization.

Table II

Olefin	Experimental *cis–trans* ratio of isomers at[a] 110°	130°	150°	170°	190°
2-Butene	0.495	0.518	0.556	0.587	0.614
2-Pentene	0.348	0.370	0.392	0.416	0.431

[a] Averages of two to six determinations for each olefin at each temperature. Isomerizations were usually started from the terminal olefin, photolyzed with HBr over a period of 1 to 8 hr, but checks starting with various mixtures of the 2-olefins gave concordant results. Length of irradiation time had no effect on the *cis–trans* ratios.

Table III. Thermodynamic Functions for Geometrical Isomerizations at 400°K

Olefin	$\Delta H°$, kcal/mole	$\Delta G°$, kcal/mole	$\Delta S°$, eu
2-Butene (this work)	−0.982	−0.52	−1.15
(Benson¹)	−1.20	−0.69	−1.2
(Maccoll³)	−0.44	−0.34	−0.25
2-Pentene (this work)	−0.977	−0.80	−0.45
(Benson⁷)	−0.73	−0.79	+0.14

ultraviolet light, gave the same analysis for isomer ratio as the mixed 2-butene isomers in the original sample (analysis of original olefin mixture: 38.3% *cis*, 61.7% *trans;* composition after mixing with HBr and carrying through the same analytical procedure as with irradiated samples: 38.3% *cis*, 61.7% *trans*). It is not likely that the loss of one isomer by HBr addition in preference to the other isomer will have affected the equilibrium ratio since it has already been shown by the author[4] that *cis*- and *trans*-2-butenes react with HBr at substantially the same rate—or, as is more likely, the isomerization is faster than either addition, and so the addition rates are not of consequence.

We find that the two olefins, 2-butene and 2-pentene, have virtually the same enthalpy difference between the *cis* and *trans* isomers. There is, however, a rather substantial difference in the *cis–trans* isomer ratios, with 2-pentene having a greater preference for the *trans* form. This probably can be ascribed to the greater bulk of the ethyl group. The data of Table III indicate a greater similarity in this work to that of Benson and co-workers[1,7] than to Maccoll and Ross.[3] The differences in entropy, particularly in the work on 2-pentene, can be explained by the rather substantial scatter of points in the experimental determination of *cis–trans* ratios. This scatter is considerably larger in the iodine and nitric oxide catalyzed isomerizations of 2-pentene as determined by Egger and Benson[7] than in their earlier work on 2-butene[1] or the work in this laboratory as described in this paper (see Figure 1). What is more disturbing is the quite substantial difference in proportion of *cis*-2-butene to *trans*-2-butene, which is much greater than the experimental error in the analytical work. It is, of course, possible that the various procedures have built-in kinetic effects of the equilibrating agent on the olefin equilibrium. If such is the case it will be very difficult to find a true equilibrium by any chemical means.

A more detailed study of these HBr-promoted olefin isomerizations is being initiated, using tritium labeling to follow the rates of hydrogen abstraction and replacement and HBr addition.

Acknowledgment. This work was supported in the form of a Summer Faculty Fellowship from the University of Rhode Island granted to the author.

(7) K. W. Egger and S. W. Benson, personal communication on forthcoming paper.