

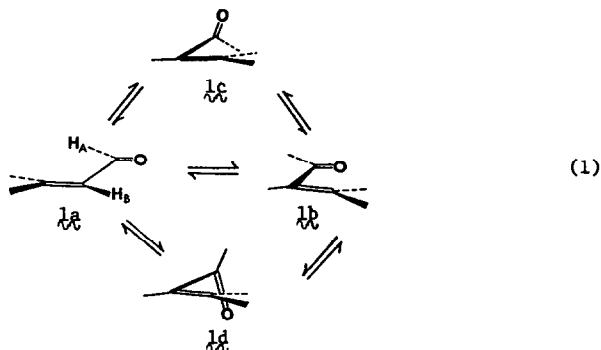
THE CONFORMATIONAL ANALYSIS OF ACROLEIN

Robert L. Lipnick*

Department of Chemistry, University of Minnesota
 Minneapolis, Minnesota 55455

(Received in USA 18 August 1972; received in UK for publication 6 February 1973)

Studies by microwave,¹ ultrasonic relaxation,² X-ray,³ nmr,⁴ and raman and infrared⁵ indicate that acrolein exists as a mixture of trans and cis conformers, with the former predominating at room temperature. While the major trans conformer is coplanar ($1a$), it is not known whether the minor conformer is coplanar ($1b$) or skewed ($1c$, $1d$).



In this study, the temperature-dependences of the averaged conformer nmr parameters have been measured for acrolein- d_2 (6) at 13 temperatures over a range of 175.6°, and these parameters related to changes in conformer population.

Acrolein- d_2 was prepared according to the scheme outlined in Figure 1. Ethyl 3,3-diethoxypropionate (2) was prepared from sodium ethoxide and ethyl propiolate (Aldrich) using the method of Ingold,⁶ b.p. 93°/17 mm (lit. 93°/22 mm). Reduction of 2 with $LiAlD_4$ in ether gave 3,3-diethoxypropanol- d_2 (3) in 69% yield, b.p. 99-102°/18 mm (lit. 98°/20 mm).⁷ Tosylation of 3 with *p*-toluenesulfonyl chloride in anhydrous pyridine afforded 3,3-diethoxypropanol- d_2 tosylate (4), an uncrystallizable oil, in 84% yield. The tosylate (4) underwent facile elimination with potassium *t*-butoxide (100% molar excess) in anhydrous dimethyl sulfoxide at room temperature to 3,3-diethoxypropene- d_2 (5), b.p. 121-123° (lit. 123.5°).⁸ Acrolein- d_2 (6) was prepared from 5 by acetal exchange in *n*-heptaldehyde containing a catalytic amount of *p*-toluenesulfonic acid.⁹

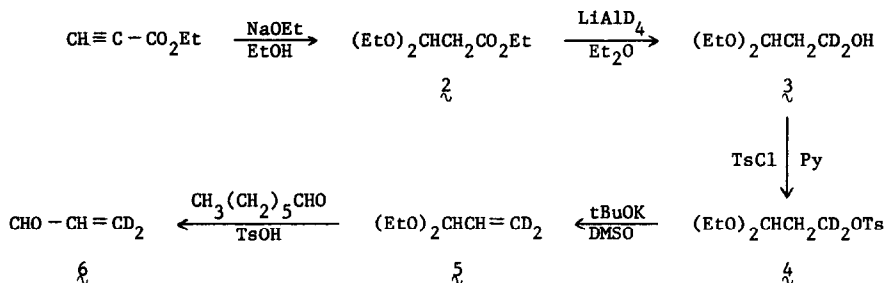


FIGURE 1

All spectra were obtained from a sealed 5 mm sample tube containing 1.07% (m/m) acrolein- d_2 (> 99% by glpc) and 0.48% (m/m) hexamethyldisilane (HMDS) (> 99% by glpc) in Reagent CS_2 , stabilized by the addition of a small crystal of hydroquinone.

The deuterium-decoupled spectrum of ξ consists of two 'equally-spaced doublets, corresponding to the aldehyde (H_A) and olefinic (H_B) protons. At each temperature, 16-22 HMDS sideband-calibrated spectra were recorded for each doublet,¹⁰ yielding line frequencies relative to HMDS, whose standard deviations ranged 0.02-0.06 Hz, with an average value of 0.03 Hz. At all temperatures, the two doublets were well-separated, and all nmr parameters were obtained from a direct first-order analysis. The vicinal coupling, J_{AB} , was derived from the average of the two doublet separations. Table 1 shows the experimental values for ν_A , ν_B , and J_{AB} at 13 temperatures.

Table 1

Temperature ^a	ν_A ^b	ν_B ^b	J_{AB} ^c
69.8	568.80	374.28	7.37
54.5	568.67	374.35	7.46
39.5	568.47	374.45	7.58
38.5	568.55	374.49	7.56
29.5	568.48	374.54	7.60
15.6	568.32	374.63	7.68
-0.9	568.02	374.79	7.76
-17.5	567.92	374.86	7.78
-37.8	567.55	375.01	7.88
-60.0	567.12	375.25	7.94
-72.5	566.79	375.37	7.99
-82.5	566.56	375.53	8.06
-105.2	565.82	375.81	8.06

a) In $^\circ\text{C}$; accurate to $\pm 1^\circ$. b) In Hz from HMDS. c) In Hz.

These parameters, in addition to the derived parameters ($\nu_A - \nu_B$) and ($\nu_A + \nu_B$), were used in an attempt to determine ΔH for the equilibrium $1a \rightleftharpoons 1b$ ($1c$, $1d$) by iterative solution of

eq. 2 where P_{-a_j} and P_{-b_j} are the j^{th} of l intensive parameters of conformers $1a$ and $1b$,

$$\ln \left(\frac{P_{-a_j} - P_{-i_j}^0}{P_{-i_j}^0 - P_{-b_j}} \right) = \frac{-\Delta H}{RT_{-i_j}} + \frac{\Delta S}{R} \quad (2)$$

respectively; $P_{-i_j}^0$ is the j^{th} of l observed parameters at the i^{th} of k temperatures, T_{-i_j} .¹¹

Solution of eq. 2 varying all of the unknowns was not achieved for any of the above parameters. Consequently, it was necessary to reduce the number of unknowns by one by holding ΔS fixed at either 0 or $R \ln 2$ (1.376)¹² e.u., corresponding qualitatively to either one planar ($1b$), or two skew enantiomers ($1c$, $1d$) for the minor conformer.

This treatment led to solution of eq. 2 for three parameter sets: v_A , $(v_A - v_B)$, and J_{AB} . Both v_B and $(v_A - v_B)$ yielded solution values of ΔH which differ appreciably from literature values (even in algebraic sign for one)¹³ and whose percent probable errors were greater than expected from similar measurements.¹⁴ As J_{AB} yielded a solution value of ΔH (Table 2) in accord with previous measurements (1.7,^{5a} 2.06,² and 2.5^{1b} kcal./mole) and gave rise to a probable error in ΔH of only 6.5%, this parameter was retained for further consideration and the others discarded. The values of ΔH and $(J_{AB})_a$ are insensitive to ΔS , and therefore have been accurately determined.

Table 2

Solution Parameters^a of Equation 1 Using Temperature-dependences of J_{AB} at Fixed Values of ΔS for Equation 2

Solution	ΔS^b (Fixed)	ΔH^c	$(J_{AB})_a$	$(J_{AB})_b$	RMS
1	0	1864±122	8.11±0.02	-3.67±1.85	0.021
2	1.376	1942±115	8.10±0.02	1.24±0.98	0.022

a) All nmr parameters are given in Hz. Subscripts a and b denote nmr parameters calculated for the trans and cis conformers, respectively. ± figures denote probable errors. b) In cal/(mole deg). c) In cal/mole.

The value of $(J_{AB})_b$ (-3.67 ± 1.85 Hz) found for $\Delta S = 0$ corresponding to one planar conformation, $1b$, is in poor agreement with the best theoretical estimate (2.4 Hz) for cis-acrolein.¹⁵ However, the solution value ($+1.24 \pm 0.98$ Hz) found if ΔS is held constant at 1.376, corresponding to two skewed enantiomers, is in good agreement with this theoretical estimate. Figure 2 shows the experimental and calculated temperature-dependences of J_{AB} for solution 2. The apparent nonplanarity of acrolein can be explained by large torsional, steric, and/or electrostatic energy contributions to the total torsional potential,^{5c} and is similar to the result found for cis-butadiene.^{14a}

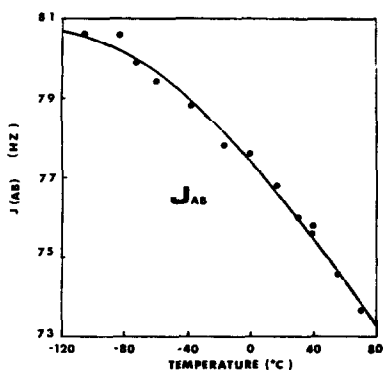


FIGURE 2. The experimental (•) and theoretical (solid line) temperature dependence of J_{AB} . The theoretical dependence is derived from solution 2 of eq. 2.

Acknowledgment: The author is grateful to the National Science Foundation for Grant No. GP-3815 which provided support for this work, and to Dr. Edgar W. Garbisch, Jr. for helpful discussions.

References and Footnotes

* Correspondence may be directed to R.L.L., 53 Winthrop Road, Brookline, Massachusetts 02146.

- (a) C. E. Cherniak and C. C. Costain, *J. Chem. Phys.*, **45**, 104 (1966); (b) R. Wagner, J. Fine, J. W. Simmons, and J. H. Goldstein, *J. Chem. Phys.*, **26**, 634 (1957).
- M. S. De Groot and J. Lamb, *Proc. Roy. Soc. (London)*, **A242**, 36 (1957).
- K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, **1**, 463 (1967-68).
- (a) A. W. Douglas and J. H. Goldstein, *J. Mol. Spectros.*, **16**, 1 (1965); (b) J. E. D. Davies, *J. Mol. Spectros.*, **29**, 499 (1969).
- (a) S. Dzhezzati, V. I. Tyulin, and V. M. Tatevskii, *Vestr. Mosk. Univ.*, Ser. II **22** (2), 14-19 (1967), see *C.A.* **63**, 109587b; (b) R. K. Harris, *Spectrochim. Acta*, **20**, 1129 (1964); (c) W. G. Fateley, R. K. Harris, F. A. Miller, and R. E. Witkowsky, *Spectrochim. Acta*, **21**, 231 (1965).
- E. H. Ingold, *J. Chem. Soc.*, **127**, 1199 (1925).
- A. Wohl and W. Emmerich, *Ber.*, **33**, 2760 (1900).
- A. Wohl, *Ber.*, **31**, 1796 (1898).
- All of the synthetic intermediates and their nondeuterated analogs gave nmr spectra that were in agreement with the assigned structures.
- The modified A-60 nmr spectrometer and experimental method have been described previously in reference 13-a.
- For a detailed discussion of the scope and limitations of this method, see E. W. Garbisch, Jr., B. L. Hawkins, and K. D. MacKay, in "Conformational Analysis: Scope and Present Limitations", E. Chiurdogu, Ed., pp. 93-110, Academic Press, New York, 1971.
- The entropy of mixing is normally used for such a case.
- Solution values at $\Delta S = 0$: $\Delta H = 691 \pm 66$ cal/mole (ν_B) and -62 ± 87 cal/mole ($\nu_A - \nu_B$). The unreliability of solution values of ΔH obtained from chemical shift data is consistent with the erratic concentration dependence of chemical shift reported for acrolein in reference 4a and ascribed to head to tail dimer equilibrium.
- (a) The Conformational Analysis of 1,3-butadiene, R. L. Lipnick and E. W. Garbisch, Jr., *J. Amer. Chem. Soc.*, **95**, 0000 (1973). (b) the Conformational Analysis of 4,4-Dimethyl-1-pentene, P. B. Woller and E. W. Garbisch, Jr., *J. Amer. Chem. Soc.*, **94**, 0000 (1972).
- A. A. Bothner-By and R. K. Harris, *J. Org. Chem.*, **30**, 254 (1965).