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The gas chromatographic separation and infrared identification of syn- and anti-acetaldoxime

Liquid acetaldoxime, neat or in solution, is known to contain the *syn* and *anti* isomers in equilibrium[1-4]. Separation of the two isomers[4] has been achieved by column chromatography, but separations by gas chromatography and infrared spectra of the pure isomers in dilute solutions have not been obtained. HADŽI AND PREMRU[3] have recorded the infrared spectra of a mixture of *syn* and *anti* isomers of acetaldoxime, acetaldoxime-d_0 and acetaldoxime-d_1 in carbon tetrachloride and assigned the bands belonging to each isomer. Since the equilibrium between the *syn* and *anti* isomers at room temperature in carbon tetrachloride is reached practically instantly, we used carbon disulphide in which the *syn* and *anti* isomers are stable long enough to record the spectra of both pure isomers at room temperature.

Experimental

Acetaldoxime was a commercial product (Th. Schuchardt), and acetaldoxime-d_1 was prepared from nitromethane-d_2. The separation was made on a Varian 1860 gas chromatograph with a flame ionization detector. Each isomer was collected in a glass trap containing carbon disulphide as the solvent, the trap being fitted at the end of the original 1:10 splitter for the 1800 Series. The temperature of the glass trap was maintained at 0°. The chromatographic separations were carried out at four temperatures. Argon was used as carrier gas and on column injection was used. A stainless-steel column, 1.50 m × 0.64 cm I.D., packed with 23.6% of Carbowax 400 on Embacell 60–100 mesh was introduced into the original air thermostat. Infrared spectra of approximately 0.005 *M* solutions of the isomers in carbon disulphide in a 10-mm cell were recorded with a Perkin-Elmer spectrometer, Model 521.

Results and discussion

The chromatographic separations were made in the temperature range 65° to 95°. In all these cases the resolution was good but results obtained at temperatures below 80° are more satisfactory than those obtained above this temperature. This is shown in Table I, where the relative resolution values according to KAISER[5] are listed. Fig. 1 represents an example of a gas chromatogram obtained at 75°.

To establish the identity of the two isomers the infrared spectra of the chromatographically separated components of acetaldoxime and acetaldoxime-d_1 were run

TABLE I

THE RELATIVE RESOLUTION VALUES OF THE *syn* AND *anti* ISOMERS OF ACETALDOXIME

Temperature (°C)	R_{21} *(min/cm)*
65	1.44
75	1.33
85	1.24
95	1.12

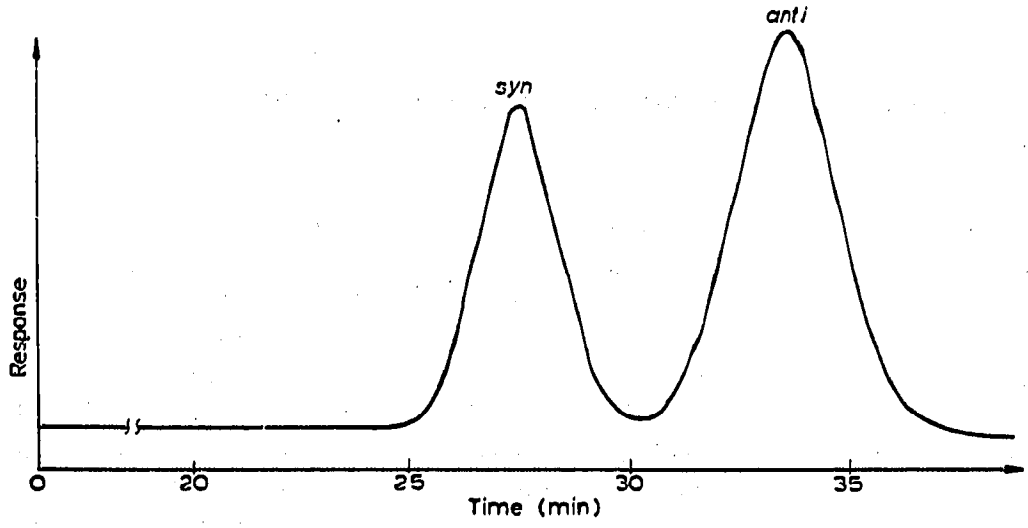

Fig. 1. Gas chromatogram of acetaldoxime at 75° on Carbowax 400.

and compared to the spectra of the original mixture of acetaldoxime and acetaldoxime-d_6.

According to ref. 3 and our own observations, differences in the frequencies for the *syn* and *anti* isomers exist in the region from about 1400 cm^{-1} to 400 cm^{-1},

TABLE II

CHARACTERISTIC FREQUENCIES IN CM^{-1} OF APPROXIMATELY 0.005 *M* SOLUTIONS OF ACETALDOXIME, ACETALDOXIME-d_6 AND THEIR ISOMERS IN CARBON DISULPHIDE

Mixture	*Acetaldoxime*	
	First component (syn)	*Second component (anti)*
1330		1330
1289		1290
1250	1250	
1124	1123	
1105		1105
970	970	
925		925
552	553	
482		483
Mixture	*Acetaldoxime-d_6*	
	First component (syn)	*Second component (anti)*
1340	1340	
1321		1320
1127	1130	
1098		1096
1050		1050
940	940	
820		820
814	812	
540	542	
478		478

while the –OH stretching of the monomeric molecule (in our spectra at 3583 cm^{-1}) is not appreciably influenced by the geometrical isomerism of the aldoximes.

Characteristic frequencies for approximately 0.005 *M* solutions in carbon disulphide of liquid, normal and C-deuterated acetaldoxime and their isomers are given in Table II.

Following the assignments of the –OH, –CH and –CD deformation vibrations for *syn*- and *anti*-acetaldoxime[3], we conclude that the first fraction of acetaldoxime and acetaldoxime-d_e consists of the *syn* isomer and the second is that of the *anti* isomer.

Conclusion

Our results demonstrate that the gas chromatographic separation of *syn* and *anti* isomers of acetaldoxime is feasible. Kinetic investigations and the complete vibrational analysis of acetaldoxime is being carried out in this laboratory.

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1 W. D. PHILLIPS, *Ann. N. Y. Acad. Sci.*, 70 (1958) 825.
2 G. J. KARABATSOS, R. A. TALLER AND F. M. VANE, *J. Amer. Chem. Soc.*, 85 (1963) 2327.
3 D. HADŽI AND L. PREMRU, *Spectrochim. Acta*, 23 (1967) 35.
4 I. PEJKOVIĆ-TADIĆ, M. HRANISAVLJEVIĆ-JAKOVLJEVIĆ AND S. NEŠIĆ, *J. Chromatogr.*, 21 (1966) 239.
5 R. KAISER, *Gas Phase Chromatography*, Vol. 1, Butterworths, London, 1963, p. 39.

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