Gas chromatography of isotopic molecules: analytical and preparative scale separations of C_2H_2, C_2HD and C_2D_2*

As a part of our program of investigation of molecular geometry and isotope effects on condensed phase phenomena, we became interested in obtaining pure samples of C_2H_2, C_2D_2, and C_2HD. The first two are easily prepared from H_2O or D_2O and calcium carbide but to our knowledge pure C_2HD has not yet been reported. This is due to the equilibration of the hydrogenic atoms during chemical preparations. We report here that we have been successful in separating macroscopic amounts (cc's at S.T.P.) of C_2HD from such equilibrium mixtures. Purities around 99 % were obtained using gas chromatography. The methods employed for analysis and separation should be useful in several different fields. Interest in analytical separations has been expressed by workers in the field of hot atom chemistry[1] and spectroscopists have long desired high purity C_2HD for measurements in regions obscured by C_2H_2 and C_2D_2 bands[2]. It is our intent to employ purified samples in measurements of isotope effects on some of the physical properties of the three isomers.

Protio-deutero isotope effects on chromatographic separations of hydrocarbons have been discussed by VAN HOOK and coworkers[3-6]. Very briefly the theory of isotope effects in condensed systems[7] leads in the first approximation to[4]

$$\ln \frac{P'}{P} = \ln R_{x'/x} = \ln \frac{V_R}{V_R'} = \frac{A}{T^2} - \frac{B}{T}$$

where V_R refers to the corrected chromatographic retention volume, the prime to the lighter isotope, A is a first order quantum correction appropriate to the lattice modes $(h\nu/kT < 2\pi)$ and B is the contribution of the changes in zero point energy of the large $(h\nu/kT > 2\pi)$ frequencies on condensation. For hydrocarbons dissolved in non-polar liquids there is a net red shift on condensation[8] due to dispersion forces. These are of such magnitude that inverse isotope effects with concomitant maxima of order 2 % per D atom result. For more polar solvents the inverse isotope effect decreases[4]. This is expected as a consequence of a stiffening of the hydrogen motions due to complexing with polar solvent groups. In the case of the ethylene–Ag^+ complex this shift is so marked that the effect becomes normal (4%/D at 0°)[9]. It is well known that acetylenic compounds are easily complexed (vapor pressure experiments on methyl acetylene[10] and acetylene[11] indicate that there is self complexing in the liquid phase which itself is strongly temperature dependent, and accounts for the marked vapor pressure isotope effect of CH_3CCD).

The theory thus suggests that separations will be most effective at low temperatures on substrates which complex with acetylene. Chromatographic considerations on the other hand require that the complexes be loosely bound in order to facilitate interphase transfer.

Experimental

Our present object was to develop a suitable analytical technique for C_2H_2, C_2HD, and C_2D_2 samples and a separation suitable for the preparation of macroscopic

amounts of C_2HD. In an initial screening program we looked at a large number of different solvents supported on 60/80 mesh Chromosorb P. The columns were thermostated usually at $-78°$. Two chromatographs, each employing helium carrier, were used. The first was a previously described "homemade" instrument[3] with a thermal conductivity detector, the second a modified Perkin Elmer F-11 chromatograph with a flame ionization detector.

Results

The results are summarized in Table I. Entries are made in order of increasing standard retention volumes. These might be construed as a measure of the net interaction between solvent and the acetylene. Correlations between the retention times and commonly accepted base strengths are not apparent. Triethylamine, which is not

TABLE I

CHROMATOGRAPHIC DATA

Columns[a]	Temperature (°C)	Flow rate (cc/min)	$t_{C_2H_2}'$ [b] (min)	$V_0(-78°)$ [c] (cc)	$R_{C_2H_2/C_2D_2}$ [d]
12 ft., 20% sec.-$C_4H_9NH_2$	-78	21	$<$ 1/2	$<$ 15	—
6½ ft., 22.5% $(C_2H_5)_2NH$	-78	26	1	30	—
8 ft., 28% H_2O-CH_3OH (2:1)	-78	16	6.7	93	—
8 ft., 20% iso-C_4H_9OH	-78	9.2	10	130	—
8 ft., 20% n-C_3H_7OH	-78	24	9.1	228	—
8 ft., 20% [e] $(C_2H_5)_3N$	-78	41	15	540	1.079
24 ft., 26% CH_3CN-C_2H_5OH (2:1)	-78	15	52	730	1.10
9 ft., 26% CH_3OH	-78	24	38.9	760	1.088
13 ft., 26% C_2H_5OH	-78	26	52.0	1340	1.078
1 ft., 26% $(CH_3)_2C=O$	-78	50	3.5	>2000	—
8 ft., 24% CH_3OH	-69	24	32.2	650	1.075
	-45	22	7.5	360	1.038
1 ft., 31% CH_3OH	-100	42	9	2400	—
8 ft., 24% C_4H_8O (THF)	-45	16	44.2	435	1.045
12 ft., 0.1 M AgNO$_3$ in 20% $C_2H_4(OH)_2$	0	Not eluted			

[a] All columns 1/8 in. copper packed (0.35 g/ft.) with 60/80 mesh Chromosorb P coated as described in the first column; percentages refer to weight per cent of liquid phase.
[b] $t_{C_2H_2} - t_{air} = t_{C_2H_2}'$
[c] $V_0(-78°) = (195/T)(V_R'j/W_l)$ where T is temperature in °K, V_R' the corrected retention volume, j the compressibility correction, and W_l the weight of liquid in the column. Reported to two significant figures.
[d] $R_{H/D} = t_{C_2D_2}'/t_{C_2H_2}'$
[e] Final analytical column 24 ft., 18% $(C_2H_5)_3N$ at $-78°$, 15 cc/min, 157 min retention, gave $R_{C_2H_2/C_2D_2} = 1.085$ and $R_{C_2H_2/C_2HD} = 1.032$.

expected to be self associated, gave the best results and was employed in the preparative work. The first five entries had elution times too short to allow meaningful measurement of the separation factors. The ratios shown in Table I were measured directly from the observed peaks without making any corrections for chromatographic nonideality. The peak shape on all of the analytical columns was similar to those shown in Fig. 1a, e, f, g or h, i.e. definitely asymmetric. In analysis 20 to 100 μl gas samples were syringe injected. The peak shapes and separation factors reported in Table I were reproducible under identical column conditions to $\pm$0.003 but only to $\pm$0.01 as the flow rate was varied. The numbers in the table are all reported at pressures near 20 p.s.i. where they are estimated as self consistent to $\pm$0.005. It is interesting to note that the separation factor at $-78°$ for all complexes is 1.08 $\pm$ 0.01. The result on the one column outside this range (CH_3CN-CH_3OH, 1:1) is complicated by the fact that it is a two-component system. (Dilution with CH_3OH was required to lower the $-40°$ freezing point of CH_3CN.) Although temperature coefficients were not a primary concern in this study, it is interesting to note that results on the CH_3OH and tetrahydrofuran columns indicate that they are marked, in accord with the theoretical considerations outlined above. Three component mixtures analyzed with the $(C_2H_5)_3N$ column indicate a definite deviation from the law of the mean on the isotope effect.

The preparative column, 29 ft. of 1/4 in. copper tubing, was packed with 60/80 mesh Chromosorb P coated with 18 % $(C_2H_5)_3N$. Samples (5 to 100 cc S.T.P.) were injected from a gas loop. A thermal conductivity detector was employed and all runs were made at $-78°$. Selected portions of the peak could be trapped out in a three foot coil of 7 mm glass tubing immersed in liquid nitrogen. A truly inordinate amount of
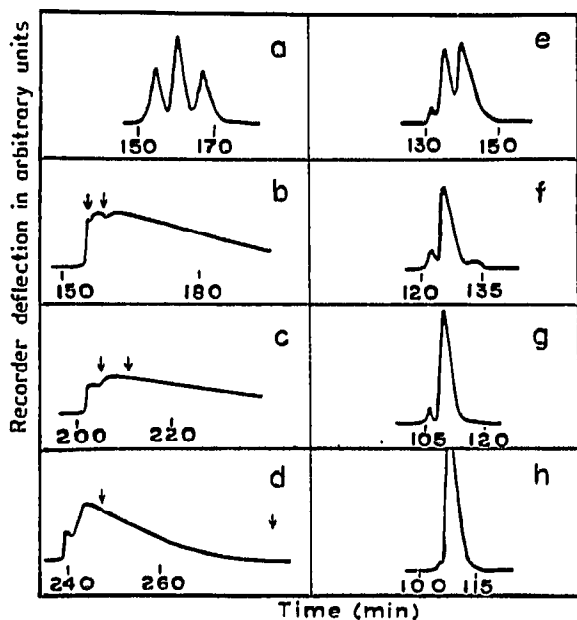

Fig. 1. Chromatograms of protio-deutero isomers of acetylene. Order of appearance on all chromatograms (from left to right): C_2H_2, C_2HD, C_2D_2. (a) Analysis column separation of $C_2H_2:C_2HD:C_2D_2 = 1:2:1$ (note e, Table I). (b), (c), (d) Successive chromatograms on preparative column ($-78°$). Arrows indicate portions trapped. Sample sizes 100 cc, 30 cc, and 5 cc. (e) Analysis of starting material for preparative separation. (f), (g), (h) Analysis of collected fractions from (b), (c), (d).

tailing developed as the sample size increased. This is to be expected from the nature of the solvent–acetylene complex which accounts for the separation. The efficiency of the preparative separation is thus quite low and multiple chromatographings are required. A series of such purifications is shown in Fig. 1. The product after three runs shows ~98 % C_2HD (~1.3 % C_2H_2, <1 % C_2D_2). The chromatographic analysis is consistent with infrared results. We see no reason why a product >99.9 % pure cannot be prepared in one or two more steps. The C_2HD stored at room temperature over mercury at order one hundred millimeters pressure was stable to disproportion over a period of at least several weeks.

To our knowledge this is the first time that preparative gas chromatography has been employed for the purification of isotopic isomers for other than the isomers of hydrogen itself.

Department of Chemistry, University of Tennessee,   W. ALEXANDER VAN HOOK
Knoxville, Tenn. 37916 (U.S.A.)   JAMES T. PHILLIPS*

1 J. DUBRIN, C. MACKAY AND R. WOLFGANG, *J. Chem. Phys.*, 41 (1964) 3267; H. J. ACHE, private communication.
2 W. J. LAFFERTY, E. K. PLYLER AND E. D. TIDWELL, *J. Chem. Phys.*, 37 (1962) 1983.
3 W. A. VAN HOOK AND M. E. KELLY, *Anal. Chem.*, 37 (1965) 508.
4 W. A. VAN HOOK AND J. T. PHILLIPS, *J. Phys. Chem.*, 70 (1966) 1515.
5 J. T. PHILLIPS AND W. A. VAN HOOK, *J. Phys. Chem.*, 71 (1967) in press.
6 W. A. VAN HOOK, *J. Phys. Chem.*, 71 (1967) in press.
7 J. BIGELEISEN, *J. Chem. Phys.*, 34 (1961) 1485.
8 Pertinent references are cited in W. A. VAN HOOK, *J. Chem. Phys.*, 44 (1966) 234.
9 R. J. CVETANOVIC, F. J. DUNCAN, W. E. FALCONER AND R. S. IRWIN, *J. Am. Chem. Soc.*, 87 (1965) 1827.
10 W. A. VAN HOOK, *J. Chem. Phys.*, 46 (1967) 1907.
11 A. KLEINENC AND O. VON FRUGNONI, *Naturwiss.*, 22 (1934) 465.