Gas-chromatographic Studies of Cadmium–Olefin Complexes

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CdF_2 deposited on a γ-alumina surface from aqueous HF solution has been found to interact sufficiently strongly with olefins and aromatic compounds to give very marked selective retardations of olefins and aromatic compounds when CdF_2–Al_2O_3 is used as the stationary phase in a gas–solid chromatographic column. These interactions are considerably modified by competition with water vapour, and are much weaker with other cadmium salts investigated.

OLEFIN complexes are well known for the univalent ions of Group IB, Cu^+, Ag^+, and Au^+, and for Hg^{2+} in Group IIB. It might therefore be expected that similar but weaker complexes would exist for Cd^{2+}, but so far as we are aware there is no reported evidence for their formation. In g.l.c. use is commonly made of the selective retardation of olefins and aromatic compounds by solutions of $AgNO_3$ in solvents such as ethylene glycol, water, or benzyl cyanide, and stability constants for the formation of these complexes can be calculated from the retention data.[1] The retardation is normally equivalent to *ca.* 1—6 carbon numbers, that is to say an olefin will emerge from the column with a retention time equivalent to a paraffin containing 1—6 more carbon atoms. This retardation corresponds to a free energy of complex formation of *ca.* 2—11 kJ mol^{-1}, and the low values must represent the difference in complexing power of the olefin and solvent (*e.g.*, ethylene glycol) molecules. When, however, $AgNO_3$ (or CuCl) is spread on an Al_2O_3 surface and the resulting material used as a stationary phase in a gas–solid chromatographic column, very much greater retardations are observed: these are so great that the olefins can only be recovered by displacement and not by elution.[2] Strong retardation is not found with Al_2O_3 modified with the more 'covalent' silver salts such as AgCl, AgBr, or AgI, nor with SiO_2 modified with $AgNO_3$ (retardations in the range 1—2·5 carbon numbers [3]).

We have found strong retardations of olefins and aromatic compounds with a column material consisting of CdF_2 deposited on an Al_2O_3 surface from 2M-HF solution. The retardations are much smaller when CdF_2 is deposited from water alone (in which CdF_2 is only slightly soluble). Only small retardations are observed with Al_2O_3 which has been treated with 2M-HF solution. Since the retardations are much smaller than those for Ag^+ ions, the cadmium complexes are presumably too weak to lead to isolable species under normal conditions.

Similar retardations are found with CdF_2 deposited on $Al_2(SO_4)_3$ or on SiO_2–Al_2O_3 but here extensive catalytic reactions occur as well. The retardations are much weaker when Al_2O_3 is modified with other cadmium

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[1] B. W. Bradford, D. Harvey, and D. E. Chalkley, *J. Inst. Petroleum*, 1955, **41**, 80; M. E. Bednas and D. S. Russell, *Canad. J. Chem.*, 1958, **36**, 1272; S. P. Wasik and W. Tang, *J. Phys. Chem.*, 1970, **74**, 2970; A. L. Harding, Part II thesis, Oxford 1972.

[2] C. G. Scott and C. S. G. Phillips, in 'Gas Chromatography 1964,' ed. A. Goldup, Institute of Petroleum, London, 1965, p. 266.

[3] T. W. Godden, B.Sc. thesis, Oxford 1966.

salts such as $CdCl_2$, $Cd(OH)_2$, $Cd(NO_3)_2$, and cadmium oxalate, or when CdF_2 is deposited on SiO_2, TiO_2, Mn_3O_4, B_2O_3, or 13X molecular sieve (all retardations in the range 0·5—2·8 carbon numbers). No selective retardation is found with a g.l.c. chromatographic column which uses cadmium stearate as a column liquid (20% on Phasesep at 100 °C).

EXPERIMENTAL

γ-Alumina (Harrington Brothers Ltd., Weir Road, London) was sieved to 100—150 BSS mesh. Al_2O_3 (10 g) was placed in a porcelain evaporating dish and impregnated three times successively with a solution containing CdF_2 (7·5 g) in 2·4M-HF (100 cm^3). In each impregnation step, 14 ml of the above solution were added and the slurry allowed to stand for 15 min. It was then heated to dryness at 150 °C, and cooled for 15 min before starting the next impregnation. The material was finally sieved. For use at 100 °C it was activated in the column for 10 h at 150 °C and then conditioned for 8 h at 100 °C. Lower selective retardations were observed with a sample which had been stored for about 2 months, and it was then necessary to activate the material at 400 °C to restore the normal retardation ability. From the adsorption isotherm it appears that 10% CdF_2 on Al_2O_3 corresponds to *ca.* 40% of a monolayer coverage of the Al_2O_3 surface with CdF_2.

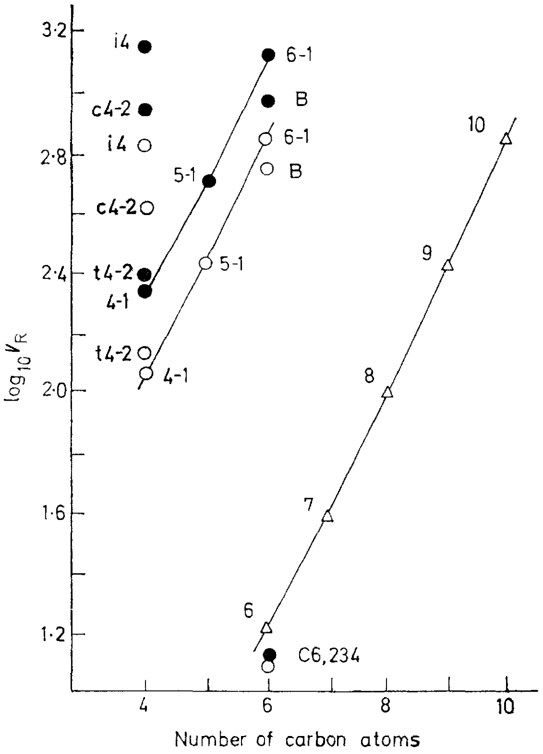

FIGURE 1 Retention volumes for various olefins (the isomeric butenes, n-pent-1-ene, and n-hex-1-ene), benzene, and n-paraffins (hexane to decane) on 10% CdF_2 on Al_2O_3 at 100 °C. Column length 6 cm, i.d. 0·25 cm, flow-rate 30 ml of nitrogen per minute. Retention volumes (uncorrected) were measured in cm^3 (at 20 °C). Open circle values were obtained with cylinder nitrogen as carrier gas, filled circle values when this had been 'dried' by passage through 13X molecular sieve (activated at 350 °C). The retention volumes of the paraffins are not changed significantly by the variation in the water-vapour pressure of the carrier gas. Key to Figures 1 and 2: 5 = n-pentane, 6 = n-hexane, 7 = n-heptane, 8 = n-octane, 9 = n-nonane, 10 = n-decane, 234 = 2,3-dimethylbutane, C6 = cyclohexane, 4-1 = but-1-ene, 5-1 = pent-1-ene, 6-1 = hex-1-ene, t4-2 = *trans*-but-2-ene, c4-2 = *cis*-but-2-ene, i4 = isobutene, B = benzene

Because of the large retention times, *e.g.*, 30 min for isobutene on a 6 cm long column at 150 °C (0·25 cm internal diameter, nitrogen carrier gas at 30 ml min^{-1}) most measurements were made with very short columns. A Pye 104 gas chromatograph was used with a flame-ionisation detector. Very small sample sizes (of the order 10^{-6} g) are required to give symmetrical peaks for olefins and aromatic compounds.

RESULTS AND DISCUSSION

Retention data for a series of n-paraffins (triangles), a series of terminal n-olefins, and the isomeric butenes and benzene (circles) are plotted in Figure 1. The regular increase of retention volume for the addition of each $-CH_2-$ group in the two series is a normal feature of both g.l.c. and g.s.c. columns, but with dried carrier gas the selective retardation over paraffins corresponds to *ca.* 4·7 carbon atoms for terminal olefins and 4·3 for benzene. At 150 °C these selective retardations rise to about 7·3 and 7·0 while at 60 °C they are 2·7 and 2·8 carbon atoms. The selective retardation of isomeric olefins, namely isobutene $\gg$ *cis*-but-2-ene $\gg$ *trans*-but-2-ene > but-1-ene is quite distinct from that found with $AgNO_3$–glycol systems where the order is but-1-ene > *cis*-but-2-ene > isobutene > *trans*-but-2-ene. Thus, apart from the sterically expected greater complexing power of the *cis*- then the *trans*-isomer, the sequence is reversed in the two systems which might have been expected to operate in a rather similar manner. Part of the explanation of this effect may lie in the greater loss in entropy of the but-1-ene molecule when it passes from the gaseous state and becomes fixed to the surface (see also data for KBr–Al_2O_3 in the Table) rather than being dissolved in a solvent.

The differences in absolute entropy of the gaseous molecules from isobutene are but-1-ene, 14; *cis*-but-2-ene, 7; and *trans*-but-2-ene, 3 which can be compared with the differential entropy loss on adsorption on CdF_2–Al_2O_3 (again relative to isobutene) as estimated from the variation of retention volumes with temperature of 13, 4, and 12 J K^{-1} mol^{-1} respectively. (Some contribution to the differences in entropy may arise from the different numbers of Cd^{2+} ions which are 'available' for complexing to unsaturated molecules of different shape.)

While cyclohexane has a slightly smaller retention volume than n-hexane (except above 130 °C) cyclohexene (*cf. cis*-but-2-ene and but-1-ene) has a very much larger retention volume than n-hex-1-ene. On the other hand, benzene has an even smaller retention than n-hex-1-ene, showing that the bonding of the aromatic ring is less strong than that of one double bond.

It was thought that CdF_2–Al_2O_3 might have a sufficiently strong interaction with isomeric xylenes to provide a useful separation. By operating under a variety of conditions (pretreatment, column temperature, use of water vapour in carrier gas) retention volume ratios for *m*-xylene : *p*-xylene were obtained ranging from 0·96 to 1·21 (the latter value at 450 °C with water vapour in the carrier gas). Similar (but not better) values have been obtained with other gas-chromatographic columns, so that it does not appear that CdF_2–Al_2O_3 provides any marked improvement on existing systems, at least under the conditions which we have tried: *o*-xylene always had a larger retention; retention volume ratios for *o*-xylene : *p*-xylene varied from 1·39 to 1·51.

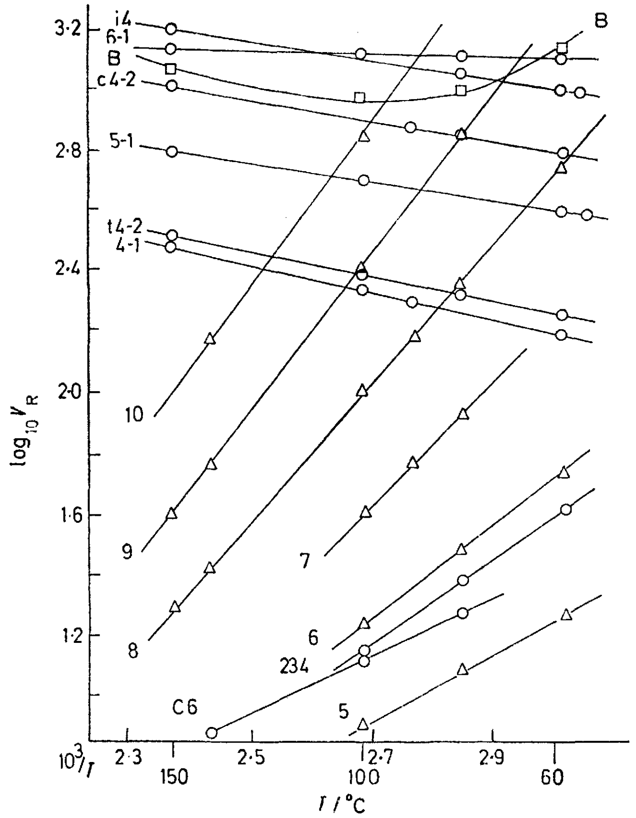

FIGURE 2 Retention volumes (as for Figure 1, ' dried ' carrier gas) as a function of temperature

When measurements were made with ordinary (white spot) cylinder nitrogen as carrier gas (without drying with molecular sieve), no substantial changes in retention volumes were noted for the paraffins, but the olefins and aromatic compound retention volumes were all decreased, as shown by the points marked with open circles in Figure 1. Much more dramatic decreases can be obtained by deliberately introducing water vapour into the carrier gas, and in this way the selective retardation of olefins relative to paraffins can be reduced to the equivalent of only one carbon atom.

Figure 2 plots retention volumes for a 10% CdF_2 on Al_2O_3 column. At each temperature the system had been allowed to come into equilibrium (see below) before the measurements were made. The paraffins have retention volumes which decrease steadily with increase of column temperature to give (approximately) straight lines on the logarithmic plot: this is the normal chromatographic experience and corresponds to exothermic interaction with the stationary phase of the column. The retention volumes of the olefins, however, change much less with temperature and actually increase with increase of temperature, a phenomenon to the best of our knowledge unique in gas chromatography. This small apparent endothermic heat of interaction is most plausibly explained in terms of competition with water vapour (present in very small concentrations even in the ' dried ' carrier gas), the water interaction with the Cd^{2+} ions being more exothermic than the olefin interaction but less favoured in terms of entropy (as it would clearly be if each active surface Cd^{2+} ion can only accommodate one olefin molecule but more than one water molecule).

Although the separation of olefins and paraffins of the same carbon number is thus markedly increased as the temperature is increased, the selective retardation of olefin isomers increases slightly with decrease of temperature, corresponding to slight decreases in the (apparently positive) heat of adsorption along the series but-1-ene > *trans*-but-2-ene > *cis*-but-2-ene > isobutene. This is illustrated by the figures in the Table, where data for a more normal salt-modified alumina are quoted for comparison.

TABLE 1

Retention volumes for the isomeric butenes (relative to but-1-ene) on 10% CdF_2 on Al_2O_3 and on 10% KBr on Al_2O_3

Olefin	But-1-ene	*trans*-But-2-ene	*cis*-But-2-ene	Isobutene
B.p./°C	−6·3	0·9	3·7	−6·6
CdF_2–Al_2O_3				
60 °C	1·00	1·16	3·81	6·46
150 °C	1·00	1·07	3·35	5·30
KBr–Al_2O_3				
60 °C	1·00	1·04	1·22	1·42
150 °C	1·00	0·97	1·12	1·05

All the experimental results discussed above were obtained with columns which had been allowed to come into equilibrium (during several hours) with the carrier gas at the temperature at which they were operated. If, however, the column had been held at a higher temperature for some period (so that it would contain a smaller equilibrium amount of adsorbed water) then it was found to retard olefins very much more markedly, often to such an extent that they were not eluted until the column had had time to rehydrate with such water

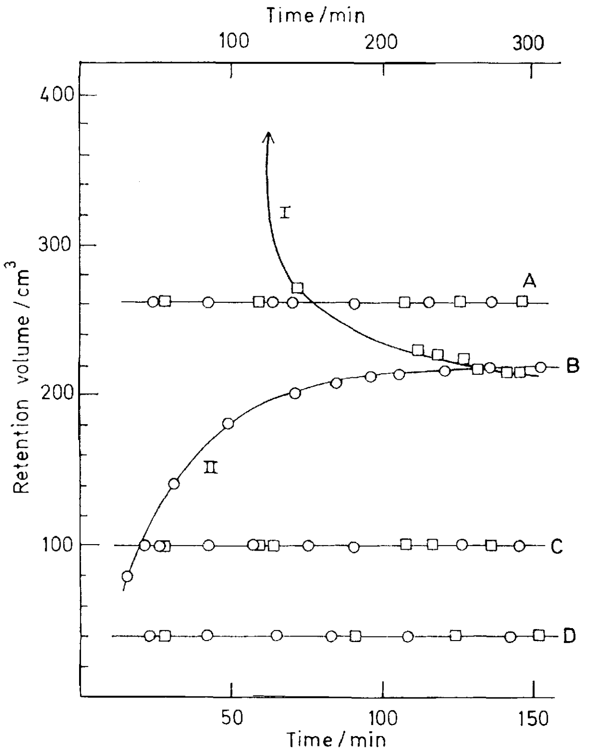

FIGURE 3 Retention volumes with conditions as for Figure 1 but with nitrogen carrier gas containing a trace of water vapour and a column which had (I) been previously heated to 140 °C (squares and upper time scale), (II) been cooled to 60 °C (circles and lower time scale); A, n-nonane; B, (I and II), but-1-ene; C, n-octane; and D, n-heptane. Curve I goes to 2720 cm^3 at 50 min and 1380 cm^3 at 110 min

as was present in the carrier gas. The time to reach equilibrium was very much reduced if water vapour was deliberately introduced into the carrier gas. Similarly, when the column had previously been cooled, the retention volumes of olefins were found to start much lower and to rise steadily to the equilibrium value. No changes were observed in the retention volumes of the paraffin hydrocarbons in either case; see Figure 3.

Although the CdF_2–Al_2O_3 columns have high efficiencies (HETP values at optimum flow rate were 0·4—0·5 mm), the large retention times for olefins and aromatic compounds probably mean that they can only have rather limited and specialised applications in analytical g.s.c. We have found them particularly suited to the determination of small traces of paraffins in olefins and aromatic compounds. Other applications may be devised which make use of the high selectivity of the olefin and aromatic compound retardations, and the ease with which these retardations can be drastically modified by change of column temperature or water-vapour pressure in the carrier gas. In contradistinction to $AgNO_3$–Al_2O_3 columns, CdF_2–Al_2O_3 columns have high thermal stability.

At higher temperatures (generally 200—450 °C) a whole series of catalytic reactions have been found to take place on CdF_2–Al_2O_3. Our preliminary series of studies shows that these can include isomerisation, polymerisation, dismutation aromatisation, methyl transfer and demethylation, cracking, hydrogenation, and hydro-cracking.

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