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Note

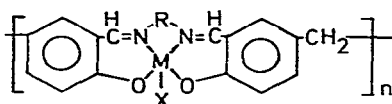
Gas chromatographic separation of the spin isomers of hydrogen at ambient temperature

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Following the synthesis of polymeric Schiff-base complexes of the general formula¹⁻³,



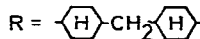
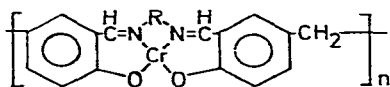
M = metal ion (+2 or +3)

X = inorganic ligand (if M³⁺)

we have elucidated their adsorption and molecular sieve properties³⁻⁵. When these complexes were used as stationary phase in a column for gas adsorption chromatography, a mixture of noble gases was separated⁴ and the efficiency was similar to that of zeolitic molecular sieves.

It is well known that zeolites are able to separate even the spin isomers and the isotopic species of hydrogen, and therefore it seemed worthwhile to find if this is also possible with polymeric Schiff-base complexes.

The numerous known methods for the separation of the spin isomers of hydrogen using different adsorbing materials⁶⁻¹⁴ all work at low temperatures, close to the boiling point of nitrogen. We succeeded in separating them at ambient temperature (296°K) using the polymeric Schiff-base complex with Cr²⁺



as stationary phase.

The complete separation of the spin isomers of hydrogen at room temperature is shown in Fig. 1a. A column, 2 m × 3 mm I.D., was packed with the carrier material of grain size 0.3-0.5 mm. For activation, the column was heated for 1 h at 523°K using helium at a flow-rate of 100 ml min⁻¹ as carrier gas. The detector was a usual thermal conductivity cell.

Besides the good separation, the hitherto unknown extremely short retention time of both spin isomers (less than 20 sec) is surprising. The peak areas show the expected⁶ ratio, 1:3. Lowering the temperature to 203°K (other conditions unchanged) had almost no influence on the retention time and peak shape of the *p*-isomer,

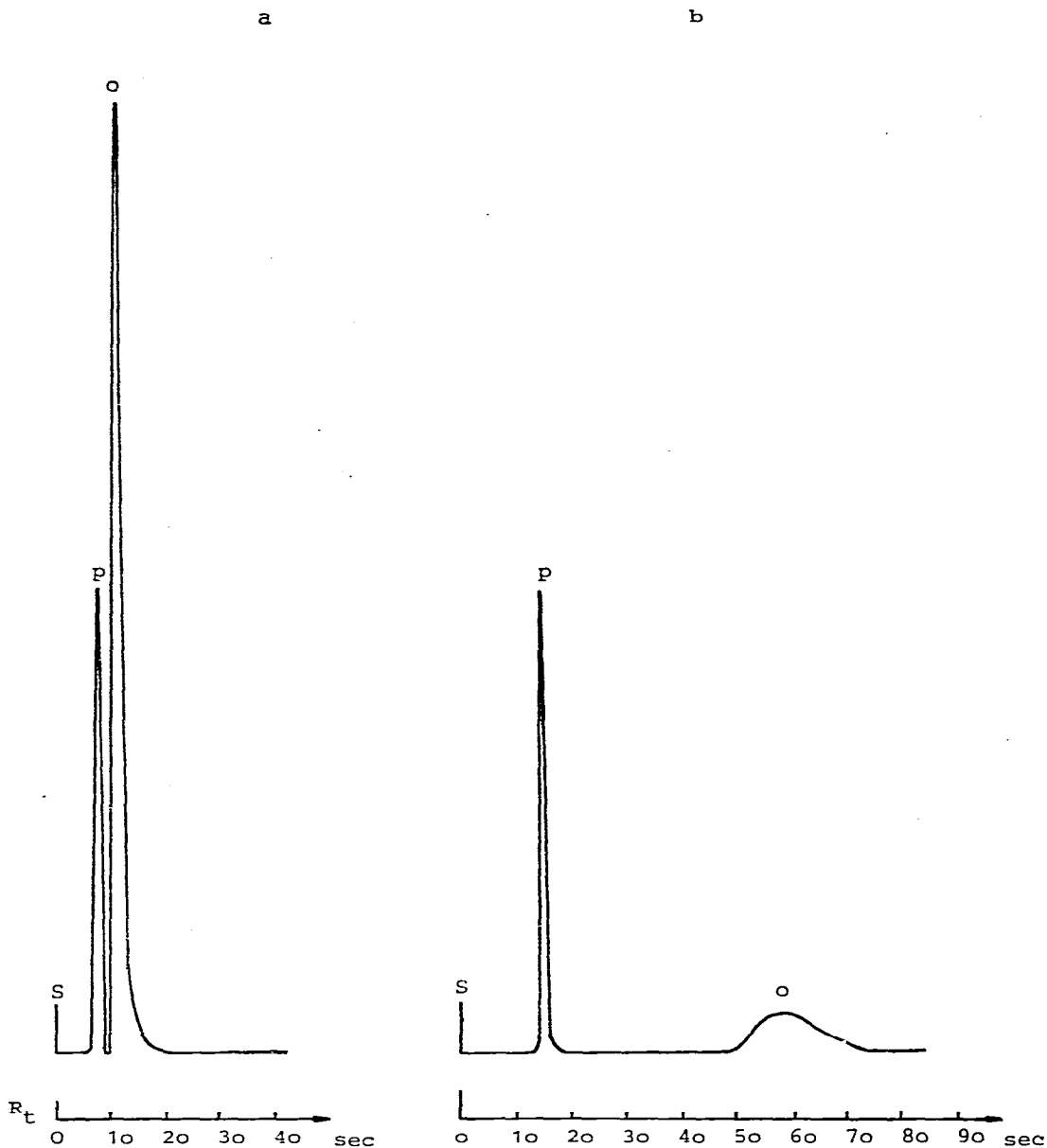


Fig. 1. Separation of the spin isomers of H₂. Carrier gas, helium at 100 ml min⁻¹; column, 2 m × 3 mm I.D.; adsorbent: polymeric Cr²⁺ Schiff-base complex. (a) 296 °K; (b) 203 °K.

whereas the *o*-H₂ peak exhibits a considerable broadening (Fig. 16). At 77°K neither of the isomers came through the column even after 30 min.

Fig. 2 (a and b) shows the separation of the D₂ isomers under the same conditions as for H₂. The peak areas again correspond⁶ to the equilibrium concentrations at room temperature (1:2).

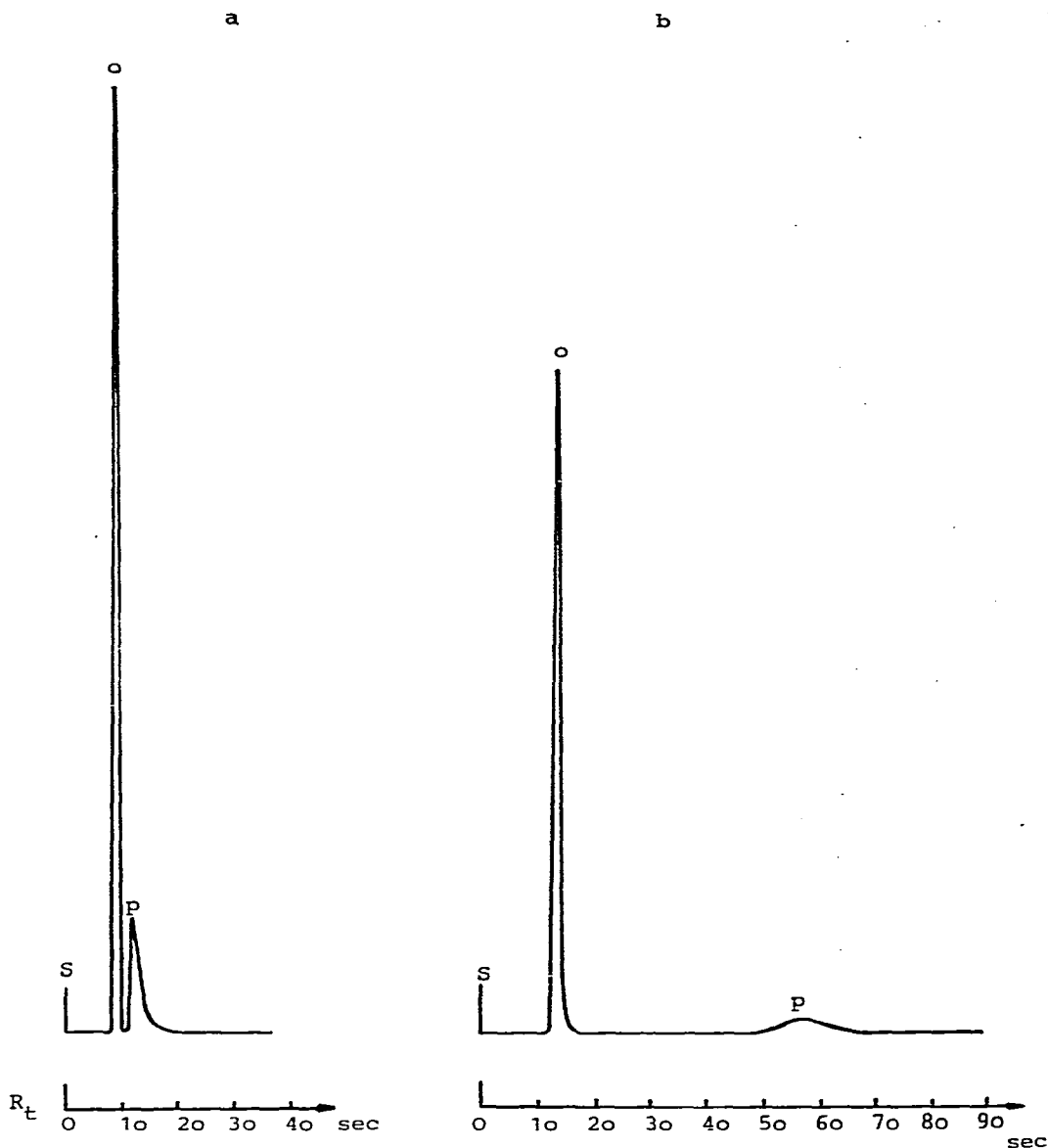


Fig. 2. Separation of the spin isomers of D_2 . Same conditions as Fig. 1.

It should be noted that the retention times of o - D_2 and p - H_2 are almost the same, as are those of p - D_2 and o - H_2 . Thus, 1:1 mixture of H_2 and D_2 gives only two peaks, one for p - H_2 and o - D_2 , and one for o - H_2 and p - D_2 (Fig. 3). So far, we have not observed any splitting due to these pairs of spin isomers.

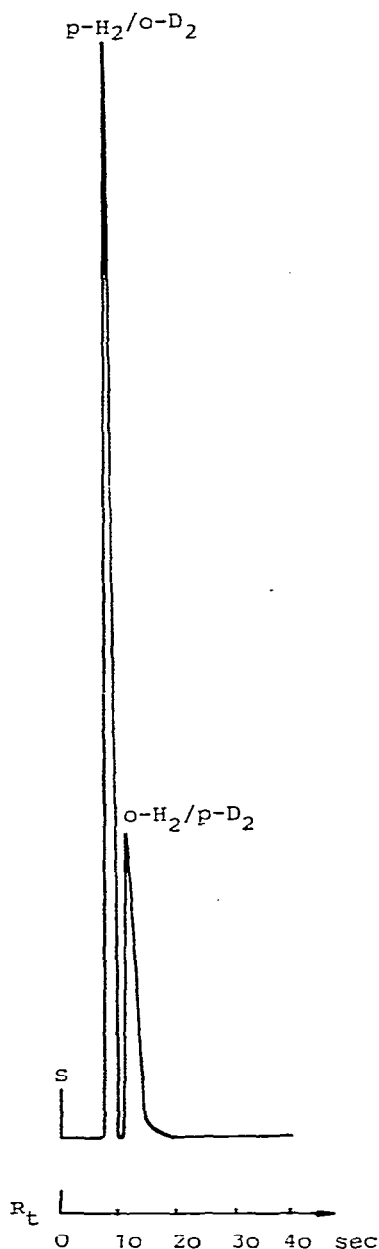


Fig. 3. Separation of a 1:1 mixture of H₂ and D₂. Same conditions as Fig. 1(a).

CONCLUSION

Using polymeric Schiff-base complexes as stationary phase in adsorption gas chromatography, it is possible to separate the spin isomers of H₂ and D₂ (but not of a mixture of both isotopes) at ambient temperature and with an extremely short retention time. This is a definite improvement on previous methods.

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