

The values Γ and a are connected by a universal relationship

$$a = \Gamma + W\rho, \quad (1)$$

where ρ is the equilibrium gas density.

Figure 1 shows three isosteres of the excess adsorption of krypton on NaA zeolite (Γ_1 , Γ_2 , Γ_3) in the region of low and elevated pressures, as well as the linear absolute adsorption isostere $a = 0.09 \text{ g} \cdot \text{g}^{-1}$, which cuts the isosteres Γ_2 and Γ_3 at points A_1 and A_2 . The coordinates of the points A_1 and A_2 allow one to determine the corresponding gas densities ρ_1 and ρ_2 because these points are the intersection points of the isostere a with

one of the isosteres Γ_2 and Γ_3 . If Γ and a in these points are known, one can calculate

$$W = (a - \Gamma_2)/\rho_1 \text{ и } W = (a - \Gamma_3)/\rho_2. \quad (2)$$

The average of two values W is $0.173 \text{ cm}^3 \cdot \text{g}^{-1}$, which is in excellent agreement with our previous estimation of this value $W = 0.166 \text{ cm}^3 \cdot \text{g}^{-1}$ (see ref. 1).

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Novel synthesis of fluoroalkyl-containing secondary alcohols using organofluoroiron compounds

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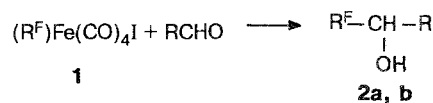
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Organoiron compounds containing fluoroalkyl groups σ -bonded with the iron atom form a well-known class of compounds.¹ Nevertheless, their use in organic synthesis, specifically for the introduction of fluoroalkyl groups into organic substrates, is practically unknown. Only two examples of this application have been reported, in which electron-enriched systems like arenes and thiols were the substrates.^{2,3}

We explored the possibility of using organoiron compounds, specifically perfluoroalkyltetracarbonyliron iodides (**1**), as the analogs of Grignard reagents in the reaction with aldehydes leading to fluorinated secondary alcohols (**2**). Following this method, alcohols **2a**, **b** were obtained from aromatic aldehydes.

The attempted reaction of complex **1** with benzaldehyde in tetrahydrofuran failed. When pyridine was used as the solvent the reaction was successful. To a solution of compound **1** (0.46 g) 1.2–1.5 mmol of an

aldehyde in 5 mL of dry pyridine was added with stirring for 5 min under an atmosphere of argon. After 15 min the reaction mixture was heated to 70 °C and stirred at this temperature for 1.5 h. The mixture was cooled, poured into 50 mL of dilute hydrochloric acid, and the product was extracted with CH_2Cl_2 (3×50 mL). The extract was washed with dilute hydrochloric acid, water, a conc. solution of $\text{Na}_2\text{S}_2\text{O}_5$, and brine, and dried with MgSO_4 . After evaporation of the solvent the residue was purified by column chromatography on SiO_2 .



$\text{R}^{\text{F}} = n\text{-C}_8\text{F}_7$; $\text{R} = \text{Ph}$ (**a**), $p\text{-NO}_2\text{C}_6\text{H}_4$ (**b**)

2,2,3,3,4,4,4-Heptafluoro-1-phenyl-1-butanol (2a), eluent, hexane—CHCl₃ (1 : 3). Yield 43 %. IR spectrum, ν/cm^{-1} : 3425 (OH). ¹H NMR (CDCl₃), δ : 3.12 (s, 1 H, OH); 5.16 (m, 1 H, CH); 7.38 (s, 5 H, C₆H₅). The characteristics are identical with those described previously.⁴

2,2,3,3,4,4,4-heptafluoro-1-*p*-nitrophenyl-1-butanol (2b), eluent, benzene, m.p. 65–66 °C. Yield 70 %. IR, ν/cm^{-1} : 3410 (OH). ¹H NMR (CDCl₃), δ : *J*, HzX: 3.23 (s, 1 H, OH); 5.39 (d, *J* = 18.5 Hz 1 H, CH); 7.97 (dd, 4 H, C₆H₄). Found (%): C, 37.58; H, 1.62; F, 40.73; N, 4.73. C₁₀H₆F₇NO₃. Calculated (%): C, 37.40; H, 1.88; F, 41.41; N, 4.36.

References

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Isotope effect in the dissolution of oxygen in chlorine pentafluoride

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The solubility of oxygen in liquid chlorine pentafluoride was studied over a narrow pressure range ($p = (3\div 5) \cdot 10^5$ Pa) and the simultaneous determination of the isotopic composition of oxygen in the liquid phase was carried out in order to further study the high solubility of oxygen in chlorine pentafluoride over a wide pressure range,¹ and to elucidate the features of the mechanism of intercalation of oxygen into liquid ClF₅, in particular, to reveal whether the separation of oxygen isotopes occurs in the course of the dissolution as was observed for water.² The basics of studying oxygen

solubility have been reported.¹ In studying the solubility we used oxygen from a cylinder with a natural abundance of the ¹⁸O isotope.

A sample (0.27 cm³) of liquid ClF₅ containing dissolved oxygen prepared for mass-spectrometric isotopic measurements was evaporated into a gas sample collector where it was cooled with liquid nitrogen in order to freeze out the chlorine pentafluoride. Oxygen for the isotopic analysis was collected into glass ampoules (cf. ref. 3). The isotopic shift ($\Delta^{18}\text{O}$) was measured to within ± 0.2 ‰. The experimental conditions corresponded to a thermodynamic heterogeneous oxygen-isotopic equilibrium.

The experimental results (Table 1) indicate that the solubility (*C*) and isotopic shift ($\Delta^{18}\text{O}$) maxima coincide. However, at a certain pressure, the isotope effect reverses its sign.

One can assume that the above phenomenon is due to changes in the structure of the solution and, hence, in the nature of the oxygen—solvent interaction.

These changes influence the fractionation of the isotopes, i.e., they increase the strength of the O₂—ClF₅ bond in comparison with the interaction of O₂ molecules in the gas phase; the zero value of $\Delta^{18}\text{O}$ points to the

Table 1. Changes in the solubility of oxygen in chlorine pentafluoride and in the isotopic shift $\Delta^{18}\text{O}$

<i>p</i> /MPa	Contact duration/h	<i>C</i> /mol. %	$\Delta^{18}\text{O}$ ‰
4.12	39	4.8	−2.3
3.82	48	5.7	−1.7
3.63	64	6.0	−1.9
3.23	104	6.1	0.0
3.14	231	6.7	+1.3
2.94	375	4.0	−1.9
2.93	735	4.0	−2.0