Gas Chromatography of Rare Earth Pivaloyltrifluoroacetone Adducts with Tri-*n*-butyl Phosphate and Tri-*n*-octylphosphine Oxide

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(Received September 2, 1971)

Recently the rare earth chelates with 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione[1] and pivaloyltrifluoroacetone (HPTA)[2,3] have been successfully gas chromatographed. It was shown that gas chromatography following the solvent extraction could be applied for the separation and determination of rare earth elements. The synergic extraction of rare earth ions was thoroughly studied using β-diketones and some organic phosphorus compounds. The high extractability was concluded to be caused by adduct formation. Thus, if the adduct compounds can be eluted, an interesting problem on the gas chromatography of rare earth metal complexes might be presented. In this paper, we wish to describe the gas chromatography of the adduct compounds of europium(III), erbium(III), and lutetium(III) with HPTA and tri-*n*-butyl phosphate (TBP), or with HPTA and tri-*n*-octylphosphine oxide (TOPO).

Five milliliters of an aqueous solution containing rare earth ions (0.01—0.1 mM in the concentration) and sodium acetate (0.2M), having the desired pH (finally pH 5.2—5.3), was shaken with 5 m*l* of benzene solution containing HPTA (0.1M) and TBP (0.1M), or HPTA (0.1M) and TOPO (0.1M), and 10—50 μl of the extract was then employed for gas chromatography. The $pH_{1/2}$ values of the extraction of europium and lutetium are 4.13 and 3.59 with HPTA only, 3.21 and 2.42 with HPTA and TBP, and 2.17 and 1.88 with HPTA and TOPO, respectively. The extracted species in the synergic extraction are $Eu(PTA)_3 \cdot 2TBP$, $Eu(PTA)_3 \cdot 2TOPO$, $Lu(PTA)_3 \cdot TBP$, and $Lu(PTA)_3 \cdot TOPO$. Typical chromatograms of europium complexes extracted are shown in Fig. 1. The retention times (min) obtained under the same conditions as described in Fig. 1 are as follows: europium, 4.4 and 5.5 with the HPTA extract,[4] 4.2 with the HPTA-TBP extract, and 7.2 with the HPTA-TOPO extract; erbium, 3.8, 4.2, and 6.6; lutetium, 2.9, 4.0, and 6.4. The sharp peaks favor the determination of each rare earth element. However, the fact that the separation factors become lower than in the case of the rare earth β-diketonates themselves, makes it unsuitable for the separation. The chromatograms of the synergic extracts which seem favorable for the determination differ a great deal from those of the tris-chelates, and the retention times of the former are generally greater except for europium-HPTA-TBP. This suggests that the adduct compounds can be eluted. For the europium-HPTA-TBP and europium-HPTA-TOPO extracts, the acetone solution of the eluted materials shows fluorescence with the same spectrum as that of the extracted benzene solution. The presence of TBP or TOPO in the eluted complexes is confirmed by comparing the IR spectra of the effluent with those of the tris-chelate, TBP, and TOPO. The results indicate that the rare earth-PTA adducts with TBP and TOPO can be gas-chromatographed without decomposition. Reproducible linear relationships are obtained between the detector response and the original concentration of aqueous europium(III) solution over the range 0.04—0.1 mM in the HPTA-TBP extraction, and 0.01—0.1 mM in the HPTA-TOPO extraction.

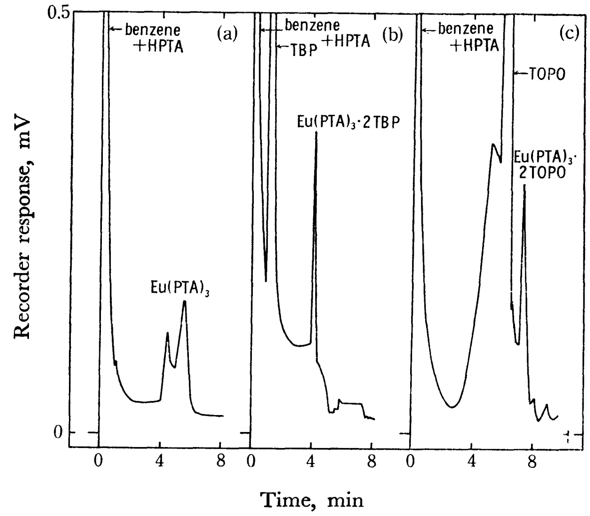

Fig. 1. Gas chromatograms of the extracts of europium(III) with (a) HPTA, (b) HPTA-TBP, and (c) HPTA-TOPO. (a) 152 μg Eu in solvent (50 μl), (b) 91 μg Eu in solvent (50 μl), and (c) 76 μg Eu in solvent (25 μl). Conditions: column, 75 cm × 3 mm i.d. stainless steel; column packing, 5% OV-101 on Chromosorb W AW DMCS (80—100 mesh); column temp., programmed from 150 to 300°C at 20°C/min; helium flow rate, 110 m*l*/min at 150°C. Detector: thermal conductivity detector, 150 mA.

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1) C. S. Springer, Jr., D. W. Meek, and R. E. Sievers, *Inorg. Chem.*, **6**, 1105 (1967).

2) T. Shigematsu, M. Matsui, and K. Utsunomiya, This Bulletin, **41**, 763 (1968).

3) M. Tanaka, T. Shono, and K. Shinra, *Anal. Chim. Acta*, **43**, 157 (1968).

4) The chromatogram of the extract shows two peaks (Fig. 1 (a)), whereas tris-chelate, $Eu(PTA)_3$, dissolved in benzene shows single peak having a retention time of 5.5 min.