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Gas Chromatography of Rare Earth Chelates of Pivaloyltrifluoroacetone*[1]

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The gas chromatographic behavior of Sc, Y, and rare earth chelates of a new β-diketone, pivaroyltrifluoroacetone (PTA), was investigated. PTA was synthesized by a Claisen condensation from pinacolin and ethyltrifluoroacetone. Sc, Y, Nd, Sm, Eu, Gd, Tb, Dy, Er, Yb, and Lu PTA chelates were prepared. Their elemental analyses and infrared spectra indicated that they were anhydrous tris chelates, and the TGA curves of the chelates proved their good volatile characteristics, showing approximately a 100% weight loss. Gas chromatograms of all the chelates and of mixtures of Sc, Y, and several rare earth chelates were obtained. Some relationships were observed between the retention time, the volatilization temperature, and the ionic radius of the central metal: With the decrease in the ionic radius, the retention time of the chelate decreased and the volatilization temperature became lower.

Recently, it has been recognized that the volatile characteristics of a number of metal β-diketone chelates make the gas-chromatographic technique of possible use for the separation of the metals. From this point of view, the chromatographic studies have been carried out on various metal chelates with acetylacetone,[1,2] trifluoroacetylacetone,[3-5] hexafluoroacetylacetone,[6] dipivaloylmethane,[7] 1,1,1,2,2,3,3,-heptafluoro-7,7-dimethyl-4,6-octanedione[8] (FOD), *etc.* By using the latter two β-diketones, Sievers and his co-workers studied the chromatographic behavior of rare earth elements in detail; as a result, they suggested the possibility of the simple and rapid separation of the individual elements.

The present authors have been attracted by the gas chromatography of metal β-diketone chelates, and have performed a systematic investigation with several β-diketones, some of which were synthesized in our own laboratory.

In this paper, the gas-chromatographic behavior of rare earth chelates with a new β-diketone, pivaloyltrifluoroacetone (PTA), will be described. The reagent possesses a trifluoromethyl group and a *t*-butyl group, both of which enhance the volatility of the chelates. Thus, rare earth PTA chelates were eluted by the gas phase, as were the dipivaloylmethane and the FOD chelates.

Experimental

Synthesis of Pivaloyltrifluoroacetone (PTA), (1,1,1-Trifluoro-5,5-dimethyl-3,5-hexanedione). The β-diketone was synthesized by Claisen condensation from pinacolin and ethyl trifluoroacetate.[9]

Ethyl trifluoroacetate was synthesized by trifluoroacetic acid and diethyl sulfate.[10,11] One mole of trifluoroacetic acid was neutralized with a sodium hydroxide solution (1.1 mol in 100 m*l* of water) and was then treated with diethyl sulfate (0.6 mol). After standing at room temperature for 3 hr, the reaction mixture was refluxed on a water bath, an ester was then obtained by distillation at 55°C. The crude ester, collected in a receiver cooled in ice water, was washed with 100 m*l* of a cold 5% sodium carbonate solution and dried over 25 g of anhydrous calcium chloride at 0°C. The product was finally purified by distillation after having been treated with concentrated sulfuric acid. In this procedure, 68 g of a pure ester with a boiling point of 60—62°C were produced.

The Claisen condensation was carried out in the following manner. To 0.55 mol of sodium methoxide

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*[1] A part of the work has been briefly reported previously: T. Shigematsu, M. Matsui and K. Utsunomiya, This Bulletin, **41**, 763 (1968).

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suspended in 100 m*l* of dry ether, 0.5 mol of ethyl trifluoroacetate and 0.5 mol of pinacolin were added successively. The mixture was then agitated for 2 hr. After the mixture had stood overnight, the ether and the ethanol were completely removed by evaporation under reduced pressure and by heating at 90°C for 6 hr. The sodium salt of PTA was then treated with 10% sulfuric acid, and the liberated PTA was extracted with ether. The ether solution was dehydrated with anhydrous calcium chloride, and the ether was evaporated off. The PTA was then converted into copper salt, the copper salt was decomposed with 10% sulfuric acid, and finally the PTA was purified by vacuum distillation. The purified product showed a boiling point of 40—41°C/17 mmHg; the yield was about 75%.

Preparation of Rare Earth Metal (III), Sc(III), and Y(III) PTA Chelates. The rare earth chelates were prepared by the method of Sievers *et al.*[8] Rare earth oxides were converted into nitrates, which were dissolved in methanol. Into the rare earth nitrate solution, a PTA methanol solution was then stirred, while the pH of the reacting mixture was maintained between 4 and 5 with a sodium hydroxide solution. The PTA chelates thus precipitated were filtered, air-dried, and recrystallized from benzene. The chelates were finally dried in a vacuum desiccator over phosphorus pentoxide.

The gas chromatograms were obtained with a Yanagimoto GCD-5DH apparatus equipped with a thermal conductivity detector. The column, 75 cm×3 mm i. d. and of stainless steel, was packed with 5% (by weight) of Dow Corning high vacuum silicone grease on Chromosorb W (60—80 mesh). Helium was used as the carrier gas. Chelate solutions were injected with a microsyringe. The thermogravimetric analysis was made with a Shimadzu Thermano Balance. About a 20-mg portion of a sample in a platinum dish was heated at a rate of 10°C/min in a nitrogen stream at a flow rate of 50 m*l*/min. The infrared spectra were measured with a Perkin-Elmer Model 521 spectrophotometer.

TABLE 1. THE MELTING POINTS OF RARE EARTH PTA CHELATES

	Mp °C	Color
Lu	160.0—163.2	White
Yb	160.2—161.0	White
Er	158.0—161.2	Pink
Dy	150.0—151.4	White
Tb	141.0—144.0	White
Gd	162.1—164.0	White
Eu	113.8—114.0	Yellow
Sm	113.1—118.0	White
Nd	126.5—128.0	Lavender
Sc	56.5— 57.0	White
Y	160.8—161.2	White

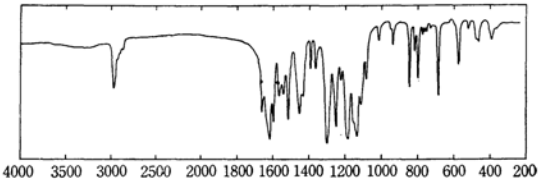

Fig. 1. IR spectrum of $Er(PTA)_3$ in KBr disk.

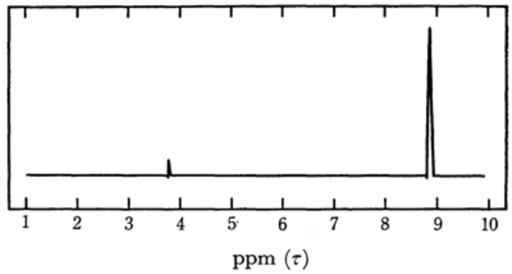

Fig. 2. NMR spectrum of $Sc(PTA)_3$. 20% $Sc(PTA)_3$ in $CDCl_3$, Standard: TMS, Temp.: 24°C

Results and Discussion

The melting points of scandium, yttrium, and rare earth chelates are summarized in Table 1, while the results of elemental analysis for several chelates are shown in Table 2. The carbon and hydrogen contents found are in good agreement with the calculated values of the tris-PTA chelates. In Fig. 1, the infrared spectrum of the erbium chelate (as a representative tervalent rare earth chelate) does not show a band attributable to OH stretching near 3400 cm⁻¹, this fact may prove that the chelates obtained are anhydrous $M^{III}(PTA)_3$-type chelates. The NMR spectrum of $Sc(PTA)_3$ is also presented in Fig. 2.

Figures 3, 4, 5 and 6 show typical chromatograms of some multicomponent mixtures. Samples, which were prepared by dissolving the PTA chelates in

TABLE 2. HYDROGEN AND CARBON CONTENTS

	PTA chelate	% C		% H	
		Calcd	Found	Calcd	Found
$Lu(PTA)_3$	$Lu(C_{24}H_{30}O_6F_9)$	37.91	37.30	3.98	4.12
$Er(PTA)_3$	$Er(C_{24}H_{30}O_6F_9)$	38.30	36.99	4.02	4.05
$Sm(PTA)_3$	$Sm(C_{24}H_{30}O_6N_9)$	39.18	39.09	4.11	4.31
$Nd(PTA)_3$	$Nd(D_{24}H_{30}O_6F_9)$	39.50	36.75	4.14	4.21
$Cu(PTA)_2$	$Cu(C_{16}H_{20}O_4F_6)$	42.34	42.49	4.44	4.55

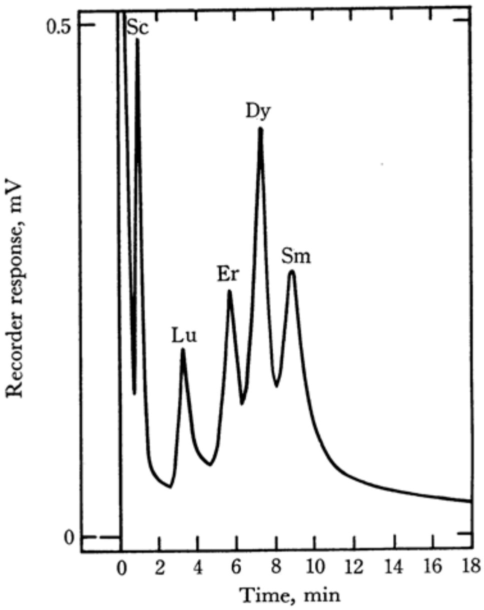

Fig. 3. The separation of $Sc(PTA)_3$, $Lu(PTA)_3$, $Er(PTA)_3$, $Dy(PTA)_3$ and $Sm(PTA)_3$. 23 μg Sc, 86 μg Lu, 83 μg Er, 123 μg Dy and 90 μg Sm in *n*-hexane (25 μ*l*). Column temp.: programmed from 170 to 270°C at 12°C/min. Injection port temp.: 270°C. Helium flow rate: 80 m*l*/min.

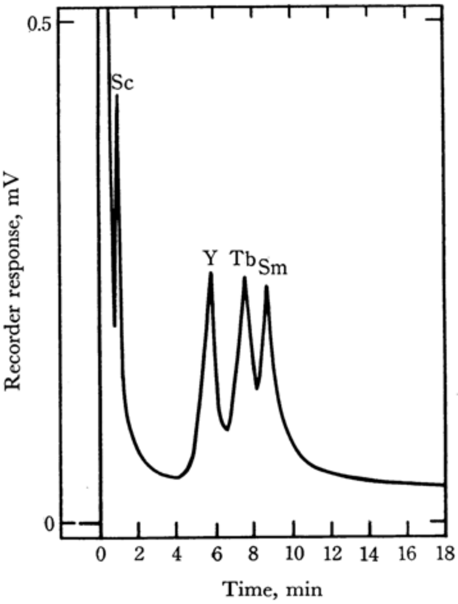

Fig. 5. The separation of $Sc(PTA)_3$, $Y(PTA)_3$, $Tb(PTA)_3$ and $Sm(PTA)_3$. 9 μg Sc, 91 μg Y, 107 μg Tb and 123 μg Sm in *n*-hexane (40 μ*l*). Conditions: same as those in Fig. 3.

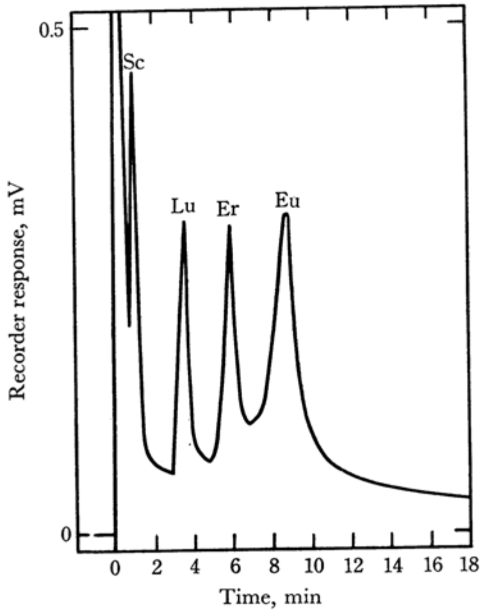

Fig. 4. The separation of $Sc(PTA)_3$, $Lu(PTA)_3$, $Er(PTA)_3$ and $Eu(PTA)_3$. 9 μg Sc, 172 μg Lu, 167 μg Er and 322 μg Eu in *n*-hexane (50 μ*l*). Conditions: same as those in Fig. 3.

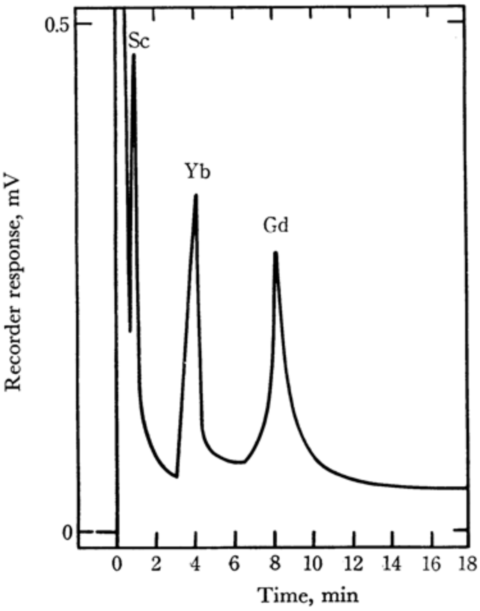

Fig. 6. The separation of $Sc(PTA)_3$, $Yb(PTA)_3$ and $Gd(PTA)_3$. 9 μg Sc, 114 μg Yb and 106 μg Gd in *n*-hexane (40 μ*l*).
Conditions: same as those in Fig. 3.

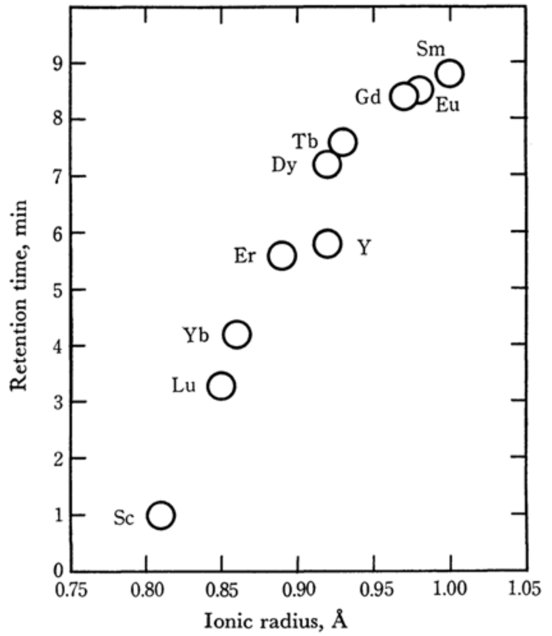

Fig. 7. Retention times for the rare earth PTA chelates as a function of ionic radius. Conditions: same as those in Fig. 3.

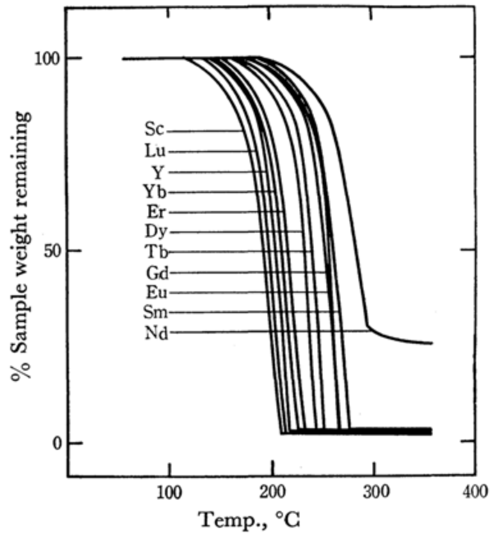

Fig. 8. Thermogravimetric curves of rare earth PTA chelates.

25—50 μl of n-hexane, were injected (at about 280°C), the column temperature was elevated from 170°C to 260°C at the rate of 12°C/min. For neodymium chelate, a higher injection temperature (*e.g.*, 320°C) was required.

The retention time of each PTA chelate was separately measured under similar condition (see Fig. 3), in Fig. 7, the values are plotted as a function of the ionic radii of the tervalent metal ions. The lower retention time corresponds well to the small ionic radius, as reported by Sievers *et al.* concerning the dipivaroylmethane[7] and FOD[8] chelates. As these figures indicate, it is not yet possible to separate all the rare earth metals individually at the same time. However, there may be a possibility for a group separation or for the separation of mixtures of some rare earth metals which do not contain any neighboring elements.

The thermogravimetric curves are shown in Fig. 8. The chelates of smaller metal ions, which show a shorter retention time, are volatilized at lower temperatures. The weight losses of all the chelates except the neodymium chelate approach 100%; this fact indicates that the PTA chelates are thermally stable in the volatilization process. The TGA curves of heavy rare earth metals and yttrium chelates may represent a combined sublimation-vaporization process, because the curves pass successively through the start of the weight loss, the melting temperature of the chelate, and the end of the weight loss.

Sievers and his collaborators[8] mentioned that a fluorocarbon substituent in a ligand markedly increased the volatility of the chelates, and that the volatile ability was also enhanced by substitution with sterically-crowded alkyl groups. Berg and Acosta[12] stated that the thermal stability of β-diketone chelates is related to the hydration (of the chelate), and that anhydrous chelates were much more stable than hydrated ones in the volatilization process.

The authors had previously studied rare earth and several other metal chelates with diisobutyrylmethane,[13] but they could not obtain satisfactory chromatograms for any rare earth metals except lutetium and erbium. Even lutetium and erbium chelates seemed to be hydrated and did not show a 100% weight loss, but one of about 75%, in the TGA curves. On the contrary, dipivaroylmethane and FOD, which possessed a more bulky alkyl group or fluorocarbon group, were proposed as useful chelating reagents for the gas chromatography of rare earth metals. The PTA presented in this investigation has a similar advantage; therefore, rare earth PTA chelates were well eluted by the gas phase. The authors will deal with the participation of the terminal group of β-diketone with the volatile characteristics of the rare earth and other metal chelates in the near future.

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