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Gas Chromatography of Aluminum, Gallium, and Indium β-Diketone Chelates

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The gas-chromatographic behavior of aluminum(III), gallium(III), and indium(III) chelates with various β-diketones was investigated. The β-diketones studied were acetylacetone and 8 synthesized, alkyl-substituted acetylacetones, benzoylacetone, dibenzoylmethane, trifluoroacetylacetone and its 5 synthesized alkyl derivatives, hexafluoroacetylacetone, benzoyltrifluoroacetone, furoyltrifluoroacetone, and thenoyltrifluoroacetone. The trifluoromethyl group increases the volatility of the chelates, while the aromatic group tends to decrease the volatility. In the alkyl-substituted acetylacetone series, the retention time of the chelates increases with an increase in the molecular weight, but it does not depend upon the volatility. On the other hand, the retention of the chelates containing the trifluoromethyl group is almost inversely correlated with the volatility.

During the past decade, the gas chromatography of volatile metal chelates has attracted much attention; many works were summarized in a monograph[1] in 1965. Beryllium(II) and aluminum(III) chelates with acetylaceton,[2-4] trifluoroacetylacetone,[2-11] and hexafluoroacetylacetone[4,12,13] have been most extensively investigated. The results indicated that the substitution of fluorine for the hydrogen of the methyl group in the ligand increased the volatility and also sometimes the thermal stability of metal chelates. Other tervalent metals, chromium(III),[3,4,6,7,14,15] gallium(III),[16,17] indium(III),[16,17] and iron(III)[9-11,18] chelates, were well studied, and the separation of these metal ions by means of gas chromatography was also examined using trifluoroacetylacetone[16,17] or hexafluoroacetylacetone.[12] However, little has been published on systematic investigations with various β-diketones which have different terminal groups, except for Tanaka and his co-workers, study[19] of the gas chromatography of some copper β-diketones chelates and Eisentraut and Sievers's study[20] of the thermogravimetry of aluminum, chromium(III), iron(III), and rhodium(III) chelates.

The present investigation was undertaken in order to evaluate the effect of the substitution of acetylacetone for methyl groups on the volatility. the thermal stability, and the gas chromatographic behavior of metal chelates. Aluminum, gallium, and indium were chosen as the central metals so that the present results could be readily compared with the results already reported. As the ligands, 21 β-diketones, acetylacetone and its alkyl derivatives, benzoylacetone dibenzoylmethane, trifluoroacetylacetone and its

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[1] R. W. Moshier and R. E. Sievers, "Gas Chromatography of Metal Chelates," Pergamon Press, New York (1965).

[2] R. D. Hill and H. Gesser, *J. Gas Chromatog.*, **1**, 11 (1963).

[3] R. E. Sievers, B. W. Ponder, M. L. Morris, and R. W. Moshier, *Inorg. Chem.*, **2**, 693 (1963).

[4] W. D. Ross, *Anal. Chem.*, **35**, 1596 (1963).

[5] K. Tanikawa, K. Hirano, and K. Arakawa, *Chem. Pharm, Bull.*, **15**, 915 (1967).

[6] D. K. Albert, *Anal. Chem.*, **36**, 2034 (1964).

[7] W. D. Ross, R. E. Sievers, and G. Wheeler, Jr., *ibid.*, **37**, 598 (1965).

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[13] W. D. Ross and G. Wheeler, Jr., *Anal. Chem.*, **36**, 266 (1964).

[14] W. D. Ross and R. E. Sievers, *ibid.*, **41**, 1109 (1969).

[15] J. Savory, P. Mushak, F. W. Sunderman, Jr., R. H. Estes, and N. O. Roszel, *ibid.*, **42**, 294 (1970).

[16] J. E. Schwarberg, R. W. Moshier, and J. H. Walsh, *Talanta*, **11**, 1213 (1964).

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[19] M. Tanaka, T. Shono, and K. Shinra, *Nippon Kagaku Zasshi*, **89**, 669 (1968).

[20] K. J. Eisentraut and R. E. Sievers, *J. Inorg. Nucl. Chem.*, **29**, 1931 (1967).

alkyl derivatives, hexafluoroacetylacetone, benzoyltrifluoroacetone, furoyltrifluoroacetone, and thenoyltrifluoroacetone were compared.

Experimental

Preparation of β-Diketones. The β-diketones were prepared by Claisen condensation, except for eight β-diketones—acetylacetone, benzoylacetone, dibenzoylmethane, trifluoroacetylacetone, furoyltrifluoroacetone, thenoyltrifluoroacetone, benzoyltrifluoroacetone, and hexafluoroacetylacetone—which were obtained from the Dojindo Co., Ltd., Research Laboratories. The alkyl-substituted β-diketones, propionylacetone, isobutyrylacetone, pivaloylacetone, diisobutyrylmethane,[21] isobutyrylpivaloylmethane, dipivaloylmethane, dipropionylmethane, and pivaloylpropionylmethane, were prepared by the condensation of the corresponding esters and ketones in the presence of sodium amide,[22] while the fluorinated β-diketones, trifluoroacetylpropionylmethane, trifluoroacetylisobutyrylmethane, trifluoroacetylpivaloylmethane,[23] trifluoroacetyl-α-methylbutyrylmethane, and trifluoroacetylisovalerylmethane, were prepared from ethyl trifluoroacetate and the corresponding ketones in the presence of sodium methoxide.[24] The crude products were converted to the copper chelates by treatment with a solution of cupric acetate in hot aqueous methanol. After recrystallization from benzene, the copper chelates were dissolved in ether and decomposed with 10% sulfuric acid. The boiling points of these β-diketones are given in Table 1, along with the symbols used in this paper.

Preparation of Aluminum(III), Gallium(III), and Indium(III) Chelates. The β-diketonates were prepared by adding a stoichiometric quantity of β-diketone, dissolved in ethanol or methanol, to an aqueous solution of the metal nitrate. The solution was either buffered with sodium acetate or adjusted to pH 6 with a 1 M ammonia solution. The metal chelate thus precipitated was filtered off, dried, recrystallized from benzene, and then dried in a vacuum desiccator over phosphorus pentoxide. Attempts to synthesize the metal chelates with HPrA, HDPrM and HPiPrM by the same procedure failed. The melting points of the chelates thus prepared are shown in Table 2; the results of the elemental analyses of the alkyl substituted β-diketonates are in good agreement with the values calculated for the (1 : 3) chelate.

The thermogravimetric analysis of metal chelates was made with a Shimadzu thermo-balance. About 20 mg of a sample placed in a platinum dish were heated at a rate of 10°C/min in a nitrogen atmosphere and at a flow rate of 50 m*l*/min. The gas chromatograms were obtained with a Yanagimoto gas chromatograph GCD-5DH equipped with a thermal conductivity detectar. The column, 75 cm × 3 mm i.d., stainless steel, was packed with 5% (by weight) Dow Corning high-vacuum silicone grease on Chromosorb W AW DMCS (80—100 mesh). Helium was used as the carrier gas. Sample solutions, prepared by dissolving the chelates in benzene, were injected at the optimum column temperature for the chelates. The injection-port temperature was maintained at 30°C above the column temperature.

Results and Discussion

Thermogravimetric Analysis. Thermogravimetric analysis is a well-established technique for surveying the volatility of various metal chelates. It presents information on whether the chelates in question are sufficiently volatile and thermally stable to give

TABLE 1. β-DIKETONES INVESTIGATED

β-Diketone	Symbol	Structural formula	Bp (°C)
Acetylacetone	HAA	$CH_3COCH_2COCH_3$	
Propionylacetone	HPrA	$CH_3COCH_2COC_2H_5$	73—73.5/19 mmHg
Isobutyrylacetone	HIBA	$CH_3COCH_2COCH(CH_3)_2$	71—72/30 mmHg
Pivaloylacetone	HPiA	$CH_3COCH_2COC(CH_3)_3$	74—75/30 mmHg
Diisobutyrylmethane	HDIBM	$(CH_3)_2CHCOCH_2COCH(CH_3)_2$	49—50/4.5 mmHg
Isobutyrylpivaloylmethane	HIBPM	$(CH_3)_3CCOCH_2COCH(CH_3)_2$	77—78/13 mmHg
Dipivaloylmethane	HDPM	$(CH_3)_3CCOCH_2COC(CH_3)_3$	96—98/27 mmHg
Dipropionylmethane	HDPrM	$C_2H_5COCH_2COC_2H_5$	65/18 mmHg
Pivaloylpropionylmethane	HPiPrM	$(CH_3)_3CCOCH_2COC_2H_5$	70/13 mmHg
Benzoylacetone	HBzA	$CH_3COCH_2COC_6H_5$	
Dibenzoylmethane	HDBM	$C_6H_5COCH_2COC_6H_5$	
Trifluoroacetylacetone	HTFA	$CF_3COCH_2COCH_3$	
Trifluoroacetylpropionylmethane	HTPrM	$CF_3COCH_2COC_2H_5$	31—31.5/26 mmHg
Trifluoroacetylisobutyrylmethane	HTIBM	$CF_3COCH_2COCH(CH_3)_2$	42—43.5/26 mmHg
Trifluoroacetylpivaloylmethane	HTPM	$CF_3COCH_2COC(CH_3)_3$	47—47.5/18 mmHg
Trifluoroacetyl-α-methylbutyrylmethane	HTMBM	$CF_3COCH_2COCH(CH_3)C_2H_5$	50—51/22 mmHg
Trifluoroacetylisovalerylmethane	HTIVM	$CF_3COCH_2COCH_2CH(CH_3)_2$	57—58/26 mmHg
Furoyltrifluoroacetone	HFTA	$CF_3COCH_2COC_4H_3O$	
Thenoyltrifluoroacetone	HTTA	$CF_3COCH_2COC_4H_3S$	
Benzoyltrifluoroacetone	HBFA	$CF_3COCH_2COC_6H_5$	
Hexafluoroacetylacetone	HHFA	$CF_3COCH_2COCF_3$	

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TABLE 2. MELTING POINTS OF ALUMINUM, GALLIUM, AND INDIUM CHELATES

Chelate	Mp (°C)	(Reference)	Chelate	Mp (°C)	(Reference)	Chelate	Mp (°C)	(Reference)
$Al(AA)_3$	192.5	(112,[25] 198[26])	$Ga(AA)_3$	194		$In(AA)_3$	181.5	
$Al(IBA)_3$	oil		$Ga(PiA)_3$	oil		$In(DIBM)_3$	96.0	
$Al(PiA)_3$	oil		$Ga(DIBM)_3$	129		$In(IBPM)_3$	96.5	
$Al(DIBM)_3$	139		$Ga(IBPM)_3$	148.5		$In(DPM)_3$	204—209	
$Al(IBPM)_3$	181		$Ga(DPM)_3$	220.5		$In(BzA)_3$	214	
$Al(DPM)_3$	257	(264—265[27])	$Ga(BzA)_3$	222		$In(DBM)_3$	251	
$Al(BzA)_3$	221	(223.5—224.0[28])	$Ga(DBM)_3$	294		$In(TFA)_3$	122—124	(118—120[29])
$Al(DBM)_3$	295—300		$Ga(TFA)_3$	125—126	(128—129.5[29])	$In(TPrM)_3$	99—102	
$Al(TFA)_3$	120	(117,[25] 120—121[29])	$Ga(TPrM)_3$	63.0		$In(TIBM)_3$	104—107	
$Al(TPrM)_3$	61.5		$Ga(TIBM)_3$	67.0		$In(TPM)_3$	112—119	
$Al(TIBM)_3$	65.0		$Ga(TPM)_3$	67.0		$In(TMBM)_3$	53.0	
$Al(TPM)_3$	71.5	(70—72[19])	$Ga(TMBM)_3$	70.0		$In(TIVM)_3$	oil	
$Al(TMBM)_3$	71.0		$Ga(TIVM)_3$	oil		$In(FTA)_3$	194—196	
$Al(TIVM)_3$	oil		$Ga(FTA)_3$	206—208		$In(BFA)_3$	137—140	
$Al(FTA)_3$	185—188	(204—205[25])	$Ga(BFA)_3$	152—154		$In(TTA)_3$	154—156	(164.6[30])
$Al(BFA)_3$	169—171	(173—174[25])	$Ga(TTA)_3$	181—183	(184—184.2[30])	$In(HFA)_3$	73.0	
$Al(TTA)_3$	198—201	(203—205[25])	$Ga(HFA)_3$	68.5—70.0	(68.0—69.5[12])			
$Al(HFA)_3$	71.5	(70.5—71.3[12])						

good gas chromatograms. The TGA curves of aluminum, gallium, and indium β-diketonates are shown in Figs. 1 to 3.

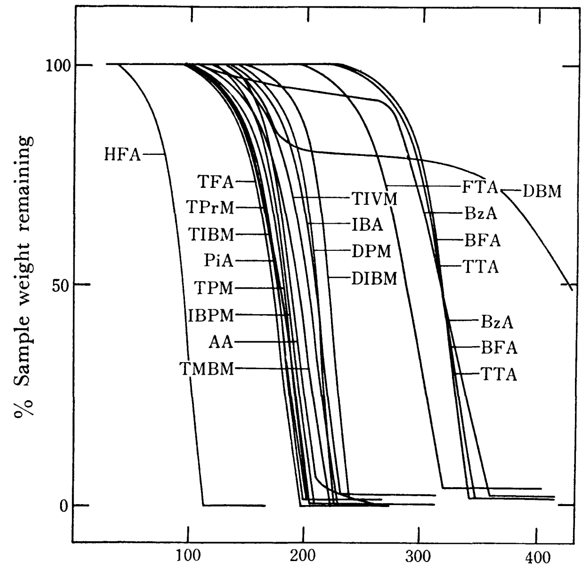

Fig. 1. Thermogravimetric curves of aluminum β-diketonates.

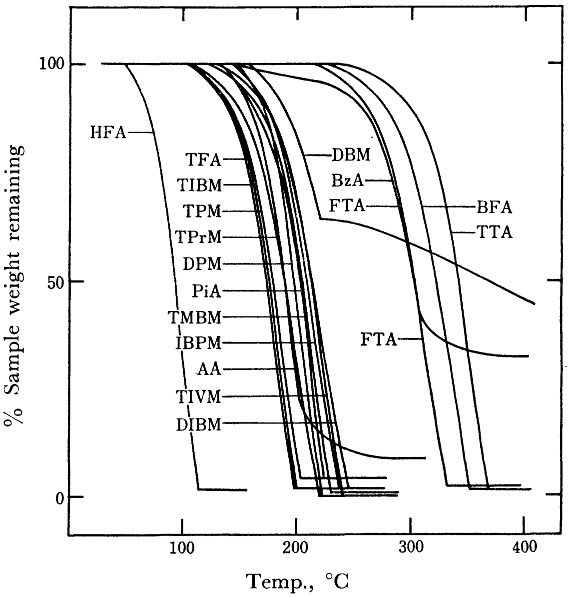

Fig. 2. Thermogravimetric curves of gallium β-diketonates.

The aluminum β-diketonates are volatile and are thermally stable, except for $Al(BzA)_3$ and $Al(DBM)_3$, which decompose over 200°C instead undergoing sublimation. The volatility increases in the following order: for alkyl-substituted acetylacetone chelates, $Al(DIBM)_3 < Al(DPM)_3 \leq Al(IBA)_3 < Al(AA)_3 < Al(IBPM)_3 < Al(PiA)_3$; for fluorinated β-diketone chelates, $Al(TTA)_3 \leq Al(BFA)_3 < Al(FTA)_3 \ll Al(TIVM)_3 < Al(TMBM)_3 < Al(TPM)_3 < Al(TIBM)_3 \leq Al(TPrM)_3 < Al(TFA)_3 \ll Al(HFA)_3$ (Fig. 1). Gallium(III) acetylacetonate does not completely sublime, and $Ga(BzA)_3$ and $Ga(DBM)_3$ decompose. The volatility increases in this order: $Ga(DIBM)_3 < Ga(IBPM)_3 < Ga(PiA)_3 < Ga(DPM)_3 < Ga(AA)_3$; $Ga(TTA)_3 < Ga(BFA)_3 < Ga(FTA)_3 \ll Ga(TIVM)_3 < Ga(TMBM)_3 < Ga(TPrM)_3 < Ga(TPM)_3 < Ga(TIBM)_3 < Ga(TFA)_3 \ll Ga(HFA)_3$ (Fig. 2). Many of the indium(III) chelates do not quantitatively sublimate, and $In(AA)_3$, $In(BzA)_3$, $In(DMB)_3$, and $In(HFA)_3$ decompose. The increasing order of the volatility is as follows: $In(DIBM)_3 < In(IBPM)_3 < In(DPM)_3$; $In(TTA)_3 < In(BFA)_3 < In(FTA)_3 \ll In(TIVM)_3 <$ In-

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[25] E. W. Berg and J. T. Truemper, *Anal. Chim. Acta*, **32**, 245 (1965).

[26] R. W. Moshier and R. E. Sievers, "Gas Chromatography of Metal Chelates," p. 141, Pergamon Press, New York (1965).

[27] *Ibid.*, p. 148.

[28] *Ibid.*, p. 147.

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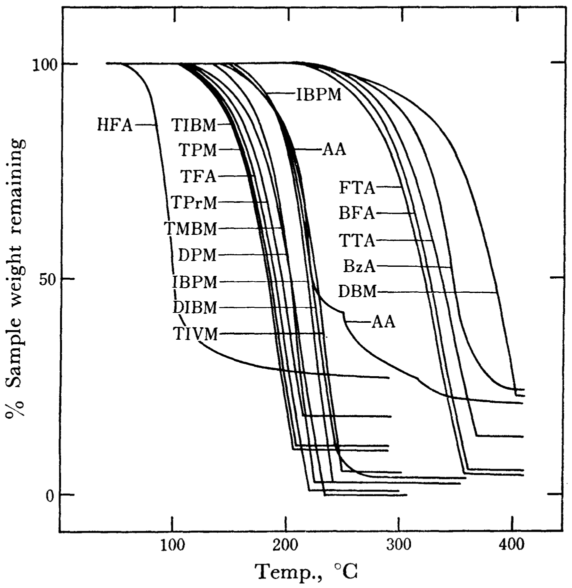


Fig. 3. Thermogravimetric curves of indium β-diketonates.

$(TMBM)_3 < In(TPrM)_3 < In(TFA)_3 < In(TPM)_3 < In(TIBM)_3$ (Fig. 3).

Usually, the substitution of the fluoromethyl group increases the volatility of the chelates, while an aryl group, such as a furyl, phenyl, or thienyl group, tends to decrease the volatility. Accordingly, FTA, BFA, and TTA chelates are less volatile, in spite of the presence of a trifluoromethyl group, and BzA and DBM chelates decompose without sublimation. However, there is no general correlation between the volatility of alkyl-substituted chelates and their substituted groups, except in the one case of indium(III) chelates, where the volatility does seem to increase in the order of substitution: $CH_3- < (CH_3)_2CH- < (CH_3)_3C-$.

Gas Chromatography of Alkyl-substituted β-Diketonates. Figure 4 shows gas chromatograms of the aluminum, gallium, and indium chelates of some β-diketones. The elution is strongly temperature-dependent. Aluminum chelates give optimal chromatograms at a column temperature of 200°C, but at this temperature the peaks of gallium and indium chelates are broad and tailed. The peak sharpens at a higher column temperature. Gallium chelates show good chromatograms at 212°C, and indium chelates, at 220°C. As may be seen in the chromatograms of $Ga(AA)_3$ and $Ga(PiA)_3$ (Fig. 5(a), (b)), a small peak or a shoulder is observed prior to the main peak. Such a confusing peak can not be removed by varying the temperature or by employing another kind of column; it might arise from a thermally-decomposed impurity.

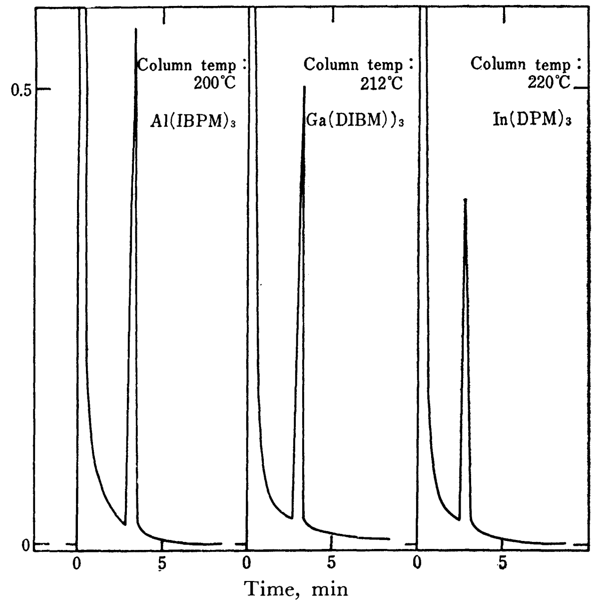


Fig. 4. Chromatograms of $Al(IBPM)_3$, $Ga(DIBM)_3$, and $In(DPM)_3$. 28 μg Al, 49 μg Ga, and 102 μg In in benzene (10 μl).

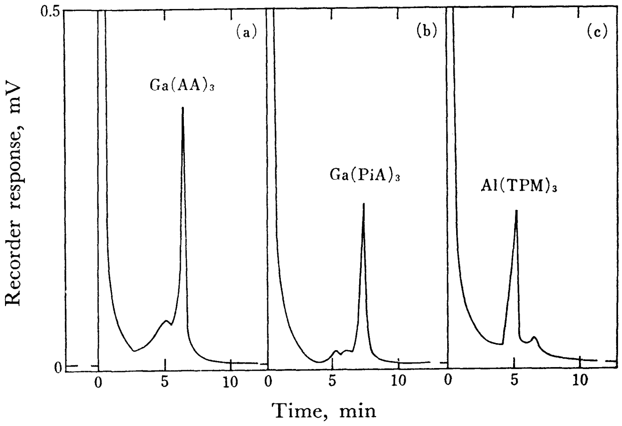
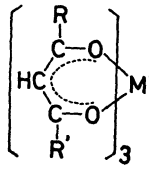


Fig. 5. Chromatograms of $Ga(AA)_3$, $Ga(PiA)_3$, and $Al(TPM)_3$. (a) 120 μg $Ga(AA)_3$, and (b) 152 μg $Ga(PiA)_3$ in benzene (20 μl). Column temperature: programmed from 100 to 250°C at 20°C/min. Helium flow rate: 95 ml/min. (c) 231 μg $Al(TPM)_3$ in benzene (10 μl). Column temperature: 178°C. Helium flow rate: 81 ml/min.

The retention data of the metal chelates with alkyl substituted β-diketones are summarized in Table 3. The retention times of the chelates increase in the following order: $Al(AA)_3 < Al(IBA)_3 < Al(PiA)_3 \approx Al(DIBM)_3 < Al(IBPM)_3 < Al(DPM)_3$, $Ga(AA)_3 < Ga(PiA)_3 < Ga(DIBM)_3 \approx Ga(IBPM)_3 < Ga(DPM)_3$, $In(DIBM)_3 < In(IBPM)_3 < In(DPM)_3$. This order is in good agreement with an empirical rule of gas chromatography that the retention time of organic compounds increases with an increase in the molecular weight. However, no correlation is obtained between the elution behavior and the volatility of the chelates observed in the TGA curve. For the separation of aluminum, gallium, and indium, DIBM, IBPM, and DPM chelates are suitable, but AA, BzA, and DBM chelates can not be used because of their smaller volatility.

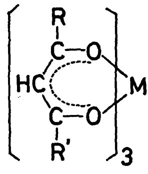
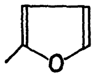
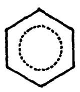
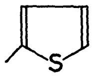
Gas Chromatography of Fluorinated β-Diketonates. Aluminum, gallium, and indium chelates with TFA, TPrM, TIBM, TPM, TMBM, and TIVM are eluted at a column temperature between 120 and 200°C. For FTA, BFA, and TTA chelates, the column temperature must rise about 100°C higher than for the above β-diketonates: $Al(FTA)_3$ and $Al(BFA)_3$ are eluted at 230°C, while $Al(TTA)_3$, $Ga(TTA)_3$, and $In(FTA)_3$ are eluted at 250°C with decomposed products. The TGA curves predict that the column temperature for $In(BFA)_3$ and $In(TTA)_3$ will be 300°C or more.

TABLE 3. RETENTION TIME OF ALUMINUM, GALLIUM, AND INDIUM CHELATES WITH NONFLUORINATED β-DIKETONES (min)

		AA	IBA	PiA	DIBM	IBPM	DPM	BzA	DBM	
	R	CH_3-	CH_3-	CH_3-	$(CH_3)_2CH$-	$(CH_3)_3C$-	$(CH_3)_3C$-	CH_3-	C_6H_5-	
	R'	CH_3-	$(CH_3)_2CH$-	$(CH_3)_3C$-	$(CH_3)_2CH$-	$(CH_3)_2CH$-	$(CH_3)_3C$-	C_6H_5-	C_6H_5-	
Aluminum		0.4	1.4	2.6	2.6	3.4	4.0	nv	nv	(column temp.: 200°C) (Helium flow rate: 80 m*l*/min)
Gallium		0.7*	—**	1.8	3.0	3.0	3.8	nv	nv	(column temp.: 212°C) (Helium flow rate: 79 m*l*/min)
Indium		nv	—**	—**	2.3	2.6	2.8	nv	nv	(column temp.: 220°C) (Helium flow rate: 75 m*l*/min)

nv: non-volatile. *: partly decomposed. **: chelates could not be synthesized.

TABLE 4. RETENTION TIME OF ALUMINUM, GALLIUM, AND INDIUM CHELATES WITH FLUORINATED β-DIKETONES (min)

		HFA	TFA	TPrM	TIBM	TPM	TMBM	TIVM	FTA	BFA	TTA
	R=CF_3 R'	CF_3-	CH_3-	C_2H_5-	$(CH_3)_2CH$-	$(CH_3)_3C$-	$C_2H_5\overset{CH_3}{\overset{\vert}{C}}H$-	$(CH_3)_2CHCH_2$-			
Aluminum		4.0	1.3	3.2	3.9	5.1	11.8	13.3	1.8	5.2	5.3[a)] 7.1
Gallium		5.3	2.7	4.8	5.9	7.2	15.8	19.7	2.5	6.0	6.2[a)] 9.0
Indium		ne	2.5	4.2	4.6	5.3	6.0	9.5	3.2[b)] 3.6	ne	ne
Operating conditions		column temp.: 90°C Helium flow rate: 47 m*l*/min.	For Al and Ga chelates, column temp.: 138°C, Helium flow rate: 67 m*l*/min. For In chelates, column temp.; 154°C Helium flow rate: 50 m*l*/min.						column temp.: 250°C Helium flow rate: 45 m*l*/min.		
Order of elution		← fast elution									late elution →

a) partly decomposed. b) decomposed products. ne: chelates were not eluted.

Therefore a column coated with 3% (by weight) silicone gum SE-30 on Chromosorb W AW DMCS (80—100 mesh) was used for these indium chelates; nevertheless, the chelates were not eluted even at a column temperature between 300 and 340°C. In the chromatograms of Al(TPrM)$_3$, Al(TIBM)$_3$, and Al(TPM)$_3$, a main peak is followed by a smaller peak (Fig. 5(c)); although no detailed study was carried out, this phenomenon might result from the *cis* and *trans* isomers, as has been reported for Cr(TFA)$_3$.[3]

The retention data of fluorinated β-diketone chelates are listed in Table 4. The table indicates that HTFA, HTPrM, HTIBM, HTPM, HTMBM, and HTIVM can be used for the separation of aluminum, gallium, and indium. An example using HTPrM is presented in Fig. 6. The retention time of fluorinated β-diketonates increases in this order: $M(HFA)_3 \ll M(TFA)_3 < M(TPrM)_3 < M(TIBM)_3 < M(TPM)_3 < M(TMBM)_3 < M(TIVM)_3 \ll M(FTA)_3 < M(BFA)_3 < M(TTA)_3$; in contrast with the alkyl-substituted acetylacetonates series, it evidently depends upon the volatility of the chelates. The increasing order of the retention time is quite the same as the decreasing order of the volatility of aluminum chelates; a similar relationship is observed for gallium chelates except for the position of TPrM and for indium chelates except for the position of TFA and TPrM.

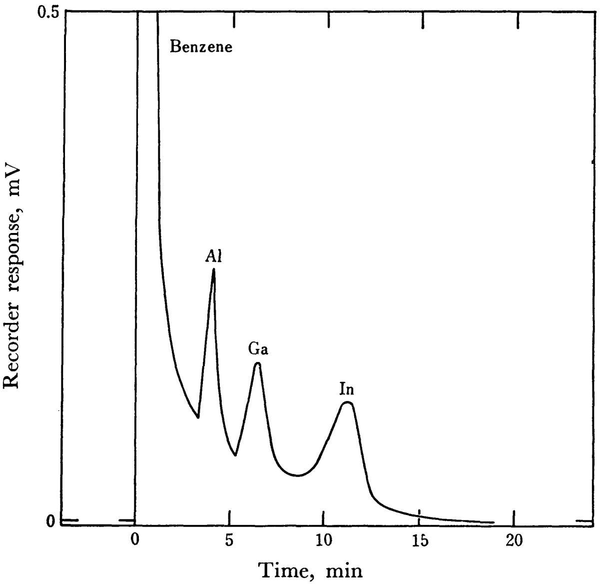


Fig. 6. Separation of aluminum, gallium, and indium TPrM chelates. 29 μg Al, 72 μg Ga, and 230 μg In in benzene (25 μl). Column temperature: 128°C. Helium flow rate: 81 ml/min.

In the present research, the substitution on the γ-position of β-diketonates was not investigated, because it had previously been reported that substitution on this position with bromine,[20] methyl,[31] or isopropyl[31] group reduced the volatility of the metal chelates.

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31) G. K. Schweitzer, B. P. Pullen, and Yi-Hung Fang, *Anal. Chim. Acta*, **43**, 332 (1968).