Kinetics of Ligand Isotopic Exchange of Tris(acetylacetonato)gallium(III) and Related β-Diketonato Complexes in Tetrahydrofuran

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The rate of isotopic exchange of tris(acetylacetonato)gallium(III)[Ga(acac)$_3$] and acetylacetone-^{14}C(Hacac) in tetrahydrofuran (THF) is expressed by the formula $R=[\text{complex}](k_1+k_2[H_2O]+k_3[\text{Hacac}])$ and the k_1, k_2, and k_3 are $\leq 2\times10^{-6}\,s^{-1}$, $0.31\times10^{-3}\,M^{-1}\,s^{-1}$ and $0.71\times10^{-4}\,M^{-1}\,s^{-1}$, at 0 °C, respectively. The activation enthalpies and entropies are 18±2 and 19±2 kcal-mol^{-1}, and −13±6 and −20±6 cal·K^{-1} mol^{-1}, for k_2 and k_3, respectively. Trichloroacetic acid gives acid catalysis. A dissociative mechanism through an intermediate containing a unidentate ligand is suggested. The isotopic exchange rate decreases in the sequence In>Ga>Al for a given β-diketonato complex, and with increase in pK_a of the β-diketone for given central metal ions.

Little information is available concerning the kinetics and mechanism of complex formation reactions of gallium(III) ions. Eigen gave the half-life of coordinated water molecules in gallium(III) perchlorate in water to be of the order of 10^{-3} s.$^{1)}$ Fiat and Connick, and Movius and Matwiyoff studied the exchange of solvent molecules coordinated to Ga(III) in water$^{2)}$ and dimethylformamide,$^{3)}$ respectively, and compared the activation parameters with those for aluminium(III). On the basis of small $\Delta H^{\ast}$ and big minus $\Delta S^{\ast}$ values, they suggested an S_N2 mechanism for the gallium(III) ions.

We found that the ligand isotopic exchange of tris-type complexes of octahedral aluminium(III) with acetylacetone$^{4)}$ and dibenzoylmethane$^{5)}$ in various organic solvents is much slower than that of coordinated solvent molecules in $[Al(H_2O)_6]^{3+}$ in water,$^{1,2,6)}$ and discussed the mechanism. We have now examined the rate of isotopic exchange of some β-diketonato complexes of aluminium(III), gallium(III), and indium(III), and found that the rate of exchange of tris(acetylacetonato)gallium [Ga(acac)$_3$] with acetylacetone-^{14}C(Hacac) is measurable in some organic solvents including tetrahydrofuran (THF). Detailed kinetic studies are given and the results compared with those of related complexes.

Experimental

Materials. *The Labelled Ligands*: Acetylacetone-^{14}C (Hacac) was prepared similarly to the method given in Ref. 4, and the specific activity was adjusted to *ca.* 0.02 μCi per mg, the water content being *ca.* 10^{-1} M. Dibenzoylmethane-^{14}C (Hdbm) was synthesized from acetic acid (12 g, 0.2 mol) containing 1 mCi ^{14}C *via* acetophenone by the usual method. On recrystallization from ethanol for three times, the yield was 29% on the basis of acetic acid, the specific activity being *ca.* 0.03 μCi per mg. Benzoylacetone-^{14}C (Hbzac) was similarly prepared by use of ethylacetate in place of ethyl benzoate. The yield was 34%, the specific activity being 0.01 μCi per mg.

The Complexes. Tris(acetylacetonato)gallium(III) was synthesized by a similar method to Moeller and Gulyas's$^{7)}$ by use of ethanol and gallium(III) chloride in place of dioxane and gallium(III) sulfate respectively. The yield was *ca.* 73%. The product was sublimed at 1 mmHg at 180 to 185 °C to give colorless crystals with mp 190 to 192 °C. Tris(benzoylacetonato)gallium(III) was prepared from gallium(III) chloride solution (0.003 mol in 3 ml of water) by adding Hbzac (0.013 mol) in ethanol (30 ml) and adjusting the pH with sodium acetate (1.2 g in 3 ml of water). The product was recrystallized from a mixture of THF and petroleum ether containing Hbzac, and washed with diethylether. The yield was *ca.* 90%. This is a mixture of *mer* and *fac* isomer, but was used without separation for the isotopic exchange studies.

Tris(1-oxo-1,3-diphenyl-2-prope-3-olato)gallium(III) [Ga(dbm)$_3$] was synthesized from gallium(III) chloride solution (0.002 mol in 2 ml of water) by treating with Hdbm (0.0089 mol in 90 ml ethanol) and sodium acetate solution (0.8 g in 3 ml of water). The crude product was dissolved in THF (11 ml) containing a small amount of Hdbm, filtered and treated with petroleum ether to give colorless crystals, which were washed with chilled diethylether and dried *in vacuo.* mp 284.5∼286.5 °C (literature value 284 °C; prepared in dioxane by use of metallic sodium in place of sodium acetate).$^{8)}$ The yield was *ca.* 80%.

Tris(benzoylacetonato)aluminium(III) [Al(bzac)$_3$] was similarly prepared according to Baly and Desch's method$^{6)}$ the yield being *ca.* 93%. Bis(1-oxo-1,3-diphenyl-2-prope-3-olato) beryllium [Be(dbm)$_2$] was prepared similarly to [Ga(dbm)$_3$] in aqueous ethanol, and crystallized from THF by adding petroleum ether. The yield was 39%. The corresponding indium (III) complexes were also synthesized similarly to those of the aluminium(III) complexes.$^{9)}$ They are sensitive towards atomospheric moisture and the organic solvents should be carefully dehydrated.

Trichloroacetic acid, THF, and the reagents for scintillation spectrometry were purified as in the literature.$^{4)}$

Kinetic Runs. The essential scheme of the experimental procedure is the same as that in Ref. 4. The gallium(III) complexes are, however, more soluble in various organic solvents, and the rate is much larger than that of the aluminium(III) complexes. Hence the procedure was slightly modified as follows. The complex (0.05 to 0.2 M) and the labelled ligand solution in THF (0.05 to 0.2 M) were kept in a thermostat, mixed swiftly and dispensed into five small glass-stoppered tubes, so that each tube contains *ca.* 2 ml of the reaction mixture. They were kept in the thermostat and taken out one by one at appropriate time intervals. The content was added into chilled petroleum ether (−20 °C) to arrest the exchange reaction. Crystalline complexes precipitated immediately or after certain lapse of time, which were filtered off or decanted, washed with cold diethyl or

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petroleum ether and dried at 60 °C for 2 hr. A weighed amount of the complex (3 to 7 mg) was dissolved in anisole (15 ml) containing 0.4% *p*-terphenyl and 0.01% POPOP [*p*-di(5-phenyl-2-oxazolyl)-benzene] and submitted to scintillation counting.

Measurements. The counting rate was recorded with the automatic counter Unilux IIA from Nuclear Chicago. The absorption spectra were recorded with a Hitachi 124 spectrometer. Water content was measured by Karl-Fischer titration.

Results and Discussion

The absorption spectra of the reaction mixtures remained unchanged throughout the kinetic runs for all the systems, and the recovered complexes were pure. McKay plots gave always linear plots. Hence no other reaction than the isotopic exchange took place under the given experimental conditions.

The rate of exchange, R is expressed by Eq. (1)

$$R = -2.3[3ab/(3a+b)][\log(1-F)]/t \qquad (1)$$

where a, b, t, and F stand for the concentrations of the complex and of the free ligand, the lapse of time and the fraction of reaction, respectively.

TABLE 1. INFLUENCE OF THE CONCENTRATION OF COMPLEX AND OF TRICHLOROACETIC ACID ON THE EXCHANGE RATE

[complex]/M	[acid]/M	$[H_2O]$/M	R/M·s	k_0/s^{-1}
0.050	0	0.036	1.1×10^{-6}	2.2×10^{-5}
0.10	0	0.036	2.2×10^{-6}	2.2×10^{-5}
0.13	0	0.036	2.9×10^{-6}	2.2×10^{-5}
0.070	0	0.025		1.4×10^{-5}
0.070	0.0029	0.025		2.2×10^{-5}
0.070	0.0053	0.025		3.0×10^{-5}
0.070	0.0074	0.025		3.6×10^{-5}

at 0 °C; [Hacac]=0.070 M

Tris(acetylacetonato)gallium(III). Kinetic Formula: The R values are proportional to the initial concentration of the complex as shown in Table 1. The variation of k_0 with water concentration under otherwise identical conditions is shown in Fig. 1, indicating the operation of two concurrent paths given in Eq. (2)

$$R = k_0a = a(k_1+k_2[H_2O]) \qquad (2)$$

Arrhenius plots of k_1 and k_2 at 0, 10, and 20 °C gave almost parallel lines and the $\Delta H^{\neq}$ are 19±2 and 18±2 kcal/mol, respectively. The dependence of k_0 upon the concentration of free ligand in the presence of differing amounts of water is illustrated in Fig. 2. The gradient indicates the ligand-catalysed rate constants, which are not affected by the water concentration. These results infer the presence of three independent paths as shown in Eq. (3)

$$R = a(k_1+k_2[H_2O]+k_3b) \qquad (3)$$

The rate constants obtained from the diagrams, and the activation parameters are listed in Table 2. Because of experimental difficulty the error for k's are *ca.* ±10%. Since the contribution of k_1 term is very small, the activation parameters for k_1 can be reckoned as those for the k_3 path.

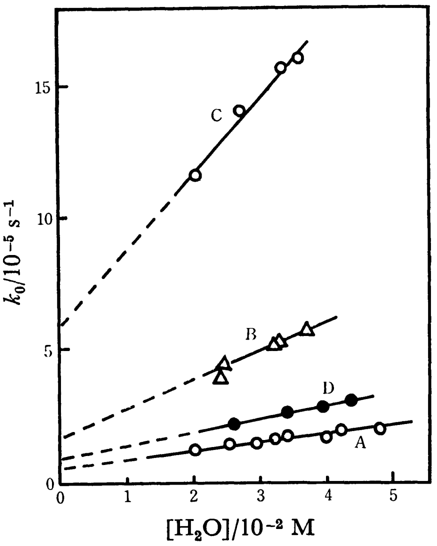

Fig. 1. Relationship between k_0 and water concentration.
A, 0 °C; B, 10 °C; C, 20 °C; D, 0 °C, [trichloroacetic acid]=0.0029 M; [Hacac]=0.070 M (for all).

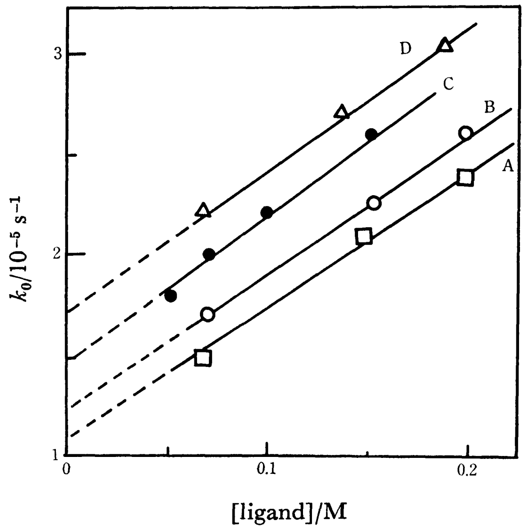

Fig. 2. Influence of ligand concentration upon k_0 in the presence of varying amounts of water for $[Ga(acac)_3]$. 0 °C; $[H_2O]$=A, 0.029, B, 0.036, C, 0.043, and D, 0.050 M.

Trichloroacetic acid catalyses the exchange reaction as shown in Table 1. The extent depends on the water concentration as seen in Fig. 1, and the overall rate in the presence of this acid is given by Eq. (4). Weaker

TABLE 2. KINETIC DATA AND ACTIVATION PARAMETERS FOR THE ISOTOPIC EXCHANGE BETWEEN $[Ga(acac)_3]$ AND Hacac-^{14}C IN THF

Temp/°C	$\frac{k_1}{10^{-6}\,s^{-1}}$	$\frac{k_2}{10^{-3}\,M^{-1}s^{-1}}$	$\frac{k_3}{10^{-4}\,M^{-1}s^{-1}}$
0	≤2	0.31	0.71
10	≤4	1.1	2.2
20	≤6	2.8	8.3
$\Delta H^{\neq}$/kcal·mol^{-1}		18±2	19±2
$\Delta S^{\neq}$/cal·K^{-1}mol^{-1}		−13±6	−20±6

TABLE 3. COMPARISON OF THE KINETIC DATA BETWEEN [Al(acac)$_3$] AND [Ga(acac)$_3$] IN THF AT 25 °C

	Al(III)	Ga(III)[b]
k_1/M^{-1}s^{-1}[a]	8.3×10^{-8}	$\leq4\times10^{-6}$
k_2/M^{-1}s^{-1}	3.3×10^{-4}	4.2×10^{-3}
k_3/M^{-1}s^{-1}	0	1.1×10^{-3}
k_1'/M^{-1}s^{-1}	1.6×10^{-4}	(1.5×10^{-3})[c]
k_2'/M^{-2}s^{-1}	2.0×10^{-2}	(4.1×10^{-2})[c]
$\Delta H^{\neq}$/kcal·mol^{-1} for k_1	21	—
$\Delta H^{\neq}$/kcal·mol^{-1} for k_2	21	18
$\Delta H^{\neq}$/kcal·mol^{-1} for k_3	—	19
$\Delta S^{\neq}$/cal·mol^{-1}K^{-1} for k_2	−7.8	−13

a) observed k_1 devided by 12, molar concentration of solvent THF. b) k's converted into the values with the aid of the activation enthalpies. c) at 0 °C.

organic acids failed to give such an acid catalysis.

$$R = a\{k_1'[\text{acid}]+[\text{H}_2\text{O}](k_2+k_2'[\text{acid}])+k_3b\} \tag{4}$$

The k_1' and k_2' are given in Table 3.

Exchange Mechanism for [Ga(acac)$_3$]: The gallium(III) complex gives much faster isotopic exchange than the aluminium(III) does. The kinetic formulae (3) and (4) are similar to those of the corresponding aluminium(III) complex.[4] We discussed that [Al(acac)$_3$] was in a rapid equilibrium with an intermediate which had one of the ligands as unidentate, and the break of the remaining bond should be the rate-determining step, on the basis of the similarity of $\Delta H^{\neq}$ values for the kinetic terms. Water and acid protons were reckoned to occupy the vacant coordination site and the free end of the unidentate ligand, respectively, and to retard the recombination of the unidentate ligand. Such occupations were considered to affect the $\Delta H^{\neq}$ values little.

The fact that k_2 and k_3 paths for the gallium(III) complex have almost equal activation enthalpies suggests that both paths would have a common rate-determining step. If water and Hacac gave nucleophilic attack towards [Ga(acac)$_3$] itself in the rate-determining step, the $\Delta H^{\neq}$ values should differ significantly, because they must have different affinities towards the substrate. We consider that the common rate-determining step would be the break of the second Ga–O bond of the unidentate ligand as shown in Fig. 3. Both water and Hacac molecule occupy the vacant coordination site of the intermediate to retard the recombination and to facilitate the break of the Ga–O bond of the unidentate ligand to some extent.

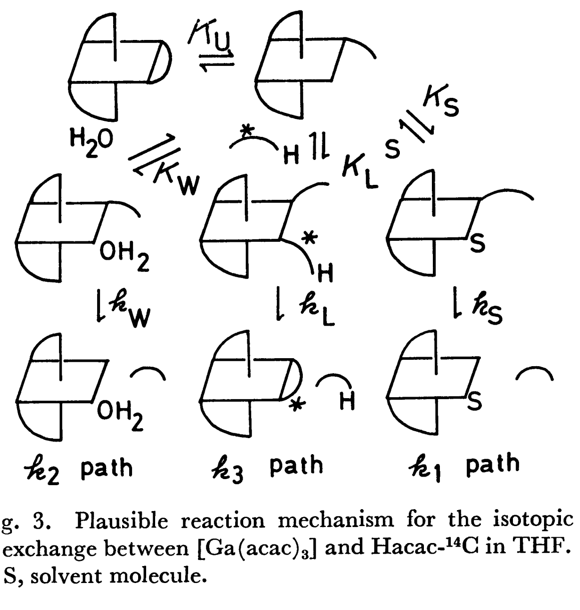

Fig. 3. Plausible reaction mechanism for the isotopic exchange between [Ga(acac)$_3$] and Hacac-^{14}C in THF. S, solvent molecule.

Pinnavaia *et al.* studied site exchange of the mixed ligand complex [Ga(acac)$_2$(dbm)] in benzene by PMR spectroscopy and obtained first-order rate constant 8.8×10^{-2} s^{-1} at 25 °C, the Arrhenius activation enthalpy and $\Delta S^{\neq}$ being 20.6±2.7 kcal/mol and 3.5±8.0 e.u., respectively.[10] They considered that a five-coordinated intermediate mechanism[11] would operate in the site exchange. This result supports our consideration that the nucleophilic interaction of the free ligand operates not on the complex itself but on the intermediate with one unidentate ligand.

When the rate and the equilibrium constants are defined as shown in Fig. 3, the k_1, k_2, and k_3 are written as follows:

$$k_1 = k_\text{s}K_\text{s}K_\text{u} \quad k_2 = k_\text{W}K_\text{W}K_\text{u} \quad k_3 = k_\text{L}K_\text{L}K_\text{u} \tag{5}$$
$$[K_\text{u}(K_\text{s}+K_\text{W}[\text{H}_2\text{O}]+K_\text{L}[\text{L}])\ll1]$$

The acid-catalyzed term would be interpreted similarly as for [Al(acac)$_3$], k_1' and k_2' terms being related to different proton carriers. The basicity of the unidentate ligand must be small and only a strong acid like trichloroacetic can give acid catalysis.

Comparison with the Mechanism for [Al(acac)$_3$]: There are two differences between the kinetic formulae for [Ga(acac)$_3$] and [Al(acac)$_3$]. The latter has a significant contribution of the k_1 path in THF, whilst the former not. The other difference is the participation of free Hacac in the rate-determining step for [Ga(acac)$_3$]. In the absence of water, (although experimentally impracticable) [Ga(acac)$_3$] and [Al(acac)$_3$] would undergo isotopic exchange *via* the ligand (k_3) and the solvent assisted path (k_1), respectively.

Tervalent gallium has a larger octahedral ionic radius (0.62 Å), than tervalent aluminium (0.51 Å), and the approach of free Hacac to the vacant cooridnation site would be easier to result in larger K_L, and hence larger k_3. Fiat and Connick[2] compared the activation parameters for the water exchange of gallium(III) and aluminium(III) perchlorate solution and suggested $S_\text{N}2$ and $S_\text{N}1$ mechanism for them, respectively. A similar trend is seen here, although the substrate should not be the complex itself but the intermediate with a unidentate ligand.

The affinities between the tervalent ion of gallium and aluminium with water, which are represented by their hydration energies, are almost equal (*ca.* 1% difference for *ca.* 1000 kcal/mol). Hence K_w values for both complexes would not differ much. Larger k_w for [Ga(acac)$_3$] than for [Al(acac)$_3$] should be responsible for larger k_2 for [Ga(acac)$_3$] than for [Al(acac)$_3$]. The difference in $\Delta H^{\neq}$ values of site exchange of gallium(III) and aluminium(III) complexes with given β-diketonato ligands is *ca.* 3 kcal/mol.[10,11] The difference in $\Delta H^{\neq}$ values for the k_2 path in Table 3 is almost equal to those for the site exchange. The ease of break of the first M–O bond of a given β-diketonato chelate would be paralleled by that of the second M–O bond. The rate-determining step for the site exchange should be either the break of the first M–O bond or the internal rearrangement of the five-coordinated intermediate. No explicit information is given as to the rate-determining step in the literatures,[10,11] but it is very likely that the break of the first M–O bond is the rate-determining step.

TABLE 4. RATE OF ISOTOPIC EXCHANGE OF SOME β-DIKETONATO COMPLEXES OF TYPICAL ELEMENT IONS IN THF

Complex	Temp./°C	b[b]	$[H_2O]$	k_0/s^{-1}
$[Al(acac)_3]$	25	0.050	0.015	4.2×10^{-6}
$[Al(bzac)_3]$	0	0.050	0.16	3.3×10^{-7}
$[Al(bdm)_3]$	0	0.050	0.015	1.0×10^{-8}
$[Ga(acac)_3]$	0	0.050	0.050	1.9×10^{-5}
$[Ga(bzac)_3]$	0	0.050	0.050	5.0×10^{-6}
$[Ga(dbm)_3]$	0	0.050	0.050	3×10^{-6}
$[In(dbm)_3]$	0	0.050	0.098	$>1\times10^{-3}$
$[Be(acac)_2]$[a]	30	1.0	—	2.1×10^{-5}
$[Be(bzac)_2]$	50	0.070	0.027	1.4×10^{-6}
$[Be(dbm)_2]$	50	0.070	0.041	1.1×10^{-6}

a) Ref. 13 b) concentration of free β-diketone.

Kinetics of Isotopic Exchange of Related Complexes. The rates are summerized in Table 4. The benzoylacetonato complexes give geometrical isomers, *mer* and *fac*. Their inter-conversion was studied by many authors by NMR spectroscopy and found to be very fast under the given experimental conditions.[10] Hence they were used without separation. Indium(III) complexes were very sensitive towards water in THF and only $[In(dbm)_3]$ allowed kinetic measurements. All the systems listed in Table 4 gave no net chemical change during the kinetic runs under the given conditions and the McKay plots were all linear. The R values were found to be proportional to the complex concentration, and k_0 values are listed. Although detailed kinetic studies were not made, we can compare the overall lability of these complexes with reference to the nature of the metal ions and of the ligands.

The following sequence shows the order of lability of acetylacetonato complexes towards isotopic exchange in organic solvents. The reaction mechanism differs from one another, and was discussed or will be discussed elsewhere.

$$\text{Ti(IV)}^{12)}>\text{In(III)}>\text{Ga(III)}>\text{Al(III)}^{4)}>\text{Be(II)}^{13)}>$$
$$\text{Pd(II)}^{14)}>\text{Co(III)}^{15)}>\text{Si(IV)}^{16)}>\text{Ge(IV)}^{17)}>\text{Cr(III)}^{12)}$$

However, so far as the gallium family elements concern, the order of lability is equal to that of water exchange. The order of lability between gallium(III) and aluminium(III) seems to be reversed, when ligands with nitrogen donors are involved (*e.g.* 8-quinolinolato[18] and EDTA[19] complexes). For ligands with oxygen donors only, the order for these two elements seems to be common, although different rate-determining steps may be involved.

Table 4 shows that the lability for a given metal ion decreases in the sequence, Hacac>Hbzac>Hdbm. The pK_a values increase in this order and the metal-ligand bond is expected to increase in this sequence. Although the metal complexes have various reaction paths for isotopic exchange, the basicity of ligands seems to give predominant influence.

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References

1) H. H. Diebler, M. Eigen, G. Ilgenfritz, G. Maass, and R. Winkler, *Pure and Applied Chem.*, **20**, 93 (1969); **6**, 105 (1963).

2) D. Fiat and R. E. Connick, *J. Amer. Chem. Soc.*, **90**, 608 (1968).

3) W. G. Movius and N. A. Matwiyoff, *Inorg. Chem.*, **8**, 925, 847 (1969).

4) K. Saito and K. Masuda, This Bulletin, **41**, 384 (1968); **43**, 119 (1970).

5) K. Matsuzawa and K. Saito, *ibid.*, **46**, 2777 (1973).

6) H. W. Baldwin and H. Taube, *J. Chem. Phys.*, **33**, 206 (1958).

7) T. Moeller and E. Gulyas, *J. Inorg. Nucl. Chem.*, **5**, 246 (1958).

8) H. Funk and A. Paul, *Z. Anorg. Allg. Chem.*, **330**, 70 (1964).

9) E. C. C. Baly and C. H. Desch, *J. Chem. Soc.*, **87**, 773 (1905).

10) T. J. Pinnavaia, J. M. Sebeson, II, and D. A. Case, *Inorg. Chem.*, **8**, 644 (1969).

11) R. C. Fay and T. S. Piper, *ibid.*, **3**, 348 (1964).

12) H. Kido and K. Saito, unpublished.

13) A. Barabas, *Inorg. Nucl. Chem. Lett.* **6**, 775 (1971).

14) K. Saito and M. Takahashi, This Bulletin, **42**, 3462 (1969).

15) K. Saito and M. Murakami, *ibid.*, **45**, 2472 (1972).

16) T. Inoue and K. Saito, *ibid.*, **46**, 2417 (1973).

17) A. Nagasawa and K. Saito, *ibid.*, **47**, 131 (1974).

18) K. Saito, M. Takahashi, Y. Miyakawa, and K. Masuda, *ibid.*, **41**, 1139 (1968).

19) M. Tsuchimoto, *ibid.*, in press.