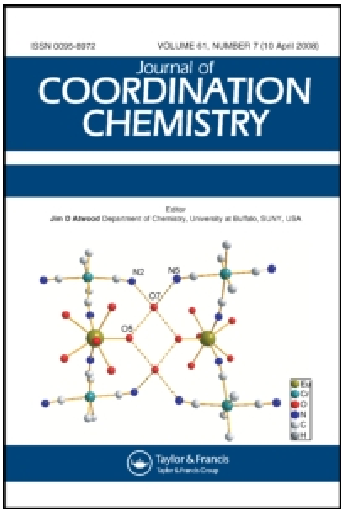

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SHORT COMMUNICATION

Thermal Reaction between Uranyl Acetate and Citric Acid in the Solid State

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INTRODUCTION

Although some quantitative investigations of the equilibria in uranyl citrate complexes in aqueous solutions have hitherto been documented,[1–5] there are few reports on the kinetics of the complexation of uranyl and citrate ions. Since such reaction is very fast in the solutions but, in a solid state slow enough to determine reaction rates and kinetic parameters, a solid-state kinetics on the complexation reaction seems of interest and significant to elucidate how the complexation occurs in the solid state. We wish to report a kinetic study of the uranyl citrate complexes obtained from a solid-state thermal substitution between uranyl acetate and citric acid or sodium citrate. The kinetic parameters for the above reaction were obtained from isothermal kinetic measurements by means of the differential thermal analysis (DTA) and the thermogravimetry (TG).

EXPERIMENTAL

Uranyl acetate was purified by recrystallization from a dilute acetic acid, and a reagent grade citric acid and sodium citrate were used without further purification. The reaction materials and products were confirmed by means of the elemental analysis and infrared spectra, and the differential thermal analysis, the thermogravimetry and isothermal kinetic measurements were performed by the use of Shimadzu TGC-20 microthermal analyzer system. About 10 mg of uranyl acetate and citric acid mixture was heated in a furnace at a heating rate of 5°C/min. The isothermal kinetic measurement was carried out at different constant temperatures in a helium stream with a flow rate of 40 ml/min. The infrared spectra were measured as nujol mulls by means of a JASCO DS-403 G spectrophotometer over the frequency range of 4000–200 cm^{-1}.

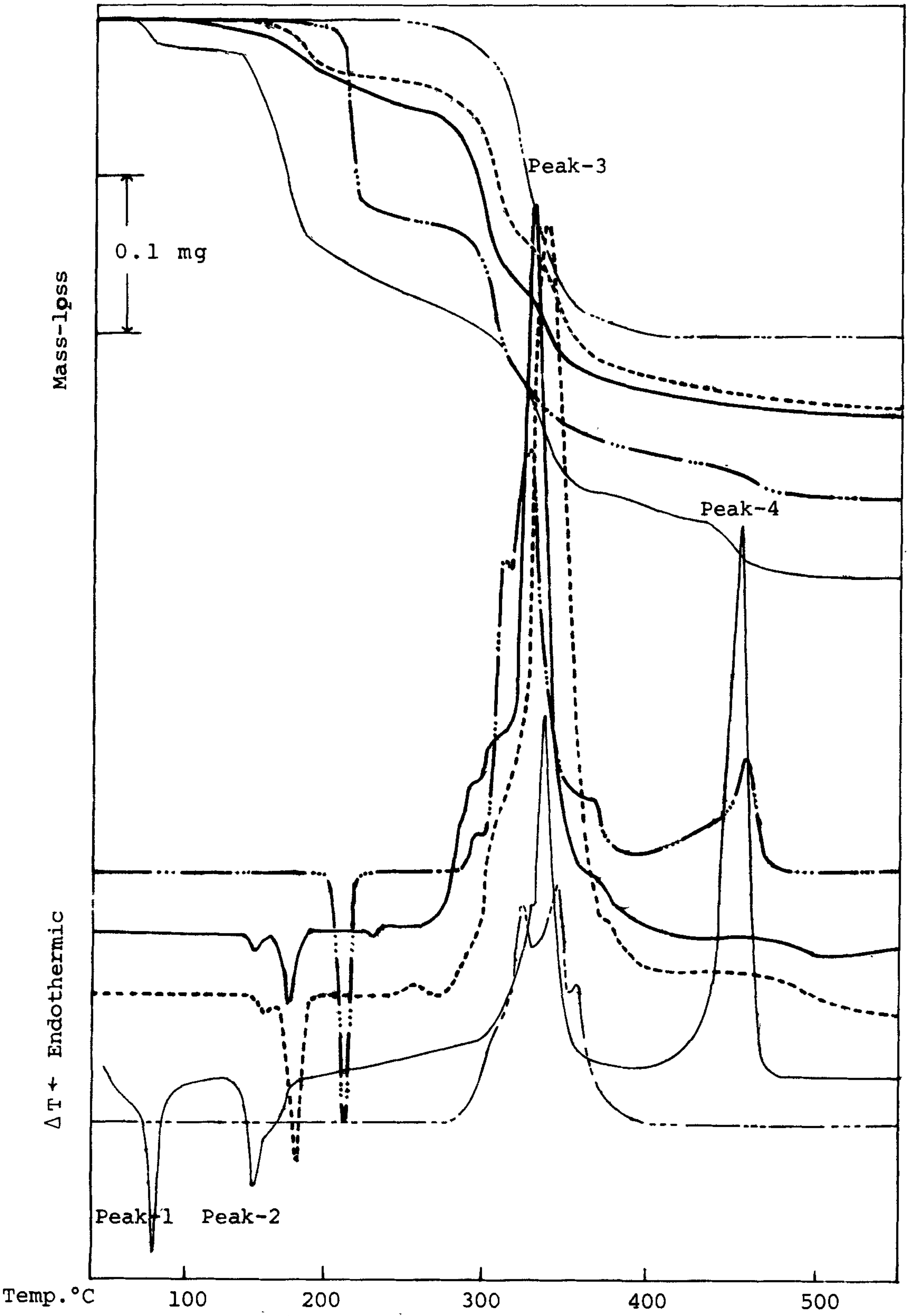
RESULTS AND DISCUSSION

DTA and TG curves for the thermal reaction in the solid state.

As can be seen from the DTA and TG curves in Figure 1 and the numerical data specified in Table I, the present thermal decomposition is apparently divided into four distinct reaction stages. The first, which is characterized by an endothermic DTA peak, is the dehydration at the temperature below 100° C. The second stage evidently consists of an endothermic ligand-substitution of the acetate by the citrate at the temperature range of 150°C–201°C. The third is the exothermic thermal-decomposition of uranyl citrate produced in the previous second-stage and probably contains an oxidative reaction with additional oxygen in air. It is also notable from that, in the third process, the evolution of carbon dioxide and water was detected similarly to the case of the thermal decomposition of uranyl acetate.[6] The fourth stage, which corresponds to the exothermic peak 4 in Figure 1, is found in only the cases of mixtures with citric acid and monosodium citrate. This is a subsequent degradation of the previous reaction product with the evolution of carbon dioxide. Therefore, apparent overall reactions involving the dual component systems can be represented according to the following steps:

$$\mathrm{UO_2(OAc)_2 \cdot 2H_2O(s) + 2H_nL(s) \rightarrow UO_2(OAc)_2(H_nL)_2(s) + 2H_2O(g)} \quad (1)$$

$$\mathrm{UO_2(OAc)_2(H_nL)_2(s) \rightarrow UO_2(H_{n-1}L)_2(s) + 2HOAc(g)} \quad (2)$$



-·-·-·- uranyl acetate (U.A.), ——— U.A. + citric acid, ▬···▬ U.A. + monosodium citrate, ▬▬▬ U.A. + disodium citrate, ········ U.A. + trisodium citrate.

FIGURE 1 DTA and TG curves of uranyl acetate-carboxylic acid mixture in the air.

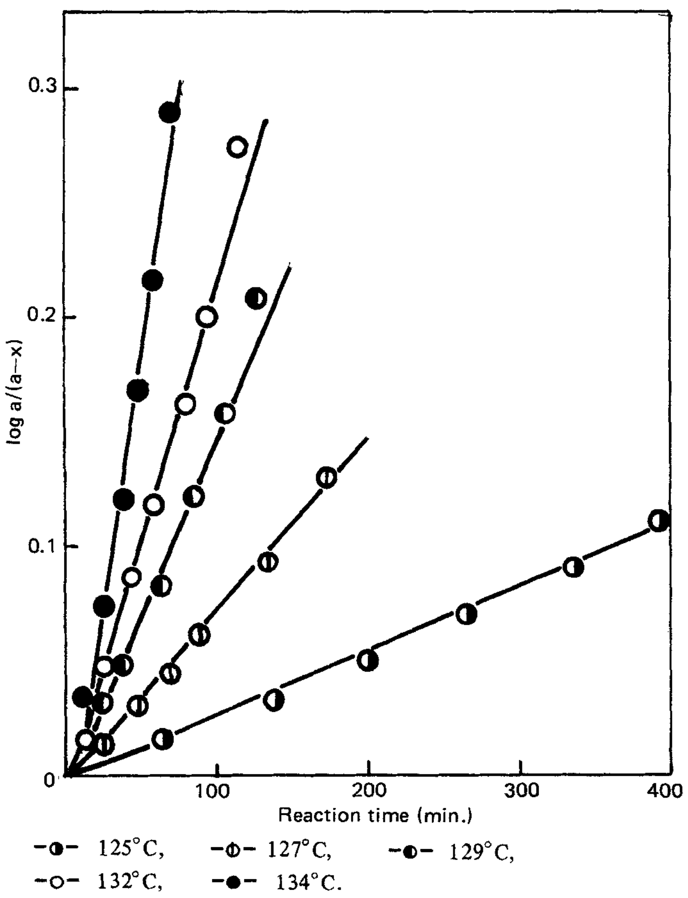


FIGURE 2. The plots of log a/(a–x) vs. reaction time for the acetate-ligand substitution of the uranyl acetate-citric acid system.

$$UO_2(H_{n-1}L)_2(s) \rightarrow UO_2CO_3(s) + (n-1)/2H_2O(g) + m\,CO_2(g) \qquad (3)$$

$$UO_2CO_3(s) \rightarrow UO_3(s) + CO_2(g) \qquad (4)$$

Analysis of the acetate-ligand substitution products

The results of elemental analysis of the reaction products in Equation (2) indicate a satisfactory coincidence between observations and calculations. Found: H,2.53; C,22.5%. Calcd for $UO_2(C_6H_7O_7)_2$: H,2.15; C,22.1%. Found: H,1.72; C, 20.7%. Calcd for $UO_2(C_6H_6O_7Na)_2$: H,1.98; C,20.2%.

Kinetic study of the acetate-ligand substitution reaction.

The isothermal kinetic measurements were performed on the present solid state reaction using a thermobalance. The plots of log a/(a–x) *vs.* reaction time t are shown in Figures 2 and 3, where "a" and "a–x"

TABLE I

DTA and mass-loss data for the thermal decomposition of uranyl acetate and mixture system.

Sample	Melting point °C (obsd.)	Peak-1† Temp, °C	Mass-loss (%) obsd/theor. (chem. form)	Peak-2† Temp, °C	Mass-loss (%) obsd/theor. (chem. form)	Peak-3‡ Temp, °C	Mass-loss (%) obsd/theor. (chem. form)	Peak-4‡ Temp, °C	Mass-loss (%) obsd/theor. (chem. form)
Uranyl acetate	–	–	–	–	–	330	32.6/28.9($4CO_2$) + 1.5($3H_2O$)	–	–
Citric acid	148–150	77	2.9/3.0(H_2O)	150 163 170	25.4/20.0 (2HOAc) + 6.0($2H_2O$)	336	21.0/23.4($5CO_2$)	450	7.4/7.4(CO_2)
Sodium citrate	202–207	–	–	201	21.8/19.3 (2HOAc) + 2.9(H_2O)	288 297 320 360	11.7 } /21.9($5CO_2$) 11.8 1.5/1.6($5H_2O$)	426	3.4/3.5($0.5CO_2$)

† Endothermic peak.
‡ Exothermic peak.

mean the mass of the reactant mixture in the initial state and the reaction time t respectively. The linear plots in these figures indicate that the acetate-ligand substitution reaction apparently obeys a first-order rate law with respect to the reactant mixture; a deviation from the straight line during the initial reaction stage is attributable to the low thermal conductivity of the powdery sample. Hence, the apparent rate law can be described using the rate constant, k_{obs} obtained from the slope of the straight line.

$$\text{Rate} = k_{obs}[UO_2(OAc)_2(H_4L)_2] \text{ in the citric acid system} \quad (5)$$

$$\text{Rate} = k_{obs}[UO_2(OAc)_2(NaH_3L)_2] \text{ in the sodium citrate system} \quad (6)$$

Table II lists the rate constants and the Arrhenius activation energies, E_a, together with the activation entropies calculated from the E_a values. For the sake of comparison, the kinetic parameters for the volatile-ligand substitution reactions of the trivalent metal complexes are also given in the same table. The rate constants for the present reactions are larger than those of the deammonation-anation reaction[7,8] of Cr(III) and Ru(III) hexaamine halides but smaller than those of the deaquation-anation reaction[9,10] of aquapentaammine complexes. However, it can be said from the activation parameters, which are differ-

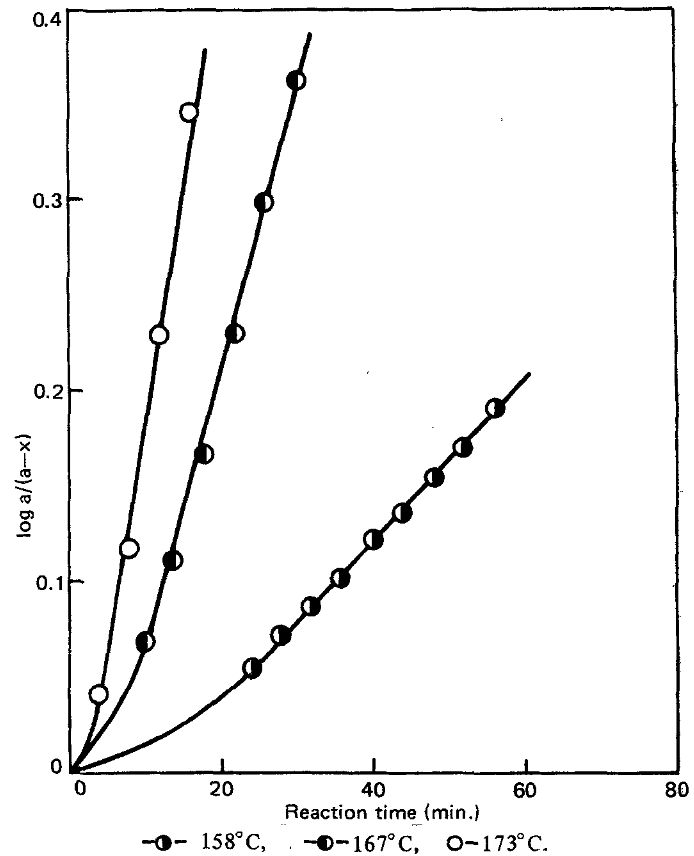


FIGURE 3. The plots of log a/(a−x) vs. reaction time for the acetate-ligand substitution of the uranyl acetate – sodium citrate system.

TABLE II

Kinetic parameters for the acetate-ligand substitution of the uranyl acetate-citric acid systems

system	$k \times 10^5$	(sec^{-1})(°C)	E_a(Kcal mol^{-1})	ΔS‡(e.u.)
$UO_2(OAc)_2 \cdot 2H_2O + H_4L$	1.06	(125)		
	2.74	(127)		
	6.14	(129)	86.6	129.6
	8.10	(132)		
	14.3	(134)		
$UO_2(OAc)_2 \cdot 2H_2O$	15.7	(158)		
$+ NaH_3L$	22.5	(162)	50.4	33.4
	52.6	(167)		
	105.8	(173)		
$[Cr(NH_3)_6]Cl_3$	2.97	(170)	30	−12
$[Cr(NH_3)_6]Br_3$	2.16	(192)	43	12
$[Ru(NH_3)_6]Br_3$	2.10	(161)		
	3.97	(172)	23.3	−29.3
$[Ru(NH_3)_6]I_3$	4.52	(144)		
	6.02	(151)	20.7	−31.6
$[Cr(OH_2)(NH_3)_5]Br_3$	24.3	(76)	36, 29.7	9.2
$[Cr(OH_2)(NH_3)_5]I_3$	16.1	(82)	19, 32.7	15.4
$[Ru(OH_2)(NH_3)_5]Br_3$	7.7	(40)	23.4	−5.2
$[Ru(OH_2)(NH_3)_5]I_3$	7.1	(40)	26.7	5.8

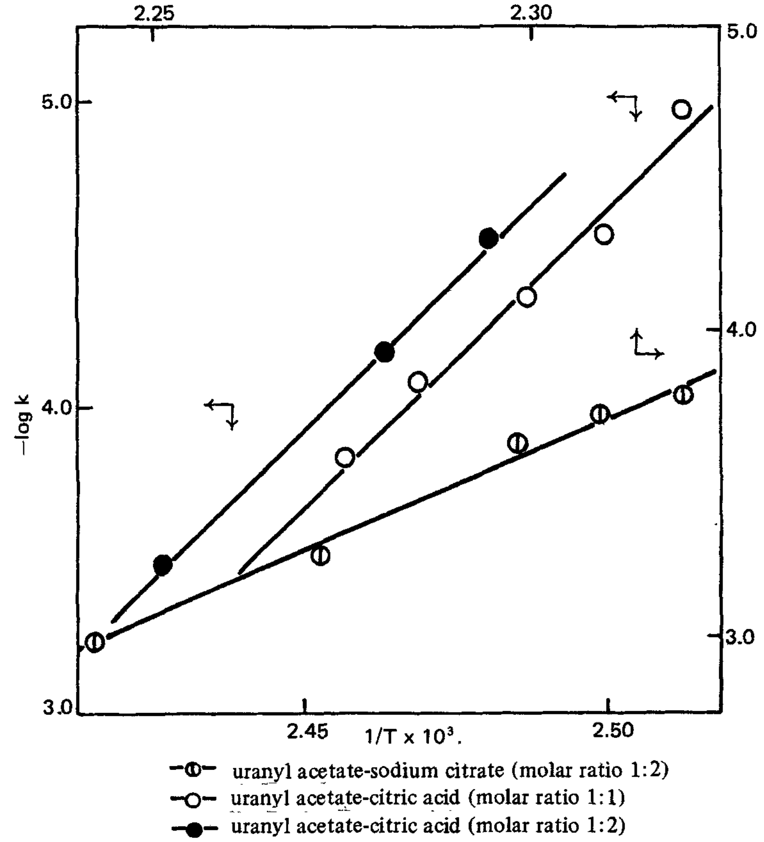


FIGURE 4. Arrhenius plots of the acetate-ligand substitution reaction.

ent from those for the above deammonation- or deaquation-anation reactions that the mechanism of the present solid-state reaction is distinctive from the previously proposed mechanisms for the reactions. In this respect, the S_N1 mechanism is generally acceptable in the case of such the reactions having the large activation energy and the positive activation entropy as the deammonations of hexaamminechromium (III) bromide and iodide.[7] In relation to this fact, the present reaction has a mechanism close to a S_N1 type rather than a S_N2 type. The citrate or sodium citrate group in the product of reaction (1) facilitates to weaken the uranyl acetate coordination bond, and then, the rate of acetic acid evolution in the reaction (2) may be controlled by these outersphere ions.

The difference between the magnitude of the activation parameters for the citric acid and sodium citrate systems may be due to the difference in the reaction intermediates, $[UO_2(OAc)_2(H_4L)_2]$, and $[UO_2(OAc)_2(NaH_3L)_2]$, and between the bond-fission energy of the uranyl-acetate linkage and that of the hydrogen-atom abstraction by the free acetate ligand.

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