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Kinetics and Mechanism of the Substitution of β-Diketonates for Acetylacetonate in Bis(acetylacetonato)(trimethyl phosphate)-dioxouranium(VI)

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Kinetics of the substitution of β-diketonates for one acetylacetonate in $UO_2(acac)_2tmp$ (acac= acetylacetonate, tmp=trimethyl phosphate) has been studied in tmp by spectrophotometric methods. The reactions proceed through intermediate complexes $UO_2(acac)_2HB$, where HB denotes various β-diketones. The formation of the intermediates are followed by intramolecular proton transfer processes from coordinated HB to one of two acac in $UO_2(acac)_2HB$. The proton-transfer step for various HB can be classified into two groups owing to the difference in the values of rate constants k_2, i.e. the substitutions of Hbza, Hhpd, and Hdbm and those of Hbta, Htta, and Htfa, k_2 of the former group giving the order of 10^{-3} s^{-1}, while that of the latter the order of 10^{-1} s^{-1}, at 25 °C, where Hbza=benzoylacetone, Hhpd=3,5-heptanedione, Hdbm=dibezoylmethane, Hbta=benzoyltrifluoroacetone, Htta=2-thenoyltrifluoroacetone, and Htfa=trifluoroacetylacetone. This can be well explained in view of the acidity of β-diketones. The addition of amphiprotic solvents, such as water and alcohols, accelerates the substitution rates, and the observed first-order rate constant k_{obsd} is expressed by $k_{obsd}=k_2+k_c$[solvent]. In the case of the addition of alcohols, k_c increases in the order: n-BuOH<i-PrOH<n-PrOH<EtOH<MeOH. This is the reverse order of autoprotolysis constants of these alcohols. Kinetic isotope effects k_c^H/k_c^D for the substitution of Hbza in tmp in the presence of H_2O (or D_2O) and CH_3OH (or CH_3OD) were determined to be 2.5 and 1.8, respectively.

In a previous paper,[1] we reported the kinetics of the substitution of dibenzoylmethanate for one acac in $UO_2(acac)_2L$, where L denotes dmso (dimethyl sulfoxide), dmf (N,N-dimethylformamide) and tmp, and proposed that the reaction started with the formation of an intermediate complex $UO_2(acac)_2Hdbm$, followed by a relatively slow proton-transfer process from coordinated Hdbm to acac. A similar proton-transfer process was also found to control the rates of β-diketonate exchange reactions in U(IV) and Th(IV) complexes.[2–4] However, the rates of these exchange reactions are much faster than those of β-diketonates in dioxouranium(VI) in spite of the similarity of the reaction mechanism.

This paper presents further information on the kinetics of the substitutions of various β-diketonates for acac in $UO_2(acac)_2tmp$. The reaction can be expressed by:

$$UO_2(acac)_2tmp + \beta\text{-diketone} \xrightarrow[\text{in tmp}]{} UO_2(acac)(\beta\text{-diketonato})tmp + Hacac.$$

The effect of water and alcohols on the rates of substitution and the kinetic isotope effects were also investigated. The kinetic results are compared with those of the previous paper.[1]

Experimental

The complex $UO_2(acac)_2tmp$ was synthesized by the same method as described previously.[1] Hacac and tmp were distilled under reduced pressure, and Hbza and Htta were recrystallized from ethanol and methanol, respectively, and dried under vacuum before use. Htfa, Hhpd, and Hbta were used without further purification. Methanol, ethanol, propanol, 2-propanol, and butanol were dried over 3- or 4-A Molecular Sieves. Merck 99.8 atom% deuterium oxide and 98 atom% methanol-d_1 were used. The water content of the solvent was below 5×10^{-3} M (M=mol dm^{-3}) as determined by Karl-Fisher titration after each kinetic run, and this degree of water content has no significant influence on the reaction rates.

The kinetic measurements were carried out on a JASCO UNIDEC-505 spectrophotometer with thermostated cell compartments (±0.2 °C) and 1-cm quartz cells for slow reaction or a Union Giken RA-401 stopped-flow spectrophotometer for fast reactions. The kinetic experiments were done under pseudo-first-order conditions ([$UO_2(acac)_2tmp$]≫[β-diketone]). The rate of the replacement of one coordinated acac in $UO_2(acac)_2tmp$ was given by $k_{obsd}[\beta\text{-diketone}]_{enol}$, where $[\beta\text{-diketone}]_{enol}$ refers to the concentration of β-diketone in the enol form and k_{obsd} refers to the rate constant for the substitution of each acac. The pseudo-first-order rate constant k_{app} was determined from the slope in plots of $\ln(A_f-A_t)$ versus time t, where A_t and A_f are absorbances at time t and infinity, respectively at the wavelength 440 nm which gives the largest absorption change by the ligand substitution. Since $UO_2(acac)_2tmp$ involves two acac molecules, each suffering the substitution in an equal probability, k_{obsd} is the half of k_{app}. Kinetic runs were performed at least twice.

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Results and Discussion

Figure 1 shows that k_{obsd} for the substitution of Hbza for acac in $UO_2(acac)_2tmp$ are independent of the concentrations of complex $[UO_2(acac)_2tmp]$. The values of k_{obsd} at various temperatures are given in Table 1. For the substitution of Htta, k_{obsd} increases linearly with $[UO_2(acac)_2tmp]$ in the low region of $[UO_2(acac)_2tmp]$, but tends to saturate in the high region. However, as seen in Fig. 2, plots of $1/k_{obsd}$ against

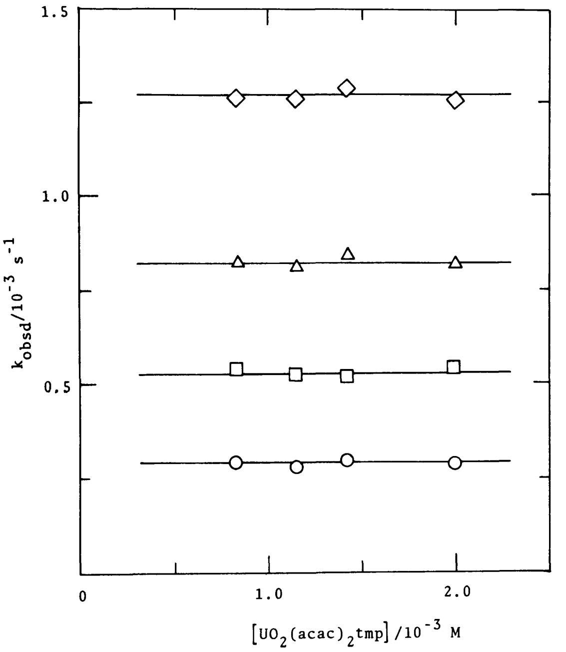

Fig. 1. Plots of k_{obsd} versus $[UO_2(acac)_2tmp]$ for the substitution of Hbza for acac in $UO_2(acac)_2tmp$: (○) 20 °C; (□) 24 °C; (△) 28 °C; (◇) 32 °C.

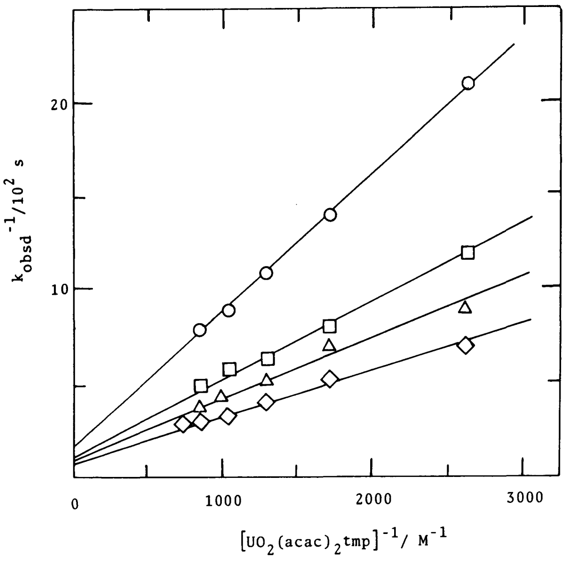

Fig. 2. Plots of $1/k_{obsd}$ versus $1/[UO_2(acac)_2tmp]$ for the substitution of Htta for acac in $UO_2(acac)_2tmp$: (○) 20 °C; (□) 24 °C; (△) 25 °C; (◇) 28 °C.

Table 1. Kinetic Data for the Substitution of β-Diketonates for acac in $UO_2(acac)_2tmp$

β-Diketonate	Parameter	Rate or equilibrium constants					$\Delta H^{\ast}$	$\Delta S^{\ast}$
		20 °C	24 °C	25 °C	28 °C	32 °C	kJ mol^{-1}	J K^{-1} mol^{-1}
bza	$k_2/10^{-4}\ s^{-1}$	2.94±0.21	5.30±0.25		8.20±0.25	12.7±0.3	87.3±4.6	−14.3±15.4
tta	q^{-1} or $k_2/10^{-2}\ s^{-1}$	6.65±1.05	7.75±1.95	8.80±2.30	11.7±4.1		48.7±10.0	−102±33
	(q/r) or K_1/M^{-1}	209 ±25	324 ±42	367 ±92	352 ±27			

Table 2. Kinetic Data for the Substitution of β-Diketonates for acac in $UO_2(acac)_2tmp$ at 25 °C

Substitution of tfa		Substitution of hpd		Substitution of bta	
$[UO_2(acac)_2tmp]$	k_{obsd}	$[UO_2(acac)_2tmp]$	k_{obsd}	$[UO_2(acac)_2tmp]$	k_{obsd}
10^{-3} M	10^{-2} s^{-1}	10^{-3} M	10^{-4} s^{-1}	10^{-3} M	10^{-2} s^{-1}
0.384	3.04	1.00	5.70	1.00	5.90
0.574	3.81	2.00	7.95	1.69	6.05
0.768	4.37	2.50	8.50	1.87	6.25
0.958	5.75	4.00	8.65	2.50	7.00
1.00	5.65	5.00	9.15	4.00	7.05
1.69	6.45			5.00	7.20
4.00	8.56				
$k_2=(1.25\pm0.22)\times10^{-1}$ s^{-1} $K_1=(7.76\pm0.37)\times10^{-2}$ M^{-1}		$k_2=(1.11\pm0.06)\times10^{-3}$ s^{-1} $K_1=(1.09\pm0.05)\times10^{-3}$ M^{-1}		$k_2=(7.55\pm0.04)\times10^{-2}$ s^{-1} $K_1=(3.15\pm0.05)\times10^{-3}$ M^{-1}	

1/$[UO_2(acac)_2tmp]$ give straight lines with intercepts yielding the expression:

$$1/k_{obsd} = q + r/[UO_2(acac)_2tmp] \quad (1)$$

where q and r are constants. The same tendency was observed for the substitutions of Htfa, Hhta, and Hhpd. The data are summarized in Table 2 with the values of q and r.

The results in the present study can be well-explained by a mechanism (Fig. 3) proposed in the previous paper.[1] In this mechanism, the reaction is initiated with the fast equilibrium between $UO_2(acac)_2tmp$ (**I**) and β-diketone in the enol form HB,[5] followed by the intramolecular proton-transfer process from coordinated HB to one of two chelated acac. According to the neutron diffraction study on $UO_2(acac)_2Hacac$,[6] Hacac is coordinated to uranium atom via a keto oxygen atom, and the plane of Hacac is located at 32.5 °C to the pentagonal equatorial plane. The structure of intermediate **II** could be similar to that of $UO_2(acac)_2Hacac$. Based on the above mechanism, assuming that the proton-transfer process (k_2 path) is the rate-determining step, k_{obsd} is given by

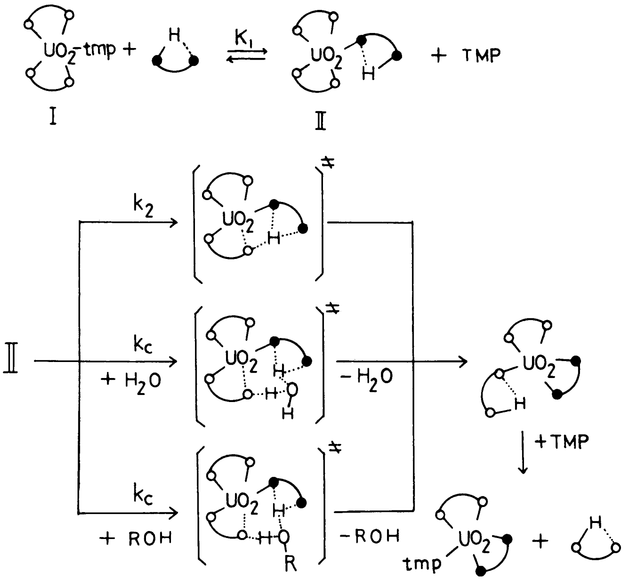

Fig. 3. Possible mechanism of the substitution of β-diketonates for acac in $UO_2(acac)_2tmp$ in tmp. $\overset{\frown}{HO\ O}$ and $\overset{\frown}{H\bullet\ \bullet}$ represent Hacac and β-diketone in the enol form, respectively.

$$k_{obsd} = k_2K_1[UO_2(acac)_2tmp]/(1 + K_1[UO_2(acac)_2tmp] \quad (2a)$$

or

$$k_{obsd}^{-1} = 1/k_2 + 1/(k_2K_1[UO_2(acac)_2tmp]) \quad (2b)$$

where $K_1=[UO_2(acac)_2HB]/([UO_2(acac)_2tmp][HB])$. In the limiting case $K_1[UO_2(acac)_2tmp]\gg1$, Eq. 2a can be simplified as $k_{obsd}=k_2$, i.e. k_{obsd} is independent of $[UO_2(acac)_2tmp]$. This is the case for the substitution of Hbza. Equation 2b is basically the same as Eq. 1, and parameters k_2 and K_1 are determined by these equations for the substitutions of Htta, Htfa, Hhpd, and Hbta. The results are listed in Tables 1 and 2. In these tables, the substitutions of HB can be classified into two groups owing to the difference of k_2 values: one is the substitutions of Hbza and Hhpd, and the other those of Htta, Htfa, and Htfa, k_2 of these groups being the order of 10^{-3} and 10^{-1} s^{-1}, respectively. The substitution of Hdbm[1] belongs to the former group. Since the k_2 path corresponds to the proton-transfer process from HB to coordinated acac, it is likely that k_2 increases with increasing acidity of HB. The acidity of HB was evaluated from data of pK_a in water-dioxane mixture (75 wt% dioxane) at 30 °C,[7,8] because pK_a of HB was not available in tmp. The values of k_2 at 25 °C and pK_a of HB are summarized in Table 3. In this table the pK_a values are considerably smaller, i.e. HB is more acidic, in the latter group. These facts indicate that the acidity of HB plays an important role for the k_2 process.

In order to examine the steric hindrance of entering HB for the substitution rate, the substitution of Hbza is compared with that of Hdbm, because Hdbm is

Table 3. Rate Constants k_2 for the Substitution of β-Diketonates for acac in $UO_2(acac)_2tmp$ at 25 °C and pK_a of β-Diketones

β-Diketone	Hbza	Hhpd	Hdbm[a]	Hbta	Htta	Htfa
k_2/s^{-1}	5.66×10^{-4}[b]	1.11×10^{-3}	2.31×10^{-3}	7.55×10^{-2}	8.80×10^{-2}	1.25×10^{-1}
pK_a[c]	12.85	13.7[d]	13.75	9.2	9.1	8.7

a) Ref. 1. b) Calibrated at 25 °C. c) In water–dioxane mixture (75 wt% dioxane) at 30 °C. d) Ref. 7.

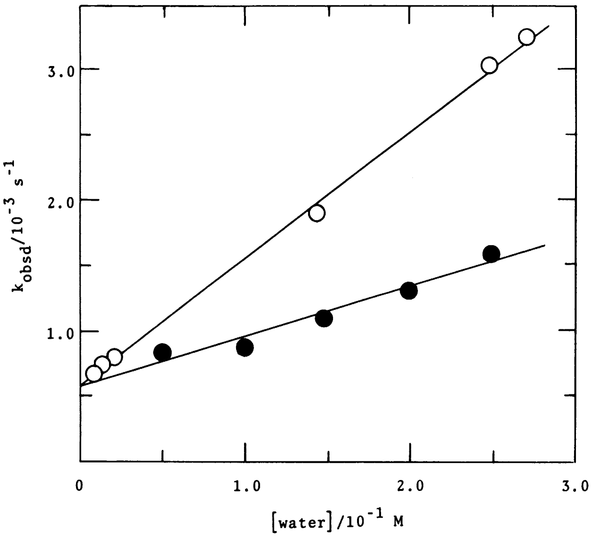

Fig. 4. Plots of k_{obsd} versus [Water] for the substitution of Hbza for acac in $UO_2(acac)_2tmp$ at 25 °C: (○) H_2O; (●) D_2O.

Table 4. Influence of Water and Alcohols on the Rate of the Substitution of bza for acac in $UO_2(acac)_2tmp$ at 25 °C

ROH	k_c 10^{-2} M^{-1} s^{-1}	pK_{auto}[a)] (25 °C)
H_2O	0.99±0.02	14.00
D_2O	0.39±0.06	14.96
MeOH	2.54±0.36	16.7
MeOD	1.42±0.12	
EtOH	2.26±0.10	18.9
n-PrOH	1.08±0.04	19.4
i-PrOH	0.71±0.04	20.8
n-BuOH	0.71±0.03	21.6[b)]

a) Ref. 9. b) Ref. 13.

much bulkier in size than Hbza and their pK_a values are similar. In Table 1, k_2 for Hbza is 5.30×10^{-4} s^{-1} at 24 °C, while 2.19×10^{-3} s^{-1} for Hdbm at the same temperature.[1)] The results that the rate is even faster for the substitution of the bulkier ligand suggest that the steric hindrance is of no significant effect.

The effect of adding water (<0.3 M) and various alcohols (<0.05 M) on the rates was investigated for the substitution of Hbza. As seen in Fig. 4, k_{obsd} increases linearly with the concentration of H_2O (D_2O). The similar linearlity was also found for all alcohols studied. Therefore, k_{obsd} can be expressed by:

$$k_{obsd} = k_2 + k_c[S] \tag{3}$$

where [S] denotes the concentrations of water and alcohols. The second-order rate constant k_c is listed in Table 4, together with the autoprotolysis constant pK_{auto}. In the case of the addition of alcohols, k_c shows a tendency to decrease with increasing pK_{auto}. This suggests that the k_c process in Fig. 3 is related to the amphiprotic property of alcohols, i.e. the ability of acting as a proton-donor and -acceptor through hydrogen bonding with intermediate **II**. Since K_{auto} is the product of the acidity constant ($ROH=RO^-+H^+$) and the constant for proton accepting equilibrium ($ROH+H^+=ROH_2^{2+}$) expressed by: $K_{auto}=[RO^-][ROH_2^{2+}]$, the role of each individual property of proton-donating or -accepting for the k_c process can not be determined strictly from these data. If the acceptor number[14)] is allowed to estimate the acid strength for prototype acids, the acidity of alcohols decreases in the order: MeOH>EtOH>*i*-PrOH, e.g. as a mutter of fact, pK_a of MeOH and EtOH are 16.68 and 18.88, respectively,[9)] indicating that the ability of proton donating of alcohols appears to be important. Water seems to behave differently, because the geometric configuration of intermediate II involving water differs from that of the intermediate involving alcohols.

The replacement of adding H_2O and CH_3OH by D_2O and CH_3OD lowers the k_c values (Table 4) and the kinetic isotope effects k_c^H/k_c^D for H_2O/D_2O and CH_3OH/CD_3OD are determined to be 2.5 and 1.8, respectively. These values are substantially small compared with the direct proton transfer in the acac-exchange reaction.[11)] Since proton transfers proceed from entering HB to leaving acac through water or alcohols, this indirect proton transfer might reduce the isotope effect in the presence of these amphiprotic solvents, particularly in such cases where proton-donor and -acceptor atoms are unsymmetrically located. This is experimentally evidenced by the fact that the smaller the difference in the acidity between two acids, HX and HY, (i.e. the more symmetrical the transition state) the larger the kinetic isotope effect for the proton-transfer reaction X^- and HY or Y^- and HX.[10)]

The activation parameters of the k_2 path for the various β-diketonates are listed in Table 5. Although

Table 5. Activation Parameters for the Proton-Transfer Rate Constant in the Substitution of β-Diketonates for acac in $UO_2(acac)_2L$

	β-Diketonate	L	Solvent	$\Delta H^{\ast}$ kJ mol^{-1}	$\Delta S^{\ast}$ J K^{-1} mol^{-1}	Ref.
1.	dbm	dmf[a)]	dmf[a)]	31.3	−177	1
2.	dbm	tmp	tmp	50.2	−127	1
3.	dbm	tmp	tmp-nm[b)]	63.4	−77.4	1
4.	bza	tmp	tmp	87.3	−14.3	This work
5.	tta	tmp	tmp	48.7	−102	This work

a) *N*,*N*-Dimethylformamide. b) tmp–nitromethane (1:1, v/v) mixture.

there is no consistency in $\Delta H^{\ast}$ in a series of the substitutions, the change in k_2 is relatively small. This is attributed to the compensation effect[12)] between $\Delta H^{\ast}$ and $\Delta S^{\ast}$, which might be resulted from the polarization of intermediate **II** as acac$\cdots$H$^{\delta+}$–B$^{\delta-}$, i.e. the larger polarization could reduce the $\Delta H^{\ast}$ values because of the weakened HB bonds and could make $\Delta S^{\ast}$ more negative as well owing to an increase of solvation towards the intermediate.

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References

1) W.-S. Jung, H. Tomiyasu, and H. Fukutomi, *Inorg. Chem.*, **25**, 2582 (1986).

2) N. Fujiwara, H. Tomiyasu, and H. Fukutomi, *Bull. Chem. Soc. Jpn.*, **57**, 1576 (1984).

3) N. Fujiwara, H. Tomiyasu, and H. Fukutomi, *Bull. Chem. Soc. Jpn.*, **58**, 1386 (1985).

4) H. Fukutomi, H. Ohno, and H. Tomiyasu, *Bull. Chem. Soc. Jpn.*, **59**, 2303 (1986).

5) Y. Ikeda, H. Tomiyasu, and H. Fukutomi, *Bull. Chem. Soc. Jpn.*, **56**, 1060 (1983).

6) M. Lenner, *Acta Crystallogr., Sect. B*, **32**, 2396 (1979).

7) a) L. G. Van Uitert, C. G. Haas, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 455 (1953); b) L. G. Van Uitert, W. C. Fernelius, and F. B. Douglas, *J. Am. Chem. Soc.*, **75**, 457 (1953); c) J. L. Ault, H. J. Harries, and J. Burgess, *J. Chem. Soc., Dalton Trans.*, **1973**, 1095.

8) According to Ref. 7a and 7b, an approximately linear relationship exists between the pK_a value of β-diketone and the mole fraction of dioxane in water–dioxane mixture, i.e. $pK_a = p + qn_2$ (p and q are constants and n_2 is a mole fraction). The pK_a value of Hhpb at $n_2 = 0.38$ was estimated by using the pK_a value (11.2) at $n_2 = 0.17$ and assuming that the q value of Hhpd is equal to that of Hacac (11.6) (Ref. 7a).

9) J. F. Coetzee and C. D. Ritchie, "Solute-Solute Interactions," Marcel Dekker, New York (1969).

10) R. P. Bell, "The Proton in Chemistry," Chapman and Hall, London (1973), Chap. 12.

11) Y. Hatakeyama, H. Kido, M. Harada, H. Tomiyasu, and H. Fukutomi, *Inorg. Chem.*, **27**, 992 (1988).

12) K. J. Laidler, "Chemical Kinetics," McGraw-Hill, London (1965).

13) C. Reichardt, "Solvent Effects in Organic Chemistry," Verlag Chemie, Weinheim (1979).

14) V. Gutmann, "The Donor-Acceptor Approach to Molecular Interactions," Plenum Press, New York (1978).