

# Kinetics of Formation and Dissociation of $[\text{Cr}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{urea})_3]^+$ : An Example of Statistically Controlled Kinetics and Equilibrium

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Kinetics of the overall reaction  $[\text{Cr}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^+ + 3 \text{ urea} \rightleftharpoons [\text{Cr}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{urea})_3]^+ + 3\text{H}_2\text{O}$  have been studied spectrophotometrically. Monophasic kinetics were observed in both directions. The reverse steps, of urea dissociation, were monitored using an analytical technique which permits direct determination of the concentration of liberated urea and does not require knowledge of extinction coefficients of intermediate species. Results imply that consecutive steps occur with rate constants in close to the statistical ratios of  $k_1:k_2:k_3 = 3:2:1$  and  $k_{-1}:k_{-2}:k_{-3} = 1:2:3$ . Rates indicate strong labilization of urea, compared to the case of mononuclear complex  $[\text{Cr}(\text{urea})_6]^{3+}$ .

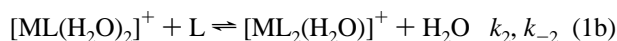
## Introduction

Complexes of the type  $[\text{M}^{\text{III}}_3\text{O}(\text{O}_2\text{CR})_6\text{L}_3]^+$  exist with a range of transition metals<sup>1</sup> and are important in several homogeneous catalytic processes,<sup>2</sup> yet their solution chemistry has been relatively little studied, particularly as regards complexes of first-row transition metals. Good equilibrium data exist to confirm the stability of the anion-bridged framework of the iron/acetate system;<sup>3</sup> and it is also known that in the case of the chromium(III)/acetate system, this framework is remarkably inert in a kinetic sense.<sup>4</sup> On the other hand, there are indications that the monodentate ligands L are relatively labile: much more easily displaced than the bridging groups and apparently more labile than the same ligands in mononuclear chromium(III) complexes. The ease of preparation of complexes with different ligands L is one indication.<sup>5</sup> A very early, and incomplete, kinetic study of the dissociation of the formate complex  $[\text{Cr}_3\text{O}(\text{O}_2\text{CH})_6(\text{O}_2\text{CH})_3]^{2-}$  is another.<sup>6</sup> More recently, Sykes and co-workers studied anation reactions of the structurally similar complex  $[\text{Ir}_3\text{N}(\text{SO}_4)_6(\text{OH}_2)_3]^{4-}$ . They were found to be substantially more facile than typical reactions at mononuclear iridium(III) or iridium(IV) centers.<sup>7</sup> Sasaki and co-workers have studied replacement of water by methanol in the ruthenium(III) and rhodium(III) complexes  $[\text{M}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^+$  ( $\text{M}_3 = \text{Ru}_3, \text{Rh}_3, \text{Ru}_2\text{Rh}$ ). They too found labilization effects, and they proposed substantially dissociative mechanisms for these and other related substitutions.<sup>8</sup> However there is still very little information on the stability or lability of similar complexes of metals of the first transition series.

One problem, commented on in particular by Sykes and co-workers,<sup>7</sup> is to evaluate rate constants for the three consecutive steps of the overall ligand replacement reaction. It is particularly

difficult when a spectrophotometric method is used, since spectra of successive reaction products usually do not differ greatly. In the case cited, this did not prevent the determination of a valid *average* rate constant, and the same is found to be true in the present work. However we differ from the previous authors in the treatment of the statistical factors, which also have to be taken into account.

Here we report kinetics of formation and dissociation of the complex ion  $[\text{Cr}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{urea})_3]^+$ , hereafter written  $\text{ML}_3$  where M denotes the substrate  $[\text{Cr}_3\text{O}(\text{O}_2\text{CCH}_3)_6]^+$  and  $\text{L} = \text{OC}(\text{NH}_2)_2$ :



A feature of the work is that, in measurements of the dissociation rates, absolute concentrations of liberated urea were determined. In this way, we could show that the rate constants are in ratios close to the statistical ratios predicted on the basis of the numbers of occupied and unoccupied ligand sites. The absolute values however are much higher than those of reactions of comparable mononuclear chromium(III) complexes.

## Experimental Section

**Preparation of Complexes.  $[\text{Cr}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{urea})_3]\text{Cl}\cdot 2\text{H}_2\text{O}$ .** Chromium trioxide,  $\text{CrO}_3$ , 5.1 g (0.051 mol), finely ground and dried over  $\text{P}_2\text{O}_5$ , was mixed with 12.0 g of glacial acetic acid. Ethanol (15 mL) was added cautiously, dropwise, with stirring under reflux, the reaction being allowed to subside completely after each addition. Urea (3.2 g, 0.050 mol) was added, and heating and stirring were continued for a further 45–60 min. Concentrated aqueous HCl (4 mL) was added slowly, followed by stirring for another 10 min. The green solution was filtered while hot, leaving no residue, then concentrated to a slurry by heating over a steam bath, and filtered again. After washing twice with 5 mL of ethanol and once with 30 mL of diethyl ether, the product was dried in air and then over silica gel for 12 h. Anal. Calcd: C, 23.2; H, 4.37; N, 10.8; Cl, 4.53. Found: C, 22.9; H, 4.36; N, 10.3; Cl, 4.47. Attempts to prepare the compound by the method of Weinland and Hachenburg<sup>9</sup> generally gave products of much lower urea content.

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**Table 1.** IR Spectral Frequencies (cm<sup>-1</sup>) and Assignments

	OC(NH <sub>2</sub> ) <sub>2</sub>	[CrL <sub>6</sub> ]Cl <sub>3</sub>	[Cr <sub>3</sub> O(OAc) <sub>6</sub> L <sub>3</sub> ]Cl·6H <sub>2</sub> O
A <sub>1</sub>	δ(NH <sub>2</sub> ) 1684 s	1683 s	1670 sh
B <sub>2</sub>	δ(NH <sub>2</sub> ) 1627 s	1578 s	1575 s
	ν(CO) 1600 s	1555 s	1545 sh
B <sub>2</sub>	ν(CN <sub>2</sub> ) 1477 s	1500 s	1500 w, sh
	ρ(NH <sub>2</sub> ) 1146 m	1175 m	1162 w
	1047 m	n.o.	n.o.
	1011 w	n.o.	n.o.
A <sub>1</sub>	ν(CN <sub>2</sub> ) 1003 w	1036 m	1033 w
B <sub>1</sub>	π(CO) 791 w	765 m	765 vw
	ω(HNH) 733 w	726 w	731 w
	δ(NCO) 601 m	635 m	obsc
	ρ <sub>r</sub> (NCN) 573 m	567 m	
	δ(NCN) 559 m	553 m	n.o.
		534 m	540 w
ν(CrO)		464 m	440 m
		390 m	410 m

[Cr<sub>3</sub>O(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]Cl·6H<sub>2</sub>O. This was prepared by reaction of freshly precipitated Cr(OH)<sub>3</sub>·xH<sub>2</sub>O with glacial acetic acid and HCl, as described elsewhere.<sup>10</sup>

[Cr(urea)<sub>6</sub>]Cl<sub>3</sub>. Following the method of Pfeiffer,<sup>11</sup> hydrated chromium(III) chloride, CrCl<sub>3</sub>·6H<sub>2</sub>O (5.4 g, 0.020 mol), recrystallized urea (7.3 g, 0.122 mol), and ethanol (20.0 g) were refluxed on a steam bath for 45 min. The green solution was filtered (no residue) and then allowed to cool in air. The green precipitate which formed within 1 h was collected, washed, and dried in air. Anal. Calcd: C, 13.9; H, 4.6; N, 32.4; Cl, 20.5. Found: C, 13.7; H, 4.5; N, 31.2; Cl, 20.3.

**Urea.** The AnalaR grade was recrystallized three times from water and dried and stored in an oven (in air, ca. 65 °C). Less purified samples gave anomalous kinetic results, typically high rate constants in the ligation experiments. This problem was traced to the presence of carbamate and/or carbonate: aged solutions, even of the recrystallized compound, again became anomalous, and increased rates were also observed when ammonium carbamate was added to the reaction mixtures. For the same reason, presumably, rapid crystallization of urea from warm saturated solutions was better than slow evaporation. Even under such conditions, large (7–10 cm) clear colorless needles were regularly obtained. IR spectra of less satisfactory products could be distinguished, but only by poorer resolution, rather by specific, assignable, impurity peaks.

**Kinetic Measurements.** Visible spectra were measured with a Hitachi U3000 spectrophotometer with temperature control by circulating water through double-walled glass cells. In a typical ligation experiment, because of the high viscosity of concentrated urea solutions, [Cr<sub>3</sub>O(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]Cl·6H<sub>2</sub>O was weighed and dissolved in aqueous perchloric acid, urea was dissolved in water, and both were equilibrated to temperature and then mixed thoroughly before being injected into the cell. Data were initially collected and stored in the Hitachi software and then transferred to Microsoft Excel for manipulation and to Microcal Origin for graphical display and functional analysis.

## Results

**IR Spectra.** High-resolution, low-temperature IR spectra of free urea and of the complexes [Cr(urea)<sub>6</sub>]Cl<sub>3</sub> and [Cr<sub>3</sub>O(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(urea)<sub>3</sub>]Cl·2H<sub>2</sub>O are summarized in Table 1.

An X-ray structure of the mononuclear complex confirms that the urea molecules are coordinated through oxygen, not nitrogen.<sup>12</sup>

Vibrational spectra of urea and its complexes have been reported in detail,<sup>13</sup> and full normal coordinate analyses have

been given.<sup>13e–g</sup> In the range 1700–1000 cm<sup>-1</sup>, free urea has bands which originate from mixtures of the C–O stretch ν(CO) (A<sub>1</sub>), the two components of the CN<sub>2</sub> stretch ν(CN<sub>2</sub>) (A<sub>1</sub>, B<sub>2</sub>), and the two components of the coupled in-plane NH<sub>2</sub> deformations δ(NH<sub>2</sub>) (A<sub>1</sub>, B<sub>2</sub>). In the present spectra, a band observed at 1600 cm<sup>-1</sup> for free urea shifts to approximately 1550 cm<sup>-1</sup> for both the mononuclear and trinuclear complexes. This is attributed to a shift in the fundamental frequency of the C–O stretch, as the double-bond character of the C–O bond is weakened on coordination. The presence of the carboxylate groups in the trinuclear complex obscures this band at room temperature, but it is resolved at 100 K.

The second type of NH<sub>2</sub> deformation in urea consists of in-plane rocking, ρ(NH<sub>2</sub>), coupled to give A<sub>1</sub> and B<sub>2</sub> components in the free urea molecule. These are assigned to a broad band at 1150–1170 cm<sup>-1</sup> in spectra of both mononuclear and trinuclear complexes, again supporting similar coordination modes in both. Two bands at 500–600 cm<sup>-1</sup> can be assigned to NCN deformation and NCN rocking, δ(NCN) and ρ<sub>r</sub>(NCN). They are separate for free urea and for the mononuclear complex but are observed as a single band for the trinuclear complex. In the case of free urea, the deformation and the rock belong to symmetry types A<sub>1</sub> and B<sub>2</sub>, respectively. The distinction seems to be retained in the monomer, but it is apparently lost in the trimer, perhaps because of the presence of the carboxylate groups.

In summary, the IR data confirm that the complex is correctly formulated as [Cr<sub>3</sub>O(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(urea)<sub>3</sub>]<sup>+</sup> and that the chromium–urea linkages are through the oxygen atoms.

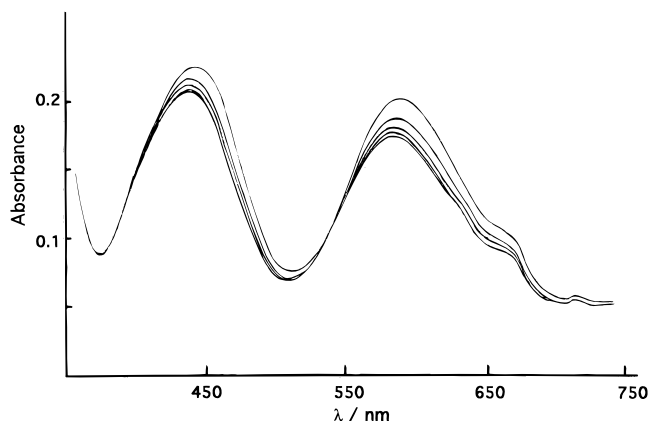
**Preliminary Measurements in Solution.** Visible spectra of [Cr<sub>3</sub>O(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(urea)<sub>3</sub>]<sup>+</sup> and [Cr<sub>3</sub>O(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup> complexes in ethanolic solution showed a slight red shift in the lower of the two main d–d bands on going from H<sub>2</sub>O to urea, as previously observed for mononuclear complexes with Cr and other metals, when the urea is coordinated through oxygen.<sup>14</sup> In ethanol, the urea complex spectrum remains unchanged for at least 1 h at room temperature, but in water it changes with time as shown in Figure 1. Detailed comparisons, and in particular the retention of the <sup>4</sup>B<sub>2</sub> and <sup>4</sup>E(<sup>4</sup>T<sub>2g</sub>)<sup>5,15</sup> bands at 660–720 nm, confirm that the final spectrum is that of the triquo adduct, retaining the trinuclear structure. The half-life of the change is approximately 30 min at room temperature. Independent measurements have shown that loss of acetate ions by the trinuclear complex is negligible over this time, at the temperature and acidity of these measurements.<sup>4</sup>

The spectral changes are reversed on adding urea. Isosbestic points are observed at ca. 535 and 400 nm, though they are not well-defined as the spectra have similar slopes at these wavelengths.

**Kinetic Measurements.** Ligation reactions were studied with urea concentrations in the range 2–7 M, at the optimum fixed wavelength of 615 nm. Although the absorbance changes were small, good quality first-order kinetics were observed with signal averaging over three or four runs. At temperatures *T* = 15–

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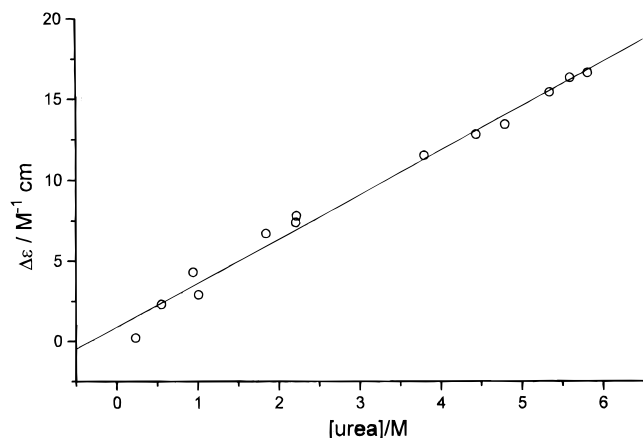


**Figure 1.** Changes in electronic spectra during the aquation of  $[\text{Cr}_3\text{O}(\text{OAc})_6(\text{urea})_3]^+$ , in water.  $[\text{Cr}_3]_{\text{T}} = 1.5 \text{ mM}$ .  $T = 25 \text{ }^\circ\text{C}$ . Time interval: 30 min.

**Table 2.** Kinetic Data for Reactions of  $[\text{Cr}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]^+$  with Urea<sup>a</sup>

$T, \text{ }^\circ\text{C}$	[urea], M	$k_{\text{obs}}$ , $10^{-4} \text{ s}^{-1}$	$T, \text{ }^\circ\text{C}$	[urea], M	$k_{\text{obs}}$ , $10^{-4} \text{ s}^{-1}$
15.0	2.0	2.931	25.0	4.0	3.421
15.0	3.0	3.247	25.0	5.0	3.472
15.0	4.0	3.378	35.0	2.0	3.010
15.0	5.0	3.582	35.0	3.0	3.251
25.0	2.0	2.983	35.0	4.0	3.346
25.0	3.0	3.264	35.0	5.0	3.567

<sup>a</sup>  $\lambda = 600 \text{ nm}$ ;  $I = 0.02 \text{ M (HClO}_4)$ ;  $[\text{Cr}_3]_{\text{T}} = 0.8\text{--}0.9 \text{ mM}$ .

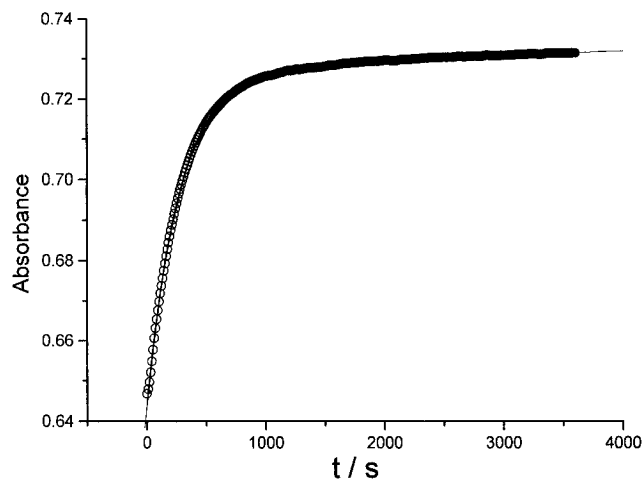


**Figure 2.** Variation of total absorbance change with urea concentration.  $\Delta\epsilon = [A(\infty) - A(0)]/I[\text{Cr}_3]_{\text{T}}$ .  $[\text{Cr}_3]_{\text{T}} \approx 0.9 \text{ mM}$ ;  $[\text{HClO}_4] = 0.2 \text{ M}$ ;  $T = 25 \text{ }^\circ\text{C}$ .

$35 \text{ }^\circ\text{C}$ , observed rate constants  $k_{\text{obs}}$  for the overall reactions are defined by

$$-(d/dt) \log |A(\infty) - A(0)| = -0.434k_{\text{obs}}t \quad (2)$$

Values of  $k_{\text{obs}}$  are listed in Table 2. The fact that ligation does not proceed to completion is confirmed by plots of  $[A(\infty) - A(0)]$  against urea concentration, which are linear for the whole of the accessible concentration range (Figure 2). At  $35 \text{ }^\circ\text{C}$ , the rate plots showed appreciable deviation from (pseudo) first order at long times. Good fits were obtained to biphasic expressions such as two consecutive exponential functions or one exponential followed by a linear drift of absorbance with time (Figure 3). Absorbance changes corresponding to the first phase fitted well to plots of the type shown in Figure 2, and the rate constants again correlated positively with urea concentration. The second phases represented only small fractions of the total absorbance changes, and they showed no dependence



**Figure 3.** Change in absorbance with time ( $\lambda = 600 \text{ nm}$ ) for the reaction  $[\text{Cr}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]^+ + \text{urea} \rightarrow \text{products}$ .  $[\text{Cr}_3]_{\text{T}} = 3.1 \text{ mM}$ ;  $[\text{urea}] = 4.0 \text{ M}$ ;  $I = 0.02 \text{ M (HClO}_4)$ . The full line is the fitted curve for the equation  $A(t) = A(0) + B \exp(-k_1t) + C \exp(-k_2t)$ .

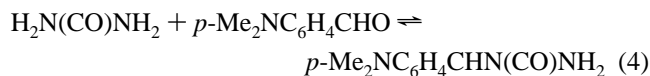
on urea concentration. They are attributed to side reactions involving break-up of the central  $[\text{Cr}_3\text{O}(\text{O}_2\text{CCH}_3)_6]$  unit and were not studied further (see comment below). Thus the ligation kinetics are described by the standard equation for approach to equilibrium

$$k_{\text{obs}} = k_{\text{aq}} + k_{\text{lig}}[\text{L}] \quad (3)$$

where  $k_{\text{aq}}$  and  $k_{\text{lig}}$  are rate constants for aquation and ligation reactions, to be defined more precisely below.

Aquation reactions were studied first at the same wavelength by starting with the triurea complex in aqueous acidic solution. First-order kinetics were observed in every experiment. Values of  $k_{\text{obs}}$  are listed in Table 3. Logarithmic plots were linear for more than 5 half-lives, corresponding to dissociation of *ca.* 2.8 urea molecules per complex (Figure 4). This was confirmed by further experiments in which the free ligand concentration was measured absolutely.

Reaction 4 is the basis of a standard colorimetric test for urea.<sup>16</sup> The reagent *p*-(dimethylamino)benzaldehyde is colorless, but the adduct is yellow with an intense absorption



maximum at  $\lambda = 430 \text{ nm}$ . Reaction 4 proved to be fast enough to serve as a direct probe of the urea concentration. Experiments confirmed that equilibrium is reached within the time of mixing of solutions, under conditions of moderate acid concentration. The reaction does not go to completion: the absorbance due to adduct increases linearly with added aldehyde concentration, the latter being in large excess over urea, but the extinction coefficient of the adduct is large compared with that of the chromium complexes at the same wavelength, and the spectrum is stable over several hours at room temperature. At fixed aldehyde concentration, the intensity is linear with urea concentration over the relevant concentration range, and calibration curves were obtained for the relevant conditions of  $[\text{H}^+]$  and temperature. The reagent was shown not to interfere with the aquation process of interest. In the kinetic experiments, initial and final absorbance readings confirmed that 3.0 molecules of urea are lost per trimer molecule and that the initial concentration of free urea was negligible. Variation of added aldehyde

**Table 3.** Kinetic data for Aquation of  $[\text{Cr}_3\text{O}(\text{OAc})_6(\text{urea})_3]^+$ <sup>a</sup>

$\lambda$ , nm	$T$ , °C	[ald], <sup>b</sup> mM	[EtOH], M	[H <sup>+</sup> ], mM	$k_{\text{obs}}$ , $10^{-4} \text{ s}^{-1}$
615	14.4	0	0	20	2.10
615	14.4	0	0	16	1.80
615	14.4	0	0	14	1.93
615	14.6	0	0	12	1.93
615	14.7	0	0	8	1.93
615	14.7	0	0	4	1.86
615	25.2	0	0	200	8.66
615	25.2	0	0	160	8.66
615	25.2	0	0	140	8.49
615	25.2	0	0	100	8.08
615	25.2	0	0	60	8.00
615	25.2	0	0	50	9.56
615	25.2	0	0	20	8.66
615	25.2	0	0	10	7.73
430	25.0	0	8.7	400	10.4 <sup>c</sup>
430	25.0	12	8.7	400	10.1 <sup>c</sup>
430	25.0	12	8.7	400	10.4 <sup>c</sup>
430	25.4	30	8.7	400	9.76 <sup>c</sup>
430	25.2	60	8.7	400	9.76 <sup>c</sup>
430	25.2	60	8.7	400	10.3 <sup>c</sup>
430	25.4	120	8.7	400	9.90 <sup>c</sup>
430	25.2	40	5.0	200	8.69
430	25.0	40	5.0	200	8.56
430	24.9	40	5.0	200	9.40
430	25.0	40	5.0	200	8.40
615	34.6	0	0	40	30.6
615	35.0	0	0	60	27.7
615	34.8	0	0	80	31.5
615	34.8	0	0	100	32.6
615	34.9	0	0	120	29.5
615	34.5	0	0	120	31.9
615	34.9	0	0	140	34.5
615	34.9	0	0	160	31.8
615	34.7	0	0	160	31.8
615	34.8	0	0	180	34.7
615	34.8	0	0	200	32.6
615	34.6	0	0	200	34.7
430	34.9	40	5.0	200	29.7
430	34.9	40	5.0	200	30.6
430	34.8	40	5.0	200	30.2

<sup>a</sup>  $I = 0.2 \text{ M}$  ( $\text{LiClO}_4$ );  $[\text{Cr}_3]_{\text{T}} = 0.8\text{--}0.9 \text{ mM}$ . <sup>b</sup> ald =  $p\text{-Me}_2\text{NC}_6\text{H}_4\text{CHO}$ . <sup>c</sup>  $I = 0.4 \text{ M}$ .

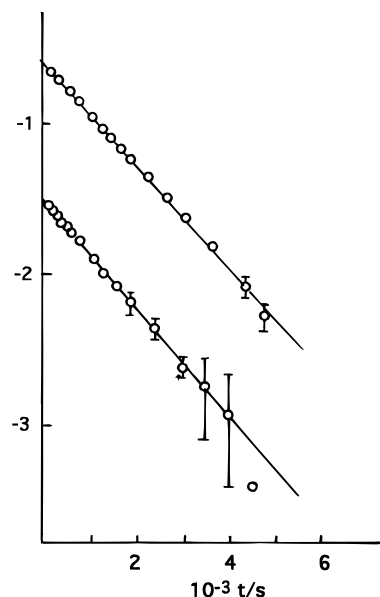
concentration over the range 0.01–0.12 M had no effect on rate. Rates were independent of  $[\text{H}^+]$  over the range 0.02–0.2 M, at  $T = 15$  and  $25 \text{ }^\circ\text{C}$ ; but at  $35 \text{ }^\circ\text{C}$  a slight upward trend was seen consistent with the expression

$$k_{\text{obs}} = k_{\text{aq}} + k_{\text{H}}[\text{H}^+] \quad (5)$$

The second term is again attributed to side reactions involving acid-catalyzed dissociation of bridging acetate ions.<sup>4</sup> Final values of  $k_{\text{aq}}$  are listed in Table 4.

## Discussion

The IR, analytical, and kinetic data make it clear that the starting material of the aquation reactions is the complex with three coordinated urea molecules,  $[\text{Cr}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{urea})_3]^+$ . The key observations of the kinetics are that aquation is monophasic over all three steps of ligand replacement; that the pseudo-first-order rate constants measured spectrophotometrically for the total mixture of chromium complexes, and for the liberated urea alone, are in good agreement; and that the specific rates of approach to equilibrium, in the directions of both aquation and ligation, are consistent. All this agrees with a statistically controlled mechanism. That is, in the reaction scheme (1a)–(1c), the successive ligation rate coefficients  $k_1$ ,  $k_2$ ,  $k_3$  are approximately in the ratio 3:2:1 and the aquation rate



**Figure 4.** First-order rate plots for aquation of  $[\text{Cr}_3\text{O}(\text{OAc})_6(\text{urea})_3]^+$ : upper curve, using added  $p\text{-Me}_2\text{NC}_6\text{H}_4\text{CHO}$  to determine liberated urea,  $\lambda = 430 \text{ nm}$ ,  $[\text{HClO}_4] = 0.4 \text{ M}$ ,  $[\text{EtOH}] = 5 \text{ M}$ ,  $[\text{aldehyde}] = 0.04 \text{ M}$ ,  $T = 25 \text{ }^\circ\text{C}$ , vertical coordinate is  $\log[A(\infty) - A(t)]$ ; lower curve, no added aldehyde,  $\lambda = 615 \text{ nm}$ ,  $[\text{EtOH}] = 0$ ,  $[\text{HClO}_4] = 0.2 \text{ M}$ ,  $T = 25 \text{ }^\circ\text{C}$ , vertical coordinate is  $\log[A(t) - A(\infty)]$ .

**Table 4.** Summary of Rate and Activation Parameters<sup>a</sup>

$T$ , <sup>b</sup> °C	[EtOH], M	$k_{\text{aq}}$ , $\text{s}^{-1}$	$k_{\text{lig}}$ , <sup>d</sup> $\text{M}^{-1} \text{ s}^{-1}$
14.5	0	$1.93 \pm 0.09$	
15	0	$2.6 \pm 0.1^d$	$0.18 \pm 0.03$
25	0	$8.5 \pm 0.5$	
25	5.0	$8.8 \pm 0.4$	
25	0	$6.4 \pm 0.4^d$	$0.49 \pm 0.10$
25	8.7 <sup>c</sup>	$10.1 \pm 0.3$	
35	0	$32 \pm 2$	
35	0	$26.3 \pm 0.4^d$	$1.3 \pm 0.2$
35	5.0	$30.0 \pm 0.4$	

$\Delta H^\ddagger$ ,  $\text{kJ mol}^{-1}$

$\Delta S^\ddagger$ ,  $\text{J K}^{-1} \text{ mol}^{-1}$

$98 \pm 1$

$102 \pm 2$

$71 \pm 4$

$-12 \pm 7$

<sup>a</sup>  $I = 0.2 \text{ M}$  ( $\text{LiClO}_4$ ). <sup>b</sup>  $\pm 0.2^\circ$ . For temperatures of individual runs, see Tables 2 and 3. <sup>c</sup>  $I = 0.4 \text{ M}$ . <sup>d</sup>  $I = 0.02 \text{ M}$  ( $\text{LiClO}_4$ ).

constants  $k_{-1}$ ,  $k_{-2}$ ,  $k_{-3}$  are in the ratio 1:2:3; also the successive differences in extinction coefficients of the four chromium complexes,  $\text{M}^+$ ,  $\text{ML}^+$ ,  $\text{ML}_2^+$ ,  $\text{ML}_3^+$ , are approximately equal. This type of reaction scheme has been analyzed many times for the case of a two-step reaction, and also for an irreversible three-step reaction,<sup>17</sup> and for analogous situations such as the equilibrium dissociation of a dibasic acid.<sup>18</sup> Vanderheiden and King also discussed a six-step reversible reaction, and they suggested on the basis of intuition that in that case also monophasic kinetics should be observed if the statistical relationships between the parameters are assumed.<sup>19</sup> In the Supporting Information we prove formally that this is correct, for any number of steps. The proof is expressed in matrix notation, but when expanded in ordinary algebra and reduced to the case of two steps, it is the same as that given by previous authors for simpler cases.<sup>20</sup> Applied to the present case, with ligand in large excess over chromium complexes, it gives

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$$\begin{aligned} A(t) - A(\infty) &= -3a(\Delta\epsilon)lK[L](1 + K[L])^{-1} \exp(-k_{\text{obs}}t) \\ &= [A(0) - A(\infty)] \exp(-k_{\text{obs}}t) \end{aligned} \quad (6)$$

where  $a$  is the total trichromium complex concentration,  $[\text{Cr}_3]_{\text{T}}$ ,  $\Delta\epsilon = \epsilon_i - \epsilon_{i-1}$ ,  $l$  is the path length,  $K = k_1/k_{-3}$ , and

$$k_{\text{obs}} = (k_1[L] + k_{-3})/3 \quad (7)$$

so that our measured  $k_{\text{lig}}$  and  $k_{\text{aq}}$  correspond to  $3k_1$  and  $3k_{-3}$ , respectively.

The experiments with added aldehyde, and with urea concentration small throughout, are described by

$$[L] - [L](\infty) = -3a \exp(-k_{\text{obs}}t) \quad (8)$$

$$A(t) - A(\infty) = -3a\epsilon l \exp(-k_{\text{obs}}t) \quad (9)$$

where  $\epsilon$  denotes the extinction coefficient of the urea-aldehyde adduct, other extinction coefficients being neglected.

The case of four consecutive reversible steps has also been dealt with in a series of studies by Sykes and co-workers,<sup>7,21</sup> mainly in reactions of the type  $[\text{M}_3\text{X}_4(\text{OH}_2)_9]^{n+} + \text{L}^- = [\text{M}_3\text{X}_4(\text{OH}_2)_{9-i}\text{L}_i]^{(n-i)+}$  ( $\text{M} = \text{Mo}, \text{W}; \text{S} = \text{O}, \text{S}, \text{Se}; n = 4, 5, 6; \text{L}^- = \text{NCS}^-, \text{Cl}^-$ ). Typically the substrate has three equivalent sites for replacement of  $\text{H}_2\text{O}$  by ligand  $\text{L}$ , and Sykes and co-workers include the statistical factor of 3 in the rate equations, writing the pseudo-first-order rate constants  $k_{\text{eq}}$  for the approach to equilibrium as

$$k_{\text{eq}} = (k_1/3)[L] + k_{-1} \quad (10a)$$

when the ligand  $\text{L}$  is in large excess over the substrate  $\text{M}$ , but

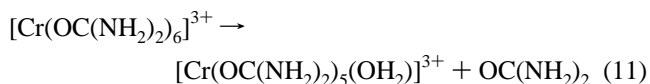
$$k_{\text{eq}} = k_1[\text{M}] + k_{-1} \quad (10b)$$

when the substrate is in excess over the ligand.<sup>21a</sup> We have preferred not to incorporate the statistical factor in the empirical rate equations.

The statistical relationship between rate constants means that each urea molecule dissociates with a probability independent of the presence or absence of other urea molecules. This is not surprising if it is assumed that the main factors which could cause differences in rate are interligand repulsions. As regards the formation reactions, under our conditions these do not

progress significantly beyond the formation of the first complex. (This accounts for the difficulty of preparing the tris(urea) adduct, referred to above, and for the nearly anhydrous conditions which were found necessary.) Thus we have no proof that the relationship between the three ligation rate constants is statistical. However the magnitude of the overall equilibrium constant suggests that it is so. In eq 6,  $K$  corresponds to the ratio  $k_{\text{lig}}/k_{\text{aq}}$ , the overall equilibrium constant for reactions 1a–1c being  $K^3$ , and this gives values of  $K$  of the order of  $0.02 \text{ M}^{-1}$  in the conventional units. But in reactions 1a–1c an  $\text{H}_2\text{O}$  molecule is displaced, and with the assignment of a “concentration”  $[\text{H}_2\text{O}] = 1000/18 = 55.5 \text{ M}$ , a more realistic equilibrium constant would be defined as  $K^{\text{true}} = [\text{ML}][\text{H}_2\text{O}]/[\text{MOH}_2][\text{L}]$ , giving  $K^{\text{true}} = 0.02 \times 55.5 \approx 1$ . More precisely, this should be written in terms of ligand and solvent activities, but the essential point is that at equilibrium the mole ratio of bound urea to bound water is of the same order as the mole ratio of free urea and water in the bulk solvent.

There is evidently not much change in the character of an individual chromium–urea bond, as a remote urea molecule is added or removed, but the character of these bonds is strongly affected by the presence of the central oxide ion. Kilpatrick<sup>22</sup> reported specific rates of aquation of the mononuclear hexakis(urea) complex:



In aqueous solution, rates were found to be zero-order in hydrogen ion, as in the present system, with  $k = 1.8 \times 10^{-6} \text{ s}^{-1}$  at  $25^\circ\text{C}$ . In the trinuclear complexes, the urea is more labile by a factor of approximately  $4 \times 10^2$ . The most obvious cause of the difference is an electronic effect of the central oxide ion of the trinuclear complex, mediated by the chromium atoms specifically to the ligands in the *trans* positions. Recently, the structure and IR spectra of the analogous fluoride adduct  $[\text{Cr}_3\text{O}(\text{O}_2\text{CC}_2\text{H}_5)_6\text{F}_3]^{2-}$  were reported.<sup>23</sup> In comparison with other complexes containing chromium–fluorine bonds, it was shown that these bonds were the longest, and the stretching frequencies were the lowest, of any so far reported. The chromium–fluorine data provided evidence of a static *trans* effect. The present results demonstrate a kinetic *trans* effect.

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**Supporting Information Available:** Kinetics are solved for a reaction scheme consisting of reagents  $A_i$ ,  $i = 1, 2, \dots, N$ , linked in all possible ways by reversible steps with first-order rate constants. The rate of approach to equilibrium and the variation of absorbance with time are obtained. For the case of four reagents linked by successive steps, with statistical relationships and pseudo-first-order kinetics, eqs 8 and 9 of the text are derived (4 pages). Ordering information is given on any current masthead page.

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