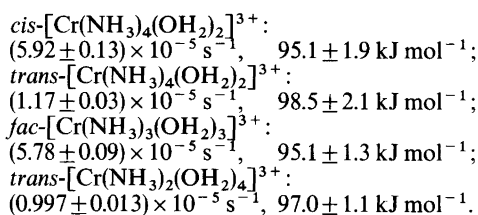


Reaction Rate Studies of the Acid Hydrolysis of Some Chromium(III) Complexes. XI. Water Exchange of *cis*- and *trans*-Tetraamminediaqua-, of *fac*-Triamminetriaqua- and of *trans*-Diamminetetraaquachromium(III) Ions in Aqueous Perchloric Acid

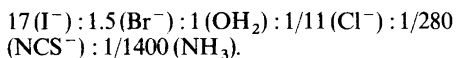
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Water exchange of *cis*- and *trans*-tetraamminediaqua-, of *fac*-triamminetriaqua- and of *trans*-diamminetetraaquachromium(III) in a 1 M perchlorate medium has been investigated. Rate constants at 25 °C for the exchange of one water ligand and activation energies are:



The rate constants correlate well with data for aquation of ammine- and halogenidochromium(III) complexes, and for a fixed set of non-reacting ligands the following relative aquation rates have been estimated for five series of complexes:



The kinetics of configurational changes of chromium(III) complexes have not been widely investigated. Recently we presented some indirect evidence in favour of the importance of water exchange for the occurrence of *trans* to *cis* isomerization of the chloride ligands in ammineaquadichloridochromium(III) complexes.¹ More direct evidence

will have to come from quantitative data for water exchange and in the present work results for *cis*- and *trans*-tetraamminediaqua-, *fac*-triamminetriaqua- and *trans*-diamminetetraaquachromium(III) are reported. When combined with literature data for pentaammineaqua-² and hexaaquachromium(III)³ this completes the series of ammineaquachromium(III) ions with equivalently coordinated water ligands.

EXPERIMENTAL

Chemicals. $[\text{Cr}(\text{NH}_3)_5\text{Br}]\text{Br}_2$,⁴ *cis*- $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{-Cl}\cdot\text{H}_2\text{O}$,⁵ *trans*- $[\text{Cr}(\text{NH}_3)_4\text{Br}_2]\text{Br}\cdot\text{H}_2\text{O}$,⁶ and *trans*- $[\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_2\text{Cl}_2]\text{Cl}$ ⁷ were prepared by literature methods. *Fac*- $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$ was obtained from Dr. P. Andersen.⁸ Ag(tos)* was prepared by the addition of *p*-toluenesulfonic acid to an aqueous solution of AgNO₃. The precipitate thus obtained was recrystallized twice from water, and dried in vacuum over solid NaOH. H₂¹⁸O (I.P. ~99 %) was obtained from 'Alfa products'. The source of other chemicals has been described earlier.⁹

Preparation of oxygen-18 enriched aquachromium(III) complexes. 0.6 mmol of $[\text{Cr}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ was treated with 1.9 mmol Ag(tos) in 1.0 ml H₂¹⁸O for 15 min at 30 °C. The reaction mixture was then frozen and excess H₂¹⁸O removed by sublimation in vacuum. The remaining solid, which is a mixture of chromium(III) complexes, AgBr and

* tos ≡ *p*-toluenesulfonate ≡ *p*-CH₃C₆H₄SO₃⁻.

unreacted excess Ag(tos), was treated with 0.01 M HClO_4 and excess Ag^+ precipitated by addition of a concentrated solution of NaBr. AgBr was filtered off and the filtrate was charged onto a 10 cm \times 2 cm column of Sephadex SP-C-25. Elution with 0.35 M NaClO_4 , pH \sim 2, removed halogenido- and *p*-toluenesulfonate complexes, after which the oxygen-18 enriched pentaammineaquachromium(III) ion was eluted with 1.0 M NaClO_4 , pH \sim 2. The eluate, about 25 ml, was diluted with the appropriate amount of 1.0 M $(\text{Na,H})\text{ClO}_4$ and immediately used for the kinetic experiments.

cis- and *trans*- $[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$, *fac*- $[\text{Cr}(\text{NH}_3)_3(\text{OH}_2)_3]^{3+}$ and *trans*- $[\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_4]^{3+}$ were prepared analogously from *cis*- $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\cdot\text{Cl}\cdot\text{H}_2\text{O}$, *trans*- $[\text{Cr}(\text{NH}_3)_4\text{Br}_2]\cdot\text{Br}\cdot\text{H}_2\text{O}$, *fac*- $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$ and *trans*- $[\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_2\text{Cl}_2]\text{Cl}$, respectively. In all cases, an amount of complex which, when dried at 100 °C, contained 0.6 mmol of coordinated halogenide ions was employed. All manipulations of oxygen-18 enriched complexes, including the ion exchange separations were carried out in the dark and at temperatures below 5 °C in order to minimize water exchange prior to the kinetic runs. The ammineaqua complexes thus prepared had spectral characteristics in complete agreement with those of ammineaquachromium(III) complexes prepared and purified by other methods.⁹⁻¹¹

Kinetic measurements. Solutions prepared as described above were protected from light and placed in a thermostatted water bath maintained at the desired reaction temperature with an accuracy

of ± 0.05 °C. 10 ml samples were withdrawn at suitable time intervals and rapidly frozen. They were next sublimed in vacuum to yield about 8 ml of slightly acid water, pH \sim 5, which was used for the mass spectrometric $^{18}\text{O}/^{16}\text{O}$ ratio determinations. The residue from the sublimation was diluted to 10 ml with water and checked spectrophotometrically to see that loss of coordinated ammonia had not occurred.

Methods of analyses⁹ and spectrophotometric measurements¹² have been described earlier.

Mass spectrometric measurements. The mass spectrometric measurements of the $^{18}\text{O}/^{16}\text{O}$ ratios, R_{sample} , were performed relative to V-SMOW (Vienna Standard Mean Ocean Water)¹³ at the Geophysical Isotope Laboratory at the University of Copenhagen. The results are given as δ -values, defined according to:

$$\delta \equiv (R_{\text{sample}} - R_{\text{V-SMOW}}) / R_{\text{V-SMOW}}$$

and the absolute $^{18}\text{O}/^{16}\text{O}$ ratio of V-SMOW: $R_{\text{V-SMOW}}$, has been found to have the value $(2005.20 \pm 0.45) \times 10^{-6}$.¹³ Experimentally the δ -values are measured most accurately when close to 0. In the present investigation they were limited to the range from -15 ‰ to $+30$ ‰. At 0 °C $p(\text{H}_2^{16}\text{O})/p(\text{H}_2^{18}\text{O}) \sim 1.018$ and it is, therefore, important that all sublimations to yield the samples for the mass spectrometric measurements are carried out reproducibly. The major source of uncertainty was found to arise from small differences in the amount

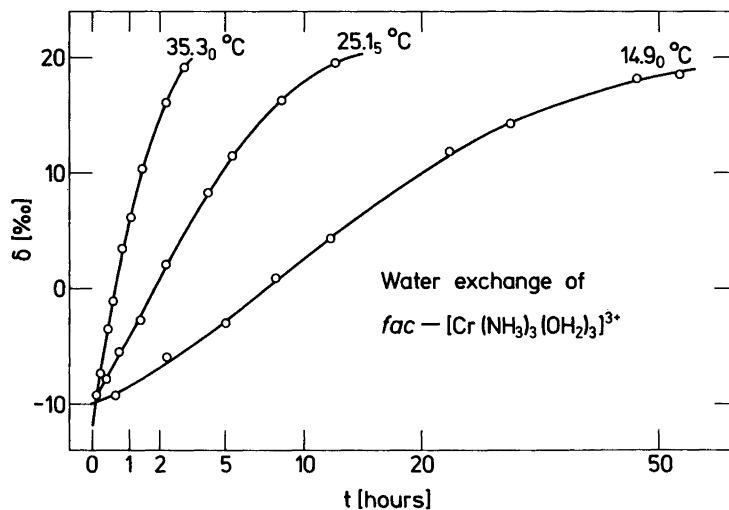


Fig. 1. Reaction kinetic experiments for water exchange in *fac*-triamminetriaquachromium(III). The experimental points, O, have been corrected for differences in the amount of sublimed water; cf. eqn. (1). The solid curves have been calculated from the rate parameters of Table 2.

of sublimed water and an empirical correction to the measured δ -values, δ_{meas} , as function of the volume of sublimed water, v , had to be used. The correction was obtained from data for about 100 samples, and could be expressed as:

$$\delta_{\text{corr}} \sim \delta_{\text{meas}} - [1.22 + 1.82(\exp(-1.56(8.75-v)) - 1)] \text{‰} \quad (1)$$

valid for 7 ml $\lesssim v \lesssim$ 9 ml of sublimed water.

Method of calculation. The corrected δ -values, $\delta_{\text{corr},t}$, as function of time, t , were approximated by a curve calculated from the expression:

$$\delta_t = \delta_0 + \delta_c [\exp(-kt) - 1]$$

(cf. the Appendix) with the three parameters: δ_0 , δ_c and k estimated by minimization of:

$$\sum_t \{ \delta_{\text{corr},t} - \delta_t \}^2 / \sigma^2(\delta_{\text{corr},t})$$

by non-linear regression analysis. $\sigma^2(\delta_{\text{corr},t})$ is the variance of $\delta_{\text{corr},t}$. Some examples of the agreement between calculated curves and the experimental data are shown in Fig. 1. The further calculations to yield activation parameters were carried out essentially as described earlier.¹²

RESULTS AND DISCUSSION

Oxygen-18 enriched ammineaquachromium(III) complexes are most conveniently prepared by

Table 1. Comparison with literature values of some rate constants for water exchange.

$[\text{Cr}(\text{OH}_2)_6]^{3+}$; 39.8 $^\circ$ C		
$10^5 k$ (s $^{-1}$)	2.06 \pm 0.11	2.11 \pm 0.11
[Cr(III)] (mM)	1.65	\sim 95
[H $^+$] (M)	0.50	\sim 0.10
[Na $^+$] (M)	0.50	—
[ClO $_4^-$] (M)	1.00	\sim 0.40
$^{18}\text{O}/^{16}\text{O}$		
monitored in	OH $_2$	$[\text{Cr}(\text{OH}_2)_6]\text{PO}_4$
Ref.	This work	3
$[\text{Co}(\text{NH}_3)_5\text{OH}_2]^{3+}$; 25.1 $^\circ$ C		
$10^6 k$ (s $^{-1}$)	5.4 \pm 0.3	5.9
[Co(III)] (mM)	2.49	100
[H $^+$] (M)	0.50	0.006–0.010
[Na $^+$] (M)	0.50	—
[ClO $_4^-$] (M)	1.00	0.31
$^{18}\text{O}/^{16}\text{O}$		
monitored in	OH $_2$	$[\text{Co}(\text{NH}_3)_5\text{OH}_2]\text{Br}_3$
Ref.	This work	14

Table 2. Rate constants for water exchange in ammineaquachromium(III) complexes.

Temp. [°C]	[H $^+$] [M]	[Cr(III)] [mM]	$^{18}\text{O}_{\text{Cr}}/\text{O}_{\text{Cr}}^{\text{tot}}$ [%]	$10^5 k^a$ [s $^{-1}$]
$[\text{Cr}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$				
15.7 $_0$	0.51	3.28	88	1.55 \pm 0.09
25.6 $_0$	0.51	3.13	87	6.23 \pm 0.06
34.8 $_0$	0.51	3.58	88	21.8 \pm 0.4
<i>cis</i> - $[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$				
15.3 $_5$	0.51	3.23	50	1.62 \pm 0.07
25.6 $_0$	0.51	2.06	49	6.0 \pm 0.3
35.2 $_5$	0.50	2.11	50	22.9 \pm 1.3
36.1 $_0$	0.51	2.46	49	24 \pm 3
<i>trans</i> - $[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$				
15.0 $_5$	0.52	1.60	50	0.316 \pm 0.019
19.9 $_0$	0.52	1.86	48	0.63 \pm 0.02
30.1 $_0$	0.51	2.08	52	2.31 \pm 0.07
30.3 $_0$	0.22	1.87	51	2.17 \pm 0.04
40.5 $_0$	0.52	2.11	55	9.13 \pm 0.17
<i>fac</i> - $[\text{Cr}(\text{NH}_3)_3(\text{OH}_2)_3]^{3+}$				
14.9 $_0$	0.52	1.39	80	1.49 \pm 0.04
25.1 $_5$	0.52	1.44	81	5.69 \pm 0.12
35.3 $_0$	0.53	1.45	86	21.6 \pm 0.3
<i>trans</i> - $[\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_4]^{3+}$				
15.1 $_5$	0.51	1.57	49	0.252 \pm 0.005
24.9 $_0$	0.52	1.03	56	1.00 \pm 0.04
35.1 $_0$	0.50	1.12	46	3.70 \pm 0.08

^a See appendix.

aquation of halogenido complexes in oxygen-18 enriched water. Direct aquation is difficult to carry out without some loss of coordinated ammonia, but both silver(I) and mercury(II) may conveniently be used to accelerate the loss of both chloride and bromide ligands. To limit isotopic dilution of the oxygen-18 enriched water it is necessary to work with non-hydrated reactants and, to maximize the yield of aqua complex, it is necessary to have salts of an only weakly coordinating anion. Several salts of both silver(I) and mercury(II) were tested and it was found that, of these, silver(I) tosylate was the best for the present purpose as it is readily prepared without water of crystallization and only minor amounts of tosylate complexes are formed in the concentrated solutions used for the preparative work. Also these complexes are robust enough to be separated from

the aquacomplexes by the ion exchange chromatographic procedure used to purify the aqua complexes.

The oxygen-18 labelled complexes were prepared from oxygen-18 labelled water which initially had an isotopic purity of about 99%. After purification the isotopic oxygen-18 purity of the aqua complexes is somewhat lower, but approximately constant for individual complexes. This is shown in Table 2 where the isotopic purity is seen to be: ~90% for the pentaammine-, ~50% for both the *cis*- and the *trans*-tetraammine- and ~85% for the *fac*-triammine complex. The *cis*- and *trans*-tetraammine-dihalogenidochromium(III) starting materials may contain some aquahalogenido complex and this can also be formed during the heating of the complexes to remove water of crystallization. The pentaammineaqua- and the *fac*-triamminetriaquachromium(III) are, however, prepared from non-hydrated starting materials. At 5 °C the half life for water exchange in all the ammineaquachromium(III) complexes is greater than 30 h. Preparation of the reactant solutions usually took about 2–3 h and the lowering of the isotopic purity of the generated ammineaquachromium(III) complexes compared to that of the reactant water can, therefore, most likely be attributed to the kinetic significance of deprotonated complexes at pH ~ 2 the condition under which most manipulations, including the ion exchange separation, were carried out; cf. Ref. 16. *trans*-Diamminetetraaquachromium(III) is generated from a complex ion which already contains two water ligands of normal isotopic distribution. This ion is seen to have an isotopic purity of about 50% and, therefore, in this case some equilibration between solvent and coordinated water must have taken place during the preparation.

Slow water exchange reactions of metal complexes

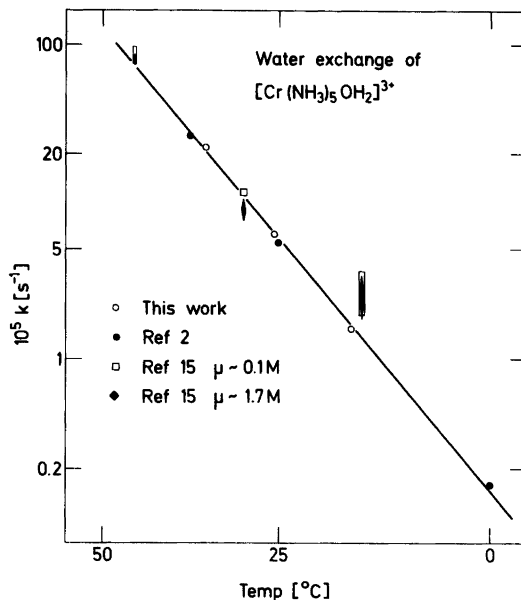


Fig. 2. Comparison with literature data of the rate of water exchange in pentaammineaquachromium(III). The experimental points have been drawn with a vertical extent corresponding to $\pm 1 \times$ the estimated standard deviations. The solid line is the basis for the parameters of Table 3.

are usually studied by oxygen-18 labelling and mass spectrometric monitoring of the $^{16}\text{O}/^{18}\text{O}$ ratio in the complex or solvent after separation, usually by precipitation of the complex. For the ammineaquachromium(III) complexes this approach is, however, not generally applicable and it was, therefore, necessary to modify established methods. This included the use of complexes, highly labelled in oxygen-18,

Table 3. Kinetic parameters for water exchange in ammineaquachromium(III) complexes.

Complex	$10^5 k^a(25\text{ °C})$ [s^{-1}]	ΔH^* [kJ mol^{-1}]	ΔS^*^a [$\text{J K}^{-1} \text{mol}^{-1}$]
$[\text{Cr}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$	5.75 ± 0.06	99.1 ± 1.4	$+7 \pm 5$
<i>cis</i> - $[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$	5.92 ± 0.13	95.1 ± 1.9	-7 ± 6
<i>trans</i> - $[\text{Cr}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$	1.17 ± 0.03	98.5 ± 2.1	-9 ± 7
<i>fac</i> - $[\text{Cr}(\text{NH}_3)_3(\text{OH}_2)_3]^{3+}$	5.78 ± 0.09	95.1 ± 1.3	-7 ± 5
<i>trans</i> - $[\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_4]^{3+}$	0.997 ± 0.013	97.0 ± 1.1	-15 ± 4
$[\text{Cr}(\text{OH}_2)_6]^{3+}$ ^c	0.246 ± 0.012	109.6 ± 1.3	$+16 \pm 5$

^a See appendix. ^b Ref. 2 and this work (see Fig. 2). ^c Ref. 3.

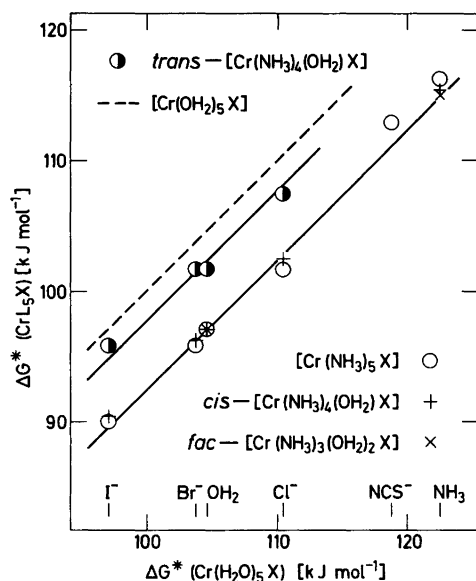


Fig. 3. Linear free energy relationships for five series of chromium(III) complexes. The straight lines have been drawn with a slope of 1 in accord with eqn. (3). The data are from Table 3 in this work and Refs. 2, 3, 10 and 17–25.

in combination with high precision mass-spectrometry. Ordinary water contains about 0.20 % of H_2^{18}O which is equivalent to a 111 mM solution. Changes of a few per cent of this value can be accurately measured, and this corresponds to changes in H_2^{18}O at the millimolar level; cf. Table 1. Fig. 1 shows some examples of kinetic runs, and in Table 1 and Fig. 2 are given comparisons of results obtained using this modified technique and earlier literature data for hexaaquachromium(III), pentaammineaquachromium(III) and -cobalt(III), all of which were studied by monitoring the oxygen-18 content in the complex ion isolated by precipitation.

In Table 2 are shown data for water exchange of *cis*- and *trans*-tetraamminediaqua-, *fac*-triamminetriaqua- and *trans*-diamminetetraaquachromium(III) in a 1 M perchlorate medium, and in Table 3 these data have been collected to give activation parameters for the reactions. The rate of water exchange of *trans*-tetraamminediaquachromium(III) is seen to be independent of the hydrogen ion concentration, and literature data in combination with the present data show that this is also the case for

pentaamminequa-^{2,16} and hexaaquachromium(III)³ at such high acidities as employed in this work. *cis*-Tetraamminediaqua-, *fac*-triamminetriaqua- and *trans*-diamminetetraaquachromium(III) have not been investigated at different hydrogen ion concentrations but comparisons with the chromium(III) complexes cited above, which contain examples of water exchange *trans* to both ammonia and water, make it very likely that the measured rate constants should be attributed to an acid independent reaction.

Fig. 3 is a comparison of the results for a number of reactions of the type:



("CrL₅" = "Cr(NH₃)₅", "*cis*-Cr(NH₃)₄(OH₂)", "*trans*-Cr(NH₃)₄OH₂", "*fac*-Cr(NH₃)₃(OH₂)₂" and "Cr(OH₂)₅"; X = I⁻, Br⁻, Cl⁻, NCS⁻, OH₂ and NH₃). The present data for X = OH₂ are in good agreement with those predicted on the basis of linear free energy relationships. The data exhibited on the figures accord with the division of ΔG^* for process (2) into two terms, depending on the non-reacting ligands and the leaving ligand, respectively:

$$\Delta G^* \sim \Delta G^*(\text{CrL}_5) + \Delta G_X^* \quad (3)$$

A summary of the data obtained using this equation is given in Table 4.

Fig. 3 clearly demonstrates the larger kinetic *trans* effect of coordinated ammonia compared to coordinated water and a further discussion of this and also of the significantly smaller kinetic *cis* effect of these two ligands will be given by us in combination with the presentation of results for those ammineaquachromium(III) complex ions

Table 4. Single ligand reactivity parameters, ΔG_X^* , at 25 °C, for aquation of chromium(III) complexes, cf. eqn. (3) and Fig. 3, and the corresponding rate constant ratios.

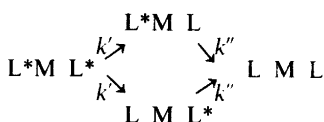
X	$\Delta G_X^* - \Delta G_{\text{OH}_2}^*$ [kJ mol ⁻¹]	k_X/k_{OH_2}
I ⁻	-7	17
Br ⁻	-1	1.5
OH ₂	0	1
Cl ⁻	+6	1/11
NCS ⁻	+14	1/280
NH ₃	+18	1/1400

which contain non-equivalently coordinated water ligands, *i.e.* *mer*-tri-amminetriaqua- *cis*-diammine-tetraaqua- and amminepenta-aquachromium(III).

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APPENDIX

In the discussion of the relative magnitude of rate constants, it is customary to apply statistical corrections when the reactivity of two or more equivalently coordinated ligands have been measured. The reaction scheme for substitution of two equivalently coordinated ligands by first order processes:



allows, in principle, the estimation of two rate constants as all the concentration *vs.* time relationships can be expressed as linear combinations of three exponential functions: $\exp(-2k't)$, $\exp(-k''t)$ and $\exp(0 \cdot t)$. This is, of course, well-known and the basis for the statistical correction with a factor 2 to $k_{\text{obs}} = 2k'$.

For an exchange process $\text{L} = \text{L}^*$ and therefore $k' = k''$. For this type of process it is usually only possible to follow the concentration of label in either the solvent: $[\text{L}^*]$, or the complex: $\{2[\text{L}^*\text{ML}^*] + [\text{LML}^*]\}$, and neither of these concentrations contains any information about $\exp(-2k't)$, as can be seen from a simple calculation, *viz.*:

$$[\text{L}^*]_t = [\text{L}^*]_0 + \{2[\text{L}^*\text{ML}^*]_0 + [\text{LML}^*]_0\} \{1 - \exp(-k''t)\}$$

and analogously for $2[\text{L}^*\text{ML}^*] + [\text{LML}^*]$.

Observed rate constants from this type of measurement should therefore not be corrected statistically. This has not always been realized in the literature.

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