

## Relaxation Spectra of Molybdate Polymers in Aqueous Solution: Temperature-Jump Studies<sup>1</sup>

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The relaxation spectra of aqueous molybdate has been determined by temperature jump at 25° and 1.0 *M* ionic strength. The pH ranged from 5.50 to 6.75; monomer concentration (*i.e.*, Na<sub>2</sub>MoO<sub>4</sub> concentration) from 0.01 to 0.25 *M*. The observed spectrum consisted of one or two relaxation effects, depending on pH and concentration. The longer, more concentration-dependent effect (1–180 msec) is most sensitive to heptamer formation; formally,  $7\text{MoO}_4^{2-} + 8\text{H}^+ \rightleftharpoons \text{Mo}_7\text{O}_{24}^{6-} + 4\text{H}_2\text{O}$ . The shorter, less concentration-dependent effect (200–500  $\mu\text{sec}$ ) is most sensitive to octamer formation; formally,  $\text{Mo}_7\text{O}_{24}^{6-} + \text{MoO}_4^{2-} + 4\text{H}^+ \rightleftharpoons \text{Mo}_8\text{O}_{26}^{4-} + 2\text{H}_2\text{O}$ . Rate constants for these two equilibria were varied until a set of constants yielding the best agreement between measured and observed relaxation time was found. The interpretation of these results depends heavily on the equilibrium constants used to describe the system. The best results were found with the equilibrium data of Aveston, Anacker, and Johnson.<sup>2</sup> The rapidity of condensation to form the heptameric isopolymolybdate species is explained by a mechanism involving reactions of protonated monomeric molybdate, which is then assumed to have octahedral coordination. These species, presumably of composition  $\text{OMo}(\text{OH})_5^-$  and  $\text{Mo}(\text{OH})_6$ , have the coordination appropriate to units of the polymer structure. The dissociation rate constant for the octamer (yielding heptamer and monomer) is larger than that for the heptamer (complete breakup to monomer), reflecting the enhanced stability of the heptamer.

Upon addition of acid to alkaline molybdate solutions, isopolyanions are formed. Equilibrium is established between monomeric molybdate and, predominantly, heptameric molybdate polymers. Despite the relative complexity of these polymolybdate ions, the steps leading to their formation are complete within a few milliseconds at moderate concentrations.<sup>3</sup>

Unlike rapid mixing studies, which are generally independent of any associated equilibrium constants, temperature-jump investigations usually depend on a sound knowledge of these constants for successful interpretation of the results. Thus, the first measurement on these systems, carried out in connection with a temperature-jump investigation of molybdenum(VI)-tartaric acid complexation using optical rotation detection, yielded relaxation spectra indicative of polymerization, which were not, however, fully interpreted, due to a lack of precise knowledge of the species present.<sup>4</sup> A temperature-jump study following further equilibrium acidity measurements on these systems confirmed the validity of the earlier kinetic measurements, and were in essential agreement with the stability constant determination, that the predominant polymeric species are heptameric and octameric.<sup>5</sup> Another relaxation study showed similar results, but differed as to the kinetic interpretation.<sup>6</sup> It is appropriate to review, briefly, the equilibrium determinations, as analysis of the relaxation data is so strongly dependent on the choice of stability constants.

Different groups of investigators have disagreed on the nature, number, and quantitative relationships among the various possible species in solution. For example, hexamers as well as heptamers were proposed by one group.<sup>7,8</sup> Other work, however, indicated that

hexameric polyanions were unlikely.<sup>2,9</sup> In a very thorough study, Aveston, *et al.*, also obtained results pointing toward the inclusion of octamers in these solutions,<sup>2</sup> which was, however, questioned.<sup>9</sup> A temperature-jump study by Asay and Eyring<sup>6</sup> found the equilibria of Aveston, *et al.*, to produce a better fit of their data than did the studies of Sillén, *et al.*<sup>9–11</sup> Our studies are also based on the Aveston, *et al.*, results, for reasons given in a following section.

We are reporting on an extensive kinetic study of equilibria in isopolymolybdate solutions by temperature jump. Wider variation of molybdate concentration in the rather restricted pH range of optimum monomer condensation and better resolution of the relaxation spectra shed new light on the kinetics of formation of polymolybdate ions.

### Experimental Section

All chemicals used were either reagent or "certified" reagent grade and were used without further purification. Stock solutions (filtered if necessary) of (Fisher) sodium molybdate, sodium hydroxide, sodium nitrate, nitric acid, and potassium nitrate were used to prepare solutions for kinetic experiments. The pH was finally adjusted by the dropwise addition of HNO<sub>3</sub> and/or NaOH solutions and measured to within 0.01 pH unit on a Sargent-Welch Model NX pH meter. The ionic strength,  $\mu$ , was 1.0 *M*, adjusted with NaNO<sub>3</sub>. (In a few experiments at an ionic strength of 0.5 *M*, KNO<sub>3</sub> was used.) This unusually high (for temperature jump) ionic strength was necessitated by the fact that high concentrations of sodium molybdate were required to produce observable effects in the pH region of the experiments; furthermore, the work of Aveston, *et al.*, was done at this ionic strength.<sup>2</sup> The indicators used were methyl red (Eastman), bromocresol purple (Fisher), and bromothymol blue (Fisher). Belmont Springs distilled water was used throughout. All solutions for kinetic experiments were degassed.

Details of the temperature-jump apparatus have already been given.<sup>12</sup> The temperature was 25 ± 1°. Each relaxation time represents the average of at least three determinations. For those experiments in which only one relaxation time was observed, semilogarithmic plots were made for most of the determinations to confirm that only a single exponential effect was present. The relative error in measurement was ±10%, except

(1) The authors gratefully acknowledge support from Public Health Service Grant GM-08893-09 from the National Institute of General Medical Sciences and partial support from a National Aeronautics and Space Administration Predoctoral Fellowship to D. S. H.

(2) J. Aveston, E. W. Anacker, and J. S. Johnson, *Inorg. Chem.*, **3**, 735 (1964).

(3) G. Schwarzenbach and J. Meier, *J. Inorg. Nucl. Chem.*, **8**, 302 (1958).

(4) R. J. Legare, Ph.D. Thesis, University of Minnesota, 1962.

(5) O. Glemser and W. Hölftje, *Angew. Chem., Int. Ed. Engl.*, **5**, 736 (1966).

(6) J. Asay and E. M. Eyring, unpublished results.

(7) M. Haeringer and J. P. Schwing, *Bull. Soc. Chim. Fr.*, 708 (1967).

(8) P. Lagrange and J. P. Schwing, *ibid.*, 718 (1967).

(9) Y. Sasaki and L. G. Sillén, *Ark. Kemi*, **29**, 253 (1968).

(10) Y. Sasaki, I. Lindqvist, and L. G. Sillén, *J. Inorg. Nucl. Chem.*, **9**, 93 (1959).

(11) L. G. Sillén, *Acta Chem. Scand.*, **18**, 1014 (1964).

(12) P. Hurwitz and K. Kustin, *Inorg. Chem.*, **3**, 823 (1964).

where noted. For those experiments in which two relaxation times were observed, all traces were plotted semilogarithmically (Figures 1 and 2). The relative error was  $\pm 25\%$  for the longer

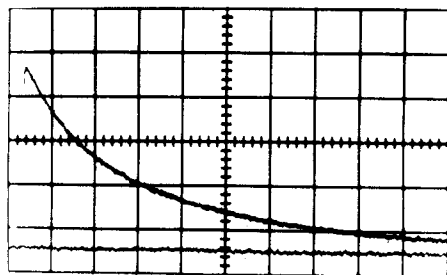


Figure 1.—Observation of relaxation time. Oscilloscopic trace for a temperature-jump experiment showing two effects. Vertical axis is proportional to change in transmittance of light following temperature jump. Horizontal axis is time; each division corresponds to 500  $\mu$ sec. The horizontal trace represents the base line, obtained by triggering the oscilloscope a second time (at the same sweep speed) 2 msec after the first trace was recorded.

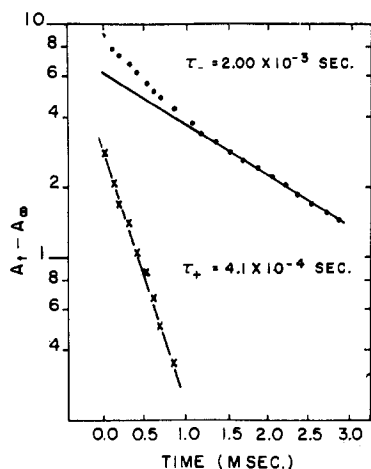


Figure 2.—Observation of relaxation time. Plot of changes in absorbance (for small changes, proportional to changes in transmittance) on an arbitrary logarithmic scale against time for the trace in Figure 1. Two close-lying relaxation times can be measured from such a plot in the following way. The dots represent the actual experimental points. The limiting slope at the longest times yields  $\tau_-$ . By subtracting from each of the initial points, the value of the limiting straight line at that point, one can calculate the values of the points represented by the "x's." The slope of the straight line through these recalculated points then yields  $\tau_+$ .

relaxation time, and  $\pm 50\%$  for the shorter one. The amplitude of the longer relaxation process was greater than that of the shorter. The problem of evaluating relaxation times differing by less than an order of magnitude has been discussed by various authors.<sup>13,14</sup>

### Concentrations in Molybdate Solutions

Reviews and discussions of the experimental problems associated with the molybdate equilibrium studies have been given by Aveston, *et al.*,<sup>2</sup> and Sasaki and Sillén.<sup>9</sup> The most comprehensive study appears to be that of Aveston, *et al.*, who used equilibrium ultracentrifugation, potentiometric acidity measurements, and Raman spectroscopy. With the results of X-ray structure determination to guide their analysis,<sup>15</sup> they de-

termined that the molybdate polymers present are heptamers and octamers. In addition, protonated forms of the heptameric and monomeric species had to be postulated to obtain agreement with acidity measurements.

As Aveston, *et al.*, pointed out,<sup>2</sup> the task of assigning the equilibria in these molybdate solutions to a unique set of species is a difficult one. Their approach was to use a variety of techniques to obtain data and then search for congruence between the separate sets of results. An entirely different approach was taken by Sillén, who tried recalculating his data,<sup>16</sup> and also that of others,<sup>2,17</sup> with refined computational techniques. Other, more recent, studies support the principal conclusions of those investigations already cited, extending the range of ionic strengths and counterions, to which the equilibria are sensitive.<sup>18-22</sup>

The purpose of this section, however, is not to review the entire literature on this problem. Instead, we wish to make clear the reasons for choosing a particular set of constants as a starting point for the temperature-jump analysis. Although closely tied to the equilibrium studies, the chemical relaxation method also affords an opportunity to check the validity of these assignments to some extent<sup>23</sup> and perhaps to recalculate some of them.

The safest conclusion appears to be that, in a sodium medium (pH > 3), the most likely polymers are heptamers and octamers. A consideration of the work of Aveston, *et al.*,<sup>2</sup> as well as the refined calculations of Sillén,<sup>16</sup> make the presence of hexamers in appreciable concentration quite doubtful. Interestingly, a comparison of Sillén's recalculations with the results of Aveston, *et al.*, indicate that the degree of protonation of some of the heptameric and octameric species had not been entirely resolved.

As the work of Aveston, *et al.*, is the most comprehensive, we have chosen to do our experiments under conditions closely approximating theirs, namely, 25°, 1 M ionic strength, and a sodium salt. Their stability constants (given in Table I) constitute the basis of the con-

TABLE I  
MOLYBDATE EQUILIBRIUM DATA (25°,  $\mu = 1.0 M$ )

$$\beta_{p,q} = [\text{H}_p(\text{MoO}_4)_q^{(2q-p)-}] / [\text{MoO}_4^{2-}]^q [\text{H}^+]^p$$

Log $\beta_{p,q}$ <sup>a</sup>		$pK_{\text{In}}^c$
$\beta_{1,1} = 3.53$	Methyl red	5.0
$\beta_{2,1} = 7.26$	Bromocresol purple	5.8
$\beta_{3,7} = 52.80$	Bromothymol blue	6.8
$\beta_{9,7} = 57.42^b$		
$\beta_{10,7} = 60.84^b$		
$\beta_{12,8} = 71.56$		

<sup>a</sup> Data from Aveston, *et al.*, ref 2. <sup>b</sup> Values reduced by 1 log unit in the final calculations reported in this article. <sup>c</sup> At  $\mu = 0.5 M$ ; data from I. M. Kolthoff, *J. Phys. Chem.*, **34**, 1466 (1930);  $K_{\text{In}}$  = indicator dissociation constant ( $\text{HIn} \rightleftharpoons \text{H} + \text{In}$ , neglecting charge).

centration calculations with a Newton-Raphson iteration on an IBM 1130 computer.

(13) M. Eigen and L. De Maeyer in "Techniques of Organic Chemistry," Vol. VIII, Part 2, A. Weissberger, Ed., Wiley, New York, N. Y., 1963, p 895, and references therein.

(14) H. Strehlow and J. Jen, *Chem. Instrum.*, **3**, 47 (1971).

(15) I. Lindquist, *Ark. Kemi*, **2**, 325, 349 (1950).

(16) L. G. Sillén, *Pure Appl. Chem.*, **17**, 72 (1968).

(17) J. P. Schwing, Dissertation, University of Strasbourg, 1961.

(18) D. V. S. Jain and C. M. Jain, *Indian J. Chem.*, **7**, 821 (1969).

(19) W. G. Baldwin and G. Wiese, *Ark. Kemi*, **31**, 419 (1970).

(20) K. F. Jahr and J. Fuchs, *Angew. Chem., Int. Ed. Engl.*, **5**, 689 (1966).

(21) G. Wiese, *Z. Naturforsch. B*, **25**, 145 (1970).

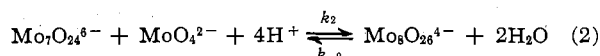
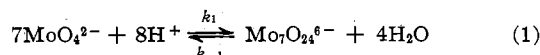
(22) H. T. Evans, *J. Amer. Chem. Soc.*, **90**, 3275 (1968).

(23) G. Schwarz, *Rev. Mod. Phys.*, **40**, 206 (1968).

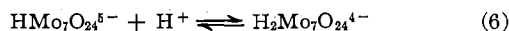
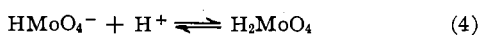
The recalculation of the data of Aveston, *et al.*, favors protonated heptamers at the expense of octamers;<sup>9,16</sup> our findings point in the opposite direction. Most convincing is the observation of two relaxation times, for this spectrum means that a minimum of three discrete molybdate-containing species must be present at appreciable concentration.<sup>13</sup> Protonated forms of  $\text{Mo}_7\text{O}_{24}^{6-}$ , although present, would not be expected to account for the behavior attributed to  $\text{Mo}_8\text{O}_{26}^{4-}$ . (Slow protolytic reactions would contribute additional relaxation processes. Preliminary ultrasonic attenuation measurements indicate, however, that these reactions are always equilibrated during the observed response to the temperature-jump perturbation.<sup>24</sup>)

### Relaxation Spectra

The reaction scheme for molybdate polymerization (at  $\text{pH} \geq 3$ , where the stability constants can account for the equilibria) can be written as shown, with the assumption that all protolytic equilibria are very rapid.<sup>13,25</sup>



Always equilibrated are



The assumption of rapid protolytic reactions allows the polymerization to be described with two rate equations

$$\frac{d[\text{Hept}]}{dt} = k_1[\text{Mon}]^7[\text{H}]^8 + k_{-2}[\text{Oct}] - k_{-1}[\text{Hept}] - k_2[\text{Mon}][\text{Hept}][\text{H}]^4 \quad (7)$$

$$\frac{d[\text{Oct}]}{dt} = k_2[\text{Mon}][\text{Hept}][\text{H}]^4 - k_{-2}[\text{Oct}]$$

where  $\text{Mon} = \text{MoO}_4^{2-}$ ;  $\text{Hept} = \text{Mo}_7\text{O}_{24}^{6-}$ ;  $\text{Oct} = \text{Mo}_8\text{O}_{26}^{4-}$ ;  $\text{H} = \text{H}^+$ . These equations were arrived at by testing different rate laws. At constant pH, with only one effect present,  $1/\tau_{\text{obsd}}$  fits a sixth-power dependence on  $[\text{MoO}_4^{2-}]$  best. From the slopes of plots of  $1/\tau_{\text{obsd}}$  against  $[\text{MoO}_4^{2-}]^6$  at constant pH,  $1/\tau_{\text{obsd}}$  was found to be related to the seventh power of  $[\text{H}^+]$ . In addition, as will be mentioned later, the complexity of the relaxation expressions may not give straightforward information on the precise composition of the activated complex. Therefore, within experimental error, the rate law for the polymerization coincides with the reaction stoichiometry.

Application of mass balance and small perturbation constraints to the above rate equations permits their solution. The reciprocal relaxation times are given by<sup>13</sup>

$$1/\tau_{+,-} = 1/2[-(a_{11} + a_{22}) \pm \sqrt{(a_{11} + a_{22})^2 - 4(a_{11}a_{22} - a_{12}a_{21})}] \quad (8)$$

The  $a_{ij}$  terms are known functions of equilibrium concentrations, rate and stability constants. The indi-

cators and protonated monomers and heptamers ( $\text{HMoO}_4^-$ , etc.) appear in the conservation relations. Their concentration changes are given in terms of the appropriate expanded stability quotients; e.g.,  $\delta[\text{HMoO}_4^-] = [\text{MoO}_4^{2-}]\beta_{1,1}\delta[\text{H}^+] + [\text{H}^+]\beta_{1,1}\delta[\text{MoO}_4^{2-}]$ . The full derivation and the  $a_{ij}$  terms are given in the Appendix.

### Analysis of Kinetic Data

The kinetic data are shown in Table II; the rate constants are given in Table III. The data where

TABLE II  
RELAXATION SPECTRA OF MOLYBDENUM(VI) SOLUTIONS<sup>a</sup>  
(25°,  $\mu = 1.0 M$ )

pH	[Mo(IV)] <sub>0</sub>	10 <sup>8</sup> [In] <sub>0</sub>	msec			
			$\tau_{\text{obsd}}$	$\tau_{-}$ , scaled	$\tau_{+}$ , scaled	
6.75	0.15	1.28 <sup>b</sup>	No effect	...	...	
6.50	0.20	1.28 <sup>b</sup>	67.5	23.8	0.204	
	0.25	1.28 <sup>b</sup>	6.23	7.56	0.204	
6.25 <sup>c</sup>	0.08	1.00	No effect	...	...	
	0.09	1.00	34.3	42.5	0.204	
	0.11	1.00	20.5	17.0	0.204	
	0.13	1.00	7.23	7.33	0.204	
	0.15	1.11	3.06	3.71	0.204	
	0.18	1.11	1.79	1.78	0.204	
	0.20	1.11	1.17	1.27	0.204	
	0.23 <sup>d</sup>	1.11	0.747	0.891	0.204	
	6.00 <sup>c</sup>	0.04	1.00	183.0	69.8	0.204
		0.05	1.00	36.4	30.6	0.204
		0.06	1.00	14.0	13.0	0.204
		0.07	1.00	6.05	6.38	0.204
0.08		1.00	3.82	3.71	0.204	
0.09		1.00	2.67	2.49	0.204	
0.10		1.12	1.78	1.86	0.204	
0.11		1.00	1.39	1.49	0.204	
0.12		1.00	1.07	1.26	0.204	
0.13 <sup>d</sup>		1.00	1.02	1.11	0.204	
0.14 <sup>d</sup>		1.00	0.883	0.997	0.204	
0.15 <sup>d</sup>		1.00	0.712	0.918	0.204	
0.16	1.00	0.973, 0.200	0.855	0.204		
0.17	1.00	0.889, 0.180	0.804	0.203		
0.18	1.00	0.887, 0.200	0.765	0.203		
0.19	1.00	0.873, 0.170	0.731	0.203		
0.20	1.00	0.779, 0.160	0.703	0.202		
5.75 <sup>c</sup>	0.03	1.00 <sup>e</sup>	14.6	15.9	0.204	
	0.04	1.11	5.19	5.11	0.204	
	0.05	1.00	2.61	2.80	0.204	
	0.07	1.11	1.62, 0.390	1.63	0.203	
	0.10	1.11	1.11, 0.220	1.20	0.202	
	0.15	1.11	1.19, 0.22	0.984	0.202	
	0.20	1.11	1.24, 0.210	0.901	0.201	
	5.50	0.01	1.30 <sup>e</sup>	156.0	82.3	0.204
0.02		1.30 <sup>e</sup>	5.62	7.38	0.203	
0.03		1.30 <sup>e</sup>	2.76, 0.540	3.27	0.202	
0.05		1.30 <sup>e</sup>	1.97, 0.460	2.07	0.200	
0.09		1.30 <sup>e</sup>	2.00, 0.420	1.64	0.198	
0.10		1.30 <sup>e</sup>	2.00, 0.330	1.60	0.197	
0.15	1.30 <sup>e</sup>	1.79, 0.360	1.48	0.196		

<sup>a</sup> All concentrations  $M$ ; subscript zero denotes total stoichiometric concentration. Concentration of Mo(VI) expressed as  $[\text{MoO}_4^{2-}]$ . <sup>b</sup> Bromothymol blue used at 580 nm. <sup>c</sup> Bromocresol purple used at 580 nm. <sup>d</sup> Analysis indicated two relaxation times, but they were inseparable. <sup>e</sup> Methyl red used at 517 nm.

TABLE III  
RATE CONSTANTS FOR MOLYBDENUM(VI) POLYMERIZATION<sup>a</sup>

$$k_1 = (9.5 \pm 1.9) \times 10^{12} M^{-14} \text{ sec}^{-1}$$

$$k_{-1} = 7.5 \pm 3.8 \text{ sec}^{-1}$$

$$k_2 = (5.0 \pm 4.5) \times 10^{23} M^{-5} \text{ sec}^{-1}$$

$$k_{-2} = (4.9 \pm 1.0) \times 10^8 \text{ sec}^{-1}$$

<sup>a</sup> 25°,  $\mu = 1.0 M$ .

only one relaxation time was observed were first analyzed with a linear least-squares routine using both an IBM 1130 and a DEC PDP-8/L computer to obtain

(24) D. Honig and K. Kustin, unpublished data.

(25) M. Eigen, W. Kruse, G. Maass, and L. De Maeyer, *Progr. React. Kinet.*, **2**, 287 (1964).

approximate values of  $k_1$  and  $k_{-1}$ . All the data were then treated by nonlinear least-squares analysis<sup>26</sup> and by a trial-and-error routine to obtain the "best fit" rate constants and to assign  $\tau_+$  and  $\tau_-$ .

Where only one relaxation time was observed, it was identified as  $\tau_-$ . Where two were observed, the longer is  $\tau_-$ , and the shorter is  $\tau_+$ . We found that the fit of  $\tau_{\text{obsd}}$  to  $\tau_{\text{calcd}}$  was least sensitive to  $k_2$ . Its value is therefore least certain; the value given is to order of magnitude validity only. The value of  $k_{-1}$  is accurate to within  $\pm 50\%$ , while those for  $k_1$  and  $k_{-2}$  are accurate to approximately  $\pm 20\%$ , relative error.

The fit between  $\tau_{-, \text{obsd}}$  and  $\tau_{-, \text{calcd}}$  is satisfactory for all but three points. For all of these experiments (pH 6.50,  $[\text{Mo}]_0 = 0.20 M$ ; pH 6.00,  $[\text{Mo}]_0 = 0.04 M$ ; pH 5.50,  $[\text{Mo}]_0 = 0.01 M$ ), the experimental error was considerably greater as the amplitude of the response was small, and the relaxation time was of long duration causing measurement difficulties due to both convection and air bubbles. Attempts to improve the fit of these three experiments deteriorated the fit of some of the other experiments, and no further adjustment was made.

Our kinetic results indicated that the values of  $\beta_{9,7}$  and  $\beta_{10,7}$  (Table I) were too large. We found that reducing both by 1 log unit gave the best fit. In the pH range of our study, this refinement caused only insignificant changes in the concentrations of the species appearing in the relaxation expressions. For those experiments in which we observed only one relaxation time,  $\tau$ , the reciprocal of the observed effect,  $1/\tau_{\text{obsd}}$ , is related to the sixth power of the  $\text{MoO}_4^{2-}$  concentration at a constant pH (Figure 3). The fit was best with

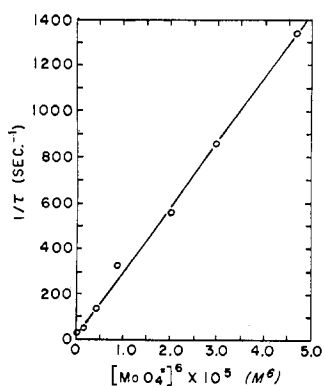


Figure 3.—Variation of the reciprocal of the relaxation time with the sixth power of the monomer concentration at constant acidity and ionic strength:  $[\text{H}^+] = 5.62 \times 10^{-7} M$ ;  $\mu = 1 M$ .

the sixth power of  $\text{MoO}_4^{2-}$  concentration; a fit to the fifth or seventh power, though not as good, could be tolerated. There was a markedly poor fit with any other lower power concentration dependence. Moreover, with unchanged values of  $\beta_{9,7}$  and  $\beta_{10,7}$  the calculated concentration dependence did not match the observed; *i.e.*, trial calculations showed  $\tau_{\text{calcd}}$  varying between 1 and 6 msec, in contrast to the observed variation between 1 and 180 msec.

The agreement between  $\tau_{+, \text{obsd}}$  and  $\tau_{+, \text{calcd}}$  is within experimental error for all the experiments at pH 6.00 and for all but one at pH 5.75 ( $[\text{Mo}]_0 = 0.07$

$M$ ). It is at the limits of experimental error for this experiment, as well as for some of those at pH 5.50 ( $[\text{Mo}]_0 = 0.15$  and  $0.10 M$ ). However, it is outside the experimental error for the remaining three experiments (pH 5.50,  $[\text{Mo}]_0 = 0.03, 0.05$ , and  $0.09 M$ ). The reasons for this disagreement are unclear. One source of error might be failure to include complexation of molybdate polymers with methyl red as has been reported.<sup>20</sup> However, this interaction should not be appreciable under our experimental conditions. The changes in  $\beta_{9,7}$  and  $\beta_{10,7}$  do not account for the lack of agreement, as the reductions in these values actually improve the fit. Therefore, we feel that the lack of good agreement for these  $\tau_+$  values is to be associated with the uncertainty in the determinations of equilibrium constants involving octamers, as  $\tau_+$  is more sensitive to their values than is  $\tau_-$ .

In Table IV the results are given separately for ex-

TABLE IV  
RELAXATION TIMES FOR MOLYBDENYM(VI)  
POLYMERIZATION<sup>a</sup> (25°,  $\mu = 0.5 M$ )

pH	$[\text{Mo(VI)}]_0$	$10^6[\text{In}]_0$	$\tau_{\text{obsd}}$ , msec
7.00	0.05	1.28 <sup>b</sup>	No effect
6.00	0.04	1.00 <sup>c</sup>	6.02
	0.05	1.00 <sup>c</sup>	2.87
	0.06	1.00 <sup>c</sup>	0.440, 2.11
	0.07	1.00 <sup>c</sup>	0.430, 1.74
	0.09	1.00 <sup>c</sup>	0.350, 1.55
	0.10	1.00 <sup>c</sup>	0.220, 1.30
	0.12	1.00 <sup>c</sup>	0.300, 1.48
	0.15	1.00 <sup>c</sup>	0.200, 1.08
5.50	0.001	1.52 <sup>d</sup>	No effect
	0.05	1.30 <sup>e</sup>	0.800, 3.35
	0.10	1.30 <sup>e</sup>	0.570, 2.99

<sup>a</sup> All concentrations  $M$ ; subscript zero denotes total stoichiometric concentration. Ionic strength adjusted with  $\text{KNO}_3$ .  
<sup>b</sup> Bromothymol blue. <sup>c</sup> Bromocresol purple. <sup>d</sup> Bromocresol green used at 580 nm. <sup>e</sup> Methyl red.

periments at ionic strength  $0.5 M$  with  $\text{KNO}_3$  instead of  $\text{NaNO}_3$ . The data differ markedly from analogous experiments at  $\mu = 1.0 M$ . At pH 6.00, for example, there were two important differences between the results at the two ionic strengths. First, the two relaxation times are observable at considerably lower total Mo(VI) concentration at  $\mu = 0.5 M$ . Second, where only one relaxation time is observed, it is significantly shorter at  $\mu = 0.5 M$ . These results agree with those of other investigators who found the equilibria to be quite sensitive, to both ionic strength and cation present.<sup>2,7,8,18-20</sup> No interpretation was attempted, as there are no equilibrium data available for these conditions.

## Discussion

The observation of two distinct relaxation times signifies that at least three discrete molybdate species are present, contributing to relaxation processes in times longer than  $100 \mu\text{sec}$ . In keeping with Aveston, *et al.*, these species are molybdate monomer, heptamer, and octamer. The validity of the assignment can be gauged by comparison of  $\tau_{\text{calcd}}$  with  $\tau_{\text{obsd}}$ .

There are, of course, many other iso- and heteropolymolybdates with different degrees of polymerization and protonation.<sup>19,20,27</sup> Relations among, and properties of, these species have been considered in

(27) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 2nd ed, 1966, pp 938-946.

(26) We wish to thank Dr. A. Gottlieb for adapting the nonlinear least-squares program (AGNLS) for use on the IBM 1130.

treating the relaxation data. For example, the discrepancies between some values of  $\tau_{+,obsd}$  and  $\tau_{+,calcd}$  are interesting with regard to Sillén's recalculations.<sup>16</sup> Sillén found that, instead of the octamer  $H_{12}(MoO_4)_8^{4-}$  (referred to, formally, as a 12,8 octamer), an 11,7 heptamer and a 9,8 octamer fit better, although he stated that this recalculation may not be very meaningful. We find that, while  $\tau_{+,calcd}$  slowly gets shorter as the pH decreases,  $\tau_{+,obsd}$  seems to get longer. This trend suggests that  $\tau_{+}$  may be less sensitive to  $[H^+]$  than our mechanism allows. Having 9 protons, rather than 12, formally involved in the formation of an octamer might account for this observation. Our changes in  $\beta_{9,7}$  and  $\beta_{10,7}$ , however, suggest less protonation of the heptamer, making an 11,7 species less probable. As mentioned, changing these constants by 1 log unit improves the fit. A greater change would not be expected on electrostatic grounds,<sup>28</sup> in the absence of any structural changes.<sup>3,29</sup> The "true" values are probably between the unreduced and the reduced values. The presence of octameric and heptameric polymers in  $Na^+$  medium at  $\mu = 1 M$  is definitive; their "formal" degree of protonation is still somewhat uncertain, however.

The structures of  $Mo_7O_{24}^{6-}$  and  $Mo_8O_{26}^{4-}$  are shown schematically in Figure 4. Aveston, *et al.*, using Raman spectroscopy, found that  $Mo_7O_{24}^{6-}$  has the same structure in solid and solution, while  $Mo_8O_{26}^{4-}$  probably does, also. These polymers,<sup>15,22,30</sup> as well as all other iso- and heteropoly molybdates,<sup>27</sup> are conceived of as being built up from  $MoO_6$  octahedra (see Figure 4). It is likely that these species have closely associated water molecules,<sup>27,30</sup> though it is not certain.<sup>2,9</sup> Positions of possible counterions are also not certain.<sup>2</sup> As can be seen from Figure 4,  $Mo_7O_{24}^{6-}$  and  $Mo_8O_{26}^{4-}$  have similar structures. Formation of the octamer from the heptamer may involve the "addition" of an  $MoO_6$  octahedral unit, along with the partial rotation of one of the  $MoO_6$  units already part of the heptamer.

Since  $MoO_4^{2-}$  in solution is surely tetrahedral (with closely associated water molecules),<sup>31</sup> how are we to understand the origin of the octahedral  $MoO_6$  unit present within the polymer? In other words, the formation of the polymer, which is a rapid process, nevertheless requires an expansion of the coordination number of molybdenum(VI) from 4 to 6. Understanding this process is the key to explaining the unusually rapid equilibration, 7 monomers  $\rightleftharpoons$  heptamer.

There is indirect evidence that the addition of a proton to (tetrahedral)  $MoO_4^{2-}$  produces expansion of the coordination sphere; *i.e.*,  $HMoO_4^-$  is probably octahedral.<sup>2,24,27,29</sup> Equilibrium studies resulted in similar ionization constants for  $H_2MoO_4$  and  $HMoO_4^-$ ,<sup>29</sup> in agreement with the conclusions drawn from rapid-mixing studies.<sup>3</sup> In the absence of structural changes,  $H_2MoO_4$  should be a stronger acid than  $HMoO_4^-$ ,<sup>28,29</sup> as it is for  $H_2CrO_4$  and  $HCrO_4^-$ .<sup>3,29,32,33</sup> The species  $HMoO_4^-$  would then be viewed as  $OMo(OH)_5^-$  and  $H_2MoO_4$  as  $Mo(OH)_6$ .<sup>3,27,29</sup>

As the stoichiometry of the heptamerization reaction

(28) Reference 27, p 218.

(29) E. F. C. H. Rohrer and J. Cruywagen, *J. S. Afr. Chem. Inst.*, **16**, 26 (1963); **17**, 145 (1964); **22**, 198 (1969).

(30) E. Shimao, *Nature (London)*, **214**, 170 (1967).

(31) R. H. Busey and O. L. Keller, Jr., *J. Chem. Phys.*, **41**, 215 (1964).

(32) Reference 27, p 528.

(33) P. Moore, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 220, (1966), and ref 3 therein.

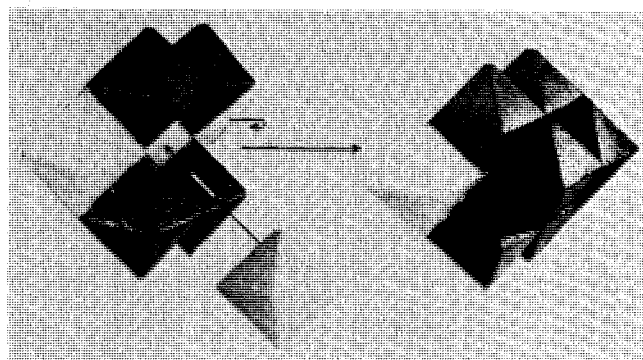


Figure 4.—Structures of isopolymolybdates. The formation of octamer from heptamer is depicted according to eq 9. The reaction is represented by showing attack of an octahedral monomer on the heptamer. As indicated by the curved arrow, one of the octahedral structural units in the heptamer effectively rotates toward the position occupied by the incoming group. Both polymers therefore have six structural units in common, all of which may be seen (at least in part) on the heptamer.

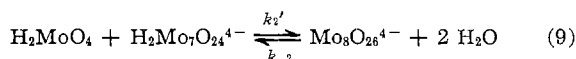
(1) shows, condensation requires oxygen elimination. Protonation of the monomeric species also enables this step to occur with a minimum of disruption. That is, the superfluous oxygen can be transferred directly to the medium most expeditiously as  $H_2O$ . The existence of H bonding aids this interaction with solvent—in the reverse, as well as forward, direction. A similar mechanism has been postulated for the hydration-hydrolysis of  $IO_4^-$  to give  $H_4IO_6^-$ , in order to explain the rapidity of this reaction.<sup>34</sup>

It should be borne in mind that, although a fast reaction technique has been applied to the study of the molybdate system, only the overall reaction leading to formation of heptamer is susceptible of measurement. By this we mean that, although the composition of the rate-determining activated complex appears to have seven monomeric units and a specified number of protons in it, we do not know the nature of its immediate precursors, *i.e.*, hexamer + monomer, pentamer + dimer, etc. However, due to the extremely low concentrations of any intermediates, reactions between, say, two trimers would have to possess extremely high bimolecular rate constants to account for relaxation times in the 1–100-msec range. These rate constants would probably exceed the diffusion-controlled limit. Therefore, it appears most likely that what occurs is a sequence of steps involving monomer as a reaction partner, with the last step rate determining.

The relaxation times observed are similar to those found previously.<sup>5,6</sup> In one of these studies,<sup>5</sup> an apparent dependence of  $1/\tau_{obsd}$  on the third power of the "monomolybdate" concentration and on the fifth power of  $[H^+]$  at "not too high  $H^+$  and Mo concentrations" was reported. In fact, it was concluded that "the primary aggregation step" is the formation of a tetramer. However, as our data indicates, the previously reported third-power dependence, based on a limited variation of concentration, does not fit as satisfactorily as the equations derived from scheme 7, *i.e.*, the fully evaluated relaxation expressions containing  $[Mon]$  to powers higher than the third (*vide* Appendix eq A9).

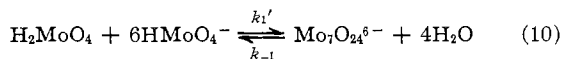
(34) K. Kustin and E. C. Lieberman, *J. Phys. Chem.*, **68**, 3869 (1964). A detailed sketch of a comparable oxygen elimination, showing the role played by H bonding, is given in this reference.

Comparison of the rate constant,  $k_1$ , for the formation of the heptamer is difficult due to the high formal order of the reaction. The reverse rate constant for heptamer dissociation,  $k_{-1}$ , is relatively low in comparison with  $k_{-2}$ , indicating that breakup of  $\text{Mo}_7\text{O}_{24}^{6-}$ , kinetically, is of relative difficulty. The order of the forward rate constant for the formation of  $\text{Mo}_8\text{O}_{26}^{4-}$ ,  $k_2$ , is also large. If we assume that the reaction occurs by eq 9 (experimentally indistinguishable from eq 2), then



$2 \times 10^7 < k_2' < 5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ . Reaction 9 may be diffusion controlled, if the upper limit prevails. It is doubtful, however, that it is actually diffusion controlled, as some structural changes are probably involved.

It seems likely that the elementary steps in forming  $\text{Mo}_7\text{O}_{24}^{6-}$  have comparable rate constants. The formation of the heptamer can be described by eq 10 (experimentally indistinguishable from eq 1; cf., also, preceding discussion) where  $k_1' \simeq 3.5 \times 10^{24} \text{ M}^{-6} \text{ sec}^{-1}$ .



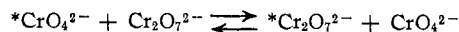
Whether or not the polymerization proceeds according to eq 9 and 10 is only speculation. The fact that  $\text{HMoO}_4^-$ ,  $\text{H}_2\text{MoO}_4$ , and  $\text{H}_2\text{Mo}_7\text{O}_{24}^{4-}$  are in considerably lower concentrations than  $\text{MoO}_4^{2-}$  and  $\text{Mo}_7\text{O}_{24}^{6-}$  would not preclude pathways involving these species. The dissociation of the octamer to heptamer and monomer is considerably faster than the heptamer dissociation ( $k_{-2} = 4.9 \times 10^3 \text{ sec}^{-1}$ ) reflecting the enhanced stability of the heptamer.

The rates of polymerization of other inorganic anions and cations have been studied by several investigators. No general mechanism has been postulated. For example, water loss has been proposed as the rate-determining step in the formation of  $(\text{FeOH})_2^{4+}$  and  $(\text{VOOH})_2^{2+}$ .<sup>35</sup> However, ring closure has also been proposed as the rate-determining step in the formation of  $(\text{FeOH})_2^{4+}$ .<sup>36</sup> In studies on the polymerization of vanadate, borate, and uranyl ions,<sup>37</sup> no convincing evidence for the presence of rate-determining water loss was found.

If anything emerges from these studies as a unifying principle, it is the fact that when expansion of the central ion's coordination number seems to be required, it is usually not in the rate-limiting process. For example, the conversion of trigonal  $\text{B}(\text{OH})_3$  to tetrahedrally coordinated borate ion is a rapid process as shown by nmr.<sup>38</sup>

A system more analogous to the molybdate is chromate-dichromate. The formation of dichromate<sup>3,33,39,40</sup> is relatively slow compared with polym-

erizations of vanadate, borate, and uranyl ions. In both monomer and dimer, Cr(VI) has tetrahedral coordination.<sup>32</sup> The relatively slow rate of condensation of Cr(VI) compared with W(VI) and Mo(VI) has been ascribed to the loss of an oxygen (probably as  $\text{H}_2\text{O}$ ) from one of the chromate tetrahedra.<sup>3</sup> In contrast, both W(VI) and Mo(VI) can simply expand their coordination. Studies of oxygen exchange in Cr(VI) solution showed that the rate of dimerization was more rapid with the pair  $\text{HCrO}_4^- + \text{HCrO}_4^-$  than with  $\text{HCrO}_4^- + \text{CrO}_4^{2-}$ .<sup>40</sup> Oxygen exchange on  $\text{CrO}_4^{2-}$  also proved to be slower than both dimerization and, possibly, exchange on  $\text{HCrO}_4^-$ . Moreover, chromate exchange with dichromate according to



is much more rapid than dimerization or oxygen exchange with water.<sup>41</sup>

Apparently, polymerization rates are favored by expansion of monomer coordination number combined with protonation or hydrolysis. In addition to poly-molybdate, this behavior seems to be important for the following polyanions. Dimers and trimers of vanadium(V) are formed from protonated  $\text{VO}_4^{3-}$ , which increases the coordination number.<sup>37d,42</sup> Tungsten(VI), like Mo(VI) forms large polyanions very rapidly.<sup>3,27,43,44</sup> With similar reasons advanced for expansion of the molybdenum(VI) coordination upon protonation, expansion of tetrahedral  $\text{WO}_4^{2-}$  has been postulated.<sup>8</sup> Bimolecular steps in these polymerizations were estimated to be  $>10^6$  and  $>10^5 \text{ M}^{-1} \text{ sec}^{-1}$  for W(VI) and Mo(VI), respectively, consistent with our findings. Recent equilibrium and temperature-jump studies of isopolytungstates are also consistent with rapid bimolecular polymerization steps.<sup>44</sup>

**Summary.**—The formation of isopolymolybdate is a relatively rapid process in view of the complexity of the reaction. Two factors have been proposed to account for this observation. The reacting form of the monomeric species has the coordination appropriate to the polymeric structure. Protonation of the monomer, which produces this state of coordination, also facilitates oxygen loss, which may be removed as, for example,  $\text{H}_2\text{O}$ .

**Acknowledgments.**—We wish to thank Mr. Daniel Lee for his help in evaluating the relaxation responses and to acknowledge the helpful communications we have had with Dr. Hartmut Diebler.

## Appendix

The concentration of each species in the rate equation (7) is replaced; for example,  $[\text{Mon}] = \overline{[\text{Mon}]} + \delta[\text{Mon}]$ . The “—” denotes the time-independent equilibrium concentration, and the time-dependent displacement  $\delta[\text{Mon}] \ll [\text{Mon}]$ ,  $[\text{Mon}]$ . Expansion of the concen-

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(36) B. A. Sommer and D. W. Margerum, *Inorg. Chem.*, **9**, 2517 (1970).

(37) (a) J. L. Anderson, E. M. Eyring, and M. P. Whittaker, *J. Phys. Chem.*, **68**, 1128 (1964); (b) M. P. Whittaker, E. M. Eyring, and E. Dibble, *ibid.*, **69**, 2319 (1965); (c) D. L. Cole, E. M. Eyring, D. T. Rampton, A. Silzars, and R. P. Jensen, *ibid.*, **71**, 2771 (1967); (d) M. P. Whittaker, J. Asay, and E. M. Eyring, *ibid.*, **70**, 1005 (1966).

(38) R. K. Momi and N. H. Nachtrieb, *Inorg. Chem.*, **6**, 1189 (1967).

(39) J. H. Swinehart and G. W. Castellan, *ibid.*, **3**, 278 (1964).

(40) R. H. Holyer and H. W. Baldwin, *Can. J. Chem.*, **45**, 413 (1967).

(41) B. N. Figgis, R. G. Kidd, and R. S. Nyholm, *ibid.*, **43**, 145 (1965).

(42) Reference 27, p 812.

(43) G. Schwarzenbach, G. Geier, and J. Littler, *Helv. Chim. Acta*, **45**, 2601 (1962).

(44) (a) O. Glemser and K. H. Tytko, *Z. Naturforsch. B*, **24**, 648 (1969); (b) K. H. Tytko and O. Glemser, *ibid.*, **B**, **25**, 429 (1970); (c) K. H. Tytko and O. Glemser, *Chimia*, **23**, 494 (1969).

trations for small perturbations results in a linearized rate equation.

$$\frac{d(\delta[\text{Hept}])}{dt} = k_1(7[\overline{\text{Mon}}]^6[\overline{\text{H}}]^8\delta[\text{Mon}] + 8[\overline{\text{Mon}}]^7[\overline{\text{H}}]^7\delta[\text{H}]) + k_{-2}\delta[\text{Oct}] - k_{-1}\delta[\text{Hept}] - k_2([\overline{\text{Hept}}][\overline{\text{H}}]^4\delta[\text{Mon}] + [\overline{\text{Mon}}][\overline{\text{H}}]^4\delta[\text{Hept}] + 4[\overline{\text{Mon}}][\overline{\text{Hept}}][\overline{\text{H}}]^3\delta[\text{H}]) \quad (\text{A1})$$

$$\frac{d(\delta[\text{Oct}])}{dt} = k_2([\overline{\text{Hept}}][\overline{\text{H}}]^4\delta[\text{Mon}] + [\overline{\text{Mon}}][\overline{\text{H}}]^4\delta[\text{Hept}] + 4[\overline{\text{Mon}}][\overline{\text{Hept}}][\overline{\text{H}}]^3\delta[\text{H}]) - k_{-2}\delta[\text{Oct}]$$

The variables  $\delta[\text{Mon}]$  and  $\delta[\text{H}]$  can be expressed in terms of  $\delta[\text{Hept}]$  and  $\delta[\text{Oct}]$  only, as follows.

Let  $\text{B} = \text{HMoO}_4^-$ ;  $\text{C} = \text{H}_2\text{MoO}_4$ ;  $\text{F} = \text{HM}_2\text{O}_7\text{O}_{24}^{5-}$ ;  $\text{G} = \text{H}_2\text{Mo}_7\text{O}_{24}^{4-}$ ; and  $\text{In} = \text{In}^-$  = indicator. Then

$$\begin{aligned} K_1 &= \beta_{1,1} = [\overline{\text{B}}]/[\overline{\text{Mon}}][\overline{\text{H}}] \\ K_2 &= \beta_{2,1} = [\overline{\text{C}}]/[\overline{\text{Mon}}][\overline{\text{H}}]^2 \\ K_3 &= \beta_{9,7}/\beta_{8,7} = [\overline{\text{F}}]/[\overline{\text{Hept}}][\overline{\text{H}}] \\ K_4 &= \beta_{10,7}/\beta_{8,7} = [\overline{\text{G}}]/[\overline{\text{Hept}}][\overline{\text{H}}]^2 \\ K_5 &= [\overline{\text{H}}][\overline{\text{In}}]/[\overline{\text{HIn}}] \end{aligned} \quad (\text{A2})$$

The following conservation relations hold for molybdate, hydrogen, and indicator

$$\delta[\text{Mon}] + \delta[\text{B}] + \delta[\text{C}] + 7\delta[\text{Hept}] + 7\delta[\text{F}] + 7\delta[\text{G}] + 8\delta[\text{Oct}] = 0 \quad (\text{A3})$$

$$\delta[\text{H}] + \delta[\text{HIn}] + \delta[\text{B}] + 2\delta[\text{C}] + 8\delta[\text{Hept}] + 9\delta[\text{F}] + 10\delta[\text{G}] + 12\delta[\text{Oct}] = 0 \quad (\text{A4})$$

$$\delta[\text{HIn}] + \delta[\text{In}] = 0 \quad (\text{A5})$$

Using (A5) and the expanded indicator equilibrium

$$\delta[\text{HIn}] = \alpha\delta[\text{H}] \quad (\text{A6})$$

where

$$\alpha = ([\overline{\text{HIn}}] + [\overline{\text{In}}])K_5/([\overline{\text{H}}] + K_5)^2$$

The assumption of rapid protolytic equilibria allows us to expand these expressions, and write the following relations for  $\delta[\text{B}]$ ,  $\delta[\text{C}]$ ,  $\delta[\text{F}]$ ,  $\delta[\text{G}]$

$$\begin{aligned} \delta[\text{B}] &= [\overline{\text{Mon}}]K_1\delta[\text{H}] + [\overline{\text{H}}]K_1\delta[\text{Mon}] \\ \delta[\text{C}] &= [\overline{\text{H}}]^2K_2\delta[\text{Mon}] + 2[\overline{\text{Mon}}][\overline{\text{H}}]K_2\delta[\text{H}] \\ \delta[\text{F}] &= [\overline{\text{H}}]K_3\delta[\text{Hept}] + [\overline{\text{Hept}}]K_3\delta[\text{H}] \\ \delta[\text{G}] &= [\overline{\text{H}}]^2K_4\delta[\text{Hept}] + 2[\overline{\text{Hept}}][\overline{\text{H}}]K_4\delta[\text{H}] \end{aligned} \quad (\text{A7})$$

Substitution of eq A6 and A7 into eq A3 and A4 enables us to express  $\delta[\text{Mon}]$  and  $\delta[\text{H}]$  in terms of  $\delta[\text{Hept}]$  and  $\delta[\text{Oct}]$  as follows

$$\begin{aligned} \delta[\text{H}] &= -R_1\delta[\text{Hept}] - R_2\delta[\text{Oct}] \\ \delta[\text{Mon}] &= S_1\delta[\text{Hept}] + S_2\delta[\text{Oct}] \end{aligned} \quad (\text{A8})$$

where  $S_1 = [Q_2R_1 - Q_3]/Q_1$ ,  $S_2 = [Q_2R_2 - 8]/Q_1$ ,  $R_1 = [Q_9Q_1 + Q_7Q_3]/\text{DEN}$ ,  $R_2 = [8Q_7 + 4Q_1]/\text{DEN}$ ,  $\text{DEN} = Q_5Q_1 + Q_7Q_2$ , and the  $Q$ 's are given by  $Q_1 = 1 + [\overline{\text{H}}]K_1 + [\overline{\text{H}}]^2K_2$ ,  $Q_2 = [\overline{\text{Mon}}]K_1 + 2[\overline{\text{Mon}}][\overline{\text{H}}]K_2 + 7[\overline{\text{Hept}}]K_3 + 14[\overline{\text{Hept}}][\overline{\text{H}}]K_4$ ,  $Q_3 = 7 + 7[\overline{\text{H}}]K_3 + 7[\overline{\text{H}}]^2K_4$ ,  $Q_5 = 1 + \alpha + 2[\overline{\text{Mon}}][\overline{\text{H}}]K_2 + 2[\overline{\text{Hept}}]K_3 + 6[\overline{\text{Hept}}][\overline{\text{H}}]K_4$ ,  $Q_7 = 1 - [\overline{\text{H}}]^2K_2$ ,  $Q_9 = 1 + 2[\overline{\text{H}}]K_3 + 3[\overline{\text{H}}]^2K_2$ . Substitution of (A8) into (A1) yields

$$\frac{d(\delta[\text{Hept}])}{dt} = \delta[\text{Hept}]\{k_1[\overline{\text{Mon}}]^6[\overline{\text{H}}]^7U_1 + k_2U_2 - k_{-1}\} + \delta[\text{Oct}]\{k_1[\overline{\text{Mon}}]^6[\overline{\text{H}}]^7U_3 + k_2U_4 + k_{-2}\} \quad (\text{A9})$$

$$\frac{d(\delta[\text{Oct}])}{dt} = \delta[\text{Hept}]\{-k_2U_2\} + \delta[\text{Oct}]\{-k_2U_4 - k_{-2}\}$$

where  $U_1 = 7[\overline{\text{H}}]S_1 - 8[\overline{\text{Mon}}]R_1$ ,  $U_2 = [\text{H}]^8(4[\overline{\text{Mon}}][\overline{\text{Hept}}]R_1 - [\overline{\text{Hept}}][\overline{\text{H}}]S_1 - [\overline{\text{Mon}}][\overline{\text{H}}])$ ,  $U_3 = 7[\overline{\text{H}}]S_2 - 8[\overline{\text{Mon}}]R_2$ ,  $U_4 = [\text{H}]^8(4[\overline{\text{Mon}}][\overline{\text{Hept}}]R_2 - [\overline{\text{Hept}}][\overline{\text{H}}]S_2)$ .

Equations A9 are of the form

$$\frac{d(\delta[\text{Hept}])}{dt} = a_{11}\delta[\text{Hept}] + a_{12}\delta[\text{Oct}] \quad (\text{A10})$$

$$\frac{d(\delta[\text{Oct}])}{dt} = a_{21}\delta[\text{Hept}] + a_{22}\delta[\text{Oct}]$$

The  $a_{ij}$  are the coefficients in (A9). The relaxation times are given by the eigenvalues of the determinantal equation

$$\begin{vmatrix} a_{11} - \lambda & a_{12} \\ a_{21} & a_{22} - \lambda \end{vmatrix} = 0 \quad (\text{A11})$$

with  $\lambda = -1/\tau$ . The two relaxation times, given by the positive and negative roots of this quadratic equation, are eq 8.