AFOSR 67-2800

DEC 12 1967

FINAL TECHNICAL REPORT TO THE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH, CHEMICAL DIRECTORATE

Project Title: LASER TEMPERATURE-JUMP STUDIES OF FAST REACTIONS

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Grant Number: AF-AFOSR-476-66-A

Grant Period: October 1, 1965 through September 30, 1967

Period Covered by this Report: December 1, 1966 to November 30, 1967

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Summary

The main objective of the research sponsored by this grant has been the development and successful operation of a laser temperature jump apparatus for measuring chemical relaxation times, τ, in aqueous solutions. From the measured τ's one can then calculate reaction rate constants for very rapid reactions in solutions. In one such study we have observed Joule heating temperature jump relaxation times in acidic, aqueous solutions of Na_2MoO_4. Overall rate constants for the equilibrium $8H^+ + 7MoO_4{}^{2-} \rightleftharpoons H_8(MoO_4)_7^{6-}$ have been calculated, and a third power dependence of monomer concentration on the reciprocal relaxation time has been confirmed. The role played by an acid-base indicator in the sample system was also considered. The large change in light absorbance of molybdate-bromocresol purple sample solutions with small changes in temperature and the associated millisecond relaxation times make this chemical system an ideal probe for comparing Joule heating and laser temperature jump devices. We duplicated our Joule heating experiments using nominal and Q-switch pulses from a neodymium doped glass laser.

We have carried out a similar kinetic study of the deprotonation of a number of azo dyes containing intramolecular hydrogen bonds. More data will be required to account for the electrostatic effects of substituents on hydrogen bonds strengths. Using another relaxation technique, we have determined the rate constants for hydrolysis of chromium (III).

Introduction

A temperature jump device for measuring rates of fast reactions in liquids that would not require high concentrations of supporting electrolyte in the sample cell and that permitted measurement of relaxation times shorter than two or three microseconds would be a significant improvement over the widely used

Joule heating device.[1-4] Rapid reactions in nonaqueous solvents of low dielectric constant and many diffusion controlled reactions in water could then be conveniently investigated by the temperature jump relaxation technique. Ertl and Gerischer[5] developed a microwave heating technique that approaches these specifications but is not completely satisfactory as a substitute for Joule heating because of the greater complexity of the instrumentation. Heating with giant laser pulses has also been suggested,[6-8] but the technique is still in the development stage.[4,9] We describe below our results obtained with a laser temperature jump apparatus in the course of a relaxation method kinetic study of aqueous sodium molybdate and subsequently of several azo dyes.

Molybdate Kinetics

A very brief report by Glemser and Holtje[10] of a Joule heating relaxation method study of the rate of aqueous molybdate polymerization appeared recently. They drew two conclusions of particular interest here. First, the equilibrium

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(1) G. Czerlinski and M. Eigen, Z. Elektrochem., 63, 652 (1959).

(2) M. Eigen and L. DeMaeyer, "Technique of Organic Chemistry," Vol. VIII, Part II, S. L. Friess, E. S. Lewis and A. Weissberger, Eds., Interscience Publishers, New York, N.Y., 1963, Chap. 18.

(3) G. Czerlinski, Rev. Sci. Instr., 33, 1184 (1962).

(4) G. Czerlinski, "Chemical Relaxation," Marcel Dekker, Inc., New York, N.Y., 1966, Chap. 10.

(5) G. Ertl and H. Gerischer, Z. Elektrochem., 65, 629 (1961).

(6) R. G. Layton and E. M. Eyring, J. Chem. Ed., 40, 338 (1963).

(7) G. Czerlinski, Q. Gibson, and H. Staerk, Biophys. Soc. Abstr., WB2 (1964).

(8) G. Czerlinski, "Rapid Mixing and Sampling Techniques in Biochemistry," B. Chance, et al., eds., Academic Press, New York, N.Y., 1964, p. 183.

(9) H. Staerk and G. Czerlinski, Nature, 207, 399 (1965).

(10) O. Glemser and W. Holtje, Angew. Chem., 78, 756 (1966).

constants for aqueous molybdate solutions reported by Aveston, et al.[11] are more consistent with the kinetic data than those given by Sasaki, Lindquist, and Sillen.[12] The equilibrium constants obtained by these two groups are compared in Table I. We used the figures of Aveston, et al.,[11] to calculate equilibrium concentrations of the various ionic species present in our sample solution, both because of Glemser's kinetic arguments and also because an ionic strength $\mu = 1.0$ M more closely approximates the $\mu = 0.5$ M characteristic of our sample solutions.

Glemser's second result[10] of particular interest here is that the reciprocal relaxation time, $1/\tau$, is proportional to the third power of the monomer concentration, $[MoO_4^{2-}]$, at pH = 5.5 and total molybdate concentration of the order of 0.01 M and to the fifth power of the hydrogen ion concentration, $[H^+]$, at molybdate concentrations of the order of 0.01 M in 0.5 M ionic strength solutions. In all Glemser's experiments the equilibrium of interest was coupled to a rapid acid-base indicator equilibrium. From these data Glemser concluded that the rate determining step in the heptamerization of molybdate is the formation of a tetramer that has not been observed by equilibrium techniques, i.e., $4MoO_4^{2-} + 6H^+ \rightleftharpoons [Mo_4O_{10}(OH)_6]^{2-}$.

Experimental Section

The sodium molybdate, $Na_2MoO_4 \cdot 2H_2O$, was Merck reagent grade. Sodium chloride used to adjust ionic strength was Wasco reagent grade. The distilled water was run through a Deeminizer and degassed by boiling. Allied Chemical reagent grade nitric acid wnd Wasco reagent grade sodium hydroxide were used to adjust pH. Paragon Testing Laboratories bromocresol purple was the acid-base indicator used.

The ionic strength of the sample solutions was adjusted to $\mu = 1/2 \sum_i z_i^2 c_i = 0.5$ M where z_i denotes the charge on the ith ion and ionic molarities c_i were

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

(12) Y. Sasaki, I. Lindquist, and L. G. Sillen, J. Inorg. Nucl. Chem., 9, 93 (1959); Y. Sasaki and L. G. Sillen, Acta Chem. Scand., 18, 1014 (1964).

TABLE I

STABILITY CONSTANTS $\beta_{p,q}$[a] FOR THE VARIOUS MOLYBDATE SPECIES PRESENT IN AQUEOUS SODIUM MOLYBDATE AT 25°C RECORDED AS $\log_{10} \beta_{p,q}$

p,q	1,1	2,1	8,7	9,7	10,7	11,7	12,8	μ[b]
Sillén[c]	3.89	7.51	57.74	62.14	65.68	68.21		3.0 M
Aveston, *et al.*[d]	3.53	7.26	52.80	57.42	60.84		71.56	~1.0 M

[a] Using the conventional notation for stability constants

$$\beta_{p,q} = \frac{[H_p(MoO_4)_q^{(2q-p)-}]}{[MoO_4^{2-}]^q [H^+]^p}$$

[b] μ = ionic strength in moles per liter, see text.

[c] See reference 12.

[d] See reference 11.

used in place of molalities. Severe shock waves in the sample cell made it impossible to carry out Joule heating temperature jump experiments at $\mu = 1.0$ M for which the data of Aveston *et al.*[11] strictly applies. Sample solutions were always thermostatted at 15°C, and since the Joule heating temperature jump effected in these kinetic studies is approximately 10° the rate constants reported are for 25 ± 1°C. The indicator concentration was generally 1×10^{-5} M in sample solutions. The pH was determined with a Radiometer Type TTT1 Titrator equipped with a PHA 630T Scale Expander calibrated in 0.01 pH units.

Our Joule heating type temperature jump apparatus is similar to that described by Hammes and Fasella[13] modified for single beam operation.[14] The vertical axis of the photographed oscilloscope trace (see, for example, the top trace of Figure 1) corresponds to relative light absorbance at the analyzing wavelength and the horizontal axis corresponds to time. For bromocresol purple the analyzing wavelength was 579 mμ. In those experiments with sodium molybdate in which no acid-base indicator was used the analyzing wavelength was 350 mμ.[15] Some of the experimental results obtained with the Joule heating apparatus are shown in Tables II and III.

Figure 2 is a schematic of our laser temperature jump apparatus. A Maser Optics Model 3100 laser head containing a 3/8 inch diameter, 6 5/8 inch long cylindrical neodymium doped glass rod (Eastman) delivers 10 joules of energy in a 2 to 3 millisecond pulse of 1.06 micron radiation. The laser is pumped by a PEK XE 17-1556 xenon flash tube with energies well below the 8600 joule maximum capability (at 3000 volts) of our capacitor bank. The laser light is focussed by lens A and is principally dissipated in a 1 mm^3 region near the center of a

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(13) G. G. Hammes and P. Fasella, *J. Am. Chem. Soc.*, **84**, 4644 (1962).

(14) G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

(15) I. Lindquist, *Acta Chem. Scand.*, **5**, 568 (1951); G. Daniels, *Gass. chim. ital.*, **90**, 1371 (1960).

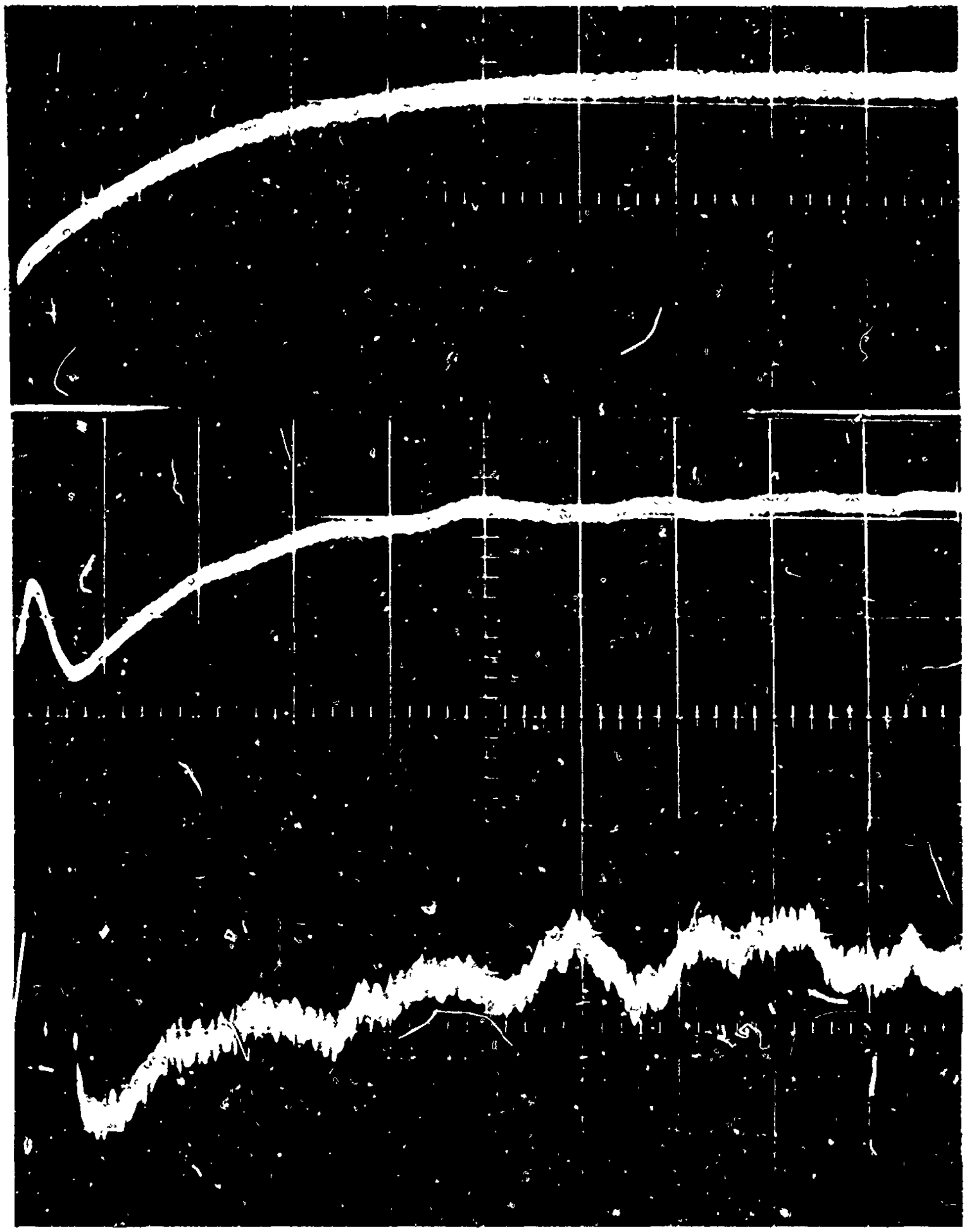

Figure 1. Temperature jump oscilloscope traces for a 0.06 M aqueous sodium molybdate solution, pH = 6.32, ionic strength 0.5 M adjusted with NaCl, and 4 x 10^{-5} M bromocresol purple at 25°C. The ordinate corresponds to relative light absorbance of the sample solution detected by a 1P28 photomultiplier tube. The abscissa is the time, 5 millisec/major division. Top trace: conventional joule heating temperature jump of sample solution. Middle trace: temperature jump effected by a "nominal" 3 millisec duration laser pulse of ∿ 10 joules at 1.06 μ from a Nd (III) doped glass rod. Bottom trace: temperature jump effected with a ∿ 1 joule "giant pulse" from the same rod Q-switched with a rotating prism. Noise in the two lower traces arises from the mercury arc analyzing beam light source.

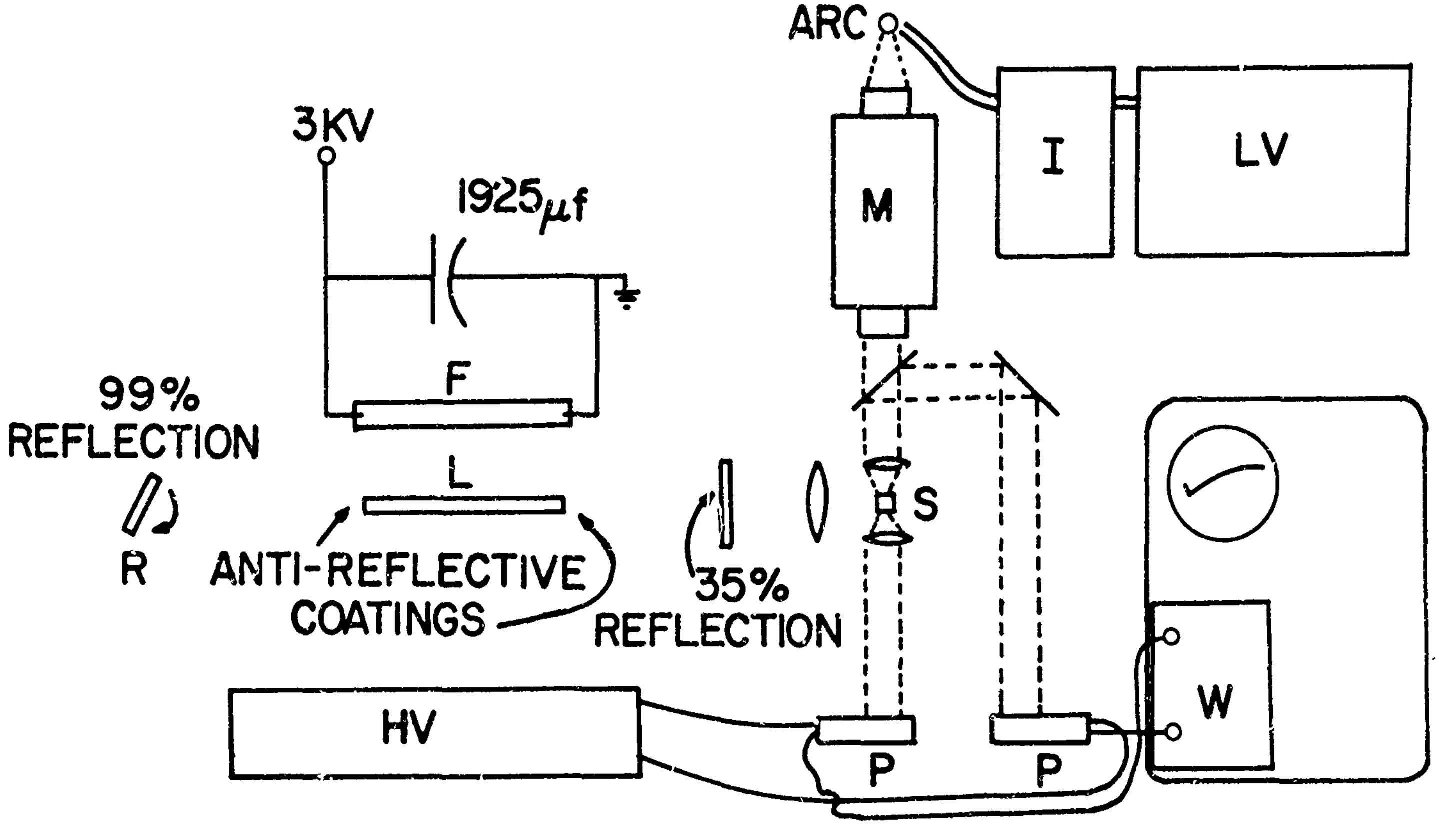

Figure 2. Schematic of the laser temperature jump apparatus: R, Beckman and Whitley Model 402 rotating prism replaced in the "nominal pulse" experiments with a stationary 99% reflecting mirror; F, a PEK XE 17-1556 xenon flash tube; L, an Eastman 3/8 x 6 5/8 in cylindrical Nd (III) glass laser rod; HV, Fluke 412B high voltage power supply; P, two 1P21 photomultiplier tubes; S, Beckman 75152 Pyrex cuvette; Bausch and Lomb high intensity grating monochromator; ARC, PEK 109 mercury arc, 100 watts; I, PEK Model 601 starter unit for initiating the arc; LV, Kepco KS 60-20 regulated D.C. power supply; W, Tektronix Type W plug-in high gain differential comparator in a 545A oscilloscope.

TABLE II

JOULE HEATING TEMPERATURE JUMP RELAXATION TIMES OBTAINED WITH AQUEOUS SODIUM MOLYBDATE SOLUTIONS AT 25°C, pH 5.5 AND IONIC STRENGTH μ = 0.5 M ADJUSTED WITH NaCl

C_0, M [a]	τ, [b] millisec	τ, [c] millisec
0.2	0.40, 2.25	
0.1	0.60, 3.75	4.09
0.08	0.54, 3.80	6.74
0.06	0.61, 3.80	20.8
0.04	0.59, 4.06	61.0
0.02	~0.97, 5.34	106.
0.015	7.25	
0.013	12.9	
0.011	14.3	
0.009	20.1	
0.007	108.2	

[a] Total concentration of Na_2MoO_4 in moles/liter.

[b] Temperature jump relaxation times determined with bromocresol purple indicator.

[c] Relaxation times determined at an analyzing wavelength of 350 mμ without indicator.

TABLE III

JOULE HEATING TEMPERATURE JUMP RELAXATION TIMES OBTAINED WITH AQUEOUS SODIUM MOLYBDATE SOLUTIONS AT 25°C, μ = 0.5 M, pH = 6.0 AND 6.5 AND 10^{-5} M BROMOCRESOL PURPLE

C_0, M	pH	τ, millisec	pH	τ, millisec
0.2	6.0	0.60, 2.69	6.5	0.15, 1.09
0.1		0.80, 3.20		5.83
0.08		0.50, 3.21		16.3
0.06		0.60, 3.45		26.4
0.04		1.3 , 6.97		
0.02		9.0 , 48.5		

rectangular 1 cm path length glass cuvette containing an aqueous sample solution. The 1.06 μ wavelength intercepts a shoulder of a strong vibrational absorption band of water[16,17] permitting direct heating of the solvent. A monochromatic analyzing light beam is directed through the cell in a 1 cm path length at right angles to and in the same horizontal plane as the laser beam. When the solution is 0.06 M in $Na_2MoO_4 \cdot 2H_2O$, 0.5 M in NaCl, and 4×10^{-5} M in bromocresol purple at pH 6.32, we observe an exponential change in the optical density at 579 mμ following the laser flash that has a time constant or "relaxation time" τ = 8.5 millisec (see middle curve of Figure 1). This result is in reasonable agreement with the τ = 9.5 millisec for this same solution measured with our conventional Joule heating temperature jump apparatus (see the top trace of Figure 1).

We have obtained similar results with a ruby laser rod of the same dimensions as the neodymium rod provided that we included 4×10^{-4} M $Cu(NO_3)_2$ and 8×10^{-4} M EDTA in the sample solution to absorb the 695 mμ ruby laser radiation. The use of the neodymium rod instead of the ruby is clearly more satisfactory since the chemistry of the sample solution is less complex. We have found similar concurrence between ruby laser and Joule heating T-jump kinetic relaxation times for the dimerization of uranyl ion[18] in $UO_2(NO_3)_2$ aqueous solutions. Of necessity the sample systems chosen must have chemical relaxation times longer than the 3 millisecond duration of the "nominal" laser pulse.

Since a Q-switched[19] laser pulse typically has a duration of the order of only 20 nanosec it would clearly be a superior temperature jump source to the

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(16) J. A. Curcio and C. C. Petty, J. Opt. Soc. Am., **41**, 302 (1951).

(17) M. R. Thomas, H. A. Scheraga, and E. E. Schrier, J. Phys. Chem., **69**, 3722 (1965).

(18) M. P. Whittaker, E. M. Eyring and E. Dibble, J. Phys. Chem., **69**, 2319 (1965).

(19) B. A. Lengyel, "Introduction to Laser Physics," John Wiley and Sons, Inc., New York, N. Y., 1966, p. 228 ff.

nominal laser pulses described above since the former would permit the measurement, in principle, of chemical relaxation times as short as 20 nsec. The bottom trace of Figure 1 was obtained with the same molybdate sample system but with a Beckman-Whitley rotating prism (Model 402) used to Q-switch the Nd (III) glass laser. The measured chemical relaxation time is 10.6 millisec in reasonable agreement with the other curves of Figure 1. The ripple in both the middle and bottom traces of Figure 1 stems from noise in the 100 watt mercury arc (PEK 109) light source producing the analyzing beam. A less noisy tungsten filament lamp (GE 6.6A/T4Q/1CL-200W) was adequate for the Joule heating experiment of the top trace in Figure 1 since less light at 579 mμ is required to detect the chemical relaxation with the larger temperature jump attendant on Joule heating. The total energy of the Q-switch pulse was found to be approximately one joule using a Ladar Systems Model LC-30 liquid calorimeter. Only a small fraction of this energy would be absorbed in the sample solution within the analyzing beam due to the comparatively high transparency of water to 1.06 micron radiation.[16]

The reason that a fourth oscilloscope trace for a more rapidly reacting chemical system than aqueous molybdate has not been included in Figure 1 is that we have not succeeded in completely eliminating the Xenon flash lamp light from the beam incident on the photocathode of each photomultiplier tube. The peak at the left hand side of the two lower traces in Figure 1 is the difference in the amounts of this scattered flashtube light reaching the two photomultiplier tubes. The introduction of a cuvette into the reference beam and the location of neutral density filters in both the sample and reference beams reduces but does not eliminate this problem. One of the great advantages of conductometric detection in laser temperature jump experiments, presently being pioneered by Stueher and coworkers,[20] is the possibility of ignoring the background of Xenon flash tube light.

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(20) J. Stuehr, private communication.

The major impediments to performing rate studies on a 0.01 microsecond time scale are the low energy of our Q-switch laser pulse and the lack of sensitivity of our photomultiplier tubes. In his Q-switch laser flash photolysis experiments in Germany, Witt[21] has circumvented these difficulties by repeating his experiments many hundreds of times and averaging the many below-noise-level signals to get a chemical time constant. The primary objection to such a procedure is the possibility that one may be bringing an artifact up out of the white noise rather than chemistry. Since we do not have funds to purchase a device for averaging very rapid transients or a larger, Q-switch laser, we have turned our attention to developing a more sensitive, fast photodetector along lines suggested by several recent workers.[22-24]

Molybdate Results and Discussion

The Joule heating relaxation times of Tables II and III permit an interesting analysis of the kinetics of isopolymolybdate formation. At pH 5.5 and total Na_2MoO_4 concentration c_0 = 0.06 M the equilibrium results of Aveston et al.,[11] indicate that the predominant equilibrium species are $MoO_4^{-2} \equiv A$, $H_8(MoO_4)_7^{-6} \equiv B$ and $H_9(MoO_4)_7^{-5} \equiv HB$. Other species present of lower concentration are $HMoO_4^{-} \equiv HA$, H_2MoO_4, $H_{10}(MoO_4)_7^{-4}$, and $H_{12}(MoO_4)_8^{-4}$. The concentrations of the predominant species are related to one another by the following equilibrium constants where H denotes hydronium ion

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(21) H. T. Witt, "Nobel Symposium V Proceedings," in press.

(22) G. Ilgenfritz, Doctoral Dissertation, Georg-August University, Goettingen, 1966.

(23) E. F. Caldin and J. E. Crooks, J. Sci. Instrum., 44, 449 (1967).

(24) M. A. Novice and J. Vine, Appl. Optics, 6, 1171 (1967).

$$H + A \rightleftharpoons HA \qquad K_1 = \beta_{1,1} \tag{1}$$

$$H + B \rightleftharpoons HB \qquad K_2 = \beta_{9,7}/\beta_{8,7} \tag{2}$$

$$8H + 7A \underset{k_{71}}{\overset{k_{17}}{\rightleftharpoons}} B \qquad K_3 = \beta_{8,7} \tag{3}$$

Since reactions (1) and (2) are protolytic reactions, we may assume their relaxation times are substantially shorter[2] than that of reaction (3).

To formulate the relaxation equation we must use the variation in concentration of some substance which appears only in reaction (3). This is impossible since all the chemical species in (3) appear at least once in reactions (1) and (2). It is therefore necessary to formulate the relaxation equation in terms of the degree of advancement ξ_3 of reaction (3). We then have

$$\frac{d(\delta\xi_3)}{dt} = k_{17}[8(H)^7(A)^7\delta H + 7(H)^8(A)^6\delta A - \left(\frac{1}{K_3}\right)\delta B] \tag{4}$$

$$= -\frac{\delta\xi_3}{\tau}$$

We also have the relations

$$\delta H = -\delta\xi_1 - \delta\xi_2 - 8\delta\xi_3 \tag{5}$$

$$\delta A = -\delta\xi_1 - 7\delta\xi_3 \tag{6}$$

$$\delta B = -\delta\xi_2 + \delta\xi_3 \tag{7}$$

If we replace δH, δA and δB in equation (4) by these values, we obtain

$$\tau = \frac{K_3}{k_{17}[8K_3(H)^7(A)^7\alpha + 7K_3(H)^8(A)^6\beta + \gamma]} \tag{8}$$

where

$$\alpha = \frac{d\xi_1}{d\xi_3} + \frac{d\xi_2}{d\xi_3} + 8$$

$$\beta = \frac{d\xi_1}{d\xi_3} + 7 \qquad\qquad \gamma = 1 - \frac{d\xi_2}{d\xi_3}$$

Making use of the equilibrium constants for reactions (1) and (2) we can readily express $d\xi_1/d\xi_3$ and $d\xi_2/d\xi_3$ in terms of measurable quantities. For instance, the former is just

$$\frac{d\xi_1}{d\xi_3} = \frac{K_1K_2(A)[8(B)-(H)] - K_1[8(A) + 7(H)]\{1 + K_2[(B) + (H)]\}}{- K_1K_2(A)(B) + \{1 + K_1[(A) + (H)]\}\{1 + K_2[(B) + (H)]\}} \tag{9}$$

The only data to which equation (8) can be legitimately applied is that in the last column of Table II which was obtained without an acid-base indicator in the sample solution. The calculated overall rate constant k_{17} for the heptamerization of molybdate obtained with this data and equation (8) is $\sim 5 \times$ [illegible] M^{-14} sec^{-1}. So large a rate constant, of course, defies sensible comparison. It is more rewarding, as Glemser and Holtje have shown,[10] to attempt to identify the rate determining step in the heptamerization from the dependence of τ^{-1} on the concentrations of MoO_4^{2-} and H^+. Our relaxation times at pH 5.5 obtained with bromocresol purple and total molybdate concentration c_0 = 0.02, 0.015, 0.013, 0.011, 0.009 and 0.007 M when fitted by least squares with the equation

$$\log \tau^{-1} = n \log (MoO_4^{2-}) + \text{constant} \tag{10}$$

yield an n= 3.06. This is in excellent agreement with the value n = 3 reported by Glemser and Holtje and would clearly indicate the formation of a tetramer as the rate determining process. However, the dissimilarity of the relaxation times in Table II obtained with and without acid-base indicator exceeds the experimental errors and thus gives rise to serious misgivings about the omission of the indicator from this interpretation of the τ^{-1} dependence on MoO_4^{2-}. A more convincing case for an identification of the rate determining step from this type of data could be made with relaxation times measured at 350 mμ without an acid-base indicator. Neither our Joule heating Plexiglas sample cell nor our analyzing beam lamp is well suited to determinations of reliable τ's at 350 mμ and total sodium molybdate concentrations of the necessary order of 10^{-2} M and less.

The real usefulness of our present familiarity with the molybdate polymerization is as an exceptionally temperature-sensitive probe for exploring the similarities of laser and Joule heating T-jump techniques. Peculiar experimental advantages of the molybdate system over the many other inorganic polymeric systems for which stability constants have been reported are solubility over a wide pH range and large amplitudes of temperature jump relaxation curves when teamed with a variety of acid-base indicators.

If we focus the laser and analyzing beams to pass through the same small region of the sample solution, we obviate the need for an impractically high energy laser pulse. Such an arrangement works regardless of whether we use a cuvette with both light paths 1 cm in length or a capillary tube in its place. We have not solved the problem of glass cuvette fracture under the shock of a Q-switch laser pulse, but we have lengthened indefinitely the life of a cuvette by blowing a ~0.5 cm hole in the glass at the points of entry and exit of the laser beam and then pulling a sleeve of Tygon tubing over the cuvette to close off those holes. The Tygon is blackened but not punctured by the Q-switch laser beam. The disadvantages are that the cell must be relocated in the laser beam after each firing and that the Tygon sleeve transmits less of the analyzing beam light.

Azo Dye Kinetics

Using the Joule heating temperature jump relaxation method, Eigen and Kruse[25]

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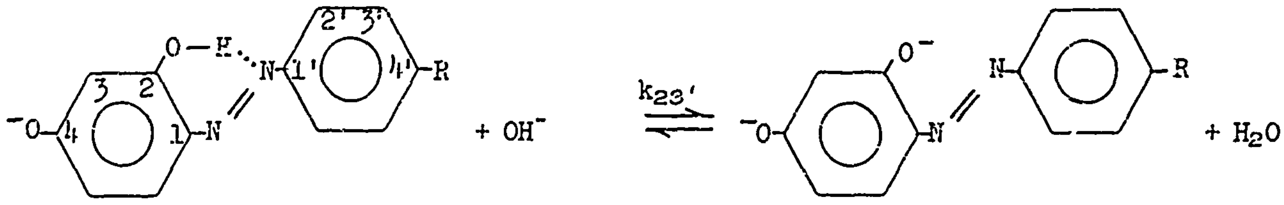
(25) M. Eigen and W. Kruse, Z. Naturforsch., 18b, 857 (1963).

measured rate constants $k_{23'}$ for the reaction



(11)

in 0.1 M ionic strength aqueous solution at 12° for 2,4-dihydroxy-4'-nitroazobenzene (I), for 2,4-dihydroxy-4'-sulfonateazobenzene (II), and for p-(2-hydroxy-1-naphthylazo)benzenesulfonic acid (III). Their values of $k_{23'}$ were 4.8×10^5, 3.6×10^5 and 3.6×10^6 $M^{-1}sec^{-1}$ respectively. The relation

$$\tau^{-1} = k_{23'}([HA] + [OH^-]) + k_{3'2} \qquad (12)$$

where [HA] denotes the equilibrium concentration of the protonated form of the azo dye and τ is the experimental relaxation time is the equation from which $k_{23'}$ is calculated. Eigen and Kruse[25] attributed the much lower value of $k_{23'}$ for these reactions than the value $k_{23'} \cong 2 \times 10^9$ $M^{-1}sec^{-1}$ for the superficially similar reaction[26] $HPO_4^{2-} + OH^- \rightleftharpoons PO_4^{3-} + H_2O$ to strong intramolecular hydrogen bonding in the protonated azo dyes. Their results raise the question whether trends of pKa and $k_{23'}$ in a larger sample of azo dyes can be correlated with electrostatic effects of ring substituents on the electronegativity of the azo nitrogen proton acceptor of the postulated hydrogen bond. Since resonance stabilization would promote a stable planar structure for the hydrogen bond about equally in all these azo dyes, this effect may be neglected.

The reason for being interested in the azo dyes as potential laser temperature jump sample systems is the extraordinarily high extinction coefficient of aqueous solutions of such compounds and the much shorter relaxation times (tens

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(26) M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, in "Progress in Reaction Kinetics," Vol. 2, G. Porter, Ed., Pergamon Press, Ltd., Oxford, England, 1964, p. 308.

of microseconds) than those reported above for aqueous molybdate solutions. Thus, the aqueous azo dyes provide a more challenging test of the capabilities of our laser temperature jump equipment.

Experimental Section

2,4-Dihydroxy-4'-nitroazobenzene (I), 2,4-dihydroxy-4'-sulfonateazobenzene (II), 4-(2-thiazolylazo)-resorcinol (IV), 6-methyl-4-(2-thiazolylazo)-resorcinol (V), and 4-(2-pyridylazo)-resorcinol (VI) were obtained from Aldrich Chemical Co., Inc. and 4-(m-nitrophenylazo)resorcinol (VII) was purchased from Distillation Products Industries, Eastman Kodak Co. The acids were recrystallized from water, and the equilibrium constants of Table IV were determined spectrophotometrically at 25° in 0.1 M ionic strength aqueous solution (adjusted with reagent grade KNO_3) following the technique of Albert and Serjeant.[27] The rate constants $k_{23'}$ also given in Table IV were calculated from equation (12) and experimental relaxation times, τ, determined by the Joule heating temperature jump technique. We verified some of the relaxation times falling in the 20 to 100 microsec time range with our laser temperature jump apparatus.

Azo Dye Results and Discussion

As in our previous kinetic studies of deprotonation of intramolecularly hydrogen bonded acids by hydroxide ion,[28] we see in Table IV that with one exception as the pKa^M increases the rate constant $k_{23'}$ for deprotonation decreases. In other words, the stronger the intramolecular hydrogen bond becomes the slower the deprotonation process is.

The relative strengths of the intramolecular hydrogen bonds as measured would have been difficult to predict _a priori_ on the basis alone of electrostatic effects of the ring substituents. For instance, the greater electronegativity of

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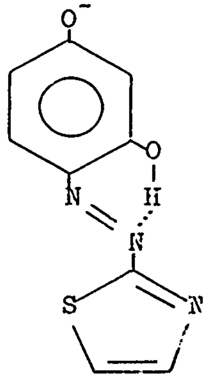
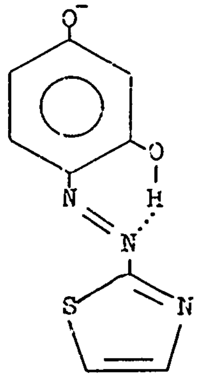
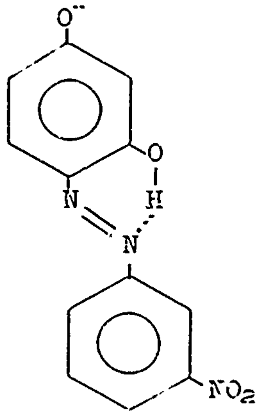
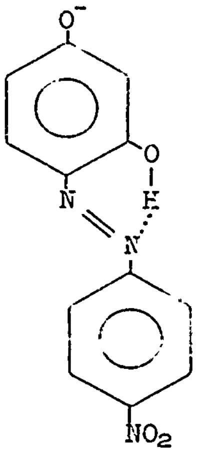
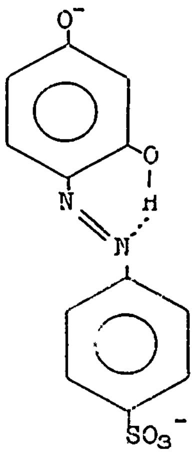
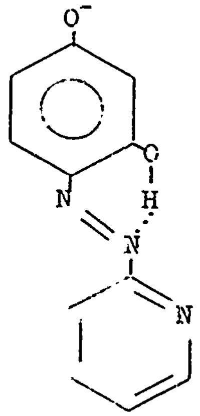
(27) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, N.Y., 1962.

(28) For references see M. H. Miles, E. M. Eyring, W. W. Epstein, and M. T. Anderson, J. Phys. Chem., 70, 3490 (1966).

TABLE IV

SPECTROSCOPIC ACID DISSOCIATION CONSTANTS AND RATE CONSTANTS FOR INTRAMOLECULAR HYDROGEN BOND BREAKING FOR A SERIES OF AQUEOUS AZO DYES AT 25°C AND IONIC STRENGTH $\mu = 0.1$ M ADJUSTED WITH KNO_3

Identifying No.	IV	V	VII	I	II	VI
Formula of HA						
$pKa^{M\,a}$	9.67 ± 0.15	10.03 ± 0.10	11.50 ± 0.04	11.67 ± 0.02	12.01 ± 0.03	12.16 ± 0.05
$k_{23}'^{\,b}$, $M^{-1}sec^{-1}$	9.5×10^7	1.6×10^8	2.1×10^6	1.3×10^6	8.6×10^5	8×10^5

[a] Mixed acid ionization constant $K_a^M = 10^{-pH}[A]/[HA]$ determined spectrophotometrically.

[b] Rate constant for the reaction $HA^{n-} + OH^- \xrightarrow{k_{23}'} A^{(n+1)-} + H_2O$ calculated from equation (12) of the text and temperature jump relaxation times.

NO_2 over SO_3^- accounts nicely for a greater decrease in charge on the azo nitrogen and hence a weaker hydrogen bond in I than in II. However, if this rationale is correct, it is difficult to explain why the para nitro group of I is less effective than the meta nitro group of VII in drawing charge away from the azo nitrogen proton acceptor. We are presently determining pKa^M and $k_{23'}$ for 4-phenylazo-resorcinol so that we may have a more satisfactory departure point for our comparisons.

Kinetics of Chromium (III) Hydrolysis

In our prowling for sample systems requiring a fast relaxation technique such as the laser temperature jump, we became interested in the hydrolysis of aqueous chromium (III). An aqueous $Cr(ClO_4)_3$ solution has a pale green color. The extinction coefficient is too low for convenient determinations of a relaxation time by spectrophotometric techniques, but we have obtained relaxation times of the order of 4 microseconds with our square wave dissociation field effect appartus.[29] We find that $k \cong 10^9\ M^{-1}sec^{-1}$ for the reaction $CrOH^{2+} + H^+ \rightarrow Cr^{3+} + H_2O$ This work as well as the above described azo dye study will be submitted for publication shortly.

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Chronological Bibliography of All Publications Produced or Anticipated Acknowledging AFOSR Support:

1. J. L. Haslam, E. M. Eyring, W. W. Epstein, G. A. Christiansen, and M. H. Miles, "Intramolecular Hydrogen Bonding in cis-Cyclopropanepolycarboxylic Acids," J. Am. Chem. Soc., 87, 1 (1965).
2. J. L. Haslam, E. M. Eyring, W. W. Epstein, R. P. Jensen, and C. W. Jaget, "Equilibrium and Kinetic Studies of the Deprotonation of the Monoanion of Several Dicarboxylic Acids in Water and in Deuterium Oxide," J. Am. Chem. Soc., 87, 4247 (1965).
3. E. M. Eyring and J. L. Haslam, "Solvent Deuterium Isotope Effects on Intramolecularly Hydrogen-Bonded Dicarboxylic Acid Monoanions," J. Phys. Chem., 70, 293 (1966).
4. J. L. Haslam and E. M. Eyring, "Deuterium Oxide Solvent Isotope Effects on N-H...O, O-H...N, and N-H...N Intramolecular Hydrogen Bonds," J. Phys. Chem., in press.
5. W. H. Inskeep, W. T. Silfvast, and E. M. Eyring, "Intramolecular Hydrogen Bonding in Aqueous Azo Dye Solutions," in preparation.
6. L. D. Rich, D. L. Cole, and E. M. Eyring, "Kinetics of Chromium (III) Ion Hydrolysis in Dilute Solutions," in preparation.

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) University of Utah Department of Chemistry Salt Lake City, Utah 84112	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

LASER TEMPERATURE-JUMP STUDIES OF FAST REACTIONS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Scientific Final

5. AUTHOR(S) (First name, middle initial, last name)

Edward M Eyring

6. REPORT DATE November 1967	7a. TOTAL NO. OF PAGES 20	7b. NO. OF REFS 29

8a. CONTRACT OR GRANT NO. AF-AFOSR-476-66	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. 9710-03 61445014 c. 681303 d.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AFOSR 67-2800

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited

11. SUPPLEMENTARY NOTES TECH, OTHER	12. SPONSORING MILITARY ACTIVITY AF Office of Scientific Research (SRC) 1400 Wilson Blvd., Arlington, Va. 22209

13. ABSTRACT

Progress is reported on three lines of investigation:

The use of Joule heating and laser temperature jump equipment to study the rate of molybdate polymerization is described in detail.

The same equipment has been used to study the rapid deprotonation by hydroxide ion of a family of azo dyes in alkaline aqueous solution that have strong intramolecular hydrogen bonds.

Preliminary results are reported of a kinetic study of the hydrolysis of chromium (III) perchlorate in acidic aqueous solutions.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Rate of reaction						
Joule heating temperature jump						
Laser temperature jump						
Molybdate polymerization						
Deprotonation						
Azo dyes						
Intramolecular hydrogen bonds						
Hydrolysis						
Chromium (III) perchlorate hydrolysis						