Differential Thermometric Measurements of the Rates of Moderately Fast Chemical Reactions in Dilute Solutions

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Abstract: By applying it to the reaction of hydrogen ion with the *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetato complex of magnesium(II), a differential thermometric technique is shown to yield rate data in acceptable agreement with those in the prior literature for reactions having half-times as short as 2 sec and involving overall temperature changes as small as 0.9 millidegree.

In a recently described[1] simple differential twin microcalorimetric apparatus for evaluating the rates of chemical reactions, the temperatures of a reaction mixture and a nearly identical reference solution are sensed by closely matched thermistors constituting two of the arms of a dc Wheatstone bridge, and the unbalance voltage of the bridge is recorded against time. The differential arrangement compensates for the thermal effects of evaporation of the solvent, power dissipation in the thermistors, heats of stirring, and heats of dilution of the added reagents. The recorded plot of differential temperature against time is easily corrected for heat exchange to obtain a plot of the extent of the reaction against time.

In the work previously described, this apparatus was used to evaluate the second-order rate constant for the alkaline hydrolysis of ethyl acetate over a range of conditions such that the half-time varied between 18 and 285 sec while the total variation of temperature resulting from the reaction varied between 15.6 and 94 millidegrees (mdeg). This paper describes the results of further work designed to reveal the lowest values of these parameters that could be handled satisfactorily. Papoff and Zambonin[2] and Wyatt[3] had employed thermometric techniques to obtain rate data for reactions having half-times as short as 3.5 and 2 sec, respectively, while Buzzell and Sturtevant[4] succeeded in evaluating a pseudo first-order rate constant for a reaction in which the overall temperature change was only 1.8 mdeg.

Exchange reactions of metal–CyDTA (*trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetate) complexes have been studied extensively by Margerum and his coworkers.[5-9] Pausch and Margerum[8] found that the replacement of magnesium(II) by lead(II) occurred by the mechanism

$$\mathrm{MgCyDTA^{2-} + H^+ \underset{k_M{}^{Cy}}{\overset{k_H{}^{MCy}}{\rightleftharpoons}} Mg(HCyDTA)^-} \qquad (1a)$$

$$\mathrm{Mg(HCyDTA)^- + Pb^{II} \longrightarrow PbCyDTA^{2-} + Mg^{2+} + H^+} \qquad (1b)$$

Using buffers containing 0.5 *F* acetate and having ionic strengths of 0.5 *M*, pH values between 5.6 and 7.25, and eight- to fortyfold excesses of lead(II), they found the reaction to be pseudo first order and to obey the rate law

$$\frac{d[\mathrm{PbCyDTA^{2-}}]}{dt} = k_H{}^{MCy}[\mathrm{H^+}][\mathrm{MgCyDTA^{2-}}] \qquad (2)$$

and they computed the value of $k_H{}^{MCy}$ at 25.0 ± 0.1° on the assumption that the measured pH values were equal to $-\log\,[\mathrm{H^+}]$.

We have employed similar solutions, with pH values between 5.2 and 6.4, to obtain pseudo first-order rate constants ranging from 0.02 to 0.3 $\mathrm{sec^{-1}}$, and have used concentrations of the magnesium(II)–CyDTA complex between 0.05 and 0.77 m*F* to obtain total temperature changes ranging from 0.9 to 11.4 mdeg.

Experimental Section

Apparatus and Technique. The calorimeter, the electrical circuitry, and most of the experimental details were identical with those previously described,[1] except that the stirring bars were replaced with Teflon-coated Roto-Stirrers (The Chemical Rubber Co.) to provide more efficient mixing in the fastest reactions. Although the output voltage of the bridge is not exactly proportional to the differential temperature, the deviation from linearity is so small over the range of differential temperatures involved in this work that it was ignored. Corrections for heat exchange were applied but were also very small.

Reagents. CyDTA monohydrate (Aldrich Chemical Co., Inc.) was suspended in water, dissolved by adding a barely sufficient volume of sodium hydroxide, and reprecipitated by neutralizing to pH 4 with hydrochloric acid. The solid product was filtered off, washed with water, and air-dried. Heating was avoided during these manipulations because solutions of CyDTA undergo thermal decomposition. Solutions of CyDTA and magnesium nitrate were standardized by accepted procedures.

At the beginning of an experiment each of the calorimetric vessels contained 80 ml of a 0.50 *F* sodium acetate solution containing 16.9 m*F* lead nitrate and enough acetic acid to yield the desired pH value. Both the original pH and that at the end of the experiment were measured with a Sargent Model DR digital pH meter; although the two pH values never differed by more than 0.002 unit, the final value is the one recorded in Table I. Both the reagent added to the reaction vessel and that added to the reference vessel contained 0.50 *F* sodium acetate, together with enough acetic acid to yield a pH of 6.38; that added to the reaction vessel also contained either 62.8 m*F* magnesium nitrate and 69.4 m*F* CyDTA or, for the experiments involving the smallest changes of temperature, 12.6 m*F* magnesium nitrate and 13.9 m*F* CyDTA.

The excess of CyDTA served to decrease the extent of dissociation of the magnesium complex. The initial concentrations of this complex given in Table I are formal concentrations and do not take dissociation into account; this of course has no effect on the computed values of the pseudo first-order rate constants obtained from eq 4 of our earlier paper.[1] Although there was a small uncompensated temperature rise in the reaction vessel as the free

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(1) T. Meites, L. Meites, and J. N. Jaitly, *J. Phys. Chem.*, 73, 3801 (1969).

(2) P. Papoff and P. G. Zambonin, *Talanta*, 14, 581 (1967).

(3) P. A. H. Wyatt, *J. Chem. Soc.*, 2299 (1960).

(4) A. Buzzell and J. M. Sturtevant, *J. Am. Chem. Soc.*, 73, 2454 (1951).

(5) D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, 2, 683 (1963).

(6) D. W. Margerum, P. J. Menardi, and D. J. Janes, *ibid.*, 6, 283 (1967).

(7) G. F. Smith and D. W. Margerum, *ibid.*, 8, 135 (1969).

(8) J. B. Pausch and D. W. Margerum, *Anal. Chem.*, 41, 226 (1969).

(9) D. W. Margerum, J. B. Pausch, G. A. Nyssen, and G. F. Smith, *ibid.*, 41, 233 (1969).

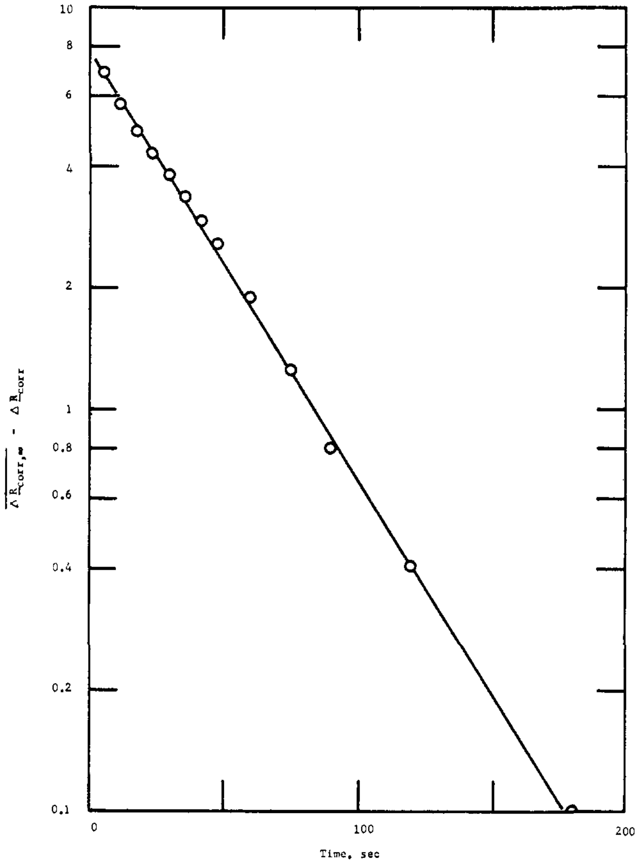

Figure 1. First-order plot of the data obtained for the reaction between 0.0538 m*F* magnesium(II)–CyDTA and 16.8 m*F* lead(II) in an 0.5 *F* sodium acetate buffer of pH 6.400. The measured differential temperatures have been corrected for heat exchange. The overall temperature change during the reaction was 0.9 mdeg, and the deviations of the points from the straight line correspond to an average error of ±10 μdeg in the differential temperature.

CyDTA initially present reacted with part of the lead(II), the fact that the computed value of *k* always became constant within 1–2 sec after the addition of the reagent showed that both this reaction and mixing were essentially complete within that length of time. Mixing was much more rapid than in our earlier work because the densities of the solutions being mixed were much more nearly equal.

Table I. Rate Constants for the Reaction of Hydrogen Ion with the Magnesium(II)–CyDTA Complex at 25° [a]

Initial concn of $MgCyDTA^{2-}$, m*F*	Final pH	Overall temp rise ($\Delta T_{corr.\infty}$), mdeg	10^2k, sec^{-1}	$10^{-4}k_H^{MCy}$, M^{-1} sec^{-1}
0.769	6.395	11.4	1.89	4.69
0.202	6.399	2.94	1.79	4.49
0.1016	6.396	1.633	1.86	4.63
0.0538	6.400	0.922	1.98	4.94
0.388	6.095	5.53	3.72	4.62
0.419	5.806	6.21	7.43	4.76
0.404	5.497	5.85	14.35	4.51
0.410	5.207	5.73	28.3	4.56
			Mean	4.65 ± 0.15 (standard deviation)

[a] All of the data were obtained in solutions containing 0.50 *F* sodium acetate. The overall temperature rise given in the third column is corrected for heat exchange, but not for the heat evolved in the reaction of lead(II) with free CyDTA initially present. The value of *k* in the fourth column is that of the pseudo first-order rate constant actually computed (so that $t_{1/2} = 0.69/k$ sec); the value of k_H^{MCy} in the fifth column is that of the apparent second-order rate constant obtained from eq 3.

Results and Discussion

Values of the pseudo first-order rate constant *k* at 25° are shown in Table I, which covers a range of overall temperature changes from 11.4 to 0.9 mdeg and a range of half-times from about 40 to 2 sec. The reliability of the technique in very dilute solutions may be assessed with the aid of Figure 1, which shows the data for an experiment in which the overall temperature change was only 0.9 mdeg. For comparison with the results of Pausch and Margerum, Table I also indicates values of the second-order rate constant k_H^{MCy} calculated from the equation

$$\log k_H^{MCy} = \log k + \mathrm{pH} \qquad (3)$$

Pausch and Margerum[8] computed $k_H^{MCy} = 6.33 \times 10^4\ M^{-1}\ sec^{-1}$ from data obtained under conditions similar to those used here, but with concentrations of lead(II) (0.33–4.50 m*F*[10]) substantially below ours (16.9 m*F*). The fact that our value of k_H^{MCy} is somewhat smaller than theirs probably means that lead(II) alters the exchange rate for the magnesium–CyDTA complex as it does that for the cadmium–CyDTA complex.[8]

The thermal capacity of the reaction vessel and its contents was evaluated at the end of each of a number of experiments by using a constant-current generator to impose a known current on a platinum resistance heater immersed in the solution for a measured length of time, and was combined with the overall temperature rise to compute the number of calories evolved in the reaction. Correcting this for the heat evolved in the reaction of the free CyDTA with lead(II), using the value $\Delta H = -12.4$ kcal/mole given by Wright, Holloway, and Reilley[11] for the enthalpy of formation of the lead(II)–CyDTA complex, gave $\Delta H = -14.0 \pm 0.6$ kcal/mole for the overall reaction $MgCyDTA^{2-} + Pb^{2+} = PbCyDTA^{2-} + Mg^{2+}$. This is in fortuitously exact agreement with the difference between the enthalpies of formation of the lead and magnesium complexes according to Wright, Holloway, and Reilley; according to Anderegg's results[12] the difference is −15.2 kcal/mole.

Values of *k* obtained at various temperatures between 24.0 and 27.1° were used to compute both the value at 25° and the enthalpy of activation by an unweighted least-squares calculation. Temperatures were evaluated by measuring the resistance of the thermistor in the reaction mixture, and were believed to be reliable to ±0.01°. The results of eight experiments gave $k = 4.6 \times 10^4\ M^{-1}\ sec^{-1}$ at 25°, in agreement with the mean in Table I, and $\Delta H^{\ddagger} = 15$ kcal/mole. Though the average deviation on the Arrhenius plot was only about ±2% in *k*, the range of temperatures was so narrow that the activation enthalpy may have an uncertainty of about ±2 kcal/mole. The activation enthalpy has not been measured previously for this reaction, but Margerum, Menardi, and Janes[6] reported $\Delta H^{\ddagger} = 16.4$ and 16.7 kcal/mole for the reactions of the manganese(II)- and lead(II)–CyDTA complexes with hydrogen ion. These values are comparable with the one obtained here.

Acknowledgment. This investigation was supported by PHS Research Grant No. GM-16561 from the National Institute of General Medical Sciences.

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(10) D. W. Margerum, personal communication, 1969.

(11) D. L. Wright, J. H. Holloway, and C. N. Reilley, *Anal. Chem.*, 37, 884 (1965).

(12) G. Anderegg, *Helv. Chim. Acta*, 46, 1833 (1966).