The Pulse Radiolysis pH-Jump in Aqueous Solutions: Applications to Lanthanide(III)–Methyl Red Systems

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(Received April 28, 1986)

Abstract

Use of the pulse radiolytic technique for studying acid–base and complex formation reactions in aqueous solutions is described. The method is based on the conversion of the hydrated electron e^-_{aq} to the anion of a strong acid, thereby obtaining a fast pH-jump. Rate constants are calculated from relaxation times measured with either spectrophotometric or conductometric detection systems. The technique has been validated with previously studied chemical systems. Rate constants for the complex formation between La^{3+} and Gd^{3+} with Methyl Red indicator have also been determined.

Introduction

Several papers have recently appeared which deal with pH-jump relaxation techniques based on the use of laser radiation [1–8]. The change in proton concentration is caused by the difference in acid–base properties of organic alcohols upon electronic excitation. The short lifetime of the excited state is, however, the limiting factor for the duration of the proton pulse.

Another pH-jump method, based on pulsed electron irradiation of 2-propanol, and its use in studies of protonation kinetics in that solvent has been described [9].

Due to the potential interest of a fast pH-jump generation in aqueous solutions, we have implemented the pulse radiolytic pH-jump method introduced by Bobrowski and Das [9] to aqueous solutions, and in the present paper we report on some new complex formation rate constants determined with this technique.

Experimental

Metal perchlorate solutions were prepared from the oxides (La_2O_3, Gd_2O_3 and Dy_2O_3, Nucor Corp., Res. Chem., 99.9%) and perchloric acid (Merck p.a.). The metal content was determined volumetrically with EDTA [10]. A sodium perchlorate solution was prepared from sodium carbonate (Merck p.a.) and perchloric acid. The salt concentration of this stock solution was found by weighing samples dried at 125 °C. The acid excess of all perchlorate solutions was determined with potentiometric titrations and Gran [11] plots. Anthranilic acid (*o*-aminobenzoic acid), tert-butanol, carbon tetrachloride (all Merck, p.a.) and Methyl Red (*o*-carboxybenzene-azodimethyl-aniline) (Fluka) were used as received.

The proton concentration of the solutions used in the kinetic measurements was adjusted with diluted NaOH solutions (~5 mM, made by diluting clear 50% NaOH in nitrogen atmosphere).

The reactions giving rise to the pulse radiolytically generated aqueous pH-jump differ slightly from the ones in alcoholic solutions [9]. For aqueous solutions deoxygenated by argon purging and containing 0.5 M tert-butanol and 2×10^{-4} M CCl_4, the main processes are

$$(H_2O \overset{e^-}{\rightsquigarrow} e^-_{aq}, H^+, \cdot OH, H_2O_2, OH^-, H\cdot, H_2 \qquad (1)$$

$$CCl_4 + e^-_{aq} \longrightarrow Cl^- + \cdot CCl_3 \qquad (2)$$

$$(CH_3)_3COH + H\cdot \longrightarrow H_2 + \cdot CH_2C(CH_3)_2OH \qquad (3)$$

$$(CH_3)_3COH + \cdot OH \longrightarrow H_2O + \cdot CH_2C(CH_3)_2OH \qquad (4)$$

Yields for reaction (1) are [12] $G_{e^-_{aq}} = 2.7$, $G_{H^+} = 3.3$, $G_{\cdot OH} = 2.7$, $G_{H_2O_2} = 0.75$ $G_{H\cdot} = 0\ 6$, $G_{OH^-} = 0.6$ and $G_{H_2} = 0.45$ (molecules/100 eV absorbed energy). In acidic solutions, OH^- will disappear by

0020-1693/86/$3.50

fast recombination with the excess of protons, and the net charge balance after the electron pulse, consists of equal amounts of e^-_{aq} and H^+. For the given concentration of CCl_4, reaction (2) (which has a rate constant [13] of 3×10^{10} M^{-1} s^{-1}) is complete within 1 μs. Thus, the net acid production is given by reactions (1) and (2).

If the concentration of CCl_4 is higher than 2×10^{-4} M, the reaction

$$CCl_4 + H\cdot \longrightarrow H^+ + Cl^- + \cdot CCl_3 \qquad (5)$$

with a rate constant [14, 15] of 4×10^7 M^{-1} s^{-1}, is not completely suppressed by reaction (3), which has a rate constant [15] of 8×10^4 M^{-1} s^{-1}. The initial fast change in proton concentration due to reaction (2), is in the latter case followed by a slower proton production by reaction (5), which must be taken into account when relaxation times are calculated from kinetic data. Typical transient conductivity signals obtained on pulsed irradiation of aqueous solutions containing tert-butanol and CCl_4 are depicted in Fig. 1.

The radicals formed in reactions (2)–(5), following irradiation, can be expected to react very slowly, if at all, with the metal complexes to be studied [16–18].

Descriptions of the pulse radiolysis setup with optical and conductometric detection systems are given elsewhere [19, 20]. The solutions were irradiated with 0.2–1.5 μs long pulses of 7 MeV electrons from a microtron accelerator. The doses used, as determined by KSCN-dosimetry, were in the range 4–20 J kg^{-1} per pulse, giving rise to an increase in proton concentration of $1–5.5 \times 10^{-6}$ mol dm^{-3}. The time resolution of the optical measurements is limited by the electron pulse width. The recovery time of the conductivity detection system from overloading by spurious signals due to electron beam stopping by the electrode is ~0.5 μs.

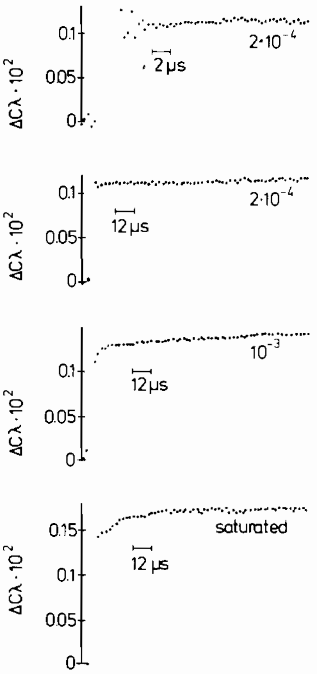

Fig. 1. Typical traces showing transient changes in conductivity, ΔCλ, on pulsed irradiation (1 krad dose) of 0.5 M tert-butanol argon saturated aqueous solutions of carbon tetrachloride. (CCl_4 concentrations are indicated in the Figure.)

The method has been validated by determining the protonation kinetics of the acid–base indicator Methyl Red (which has previously been investigated with the E-jump method [21]), and the complex formation between Dy^{3+} and anthranilate (which is known from a T-jump study [22]). A comparison of our results with the rate constants from the literature is given in Table I. A modification of the HALTA-

TABLE I Comparison of Literature Reaction Rate Constants in Aqueous Solutions with Values Obtained by the Pulse Radiolytic pH-Jump Method at ~20 °C and 0.5 M tert Butanol. HAnt and HInd stand for Anthranilic Acid and Methyl Red respectively. The Ionic Strengths were adjusted with $NaClO_4$

Detection system and ionic strength	$\overrightarrow{k}$ (M^{-1} s^{-1})	$\overleftarrow{k}$ (s^{-1})	log ($\overrightarrow{k}/\overleftarrow{k}$)
$H^+ + Ind^- \rightleftharpoons HInd$			
optical ($I \simeq 0$)	$(4.5 \pm 0.3) \times 10^{10}$		a
conductivity ($I \simeq 0$)	$(4.3 \pm 0.2) \times 10^{10}$		a
ref. 21 ($I \simeq 0$)	3.5×10^{10}	4.8×10^5	4.86
$Dy^{3+} + Ant^- \rightleftharpoons DyAnt^{2+}$			
conductivity ($I \simeq 0$)	$(6.5 \pm 1.6) \times 10^7$	$(2.2 \pm 1.2) \times 10^4$	3.5 ± 0.3
optical ($I = 0.1$)	$(1.9 \pm 0.13) \times 10^7$	$(1.5 \pm 0.12) \times 10^4$	3.1 ± 0.05
ref. 22 ($I = 0.2$)	$(1.8 \pm 0.27) \times 10^7$	$(1.5 \pm 0.24) \times 10^4$	3.08 ± 0.1

[a] The equilibrium constant was determined spectrophotometrically to be 4.93 ± 0.05 (0.1 M $NaClO_4$, 0.5 M tert-butanol, ~20 °C), and estimated to 5.1 at $I \simeq 0$).

FALL computer program [23] to include activity coefficient corrections according to the Davies equation, was used to calculate the concentration variable, $F(c)$, in the relationship

$$\tau^{-1} = \overrightarrow{k} F(c) + \overleftarrow{k} \qquad (6)$$

from which rate constants are calculated [24].

Results and Discussion

A standard method in the study of fast kinetics, is the use of acid–base indicators when direct spectrophotometric monitoring of the reacting species is not possible. This has been the case in some studies of the kinetics of complex formation between lanthanide(III) ions and anthranilate [22, 25] or acetate [25, 26].

It is known, however, that many azo dyes form complexes with lanthanides [27]. Therefore, an assessment of the effect of metal–indicator interaction on the rate constants for the lanthanide systems studied with an acid–base indicator was needed.

The kinetics of complex formation between La^{3+} and Gd^{3+} with Methyl Red in aqueous solutions containing 0.1 M $NaClO_4$ and 0.5 M tert-butanol was thus studied with the pulsed irradiation induced pH-jump technique, using spectrophotometric monitoring. The results are presented in Table II. The equilibrium constants obtained can be compared with values for another azo dye, PAR (4-(2-pyridylazo)-resorcinol) [28], *i.e.*

$$Gd^{3+} + HPAR^{-} \rightleftarrows Gd(HPAR)^{2+}$$

$$\log K_{eq} = 4.28 \pm 0.03$$

Analysis of the effects of the superposition of two not well separated relaxation processes (the metal–ligand and the metal–indicator reactions) on the determination of relaxation times has already been given in the literature [29, 30]. An estimate of the effect of the Dy(III)–Methyl Red reaction on the experimentally determined rate constants for the Dy(III)–anthranilate system [22], can be obtained if the KINRATE computer program [31] is used to solve the set of ordinary stiff differential equations describing such chemical system. Numerical calculations were thus performed with the KINRATE program for two aqueous solutions (see Table III). Values of $1/\tau$ were determined by standard least squares fitting of the numerical results, and the rate constants were calculated from τ^{-1} and $F(c)$ values (cf. eqn. (6)) with $F(c)$ calculated assuming that there is no complex $Dy(Ind)^{2+}$.

As is well known [29, 30], the relaxation times obtained from the superposition of two overlapping relaxing processes depend on the relative amplitudes of the two relaxations, and therefore, the results

TABLE II. Reaction Rates for the Complex Formation between La^{3+} and Gd^{3+} with Methyl Red. Values obtained with the Pulse Radiolytic induced pH-Jump (Spectrophotometric Detection) in 0.5 M tert-Butanol and 0.1 M $NaClO_4$ Aqueous Solutions at ~20 °C

Lanthanide(III)	$\overrightarrow{k}$ (M^{-1} s^{-1})	$\overleftarrow{k}$ (s^{-1})	$\log (\overrightarrow{k}/\overleftarrow{k})$
La^{3+}	$(3.7 \pm 0.3) \times 10^7$	$(6.2 \pm 3.4) \times 10^3$	3.8 ± 0.3
Gd^{3+}	$(3.5 \pm 0.2) \times 10^7$	$(5.6 \pm 1.3) \times 10^3$	3.8 ± 0.1

TABLE III. Results of Numerical Calculations with the KINRATE Computer Program. The Relaxation after an instantaneous pH-jump was simulated for Pairs of Solutions[a] and Values of τ^{-1} were Determined by Least-squares Fitting of [HInd] *vs.* Time[b].

Rate constants used in the calculations	Rate constants obtained	
	$\overrightarrow{k}_{ML} \times 10^{-7}$	$\overleftarrow{k}_{ML} \times 10^{-4}$
$\overrightarrow{k}_{MI} = 1.8 \times 10^7; \overleftarrow{k}_{MI} = 1.0 \times 10^4$	1.38 ± 0.04	1.01 ± 0.06
$\overrightarrow{k}_{MI} = 3.6 \times 10^7$ $\overleftarrow{k}_{MI} = 1.0 \times 10^4$	3.10 ± 0.05	1.01 ± 0.04
$\overrightarrow{k}_{MI} = 0.9 \times 10^7$ $\overleftarrow{k}_{MI} = 1.0 \times 10^4$	0.67 ± 0.07	0.68 ± 0.12
$\overrightarrow{k}_{MI} = 1.8 \times 10^7$ $\overleftarrow{k}_{MI} = 2.0 \times 10^4$	1.21 ± 0.06	2.88 ± 0.10
$\overrightarrow{k}_{MI} = 1.8 \times 10^7$ $\overleftarrow{k}_{MI} = 0.5 \times 10^4$	1.36 ± 0.03	0.35 ± 0.05

[a] Composition of solution 1: $[Dy^{3+}]_T = 0.267$ mM; $[Ant^-]_T = 0.043$ mM; $[Ind^-]_T = 9$ μM; pH = 5.5; solution 2: $[Dy^{3+}]_T = 2.56$ mM; $[Ant^-]_T = 0.086$ mM; $[Ind^-]_T = 9$ μM; pH = 5.5. [b] Rate constants were calculated using eqn. (6). The following parameters were not varied between the calculations: $H^+ + Ant^- \rightleftarrows HAnt$, $\overrightarrow{k}_{HL} = 2 \times 10^{10}$, $\overleftarrow{k}_{HL} = 3.476 \times 10^5$; $H^+ + Ind^- \rightleftarrows HInd$, $\overrightarrow{k}_{HI} = 3.7 \times 10^{10}$, $\overleftarrow{k}_{HI} = 3.7 \times 10^5$; $Dy^{3+} + Ant^- \rightleftarrows Dy(Ant)^{2+}$, $\overrightarrow{k}_{ML} = 1.8 \times 10^7$, $\overleftarrow{k}_{ML} = 1.0 \times 10^4$.

obtained will depend on physical factors like temperature, monitoring technique, perturbation method, etc. In our numerical simulations we have only examined the variation of [HInd] *versus* time after an initial $[H^+]$-jump, and therefore the results have inherent limited applicability. However, our results show that an error of ~25% in the values of $\vec{k}$ is made if the $Dy(Ind)^{2+}$ reaction is not taken into account. The error depends only slightly on total indicator concentration and initial pH of the solutions. On the other hand, there is a strong dependence on the rate constants for the metal–indicator reactions, as seen in Table III. This might be so because [HInd] is the monitored chemical species.

It should be concluded that although the literature values for the rate constants of complex formation between lanthanide(III) and anthranilate [22, 25] might be in error, the magnitude of that error is difficult to ascertain. One should also avoid, when possible, the use of acid–base indicators when studying lanthanide complex formation kinetics.

In the Gd(III)–picolinate system [32], where $\vec{k}$ has a value of $\sim 5 \times 10^8$ (0.1 M $NaClO_4$, 0.5 M tert-butanol, spectrophotometric detection with Methyl Red), two distinct relaxation times are found experimentally. The larger relaxation time corresponds to the rate constants reported in Table II. In this chemical system the precise evaluation of the rate constants for metal ion complex formation is possible, even in the presence of the metal–indicator reaction, due to the wide separation of the relaxation times.

Acknowledgement

The financial support of the Swedish Natural Science Research Council is gratefully acknowledged.

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