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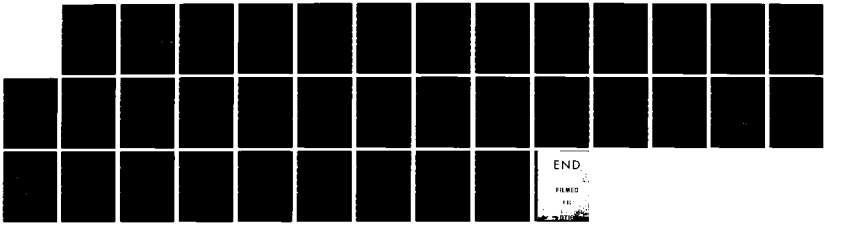

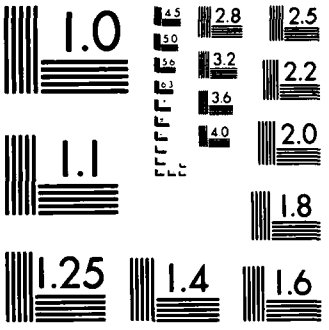

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Flash photolysis of neutral red between pH 1.3 and pH 11 yields the triplet species $^3DH_2^{+2}$, $^3DH^+$, and ^3D. Both $^3DH_2^{+2}$, and ^3D exhibit first order decay with rate constants of $1.6 \pm 0.3 \times 10$ s^{-1}, but $^3DH^+$ decays within the lifetime of the flash. Over the entire pH range, ascorbic acid quenches the triplet, forming the semireduced radicals $DH_3^{\cdot+2}$, $DH_2^{\cdot+}$ and $DH^{\cdot}$, all of which exhibit second order decay with $k = 1.8 \pm 0.4 \times 10^8$ M^{-1} s^{-1}, most probably by

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recombination with semioxidized ascorbic acid. the dependence of the rate of decay of radical neutral red on the identity of reversible reductants supports the back-electron transfer mechanism, as does digitial simulation of complex radical disproportionation schemes. In contrast to the efficient reduction of triplet neutral red by ascorbic acid, its reduction by EDTA is quite inefficient.

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Transient Photochemistry of Neutral Red

by

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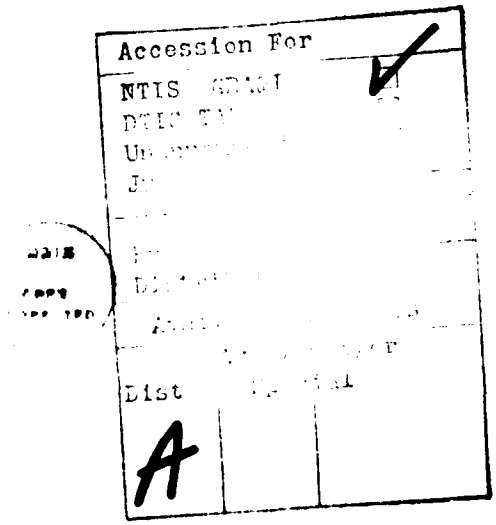
Short Running Title: Transient Photochemistry of Neutral Red

Subheadings	Keywords
neutral red	transient species, triplets, semireduced radicals
transient spectra	neutral red, decay rates, acidity constants
semireduced radicals	formation, decay, influence of reducing agents, acidity constants
triplets	acidity constants, decay rates, reduction

ABSTRACT

Flash photolysis of neutral red between pH 1.3 and pH 11 yields the triplet species $^3DH_2^{+2}$, $^3DH^+$, and ^3D. Both $^3DH_2^{+2}$, and ^3D exhibit first order decay with rate constants of 1.6 ± 0.3 x 10^4 s^{-1}, but $^3DH^+$ decays within the lifetime of the flash. Over the entire pH range, ascorbic acid quenches the triplet, forming the semireduced radicals $DH_3^{+\cdot 2}$, $DH_2^{+\cdot}$ and DH·, all of which exhibit second order decay with k = 1.8 ± 0.4 x 10^8 $\underline{M}^{-1}$ s^{-1}, most probably by recombination with semioxidized ascorbic acid. The dependence of the rate of decay of radical neutral red on the identity of reversible reductants supports the back-electron transfer mechanism, as does digital simulation of complex radical disproportionation schemes. In contrast to the efficient reduction of triplet neutral red by ascorbic acid, its reduction by EDTA is quite inefficient.



INTRODUCTION

Although the transient photochemistry of thiazine dyes such as methylene blue (Wildes et al., 1977) and thionine (Bonneau et al., 1974) has been the subject of intensive study, the transient photochemistry of the azine dyes has received little attention. We report here such a study of neutral red (3-amino-6-dimethylamino-2-methylphenazine hydrochloride). Neutral red has long been used as both an acid-base indicator (Bishop, 1972), and a biological stain (Clark and Perkins, 1932), but its transient photochemistry has been the subject of only one brief study (Chibisov et al.,1969) which reported semireduced radical peaks at pH 4 and pH 11. Because both the triplet species and the semireduced radical species play critical roles in the photoredox reactions of dyes (Ohno and Lichtin, 1980), knowledge of the properties of these excited states is necessary for proper understanding of such processes. The present study establishes the major features of the acid-base behavior, the visible spectra and the decay kinetics of both the semireduced radical species and the triplet species of neutral red. In some respects, the properties of these excited state species of neutral red are similar to those of the thiazine dyes methylene blue (Wildes et al., 1977) and thionine (Bonneau et al., 1974) and the azine dye safranin-O (Baumgartner et al., 1981), but there are important differences which distinguish neutral red from the other dyes.

MATERIALS AND METHODS

Neutral red was recrystallized thrice from 50% aqueous methanol and other chemicals were reagent grade, and were used without further purification. Except as noted in certain studies with EDTA as reducing agent, 2×10^{-6} M dye in aqueous 1×10^{-3} M phosphate buffer was used throughout. Prior to flash photolysis, the dye solution in a 10 cm quartz or borosilicate cell was rigorously freed of oxygen by 7 successive freeze-pump-thaw cycles under a vacuum of 10^{-5} torr. Spectroscopic transients were secured using the xenon flash photolysis unit described by Strong and Perano (1967), which permitted monitoring the transient absorption between 350 nm and 820 nm beginning 50 μs after flash initiation. Before reaching the sample cell, the flash lamp beam passed through a uranyl nitrate solution and a copper sulfate-methylene blue solution to limit the sample illumination to wavelengths between ca 450 nm and 550 nm, the range which corresponds to the absorption band of ground state neutral red. Kinetic data were subjected to linear regression analysis and only data sets with regression coefficients of 0.985 or higher were used to compute rate constants.

RESULTS AND DISCUSSION

Triplet State Characteristics

Transient absorption spectra obtained from pH 1.3 to pH 11.0 in the absence of reducing agents, representative examples of which are in Figure 1, were used to estimate the

acidity contants of the triplet state. Strong absorption by ground state dye from ca 440 nm to 550 nm precludes characterization in this range of transient spectra, the essential features of which are as follows. Between pH 1.3 and pH 4.2, the transient absorption spectrum consists of two bands with maxima at 390 nm and 680 nm, the intensities of which are essentially pH independent. Above pH 4.2 the 680 nm band decreases in intensity, the 390 nm band broadens and both peaks shift toward shorter wavelengths. At pH 5.1, the 680 nm peak has shifted to 650 nm and the 390 nm peak has shifted to 380 nm. Accompanying these spectral shifts is a sharp drop in the lifetime of the triplet species, which becomes so short that above pH 6 the triplet absorption follows the decay of the flash and cannot be detected 50 μs after flash initiation. Triplet absorption remains undetectable until ca pH 9.2, at which point the triplet lifetime has increased sufficiently to reveal the bands at 380 nm and 650 nm and a new band at 580 nm. Increasing the pH from 9.2 to 11 causes the intensity of the 650 nm band to fall nearly to zero and the intensity of the 580 nm band to increase to a limiting value, while the intensity of the 380 nm band remains essentially constant.

No transients were observed in the presence of oxygen, a result which together with the reactivity of these transient species with reducing agents (see next section) indicates that they are triplet species. Because the pK_a of neutral red is 6.8 (Bartels, 1956), both the acidic and basic forms of ground

state neutral red give rise to triplet species. From pH 1.3 to pH 4.2 and from pH 9.2 to pH 11.0, the decay rate of the triplet species is fixed, independent of pH. Throughout both pH domains, the transient depletion of the ground state dye shows the triplet concentration 50 μs after flash initiation to be 1.3×10^{-7} M. That is, at this point the triplet yield is equivalent to ca 6-7% of the concentration of ground state dye, as compared to ca 50% triplet yield for safranin-O under similar excitation conditions in the same apparatus (Baumgartner et al., 1981). In these studies, the ground state absorption was held approximately constant by centering the irradiation at the ground state isosbestic point of 480 nm. It is noteworthy that over the entire pH range where the triplet can be detected, the triplet yield remains virtually fixed at 6-7%. This estimate of the triplet yield is based on the usual assumption that the triplet species do not absorb significantly at 500 nm, the wavelength at which we monitored the ground state depletion. Although Figure 1 suggests that this assumption is valid, it is possible that the triplet species do absorb at this wavelength. Therefore, the estimates of triplet yield are minimum values, while the estimates of the triplet absorptivities are maximum values.

The molar absorptivity of each triplet species was determined from the ground state depletion and the transient triplet absorbance at a pH which ensures that only one triplet species is present. These values along with the first order

rate contants for triplet decay are reported in Table I. In view of the structural similarity of neutral red to thionine, oxonine and safranin-O, we have adopted the notation of Bonneau et al., (1973) for the triplet state whereby the most highly protonated triplet species in the pH range of interest is denoted $^3DH_2^{+2}$.

The pH dependence of the transient triplet absorption bands indicates that the acidic triplet undergoes stepwise loss of two protons as described by Equation 1.

$$^3DH_2^{+2} \underset{}{\overset{K_{a_1}}{\rightleftharpoons}} {}^3DH^+ + H^+ \overset{K_{a_2}}{\rightleftharpoons} {}^3D + H^+ \qquad (1)$$

Figure 2 reports the pH dependence of the normalized absorbance at 680 nm and at 580 nm 50 μs after flash initiation. Although these plots are qualitatively similar to those for a number of other dyes (Knowles, 1971), they cannot be used to determine exact values of the pK_as of $^3DH_2^{+2}$ and $^3DH^+$. The reason is that the decay of the intermediate triplet, $^3DH^+$, is much faster than that of $^3DH_2^{+2}$. In fact, it is so rapid that between pH 6 and pH 9 it follows the decay profile of the flash lamp and no triplet absorption can be detected 50 μs after flash initation. Because $^3DH^+$ decays much more rapidly than does $^3DH_2^{+2}$, formation of $^3DH^+$ above pH 4 increases the rate of $^3DH_2^{+2}$ decay. This coupling occurs because proton transfer is much faster than decay of $^3DH_2^{+2}$ (Schulman, 1976), so that throughout its lifetime, $^3DH_2^{+2}$

disappears by conversion to $^3DH^+$ as well as by direct decay to the ground state. This second decay route lowers the concentration of $^3DH_2^{+2}$ throughout its lifetime, and as a result, the pH at which the normalized absorbance of $^3DH_2^{+2}$ falls to 0.5 is lower than the pK_a of $^3DH_2^{+2}$. The interaction of $^3DH^+$ with ^3D is analogous to its interaction with $^3DH_2^{+2}$, and similar considerations show that the pH at which the normalized absorbance rises to 0.5 is higher than the pK_a of $^3DH^+$. That is, the lower limit of pK_{a_1} is 4.8 and the upper limit of pK_{a_2} is 9.5. Determination of the precise values of the pK_as requires knowledge of the decay kinetics of $^3DH^+$, which in turn requires that absorption measurements be made sooner after flash initiation. Despite this limitation, however, the estimated pK_as of triplet neutral red (>4.8, <9.5) agree reasonably will with the triplet pK_as of the related dyes thionine (6.3, 8.9) (Fischer, 1964; Faure et al., 1967; Bonneau and Pereyre, 1975) and safranin-O (7.5, 9.2) (Baumgartner et al., 1981).

Both $^3DH_2^{+2}$ and ^3D exhibit strictly first order decay over 2-3 halflives. The absence of a transition to second order kinetics late in the life of the triplet species shows that triplet-ground state interaction forming semireduced and semioxidized dye, which was suspected to occur with safranin-O (Baumgartner et al., 1981), is not significant for neutral red. All transients decays return to the baseline within ca 0.2 ms and the ground state absorption spectrum is unchanged

after samples are subjected to as many as 50 flashes, thus confirming that triplet formation is reversible and that no long-lived species are formed.

Semireduced Radical Formation

We have examined the one-electron reduction of triplet state neutral red by several reducing agents, with emphasis on the behavior of ascorbic acid and EDTA. With 2×10^{-4} M ascorbic acid as the reductant, between pH 1.3 and pH 11, the concentration of semireduced radical 50 μs after flash initiation estimated from the transient decrease in ground state absorption at 500 nm corresponds to ca 6% of the ground state dye concentration. The similarity of this value to the concentration of triplet formed in the absence of reducing agents and the observation that 2×10^{-4} M ascorbic acid completely quenches the triplet indicate that over the entire pH range, conversion of triplet neutral red to the semireduced radical is essentially quantitative.

Several aspects of the formation of the semireduced radical by ascorbic acid are significant. First, addition of this reducing agent does not decrease the relative yield of neutral red fluorescence, a result which eliminates singlet state neutral red as a direct pathway to the semireduced radical. Second, the total quenching of the triplet transient indicates that conversion of triplet neutral red to the semireduced radical takes place with high efficiency. Even between pH 6 and pH 9, where the triplet decay is so rapid that

it follows the flash lamp decay, the concentration of semireduced neutral red remains at the level observed outside this pH range, where the triplet lifetime is much longer. The ability of the reduction pathway to compete successfully with triplet decay under these extreme circumstances shows clearly that the rate of triplet reduction by 100 fold excess ascorbic acid is much faster than the rate of triplet decay.

In contrast to the highly efficient reduction of triplet neutral red by ascorbic acid from pH 1.3 to pH 11, its reduction by EDTA over this pH range is quite inefficient. For example, over the entire pH interval, 2×10^{-4} M EDTA does not react to a detectable extent with triplet state neutral red. Unfortunately, the low reactivity of EDTA below pH 6 (Bonneau et al., 1974) and the limited solubility of neutral red above pH 7 limit severely the scope of a systematic study of the reduction of triplet state neutral red by EDTA. Transient experiments at pH 6.5 with 2×10^{-3} M EDTA yield small quantities of semireduced dye, equivalent to ca 0.3% of the ground state dye concentration. The low reactivity of EDTA with triplet state neutral red stands in contrast to its high reactivity with the triplet states of thionine, methylene blue (Bonneau et al., 1973; Bonneau et al., 1974) and safranin-O (Baumgartner et al., 1981) both of which EDTA reduces with high efficiency above pH 6. This difference may reflect the fact that the concentration of $^3DH_2^{+2}$ which exists under these conditions is much lower in the case of neutral

red than in the case of the other dyes. The estimated pK_as of $^3DH_2^{+2}$ noted in the previous section support this explanation.

Semireduced Radical Spectra

Representative transient spectra of semireduced neutral red secured 1 ms after flash initiation and reported in Figure 3 illustrate the major spectral features of these species. Below pH 6.5, there is a sharp absorption band centered at 390 nm and a broad band centered at 690 nm. Chibisov et al., (1969) reported only the long wavelength band at pH 4. Above pH 8.5 there are two absorption bands at 380 nm and 710 nm. Chibisov et al., (1969), report only a band below 600 nm at pH 11. Neither the wavelengths of the two absorption bands nor the intensity of the shorter wavelength band is sufficiently pH sensitive to be useful for monitoring the acid-base chemistry of semireduced neutral red, but the strong pH dependence of the intensity of the longer wavelength band is ideally suited for this purpose. The normalized absorbance-pH plot at 690 nm reported in Figure 4 displays distinct transitions centered at pH 2.6 and pH 7.8, each of which corresponds to a pK_a. Chibisov et al., (1969), report a single pK_a of about 7, but made no measurements below pH 4. Because the rate constant for decay of semireduced neutral red is pH independent (see following section), these transitions can be asssociated directly with the two pK_as of semireduced neutral red. Thus, the acid-base chemistry of semireduced neutral red can be described by Equation 2 in which the

formula of the most highly protonated species is denoted $^{3}DH_{3}^{+2}\cdot$.

$$DH_{3}^{+2}\cdot \underset{}{\overset{K_{a_1}}{\rightleftharpoons}} DH_{2}^{+}\cdot \underset{+H+}{\overset{K_{a_2}}{\rightleftharpoons}} DH\cdot \qquad (3)$$

This choice of notation is suggested by the similarity of the second pK_a of the neutral red radical (7.8) to the pK_a of the species $DH_2^+\cdot$ of thionine (8.2, Fisher, 1964; Bonneau et al., 1968; Faure et al., 1967), oxonine (7.6, Michaelis and Granick, 1941) and safranin-O (9.5, Baumgartner et al., 1981). Molar absorptivities, absorption maxima, and decay constants of the three neutral red radical species along with their pK_as are summarized in Table II. As a check on the correctness of the pK_a values, the solid line in Figure 4 is the theoretical line constructed from the pK_as and the limiting absorbances. The close agreement of this theoretical line with the experimental points confirms that these pK_a values are consistent with the data.

Semireduced Radical Decay

Over the entire pH range, the decay of neutral red formed by ascorbic acid reduction follows second order kinetics with a rate constant of $1.8 \pm 0.4 \times 10^{8}$ M^{-1} s^{-1}, independent of pH. The two simple processes consistent with these kinetics are the disproportionation of the semireduced radical and the back transfer of an electron from the semireduced radical to oxidized ascorbic acid. The corresponding reactions are defined by Equation 3 and Equation 4, respectively, where AA

and $AA^{\cdot+}$ represent ascorbic acid and its one electron oxidation product. Although Equations 3 and 4 apply specifically to the pH range 2.6-7.8, similar expressions involving $DH_3^{+\cdot 2}$ and $DH^{\cdot}$ apply at higher and lower pH values.

$$DH_2^{+\cdot} + DH_2^{+\cdot} \longrightarrow DH_3^{+} + DH^{+} \qquad (3)$$

$$DH_2^{+\cdot} + AA^{\cdot+} \longrightarrow DH^{+} + AA + H^{+} \qquad (4)$$

There are two pieces of evidence which indicate that Equation 3 is not an important pathway for decay of semireduced neutral red. The first is that from pH 1.3 to pH 11 there is no detectable deficit in the concentration of ground state neutral red within 20 ms after subjecting the neutral red-ascorbic acid system to 50 successive flashes, indicating that no ground state neutral red is permanently converted to leuco dye. Since leuco neutral red is reported to be oxidized only slowly near neutral pH on the time scale of potentiometric studies (Clark and Perkins, 1932), the rapid and complete regeneration of ground state neutral red in this pH range in the present study suggests that formation of leuco dye is not significant.

The second and more direct indication that Equation 3 is not the major pathway for the disappearance of semireduced neutral red when a reversible reducing agent is used is the strong dependence of the rate constant for this process on the

identity of the reducing agent. For example, at pH 7.5 with p-phenylenediamine as the reductant, the decay constant of the semireduced radical is 2.5 x 10^9 $\underline{M}^{-1}$ s^{-1}, a value more than 10 fold higher than that observed with ascorbic acid as reductant. Under these conditions the one-electron oxidation product of p-phenylenediamine is a significantly better oxidant than the one-electron oxidation product of ascorbic acid, (Steenken and Neta, 1979). The fact that semireduced neutral red decays <u>ca</u> tenfold more rapidly in the presence of oxidized p-phenylenediamine than in the presence of oxidized ascorbic acid is consistent with the back electron transfer mechanism of Equation 4, but rules out the radical disproportionation mechanism of Equation 3.

Because radical disproportionation is an efficient process for the disappearance of the semireduced radical species of a number of dyes, we considered the more complex mechanism defined by Equations 5 and 6 in which Ox and Re denote the

$$DH_2^+\cdot + DH_2^+\cdot \longrightarrow DH_3^+ + DH^+ \qquad (5)$$

$$DH_3^+ + Ox \longrightarrow DH_2^+\cdot + Re \qquad (6)$$

oxidized and reduced forms of the reducing agent. In this mechanism, a fast radical disproportionation step is followed by a slower step which converts leuco dye to semireduced radical. Because coupling the two steps complicates

analytical solution of the kinetic equations, we used digital simulation to obtain numerical solutions under appropriate conditions. Figure 5 demonstrates the influence of the rate of the coupled reaction between the oxidized form of the reducing agent and the leuco dye on the second order rate plot for disappearance of the semireduced radical. In this simulation, k_1, the rate constant of Equation 5 is set at 2×10^8 $\underline{M}^{-1}$ s^{-1}, while k_2 is varied from 0 to 2×10^{10} $\underline{M}^{-1}$ s^{-1}.

As anticipated, the second order kinetic plots are linear if k_2 is either much larger than k_1 or much smaller than k_1. However, for either condition, the slope of the second order kinetics plot is nearly independent of the value of k_2. That is, under the conditions which give reasonable second order kinetics plots, the apparent rate constant for disappearance of the semireduced radical is virtually insensitive to the reactivity of the oxidized form of the reducing agent. In fact, over the entire range of k_2, the value of the apparent second order rate constant varies by only a factor of two. These predictions of the model are clearly inconsistent with the tenfold increase in the rate of disappearance of semireduced dye when ascorbic acid is replaced with p-phenylenediamine, ruling out the disproportionation-regeneration mechanism of Equations 5 and 6. Thus, the only mechanism consistent with all of the kinetic data is the back electron transfer process of Equation 4.

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TABLE I

Properties of Neutral Red Triplet Species

Species	pk_a	Absorption Maxima (nm)	Molar Absorptivity ($M^{-1}cm^{-1}$)	Decay Constant (s^{-1})
$^3DH_2^{+2}$		390 680	8,000 12,000	$1.6 \pm 0.3 \times 10^4$
$^3DH^+$	4.8			
	9.5			
^3D		380 580	5,800 7,300	$1.6 \pm 0.3 \times 10^4$

TABLE II

Properties of Semireduced Neutral Red Species

Species	pk_a	Absorption Maxima (nm)	Molar Absorptivity ($M^{-1}cm^{-1}$)	Decay Constant ($M^{-1}s^{-1}$)
$DH_3^{+2}\cdot$		390 690	8200 1000	$1.8 \pm 0.4 \times 10^8$
	2.6			
$DH_2^{+}\cdot$		390 690	8200 5800	$1.8 \pm 0.4 \times 10^8$
	7.8			
$DH\cdot$		380 710	7000 8100	$1.8 \pm 0.4 \times 10^8$

FIGURE CAPTIONS

Figure 1 Transient absorption spectra of triplet species
open circles - pH 2.8
closed circles - pH 9.8

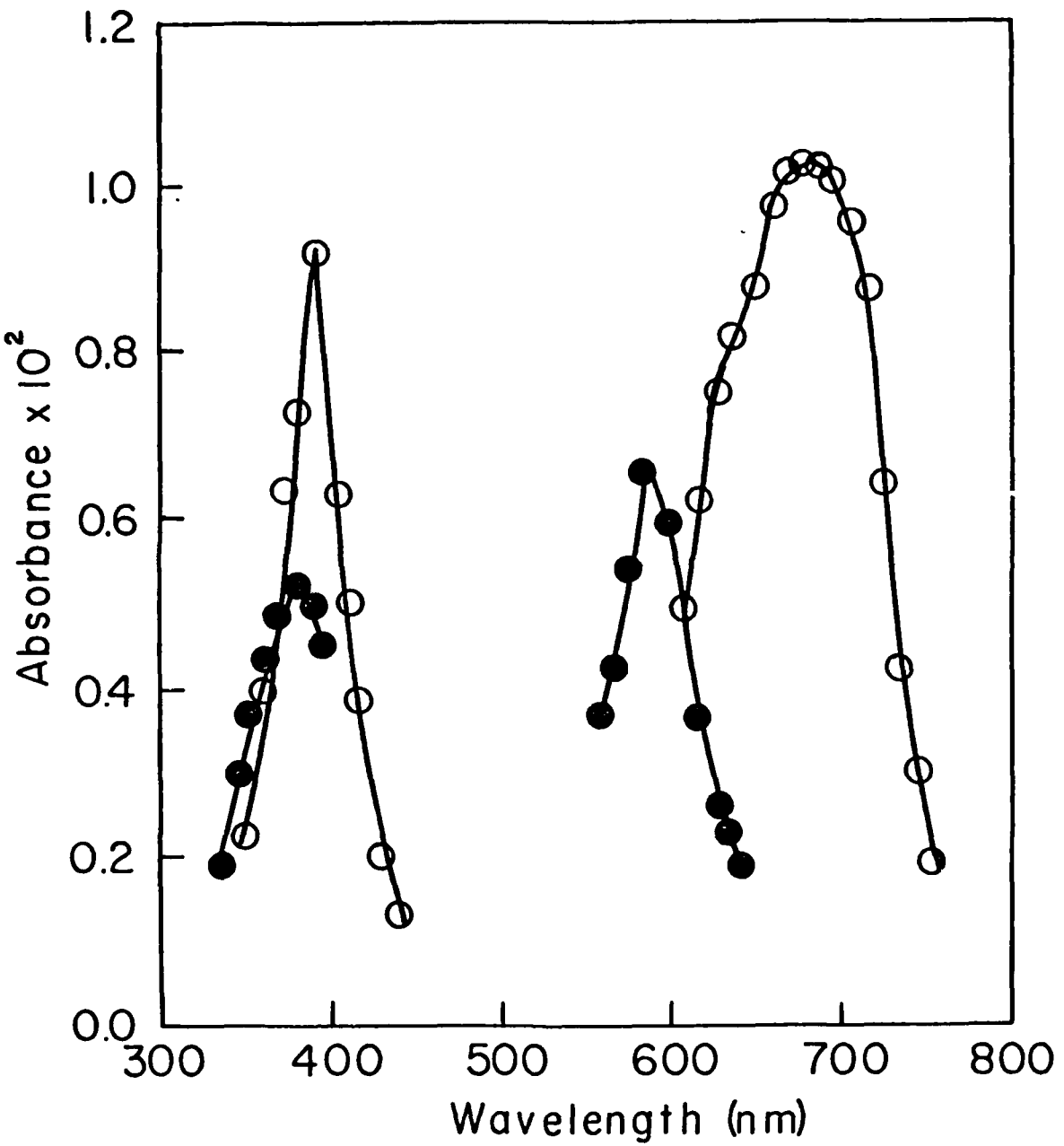
Figure 2 Normalized absorbance - pH plot for triplet species
open circle - acidic triplet at 680 nm
closed circles - basic triplet at 580 nm

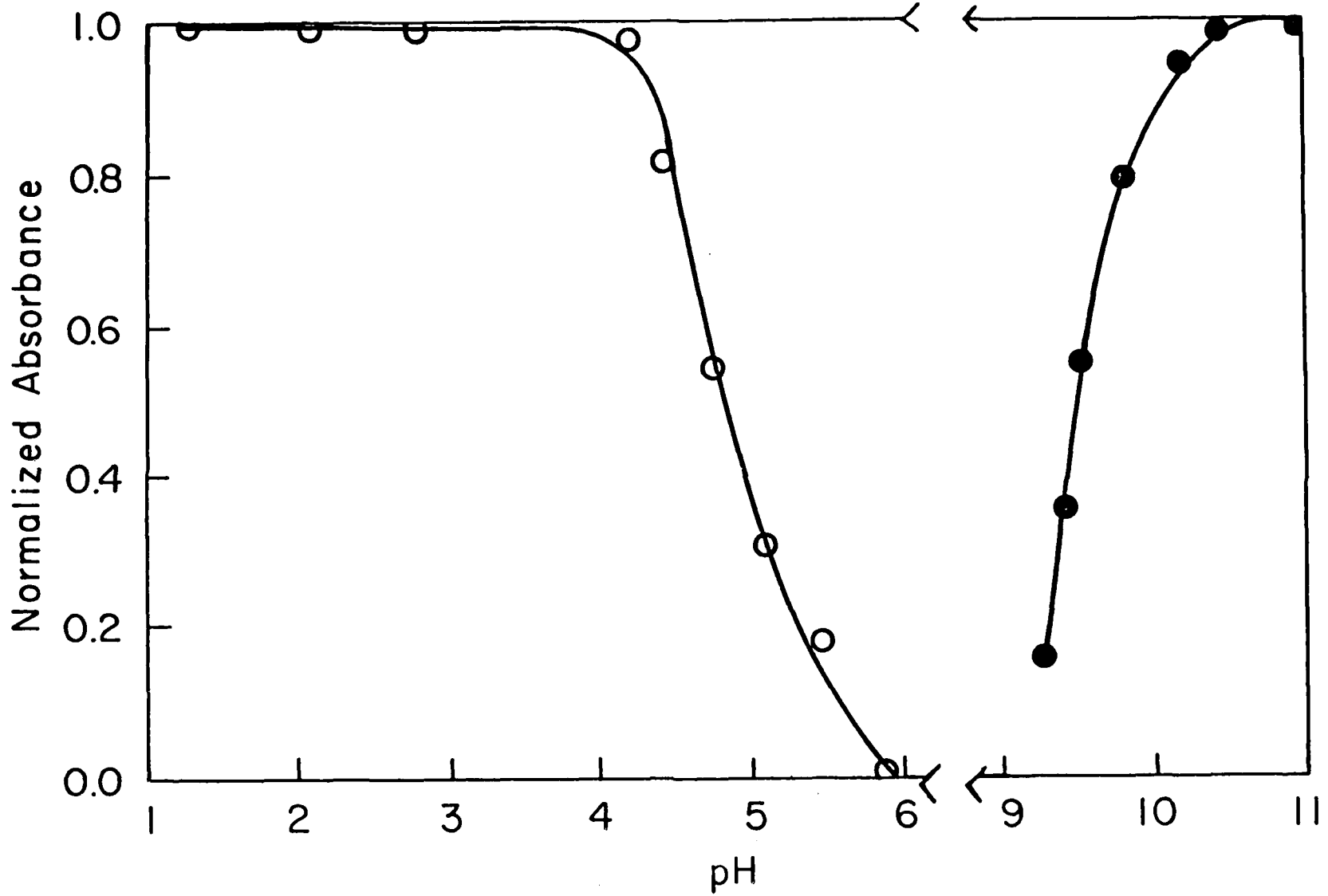
Figure 3 Transient absorption spectra of semireduced radicals
open circles - pH 2.8
closed circles - pH 9.8

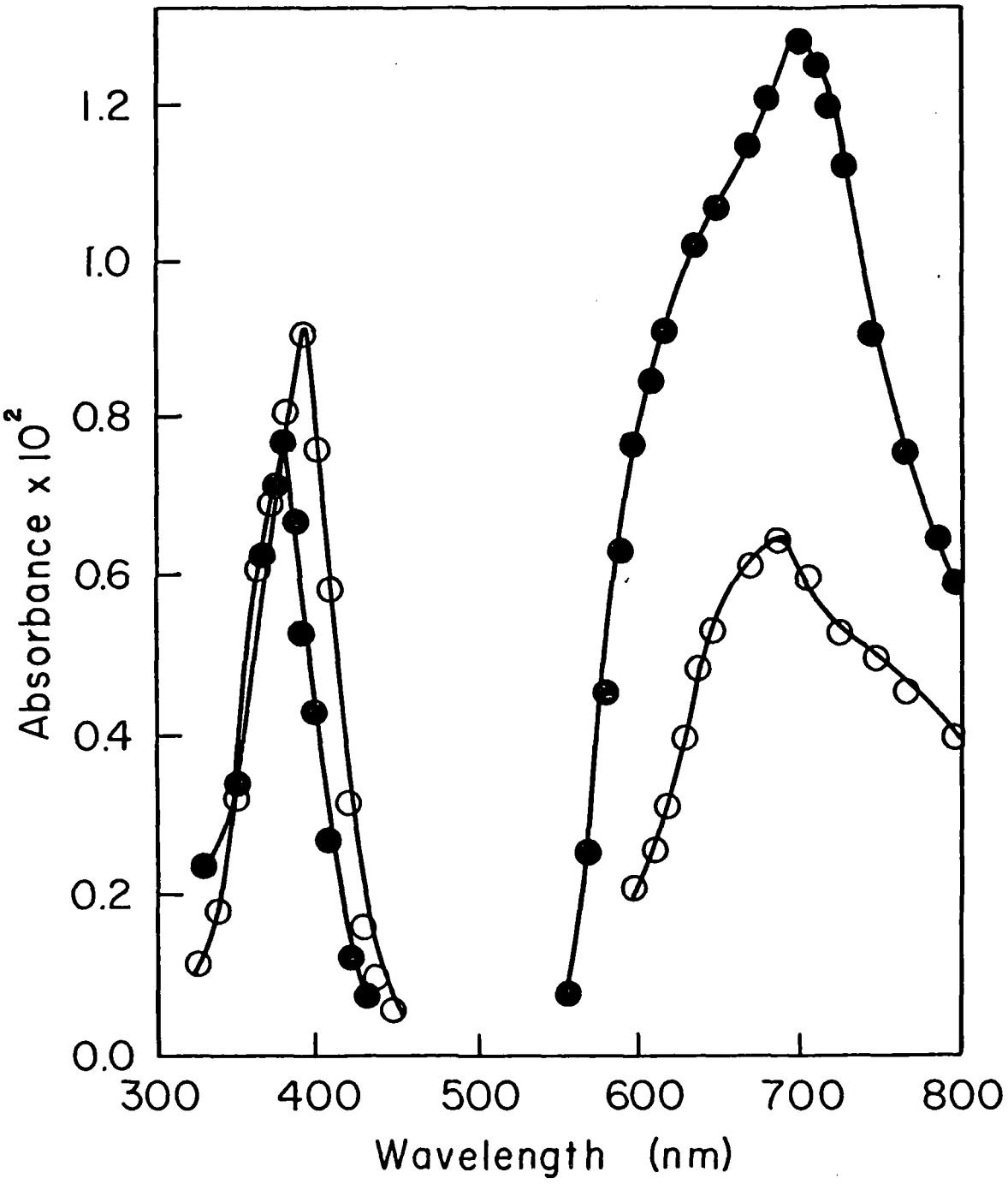
Figure 4 Normalized absorbance-pH plot for semireduced radicals at 690 nm

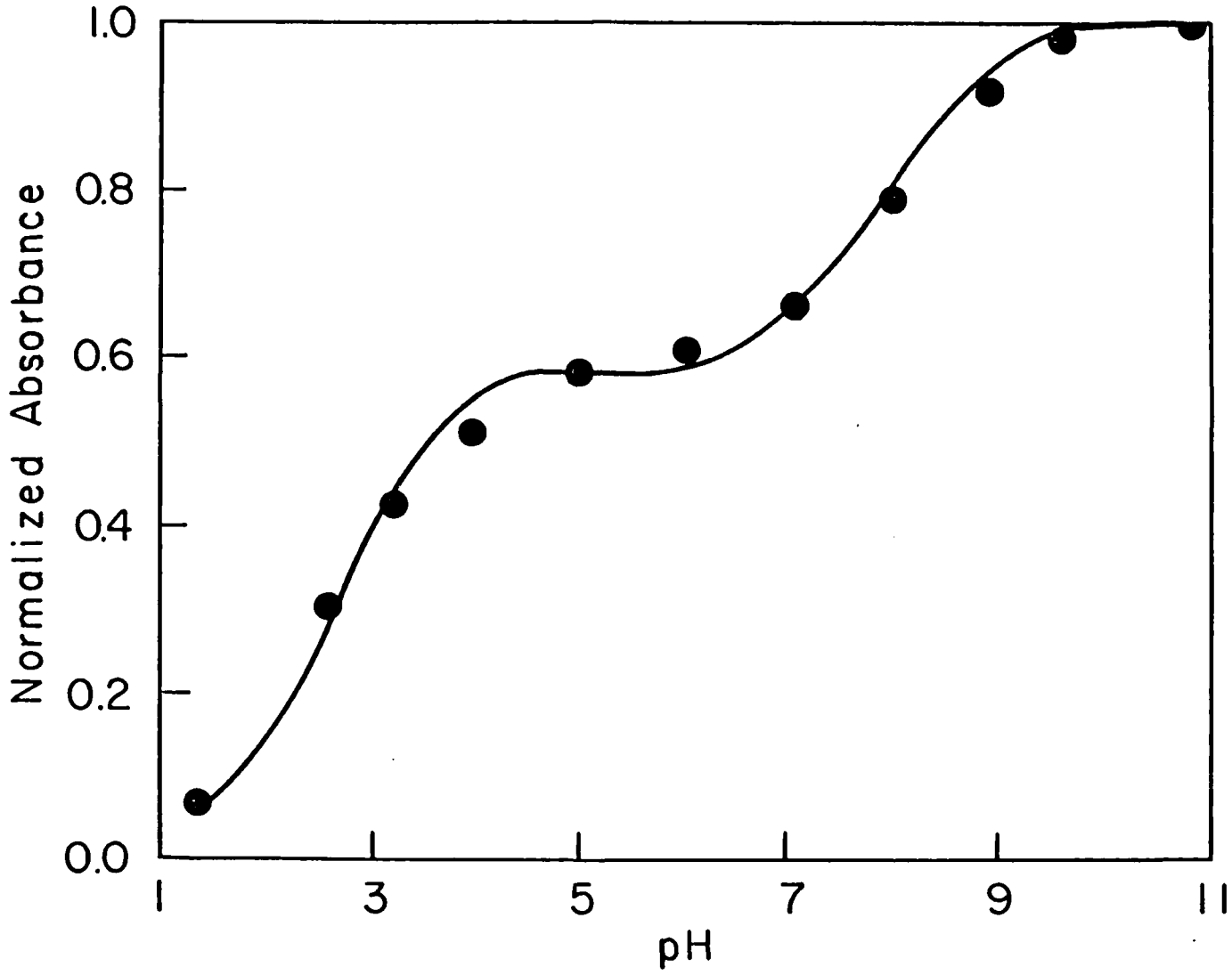
Figure 5 Digitally simulated second order plots for disappearance of semireduced radical by mechanism of Eqns 5 and 6 with $k_1 = 2 \times 10$ $\underline{M}^{-1} s^{-1}$.

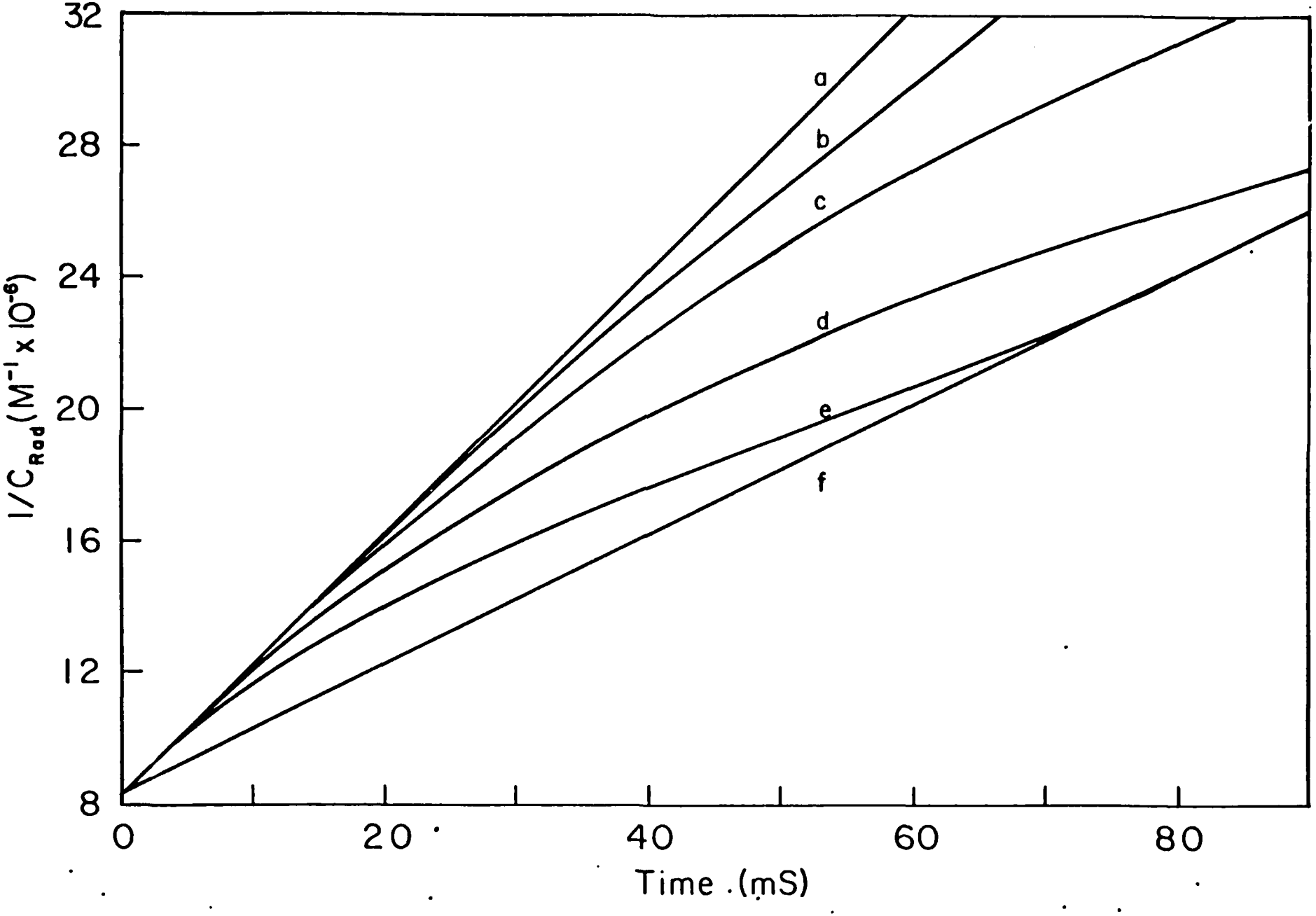
plot	k_2 $\underline{M}^{-1}s^{-1}$
a	0
b	$2x10^7$
c	$6x10^7$
d	$2x10^8$
e	$6x10^8$
f	$2x10^{10}$


1.2
1.0
0.8
0.6
0.4
0.2
0.0
Absorbance x 10²
300
400
500
600
700
800
Wavelength (nm)


Normalized Absorbance
1.0
0.8
0.6
0.4
0.2
0.0
1
2
3
4
5
6
9
10
11
pH


1.2
1.0
0.8
0.6
0.4
0.2
0.0
Absorbance x 10²
300
400
500
600
700
800
Wavelength (nm)


1.0
0.8
0.6
0.4
0.2
0.0
Normalized Absorbance
1
3
5
7
9
11
pH


32
28
24
20
16
12
8
0
20
40
60
80
Time .(mS)
$1/C_{Rad}(M^{-1} \times 10^{-6})$
a
b
c
d
e
f

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