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PHOTOINDUCED ELECTRON TRANSFER IN RIGID SOLUTION: TIME RELATED QUENCHING OF TRIPLET ZINC TETRAPHENYLPORPHINE

M.A. Kahlow
(M.S. Thesis)

December 1983

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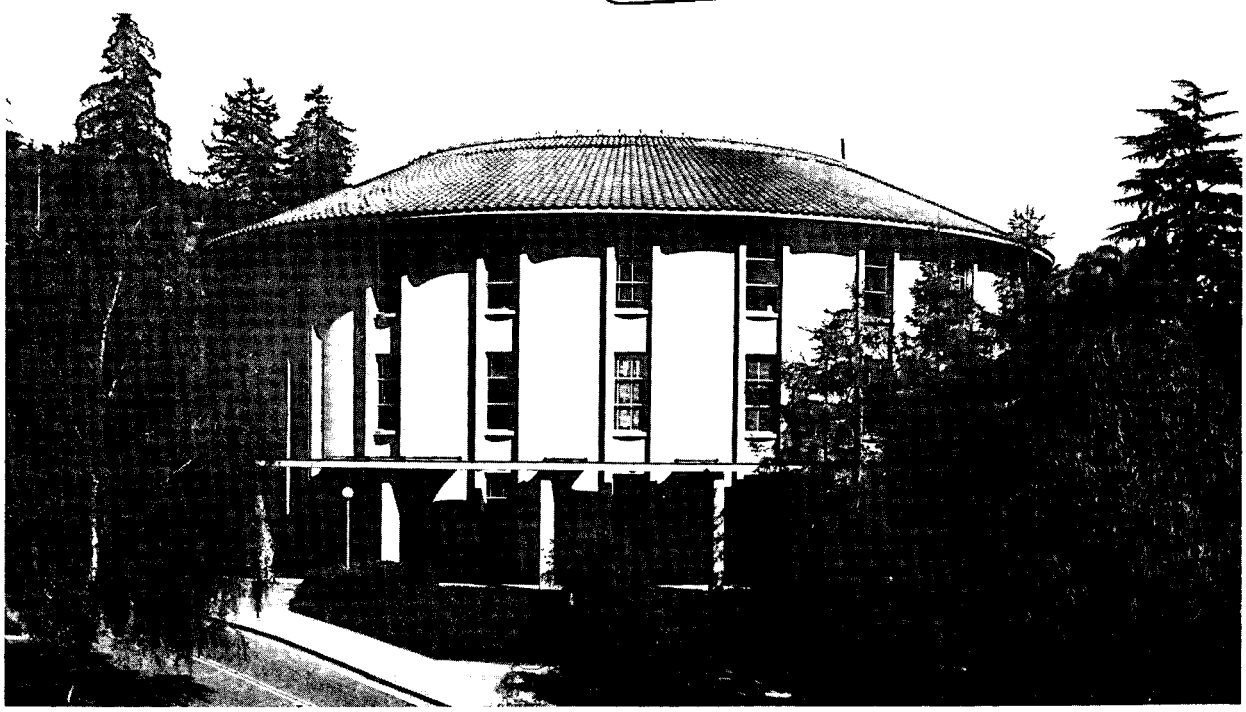

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PHOTOINDUCED ELECTRON TRANSFER IN RIGID SOLUTION: TIME RELATED QUENCHING OF TRIPLET ZINC TETRAPHENYLPORPHINE

Michael A. Kahlow
(M.S. Thesis)

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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ABSTRACT

A model has been developed to describe the behavior of photoinduced electron transfer between randomly distributed reactants in rigid media. Using this model, we have determined the distance dependence of electron transfer from triplet zinc tetraphenylporphine (ZnTPP) to methylbenzoquinone (MBQ) in sucrose octaacetate glass at 21° C. The observed decay of triplet ZnTPP is well described by an exponential dependence of the electron transfer rate with distance, in agreement with other works. However, at 31° and above, the observed kinetics are no longer consistent with this treatment. This may be due to the onset of diffusion at these higher temperatures, with the result that the distances between porphyrin and quinone are no longer fixed on the experimental time scale.

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INTRODUCTION

In recent years much attention has been focused on the electron transfer reactions from electronic excited states of molecules. A relatively inert molecule can, with the absorption of a photon of light, become both a strong oxidant and a strong reductant.

Excited, such a molecule can accept or donate an electron from or to another chemical species, yielding reducing and oxidizing products. These two energetic products can then separate, or react with each other. These two electron transfer reactions will be called the forward and back reactions, respectively. The back reaction typically gives back the original two molecules, both in their ground electronic states.

Many hope that an understanding of these two reactions will let one separate the intermediate products before the back reaction. This is an important step in achieving the elusive goal of "artificial photosynthesis" -- the direct conversion of light energy (a photon) to a storable form of chemical energy [1].

The relative rates of the forward and back reactions are the important factors in this endeavor. To increase the overall

yield of products, one should have a system with a relatively fast forward reaction and a slow back reaction. Many workers have used microscopic organizations to physically separate the initial photoproducts, usually with some form of phase boundary. Micelles [2], microemulsions and polyelectrolytes [3], vesicles and polymerized vesicles [4], soluble polymers [5], colloids [6], and semiconductor dispersions [7] have all been used for this purpose, with varying degrees of success.

However, these studies often leave key questions unanswered -- namely, what is the distance of separation of the chemical species, and how is their rate of reaction affected by this separation? These are not easy questions to answer. But if we could answer them, we could simplify the design of such microscopic organizations. To this end, we decided to study the effect of distance of separation on electron transfer rates.

One recent approach is the covalent linkage of a porphyrin molecule to a quinone [8,9]. This sets the distance, and, depending on the nature of the linkage, sometimes also the relative orientation. One then follows the kinetics of electron transfer from the porphyrin excited singlet and triplet states to the quinone and back through flash photolysis.

However, the syntheses of these molecules are difficult. Therefore, we looked for another method. We chose to isolate the donor and acceptor molecules (in this experiment, zinc tetraphenylporphine [ZnTPP] and methylbenzoquinone [MBQ]) in random fashion in a rigid solution, sucrose octaacetate [SA]. The distances are fixed -- diffusion is (in theory) eliminated.

Much of the previous work on electron transfer in rigid, random media (glasses) has been done by John Miller at Argonne National Laboratory [10-14], although other groups have published in the field [15-18]. Pulse radiolysis studies by Miller and co-workers has shown that electron transfer rates depend exponentially on distance:

$$k(r) = \nu \exp\left[-(r-R_0)/a\right] \tag{1}$$

where k(r) is the distant dependent first order rate constant, ν is a pre-exponential frequency factor, r is the center to center distance of the electron donor and acceptor, R_0 is the sum of the crystallographic radii, and a is a scaling factor dependent on the interaction of the donor and acceptor wave

functions through the solvent potential barrier. This result is also predicted by theory [19-21].

Miller and co-workers have also recently shown that, for photoinduced electron transfer from or to a molecule in an electronic excited state, the steady state emission quenching follows a simple exponential behavior [13,14]:

$$I/I_o = \exp\left[-\frac{4}{3}\pi c R_q^3\right] \qquad (2)$$

where I/I_0 is the fraction of quenching, c is the concentration, in (molecules/unit volume) and R_q is a "quenching radius". The quenching radius is defined as the donor-acceptor distance at which the rate of decay of the excited state is equal to the rate of electron transfer. This applies to both singlet state [13] and triplet state [14] reactions.

Our intention was to observe the time resolved kinetics of the reaction between the triplet state of ZnTPP and MBQ, using flash photolysis. This theory was first explored in the work of Inokuti and Hiriyama [22] on electron exchange (analogous to electron transfer). Until this last year, the only time

resolved work on such systems was that of Namiki et al [23], on the quenching of indole fluorescence by chloromethanes in rigid ethanol glass. They use an expression for the kinetics that assumes a random distribution of quenching molecules, and that the molecules are points with no volume. In our work, quenching of the excited singlet porphyrin prior to intersystem crossing to the triplet leaves us with a nonrandom distribution of distances for triplet state reactions. Thus, this model cannot be used for our work.

While we were conducting our experiments, McLendon and co-workers [18] published the results of similar work. [24] Their model, like ours, does not require a random distribution, or the assumption that the molecules have no volume. Their expressions will be compared below to those used in this work.

The Model -

Our model for the quenching of the triplet state is a form of the nearest neighbor approximation of Huddleston and Miller [25], modified to account for the decay of the donor excited state. In this model, the electron donors are considered to react only with the nearest acceptor molecule. With this approximation, the survival probability becomes:

$$P_{nn}(+) = e^{-k_1 t} \int_{r = R_0}^{r = \infty} \omega dr \quad (r) e^{-k_2(r)t} \tag{3}$$

where $k_2(r)$ is the distance dependent rate constant for electron transfer between a donor and acceptor separated by a distance r, and $\omega(r)$ is the nearest neighbor distribution function [26]

$$\omega(r) \alpha 4 \pi c r^2 \exp\left[- \frac{4}{3} \pi c r^3 \right] \tag{4}$$

Note that $\omega(r)$ must be normalized so that

$$\int_{r = R_0}^{r = \infty} dr \, \omega(r) = 1 \tag{5}$$

The constant k_1 is the first order rate constant for deactivation of the donor excited state in the absence of quencher; the exponential in front of the integral thus provides for the natural decay of the excited state.

This nearest neighbor approximation suggests an intuitive way of understanding these reactions. If we make the additional

assumption that electron donor - acceptor pairs do not interact with other donor - acceptor pairs, we can consider each pair separately. This is a reasonable assumption; if we differentiate equation (4) and solve for the most probable distance between molecules, we find that this distance is:

$$r_{mp} = 6.42 \left(\frac{1}{M} \right)^{1/3} \quad (\mathring{A}) \qquad (6)$$

where M is the concentration in moles per liter, and r_{mp} is in Angstroms. With the donor concentrations used in this study (1×10^{-4} M), the most probable distance between donor molecules is 135 Angstroms. For the acceptor concentrations used (0.015 to 0.105 M), the most probable donor - acceptor and acceptor - acceptor distances range from 13.6 to 26.0 Angstroms.

We can consider each donor - nearest acceptor pair to be a "supermolecule", with the interaction between the pair dependent on the distance between them. The rates of reaction for each isolated pair is then first order, though dependent on distance. The kinetic scheme for each pair is then:

$$\begin{tikzcd} {}^3PQ \arrow[r, "k_2(r)"] \arrow[rr, bend right, "k_1"'] & {}^3P^{+\cdot}\,Q^{-\cdot} \arrow[r, "k_3(r)"] & PQ \end{tikzcd}$$

where

k_1 is the normal first order rate constant for decay of the donor excited state.

$k_2(r)$ is the first order distance dependent rate constant for electron transfer from the excited donor to the acceptor.

$k_3(r)$ is the first order distance dependent rate constant for electron transfer from the reduced acceptor to the oxidized donor (The back reaction).

Solving for the survival probability as a function of distance of separation and time for an isolated donor - acceptor pair gives

$$P_{nn}(r,T) = e^{-(k_1 + k_2(r))} \tag{7}$$

Summing over all the possible donor - acceptor distances and weighting for the distribution of distances $\omega(r)$ gives equation (3).

This expression does not consider the relative orientation of the two reacting species. It would be desirable to determine the dependence of the electron transfer rate on orientation, as well as on distance. Huddleston and Miller [25] considered the effect of random orientation on the decay. They found that the experiments were likely to be insensitive to the orientation, simply giving the angle-averaged electron transfer rate at a distance r. Thus, we neglect the effect of orientation of the donor - acceptor pairs.

One can set up a series of differential equations based on the kinetic scheme. From these, we have also solved for the concentration of separated photoproducts with time, dependent on the rates k_1, $k_2(r)$, and $k_3(r)$. The somewhat complicated expression for the fraction of reacting pairs present as the radical photoproducts is:

$$P_b(+) = \int_{r = R_0}^{r = \infty} dr\ (r)\ \frac{k_2(r)}{k_3(r) - K_2(r) + k_1} \left[e^{-\ k_2(r) + k_1\ +} - e^{-k_3(r)^+} \right] \quad (8)$$

In this study, we tried but were unsuccessful to observe the reduced quinone - oxidized porphyrin intermediates.

Physical Basis of the Rate Equation (1) -

It may be helpful to relate equation (1), the expression for the rate of electron transfer over a distance, to physical quantities. First, consider the simple case of an electron of energy E tunnelling through a barrier of potential energy V and width d, where V is greater than E. The probability of the electron tunnelling through the barrier, if the probability is small compared to one, is given by [19]:

$$P = \frac{16EV}{(E + V)^2} \exp\left[- \frac{2d\sqrt{2mV}}{\hbar} \right] \tag{9}$$

where P is the probability of tunnelling (as compared to reflection), and m is the mass of the electron.

A more general formulation suitable for any shape of barrier uses the 'WKB approximation' [27],

$$P = C \exp\left[- \frac{2\sqrt{2m}}{\hbar} \int \sqrt{V(x)}\, dx \right] \tag{10}$$

where C is a proportionality constant, x is the coordinate of the electron travelling through the barrier, and V(x) is the height of the barrier over the total energy of the electron as a function of x. The square root of the potential is integrated from the entry point of the barrier to the exit point.

Devault [19] associates this expression with Miller's [11,12] rate equation, letting [28]

$$a = \frac{\hbar}{2\sqrt{2mV}} \tag{11}$$

where V is a sort of average barrier height. Values of a in the literature have ranged from 0.5 [23] to 1.0 Angstroms [11,25]. These values correspond to average barrier heights of 1 to 4 eV, physically realistic values.

For an analysis of the origin of ν in equation (1), one could do worse than go to the work of Namiki et al. [23] They start with the following expression for the rate:

$$k(r) = \frac{2\pi}{\hbar} \; Vif(r)\Big|^2 \sum_f \Big|\langle x_i \; x\rangle_f\Big|^2 \; \delta(E_i - E_f) \tag{12}$$

where r is the distance between the donor and acceptor molecules, $V_{if}(r)$ is an overlap of the donor and acceptor electronic wave functions, $\langle \chi_i | \chi_f \rangle$ is the Franck - Condon vibrational overlap between initial and final states, and E_i and E_f are the energies of the initial and final states, respectively.

Approximating $V_{if}(r)^2$ by

$$\left|Vif(r)\right|^2 = \left|Vif(0)\right|^2 \exp\left(\frac{-r}{a}\right) \tag{13}$$

gives

$$k(r) = \nu \exp\left(\frac{-r}{a}\right) \tag{14}$$

Which is equivalent to Miller's rate expression, where ν is the electron transfer rate at zero separation,

$$\nu = \frac{2\pi}{} \left|V_{if}(0)\right|^2 \sum_f \left|\langle \chi_i | \chi_f \rangle\right|^2 \delta(E_i - E_f) \tag{15}$$

Thus, the frequency factor is dependent on the overlap of the electronic wave functions at zero distance, and the Franck - Condon vibrational overlap of the reactants and products.

Another Model -

McLendon and co-workers [18] recently used an alternate expression for the survival probability of the donor excited state, derived from the work of Inokuti and Hiriyama [17]. This expression, which takes into account the probability of electron transfer to all acceptor molecules rather than considering only the nearest neighbor interactions, is given by:

$$P(t) = \exp\left[-k_1 t\right]\left[\int_{R_1}^{R_2} dr\, \omega'(r)\, 4\pi r^2 \exp\left[-tn(r)\right]\right] \qquad (16)$$

Here R_1 is the center to center distance of closest approach for the donor acceptor pair, and N is the average number of acceptor molecules whose centers are located within a distance R_2 or less from a donor molecule. $\omega'(r)$ is proportional to the probability of an acceptor molecule being located in a fixed volume element at a distance r from the donor. Note that this

is defined differently than the distribution in the nearest neighbor approximation.

n(r) is the rate of electron transfer, given by the relation

$$n(r) = \frac{1}{\tau} \exp\left[\left(\gamma\left(1 - \frac{r}{R_a}\right)\right)\right] \tag{17}$$

R_q is the so-called "critical distance" for electron transfer [11,29]. This is defined such that $k_2(R_q) = 1/\tau$, where tau is the normal lifetime of the donor excited state.

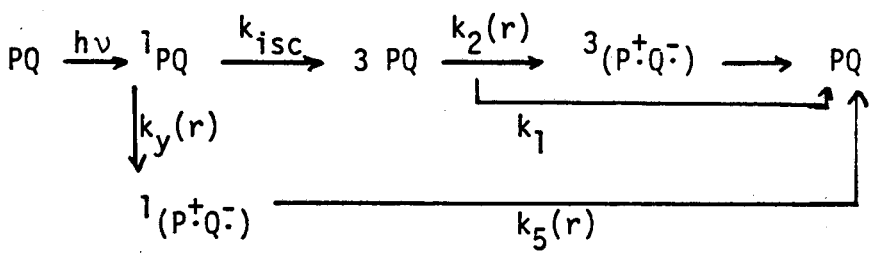
Equation (16) is related to equation (1) by the following identities:

$$a = \frac{R_0}{\gamma} \quad \text{and} \quad \nu = \frac{e^{\gamma}}{\tau} \tag{18}$$

We see that the rate expressions used in this work and that of McLendon and co-workers are equivalent.

Effect of Singlet State Electron Transfer on Triplet Reactions -

One last matter needs to be addressed: How does electron transfer quenching of the singlet state of the porphyrin by the quinone, before intersystem crossing to the triplet, affect the observed triplet kinetics? If one considers the reactions of the singlet state, the kinetic scheme is expanded -



where k_f is the first order rate constant for singlet decay to the ground state, and k_{isc} is the rate constant for intersystem crossing. $k_4(r)$ is the first order distance dependent rate constant for singlet electron transfer to the quinone, and $k_5(r)$ is distance dependent rate constant for the back reaction.

Those pairs that are close enough such that $k_4(r)$ is much greater than k_{isc} will react through the singlet state. The time resolution of our equipment is such that all of the singlet

state reactions are over before we can measure our first time point. The lifetime of the singlet state, $\tau_s = 1/(k_f + k_{isc})$, is 2.7 ns. Thus, when we start our measurements, the distribution of triplet donor - acceptor distances is already depleted at short r, because of singlet state reactions.

The approximation we use for this nonrandom distribution is to consider that all donor - acceptor pairs within the steady state singlet quenching radius, ${}^1R_q$, react through the singlet state, while none of those with separation greater than ${}^1R_q$ do. The quenching radius ${}^1R_q$ is determined by application of equation (2) to the results of steady state fluorescence quenching experiments.

Including this modification into the distribution function is done simply by setting $\omega(r) = 0$ if r is less than or equal to ${}^1R_q$. It will be shown that these approximations, namely, neglecting all acceptor molecules other than the closest one to a given donor, and describing the singlet quenching as a step function, do a good job of describing the behavior of real systems.

EXPERIMENTAL

Sucrose octaacetate (SA) (Sigma) was dissolved in an excess of absolute ethanol, heated in the presence of activated charcoal, filtered, boiled down to a smaller volume, and recrystallized. The white powder or small white needles were filtered and rinsed with cold absolute ethanol, then placed in a vacuum desiccator until dry.

Chromatography of zinc tetraphenylporphine (ZnTPP) (Strem) with 1/1 dichloromethane/hexane on silica separated a red band from two others. This purification gave a product with a measured first order lifetime of 1.1 mS in methyltetrahydrofuran (compared to previously measured lifetimes of 1.25 and 1.15 mS in toluene and pyridine, respectively [30]).

Methylbenzoquinone (MBQ) (Eastman, technical grade) was first recrystallized from heptane, and then sublimed.

Sample Preparation -

A stock solution of ZnTPP in SA was prepared by adding 0.0014 g (2.0×10^{-6} moles) of ZnTPP to 25.00 g (19.67 ml) of SA. This mixture was heated to 160° C under nitrogen with

stirring to dissolve the porphyrin and give a solid solution with a concentration of 1.05×10^{-4} M at 25° C. It was cracked by immersion in liquid nitrogen, and stored in a light proof container under nitrogen.

This solution and sufficient quinone to give both the desired concentration and a total mass of 3.0 g were placed in a 10 x 10 mm I.D. glass cell which was attached to a glass tube and a standard taper fitting. SA has a density of 1.271 g/ml, yielding a sample volume of about 2.4 ml. (The amount of added quinone was small enough to neglect in computation of the volume.) Samples were then evacuated, and sealed off under vacuum. After this, they were placed in a 120° to 140° oven for 30 minutes to one hour to melt. The samples were turned occasionally while being heated to help in mixing. All samples in a given experiment were prepared at the same time.

Samples for earlier experiments (most of which will not be discussed here) were prepared in a slightly different manner. A stock solution of ZnTPP in SA was prepared by dissolving 0.0038 g ZnTPP (5.6×10^{-6} moles) in 2.00 g SA, by the method described above. This gave a stock solution of 3.56×10^{-3} M, which was stored in a lightproof container under nitrogen. Into 3 x 9 mm I.D. cells were placed 0.0562 g of this stock solution, along

with the quinone and enough SA to make up a total mass of 2.00 g. Samples were then prepared as above.

Measurements were performed within several hours after sample preparation.

Properties of SA glasses -

With gentle, gradual warming or cooling, these glasses seem to be stable to cracking down to at least 2° C. However, upon rapid cooling from room temperature, or rapid heating from temperatures below 10° C, they can crack.

Zinc tetraphenylporphine in sucrose octaacetate is not stable in the presence of both light and oxygen. Nor is it stable in the presence of both heat and oxygen. However, under vacuum at room temperature, it seems to be stable for several months, even under normal room lighting conditions.

Intense light in the visible absorption band of the quinone (about 430 nm) results in a permanent photochemical reaction, as evidenced by a color change. However, light in the low energy porphyrin absorption bands does not result in any apparent

irreversible reaction, indicating that this photochemistry probably involves a quinone excited state.

Sucrose octaacetate glasses do not readily crack. Cracked samples will anneal at 30° C within two hours -- this might indicate that diffusion is taking place at an observable rate. (Annealling does not occur for days at 22° C.) At 45° C, SA glasses will flow, noticeably changing their shape in about one half hour. Thus, sucrose octaacetate should have a measurable viscosity at 45° C, and might not be a suitably rigid media at this temperature.

Steady State Fluorescence Measurements -

Samples for steady state fluorescence measurements were prepared by addition of the 3.56×10^{-3} M ZnTPP stock to a weighed amount of SA. After melting, this mixture was poured into standard quartz 10 x 10 mm cells, and allowed to cool. All these operations were performed under nitrogen. The final concentration of porphyrin was 1×10^{-4} M in all samples.

For fluorescence depolarization experiments, a sample of about 10^{-4} M Rhodamine 6G (tetrafluoroborate) was prepared by adding a methanol solution of the dye to a vial, and evaporating

the methanol. Sucrose octaacetate was added, and heated with a heat gun in the air. The solution was poured into a silica cell while still melted.

Steady state fluorescence measurements were performed with a Perkin - Elmer MPF-2A fluorescence spectrophotometer.

Flash Photolysis -

The apparatus consisted of a Candella flashlamp pumped dye laser (using Rhodamine 110 as the dye) with a fast double beam spectrophotometer. Essentially, it is the same system previously described by J. M. Yang [31], with minor modifications.

The laser can put out up to 0.2 J per pulse, with a width pulse width of about 500 ns (full width half maximum). In these experiments, the laser intensity was much lower than the maximum, set below the level needed to saturate the sample or cause two photon events.

It was found that a simple coaxial flashlamp will give adequate laser performance, in contrast to earlier work that indicated a more complicated flashlamp assembly was required [31].

The kinetics were followed by time resolved absorption. The laser beam struck the sample at an angle of about 10° relative to the detection beam, on the same face. This is different than the perpendicular crossed beam set-up used by Yang. The absorbance of the sample was monitored with a 75 watt xenon lamp, powered by a Lambda regulated power supply. A home built lamp starter was used to start the lamp. The detector used was essentially the same as the D.C. detector described by J. M. Yang. The lamp output was focused and split into two paths. One beam was directed through a cut-off filter, through the sample, and onto the first detector. An narrow band interference filter or monochromator was placed in front of this detector. The other beam was directed onto a second detector which has been modified to give a higher signal to noise ratio than the previously arrangement. The output from the two detectors was then ratioed to minimize problems due to lamp fluctuations.

The response time of the detectors was about 100 ns. Thus, with a laser pulse width of about 500 nS, we are limited to observation of processes of a conservative timescale of 5 microseconds or longer. This precluded monitoring of the kinetics of singlet state reactions, which are about 3 orders of magnitude faster.

The detector output was linear with light intensity up to transient optical density changes of 0.08. These detectors did not work well for larger O.D. changes.

This output was collected on a Nicolet Explorer IIIA digital oscilloscope. The scope was triggered by the laser beam through a separate detector. A home built signal averager read the date and averaged it. Typically, 25 to 250 laser pulses were needed to give a signal to noise ratio of about 50. These data was then read into the LCB VAX 11/780, using the CALDAF system of programs.

Further data processing was done by programs on the VAX.

Plotting was done with the aid of DAPGRAPH, a general purpose XY plotting program written for the VAX by Dave Pearlman.

RESULTS

The concentration of the triplet state of ZnTPP was followed by monitoring its absorbance transient at 840 nm [30] immediately after illumination by a laser pulse at 567 nm.

The laser pulse reproducibility was poor. Therefore, the absolute absorbance change was scaled to a relative concentration, to allow for better comparison between different measurements. For solutions with no added quinone, the absorbance at time = 0 was taken as equal to one, and the other points scaled accordingly. For solutions with quinone, the initial absorbance was set equal to one minus a correction factor for quenching of the singlet state by the quinone.

The photophysical properties of ZnTPP and MBQ are summarized in Table 1.

Kinetics of ^{3}(ZnTPP) Decay -

Without quinone, the triplet showed nearly perfect first order kinetics. Transients were fitted to a single exponential, with baseline correction, of the form $y = A + B \exp(-Ct)$. The baseline correction was typically negligible, and no deviation from first order behavior was seen. (See Figure 1.)

Table (1) Photophysical properties of ZnTPP and MBQ

	Solvent	ϕ_f	τ_s /ns	E_s /eV	ϕ_t	300 K τ_t /ms	E_t /eV
ZnTPP	toluene	.04	2.7	1.9	.88	1.25	1.5
MBQ	none (gas phase)			2.75			2.30

Data for ZnTPP is taken from ref. 33, except for the triplet and singlet energies. These were estimated from the wavelength of the emissions.

Energies for MBQ are estimated from the gas phase energies for benzoquinone, given in ref. 36.

Figure (1)

Decay of triplet ZnTPP, monitored by absorbance at 840 nm. 1×10^{-4} M ZnTPP in sucrose octaacetate, 21° C, with fit and residuals plot.

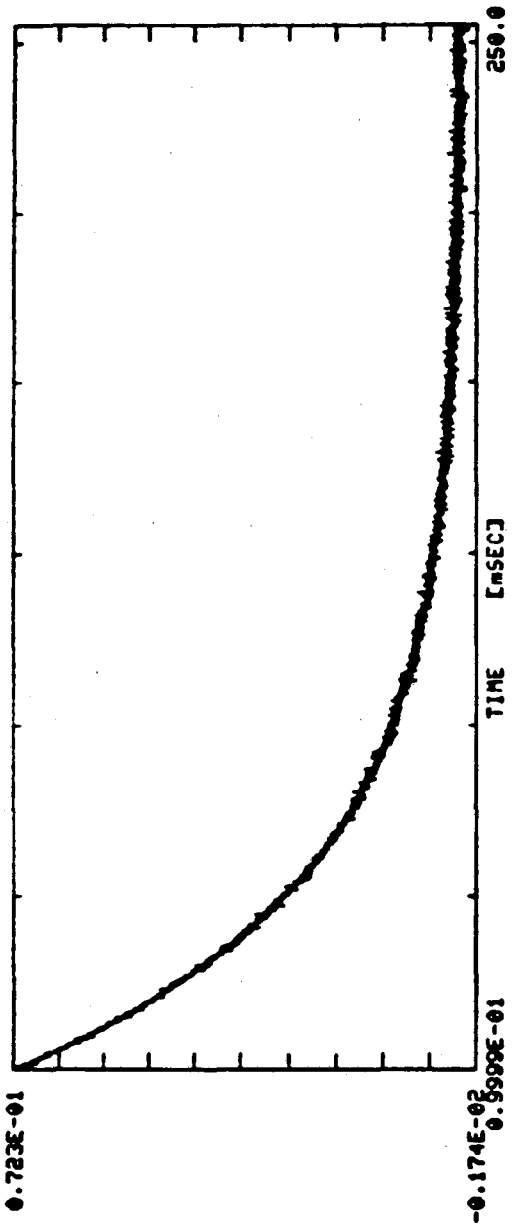
Fitted to -

$y = A + B \exp(-Ct)$

$A = 7.5 \times 10^{-4}$

$B = .0713$

$C = 23.0$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-0.174E-02
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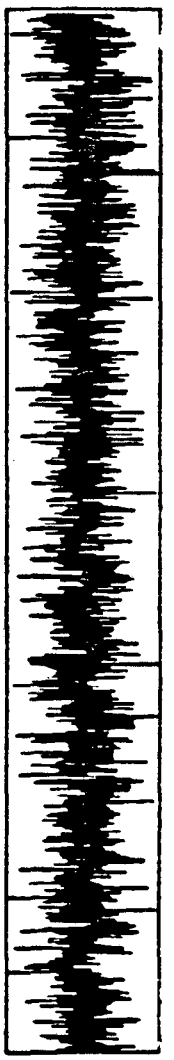
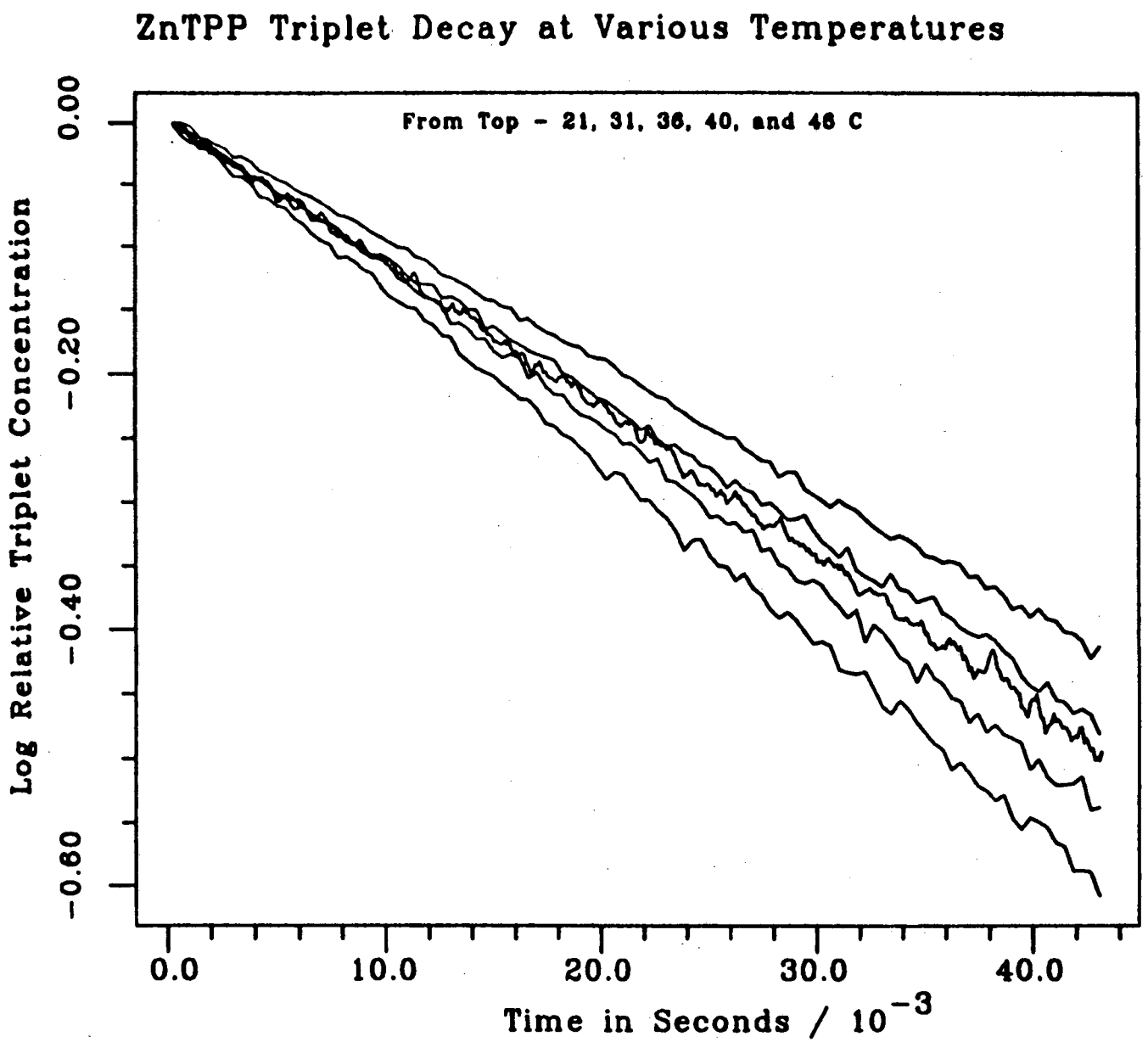


Figure (2)

Effect of temperature on ^{3}(ZnTPP) decay, no added quinone.


ZnTPP Triplet Decay at Various Temperatures
From Top - 21, 31, 36, 40, and 46 C
Log Relative Triplet Concentration
0.00
-0.20
-0.40
-0.60
0.0
10.0
20.0
30.0
40.0
Time in Seconds / 10^{-3}

At 21° C, the 1/e lifetime of the triplet state was 43 ms. This is surprisingly long, as the lifetime in fluid solvents at room temperature is near 1 ms [30,32], and even in 2-methyl-tetrahydrofuran glass at 77 K it is only 26 ms [32]. As the temperature is increased, the triplet lifetime decreases, dropping to 31 ms at 46° C. The decay curves are displayed in figure 2. The lifetimes determined from these transients are given in table 2.

The rate constants for triplet deactivation as a function of temperature are displayed in an Arrhenius plot in figure 3. This gives an apparent activation energy for triplet deactivation of about 10 kJ/mol, or 0.1 eV per molecule. This is less than the energy difference between the singlet and triplet states (0.4 eV).

Effect of added quinone -

Added Methylbenzoquinone [MBQ] quenched the fluorescence of ZnTPP in sucrose octaacetate. Quenching was measured for a number of quinone concentrations. According to the steady state quenching model of Miller [13,14]:

$$\frac{I}{I_o} = \exp\left[-\frac{4}{3}\pi c R_q^3\right] \qquad (2)$$

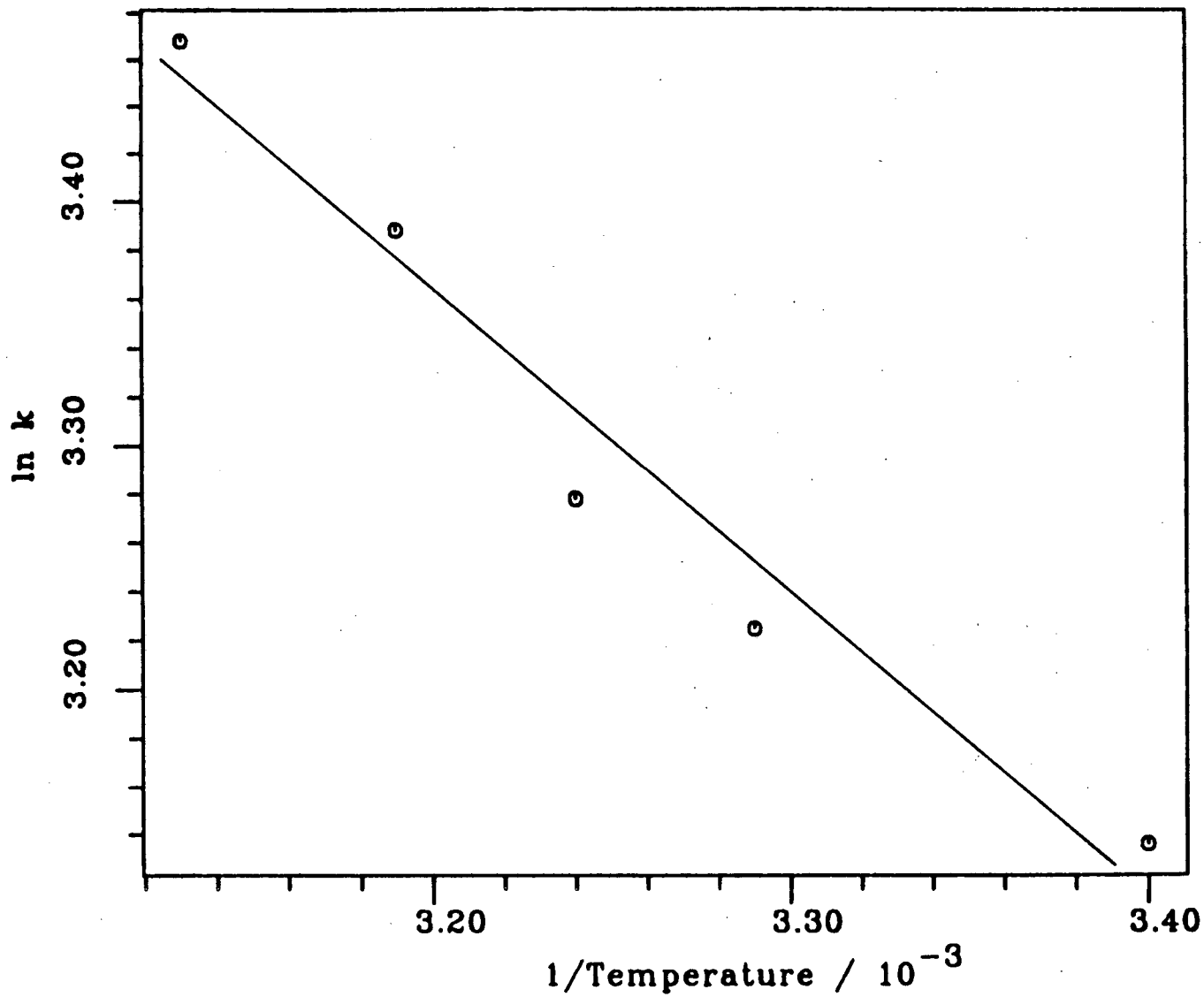
Table (2) 1/e lifetime of ^{3}(ZnTPP) in sucrose octaacetate as a function of temperature

T_o /C	τ /ms
21	43.4
31	39.9
36	37.7
40	33.8
46	31.2

Figure (3)

Arrhenius plot of the rate constant for ^{3}(ZnTPP) deactivation vs. temperature.

ln Triplet Decay Rate v. 1/T



where R_q is the quenching radius. Figure 4 displays a plot of $\ln(I_0/I)$. This plot gives a value of about 11 Angstroms for ^1R_q, the singlet state quenching radius.

The steady state fluorescence quenching was found to be independent of temperature, over the temperature range of 21° to 45° C.

The singlet quenching must be taken into account to analyze the data from solutions with added quinone. For these solutions, all of the singlet quenching took place before measurements started. This is true because the singlet lifetime of ZnTPP is only 2.7 ns [32]. The fraction of porphyrin quenched in its singlet state was computed using the above equation, with a quenching radius of 11 Angstroms. The initial concentration of triplet porphyrin was then taken as equal to 1 minus the fraction of fluorescence quenching. The rest of the transient was then scaled accordingly.

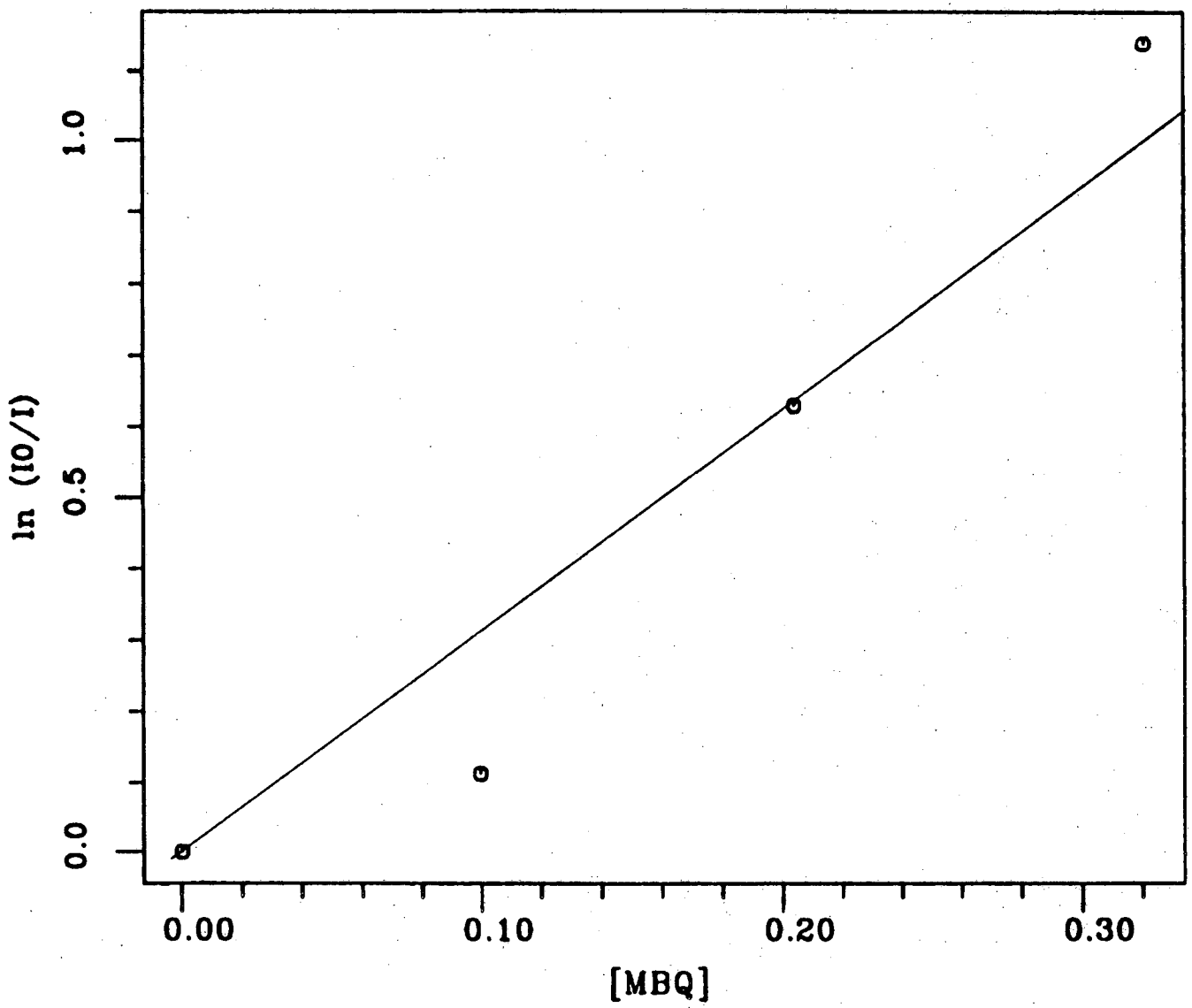
Plots of the effect of concentration on the quenching are shown for temperatures of 21°, 31°, 36°, 40°, and 46° are shown in Figures 5 through 9.

Looking at these plots, we see a huge increase in quenching as the temperature is increased only 25°, from 21° to 46°. For

Figure (4)

Steady state quenching of ZnTPP fluorescence by MBQ.

Quenching of ZnTPP Fluorescence by MBQ

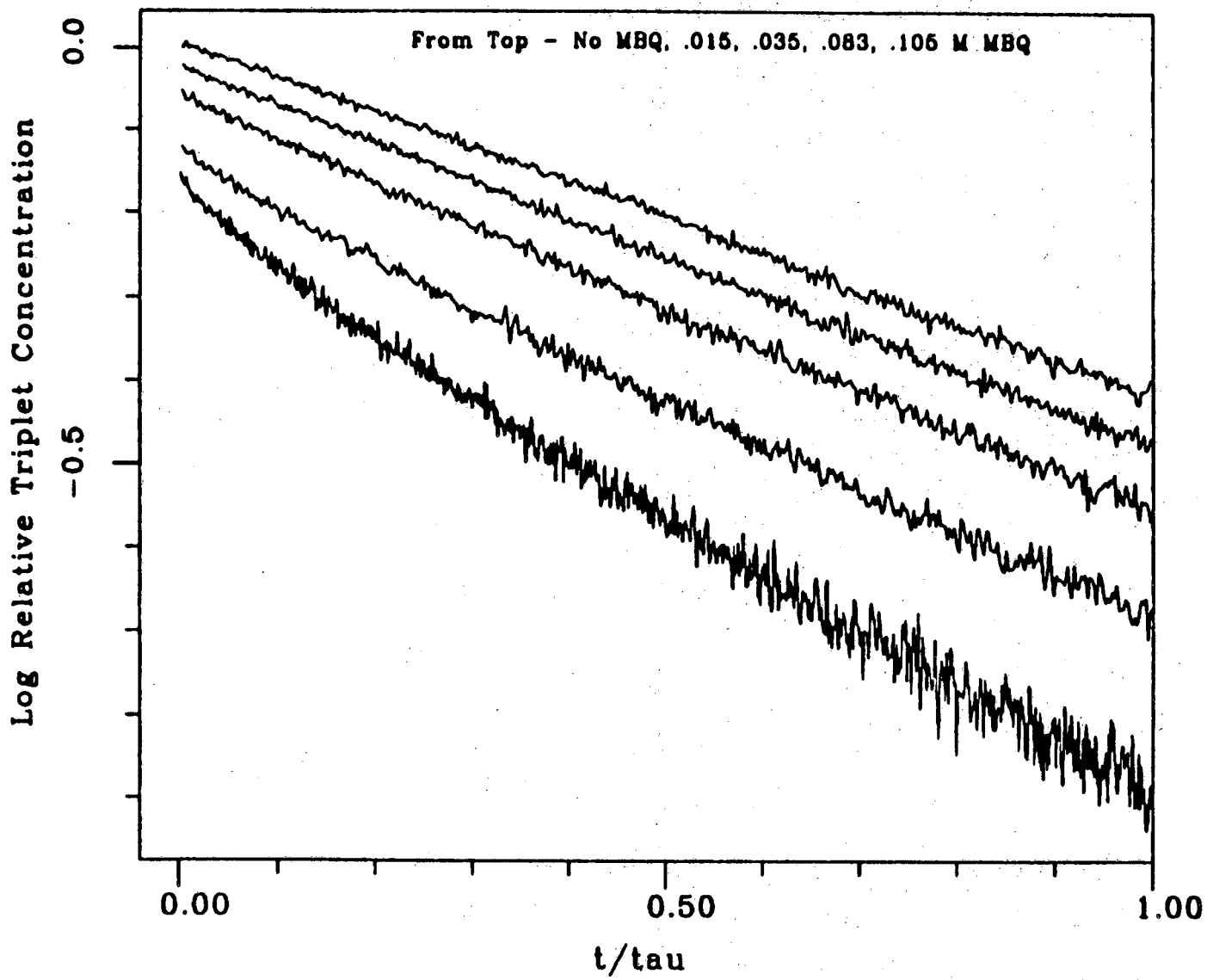


Figures (5-9)

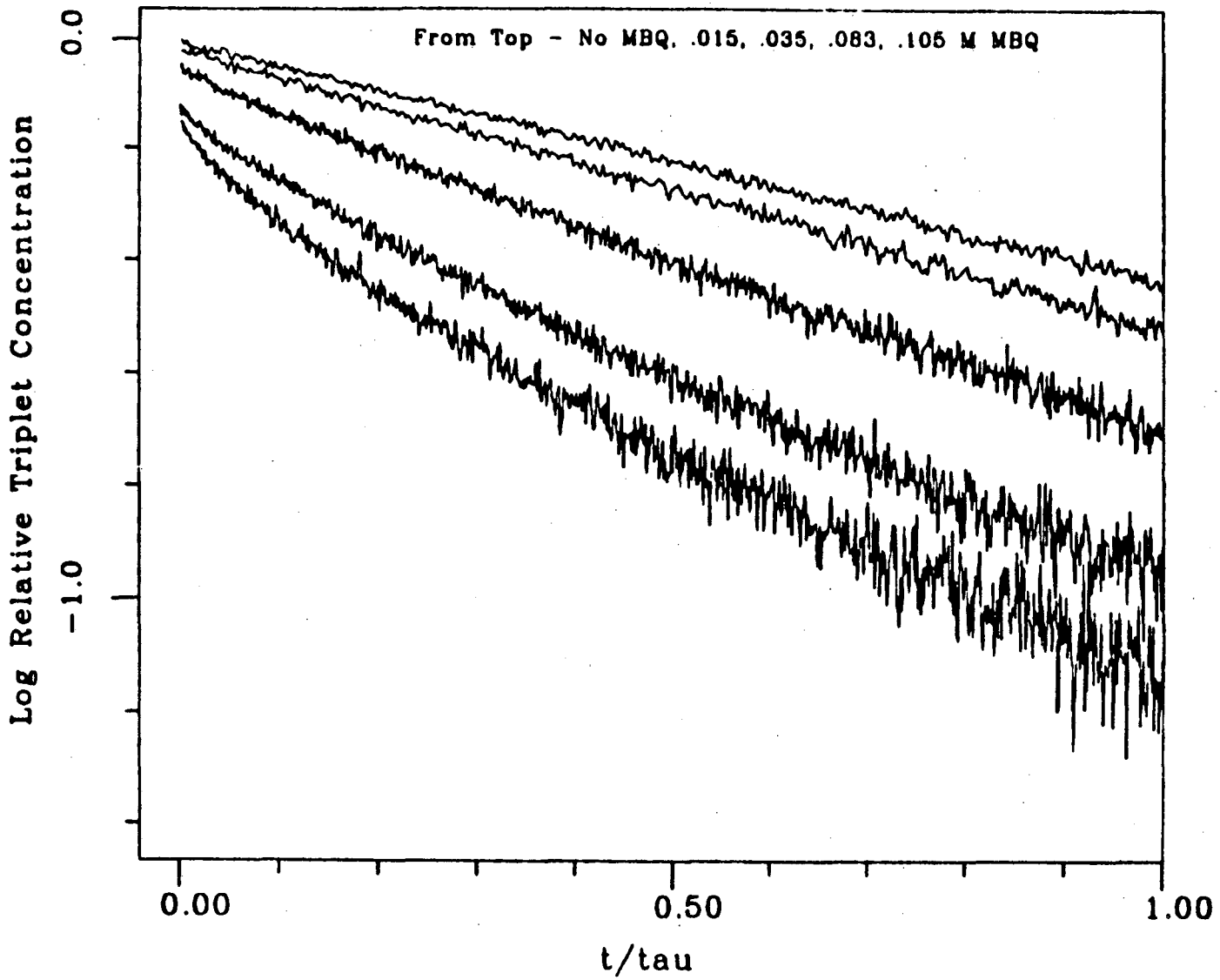
Decay of ^{3}(ZnTPP) with no quinone, and with 0.015, 0.035, 0.083 and 0.105 M quinone

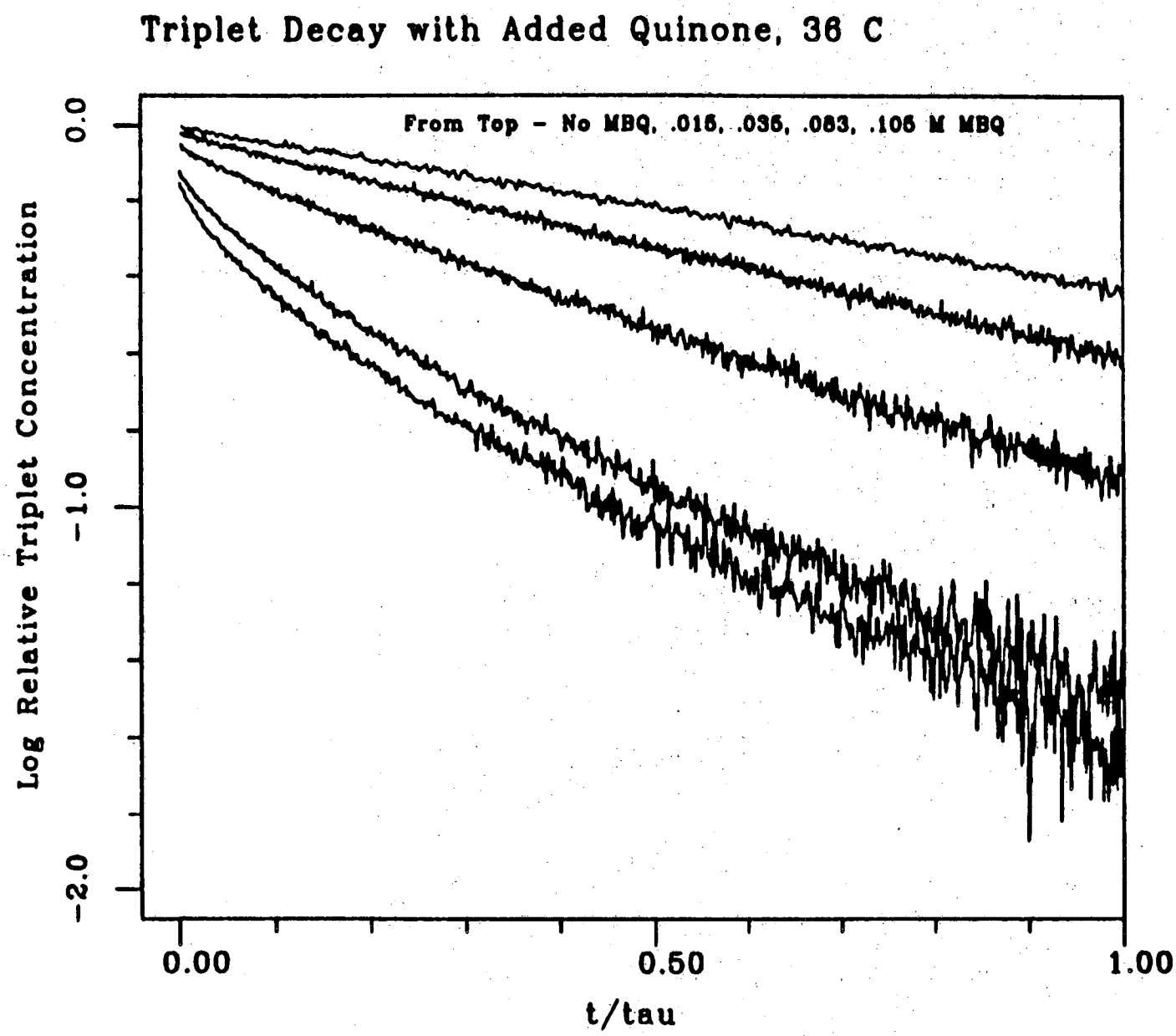
Temperature (in ^{o}C)	
21	Figure (5)
31	Figure (6)
36	Figure (7)
40	Figure (8)
46	Figure (9)

Triplet Decay with Added Quinone, 21 C

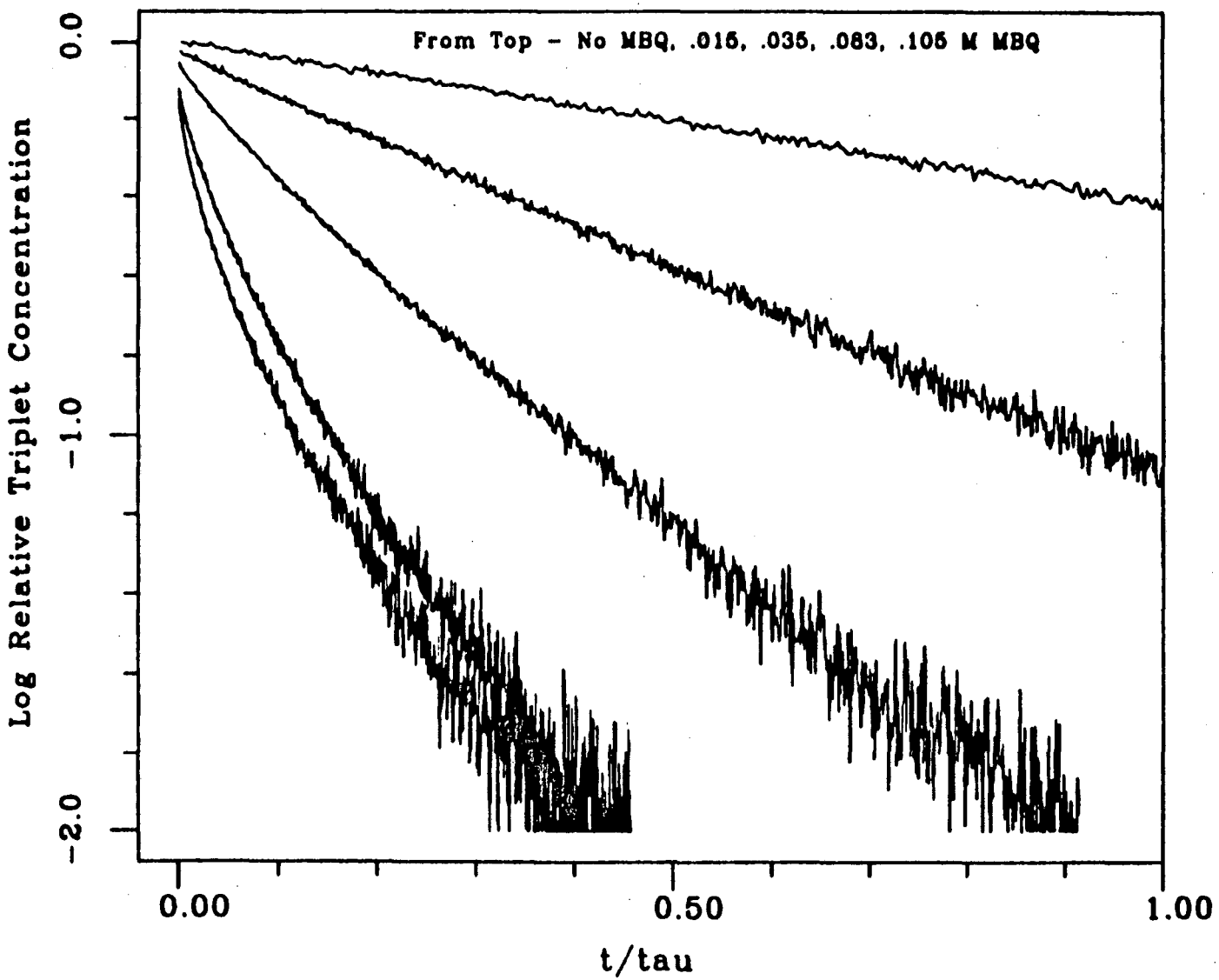


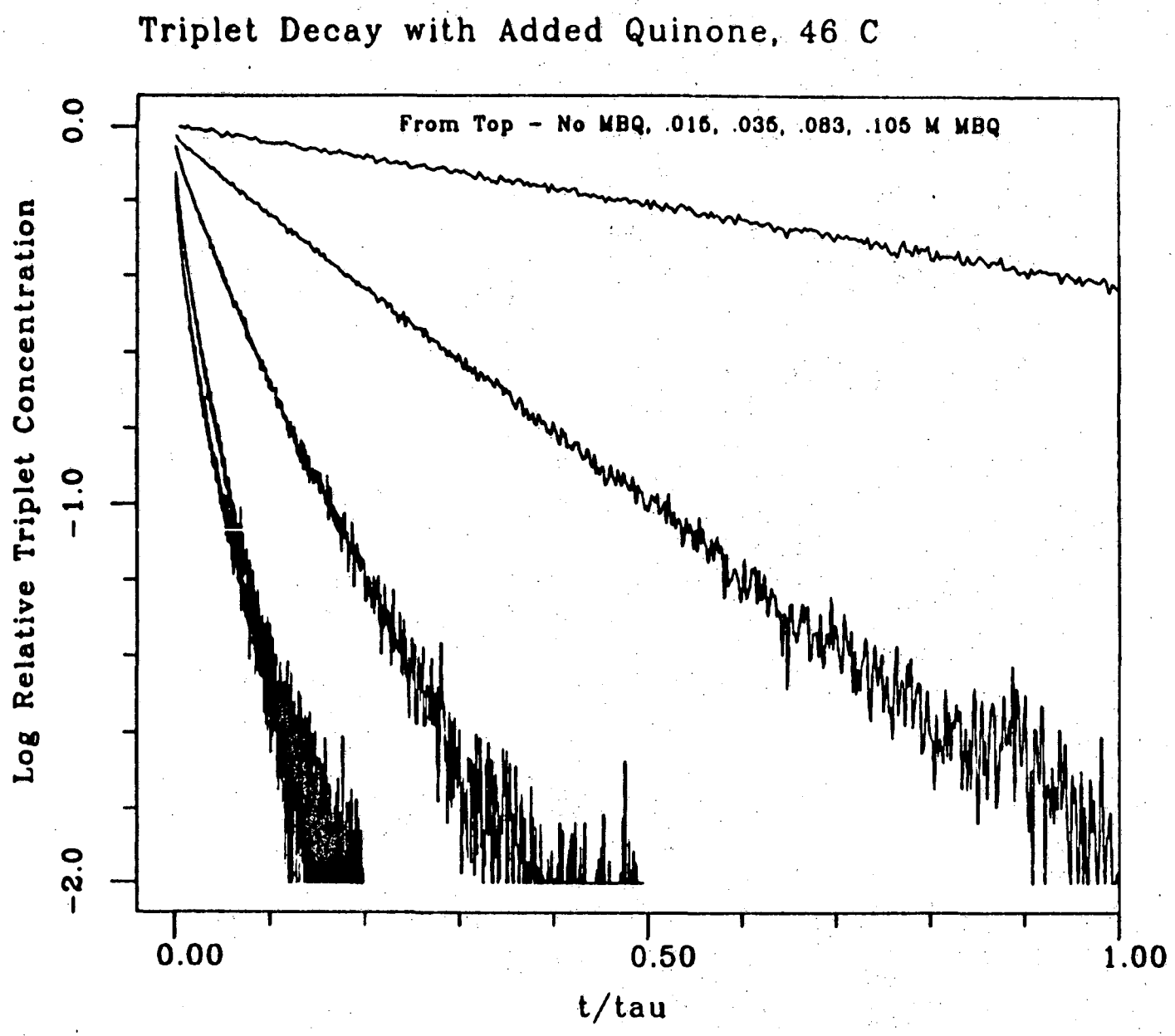
Triplet Decay with Added Quinone, 31 C




Triplet Decay with Added Quinone, 36 C
From Top - No MBQ, .015, .035, .083, .105 M MBQ
Log Relative Triplet Concentration
0.0
-1.0
-2.0
0.00
0.50
1.00
t/tau

Triplet Decay with Added Quinone, 40 C




Triplet Decay with Added Quinone, 46 C
From Top - No MBQ, .015, .035, .083, .105 M MBQ
Log Relative Triplet Concentration
0.0
-1.0
-2.0
0.00
0.50
1.00
t/tau

a more direct comparison, the transients for [MBQ] = 0.015 and 0.105 M at different temperatures are displayed in Figures 10 and 11. This increase in rates is reversible. One can measure the decay at 20° C, increase the temperature to 45° C and measure the decay, then return to 20° C and reproduce the first curve immediately. For example, see Figure 12.

Simulations and Fitting -

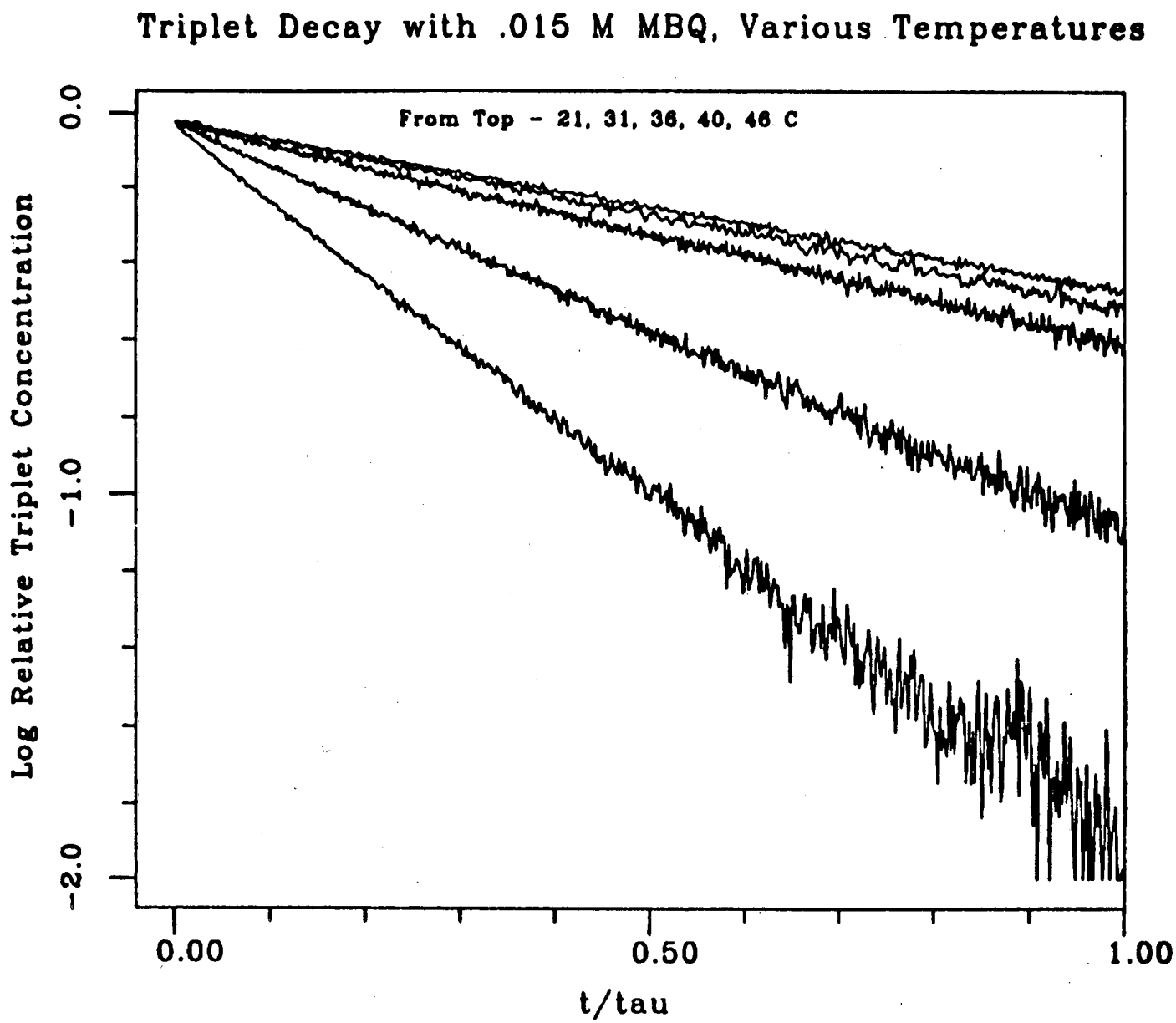
A computer program [33] was written to simulate decay behavior using the relation discussed in the introduction:

$$P(t) = \exp(-k_1 t) \int_{r = {}^{1}R_q'}^{r = R_2} dr\,\omega(r)\exp \nu t \exp\left[-\frac{(r - R_0)}{a}\right] \qquad (19)$$

The integration is performed numerically from ${}^{1}R_q'$ to R_2. ${}^{1}R_q'$ is a modified singlet quenching radius, computed numerically with the nearest neighbor probability distribution set equal to zero for distances closer than the donor - acceptor edge to edge radius (estimated as 9 Angstroms). Therefore, ${}^{1}R_q'$ is slightly larger than ${}^{1}R_q$, the quenching radius obtained from equation (1). R_2 is taken to be large enough that the integration converges - for these experiments, R_2 = 100 Angstroms is sufficient.

Figures (10,11)

Effect of temperature on the decay of ^{3}(ZnTPP) with 0.015 M quinone (figure (10)), and 0.105 M quinone (figure (11)).


Triplet Decay with .015 M MBQ, Various Temperatures
From Top - 21, 31, 36, 40, 46 C
Log Relative Triplet Concentration
0.0
-1.0
-2.0
0.00
0.50
1.00
t/tau

Triplet Decay with .105 M MBQ, Various Temperatures

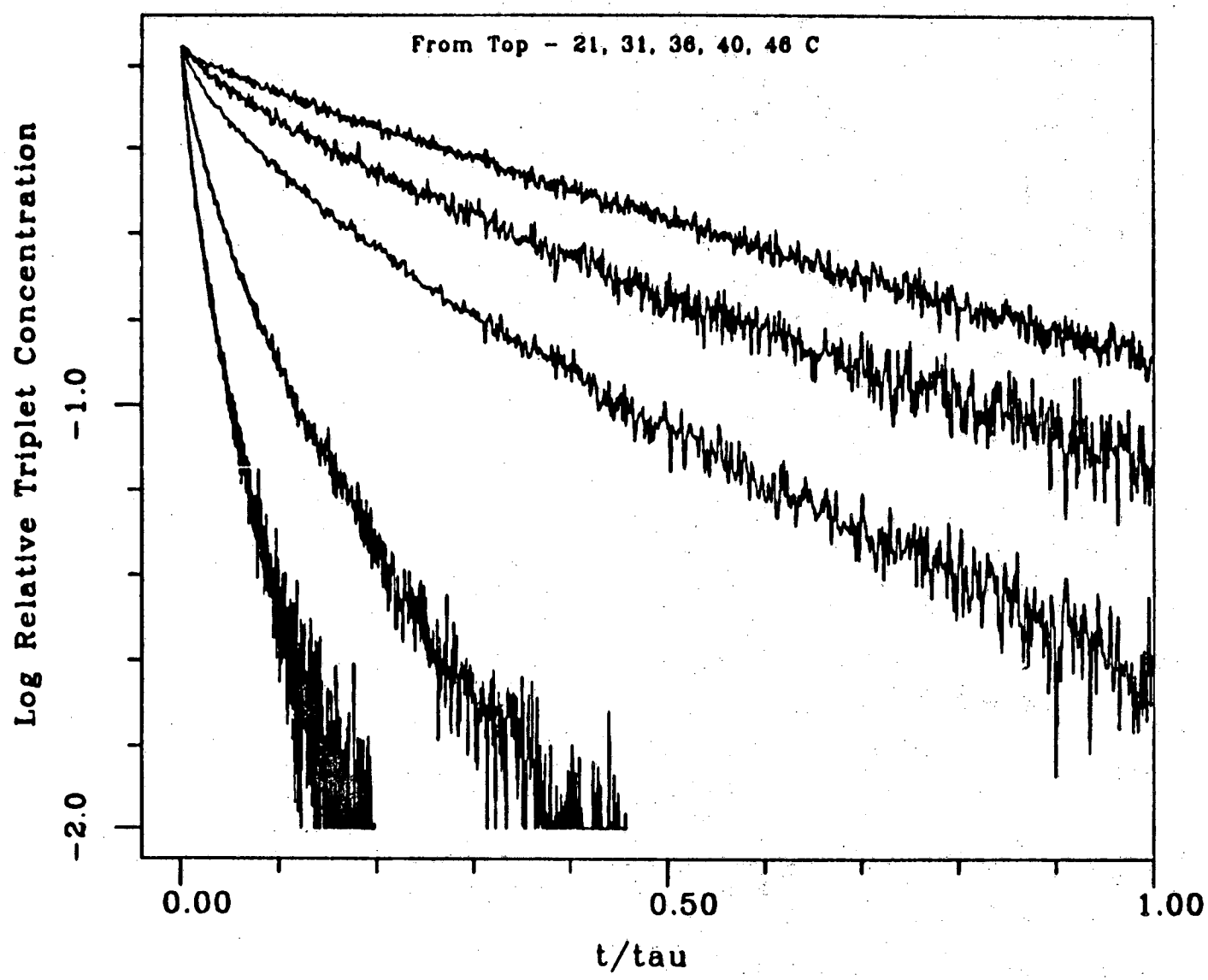
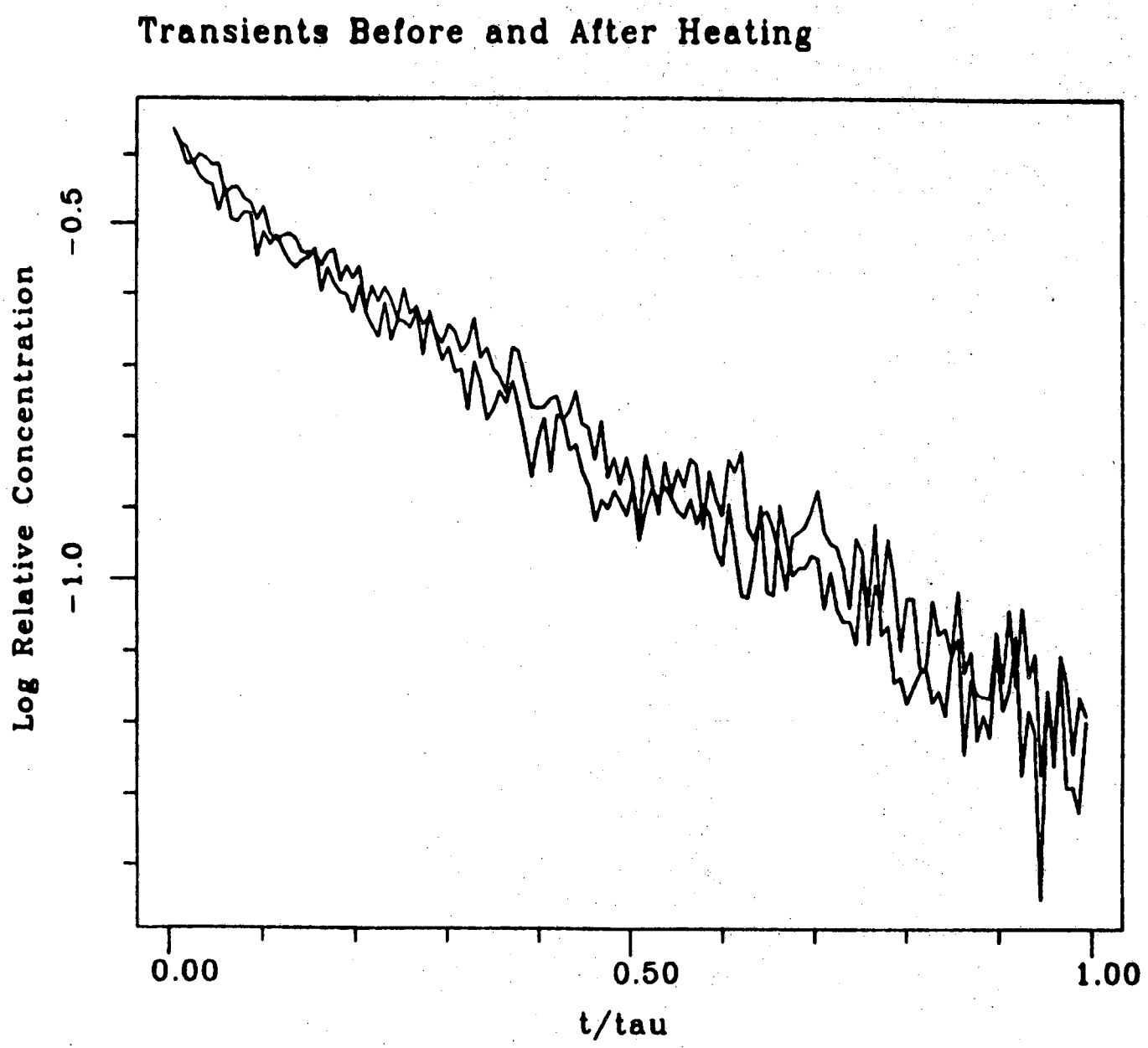


Figure (12)

Reproducibility of the temperature effect. Transient optical density of ^{3}(ZnTPP) at 640 nm, 0.25 M quinone, 20° C. Measurements were taken several hours apart, before and after heating to 45° C.


Transients Before and After Heating
Log Relative Concentration
-0.5
-1.0
0.00
0.50
1.00
t/tau

In these simulations, the a parameter is set at 0.75 Angstroms, and ν is varied from 0 to 10^{12}. Simulations were done for concentrations of 0.015, 0.035, 0.083, and 0.105 M quinone. Those simulations are shown in Figures 13 through 16.

Shown in Figures 17 through 20 are simulated curves with the corresponding experimental curves, for T = 21°. With the exception of the highest concentration (0.105 M quinone), the experimental curves match the simulated curves very nicely, for times up to $t/\tau = 1$. The 0.105 M curve matches expected behavior only up to $t/\tau = 0.4$. The curves at all concentrations are consistent with a value of $\nu = 10^4 - 10^5$.

In Figures 21 through 24 are similar plots, but with for T = 31° C. In contrast to the 21° behavior, none of these experimental curves follow the simulated ones; at least, not for times greater than $t/\tau = 0.1$. At greater times, the quenching is larger than expected by the model. For still higher temperatures, this deviation is even more pronounced.

From looking at these plots, it is seen that the scaling of the experimental data (the value of the initial optical density) is very crucial. Thus we decided to fit the unscaled data (change in absolute optical density v. time) to a curve of the form of equation (19), with the a parameter fixed at 0.75

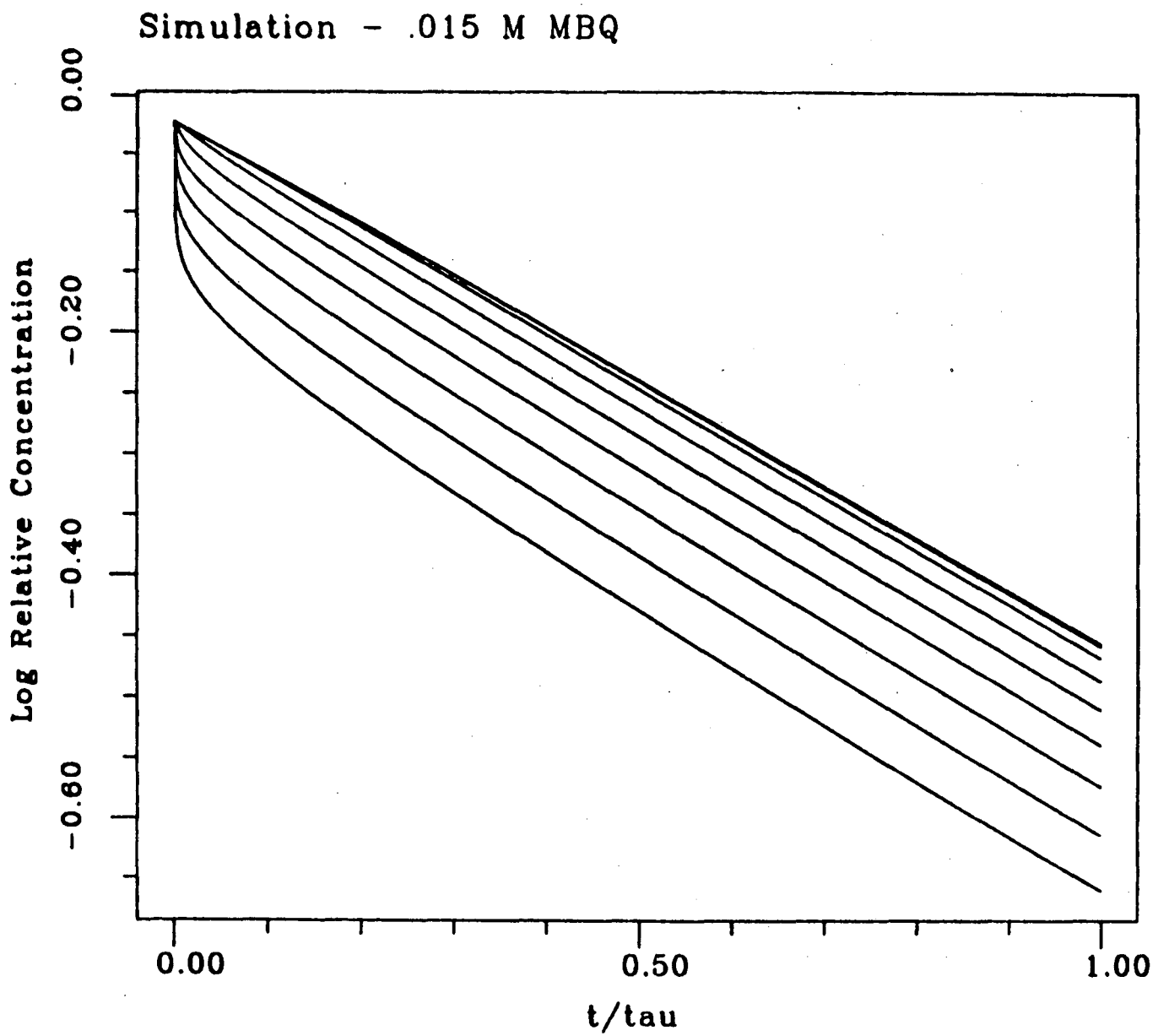
Figures (13-16)

Computer simulations, $\nu = 0, 10^3$ to 10^{10} s^{-1} in multiples of 10.

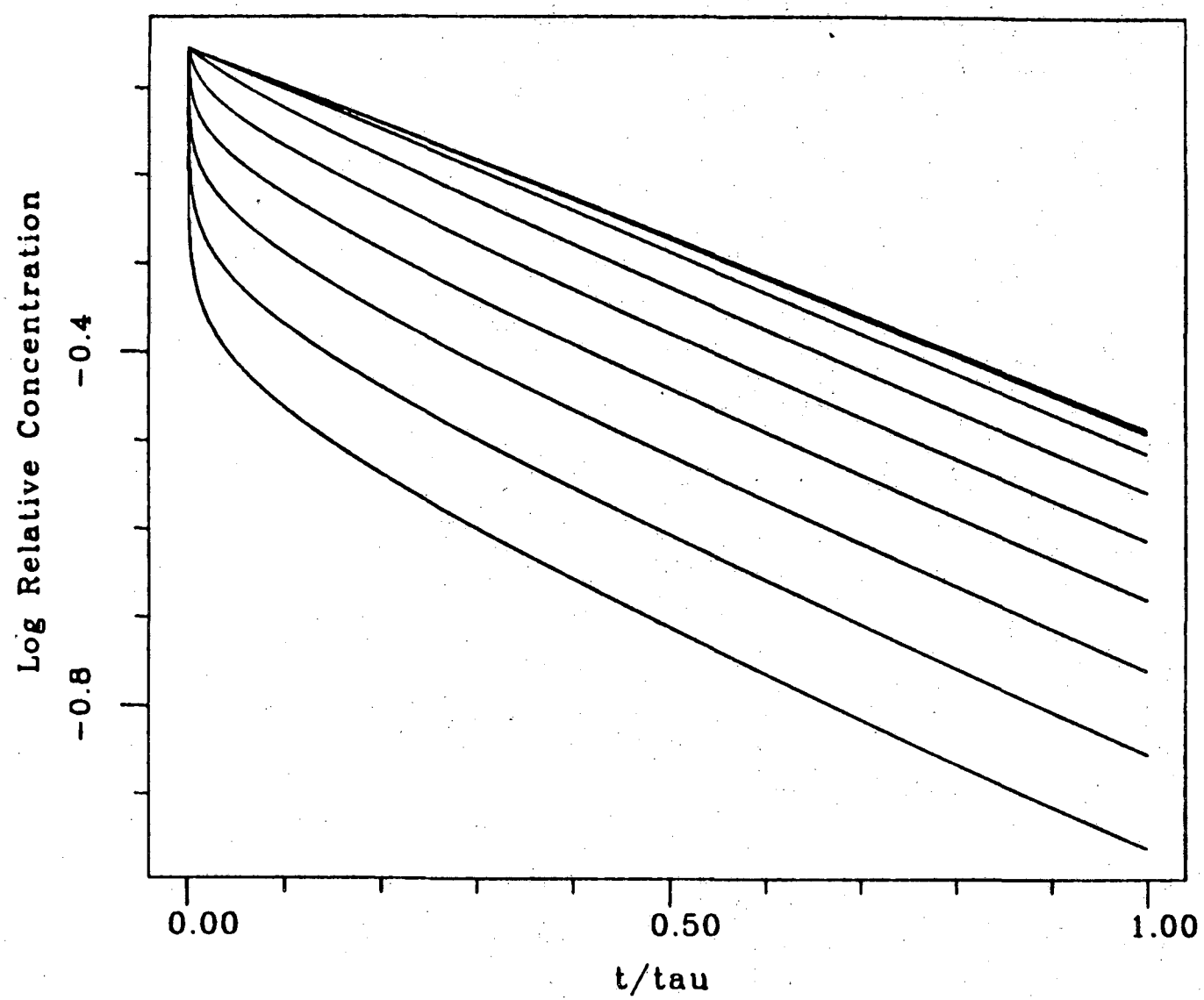
Donor lifetime = 43.4 ms.

Singlet quenching radius = 11 Angstroms.

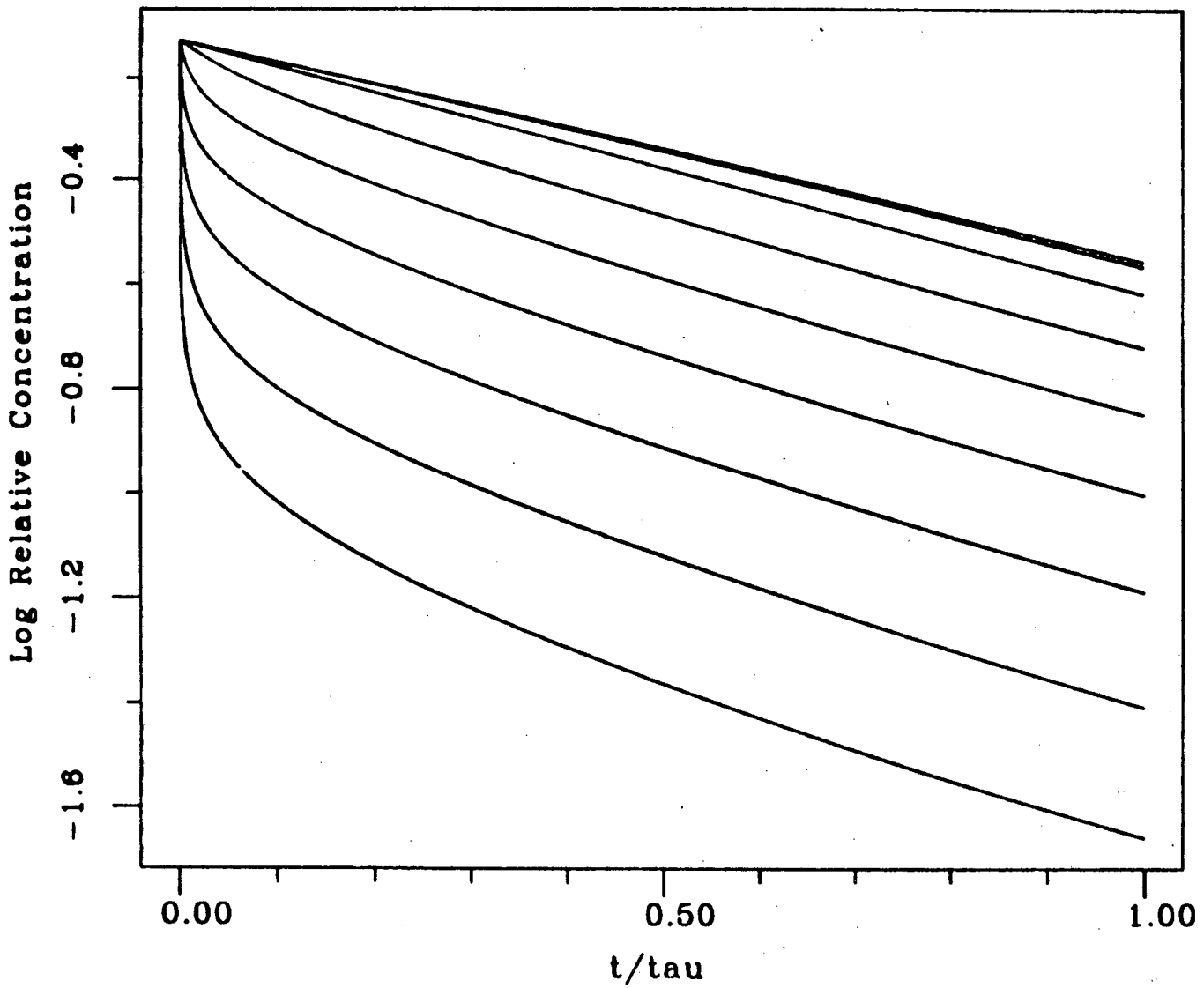
Acceptor concentration /M	
0.015	Figure (13)
0.035	Figure (14)
0.083	Figure (15)
0.105	Figure (16)

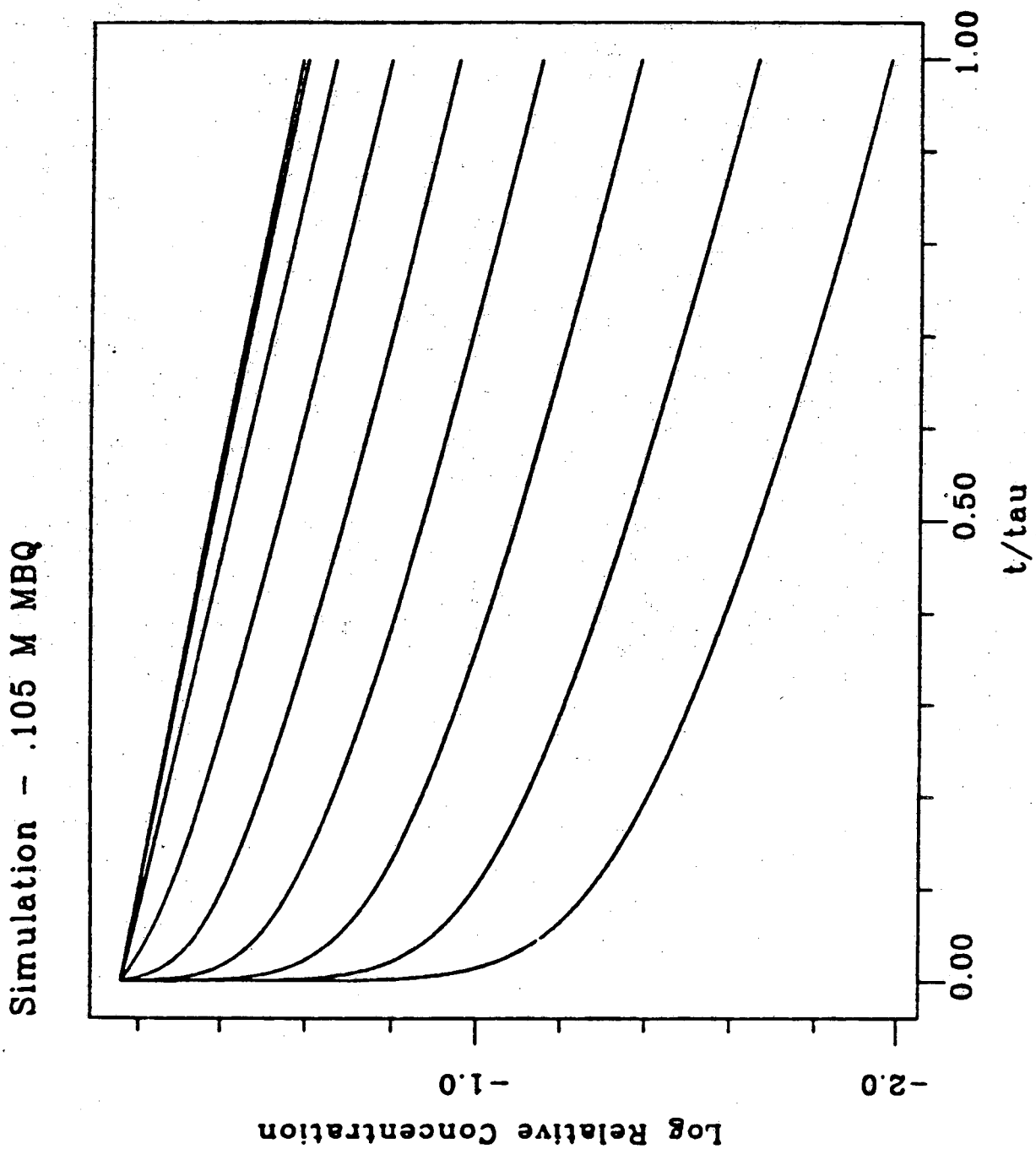

Simulation - .015 M MBQ
Log Relative Concentration
0.00
-0.20
-0.40
-0.60
0.00
0.50
1.00
t/tau

Simulation - .035 M MBQ



Simulation - .83 M MBQ




Simulation - .105 M MBQ
Log Relative Concentration
-1.0
-2.0
0.00
0.50
1.00
t/tau

Figures (17-20)

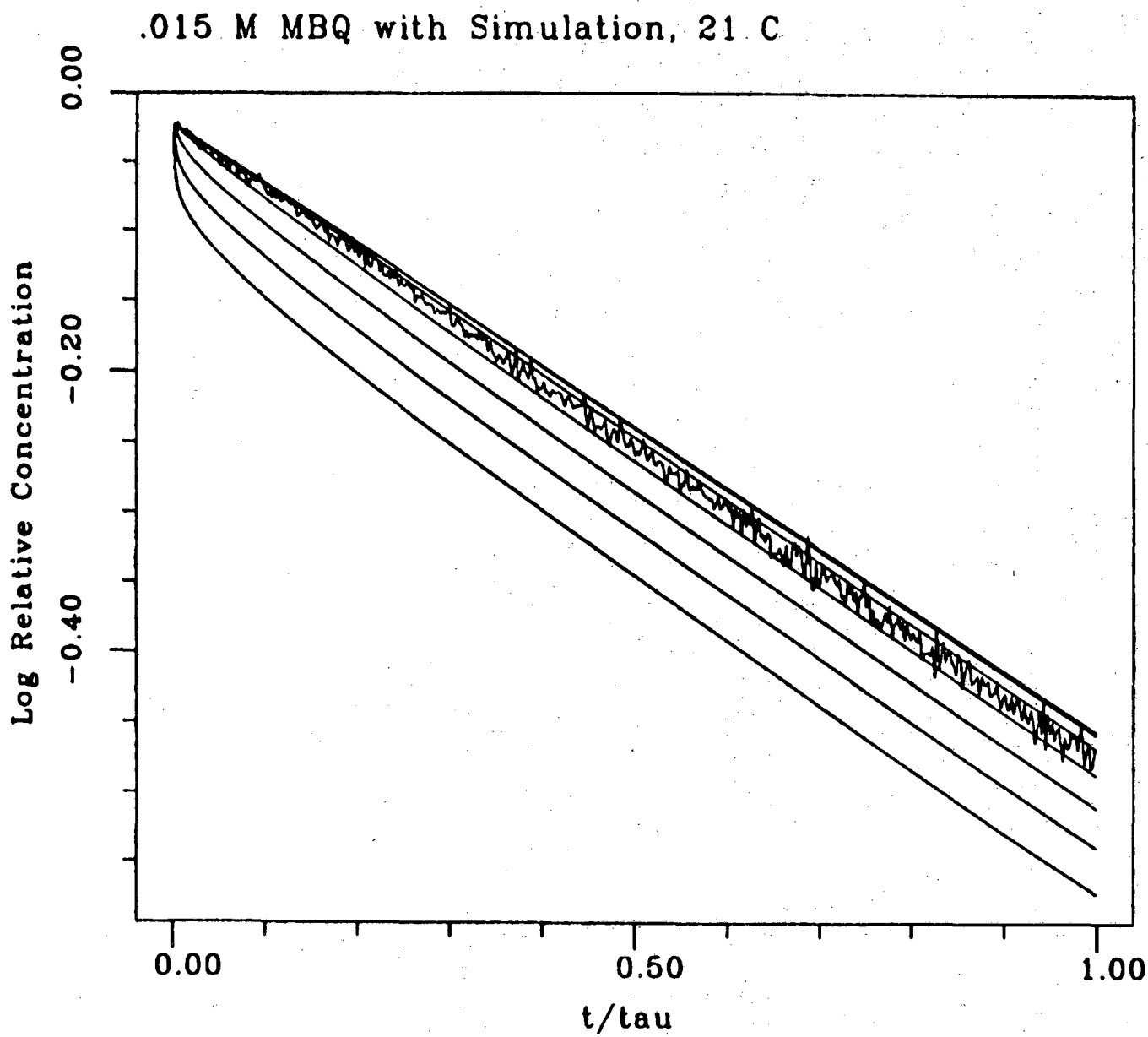
Simulations with overlayed experimental transients, 21° C

Simulated ν = 0, 10^{3} to 10^{8} s^{-1}.

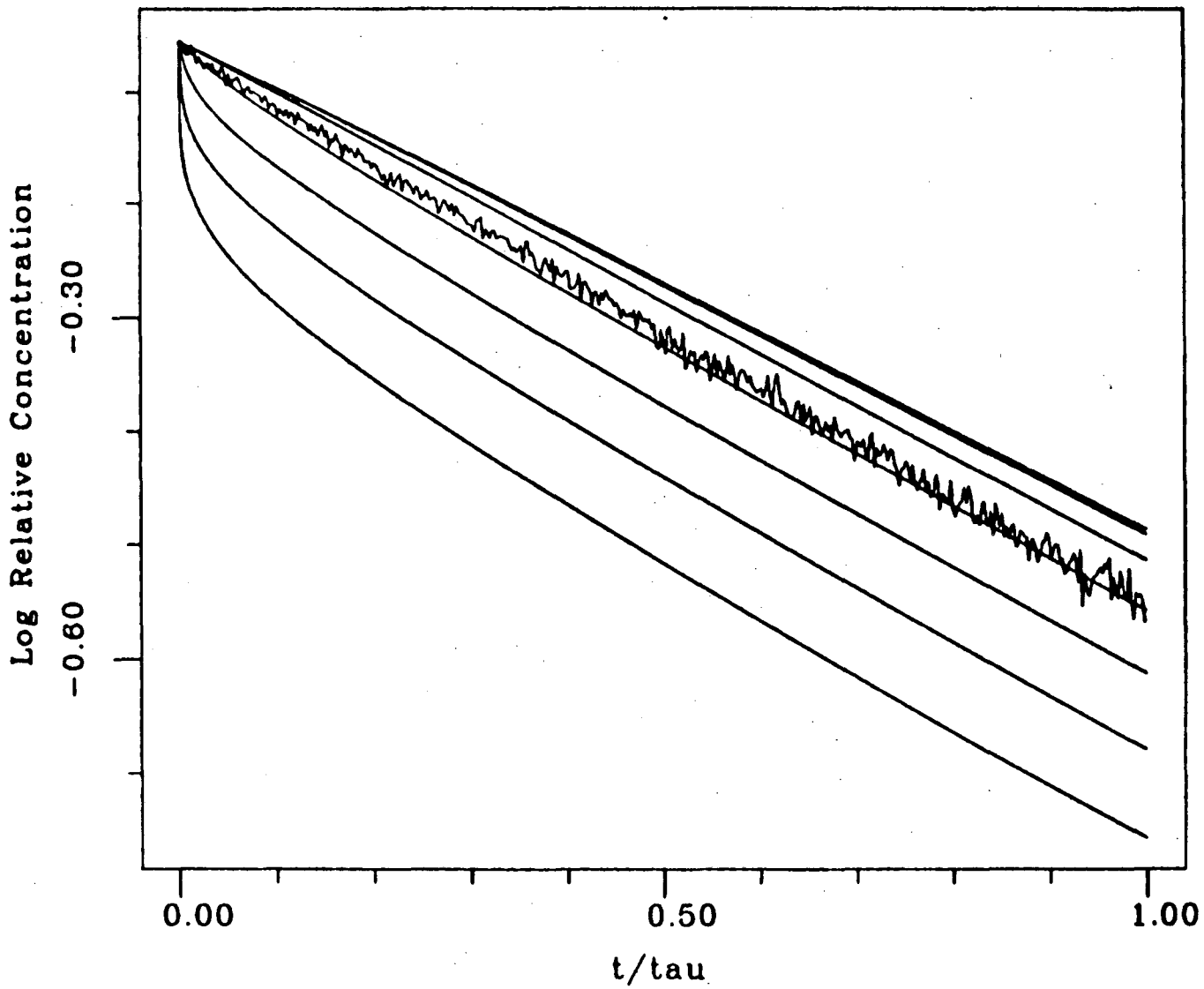
Donor lifetime = 43.4 ms.

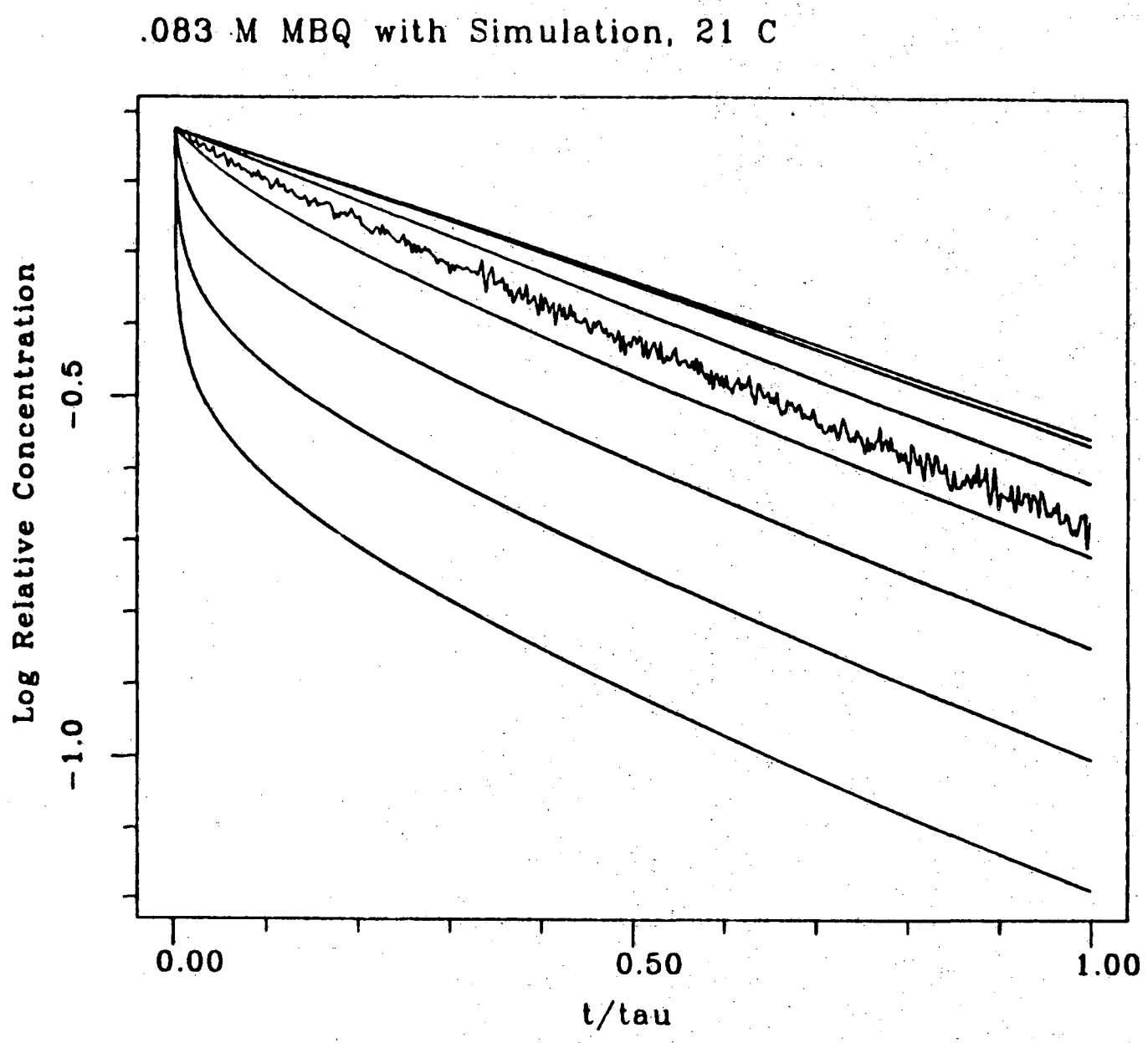
Singlet quenching radius = 11 Angstroms.

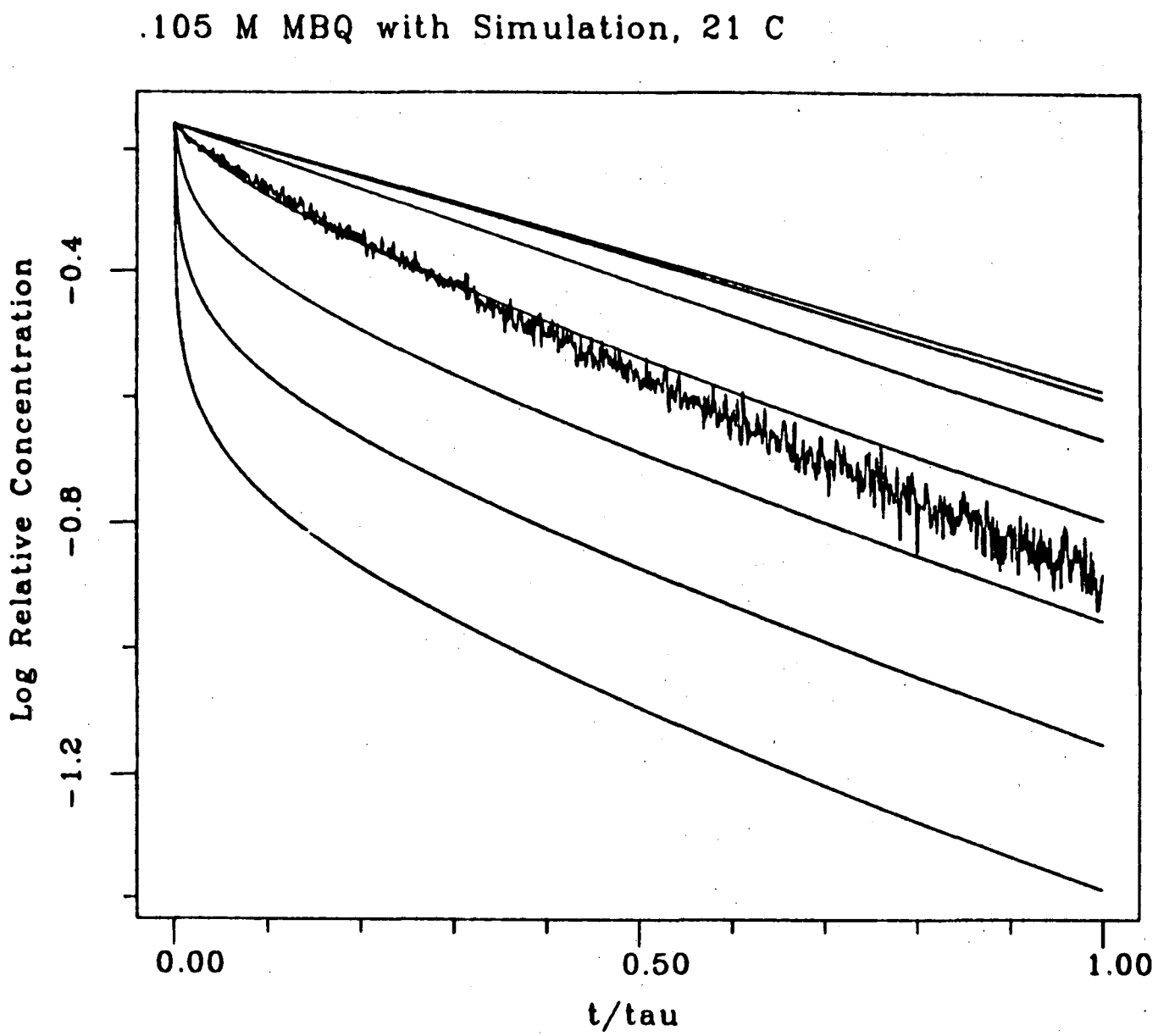
Acceptor concentration /M	
0.015	Figure (17)
0.035	Figure (18)
0.083	Figure (19)
0.105	Figure (20)


.015 M MBQ with Simulation, 21 C
Log Relative Concentration
0.00
-0.20
-0.40
0.00
0.50
1.00
t/tau

.035 M MBQ with Simulation, 21 C




.083 M MBQ with Simulation, 21 C
Log Relative Concentration
-0.5
-1.0
0.00
0.50
1.00
t/tau


.105 M MBQ with Simulation, 21 C
Log Relative Concentration
-0.4
-0.8
-1.2
0.00
0.50
1.00
t/tau

Figures (21-24)

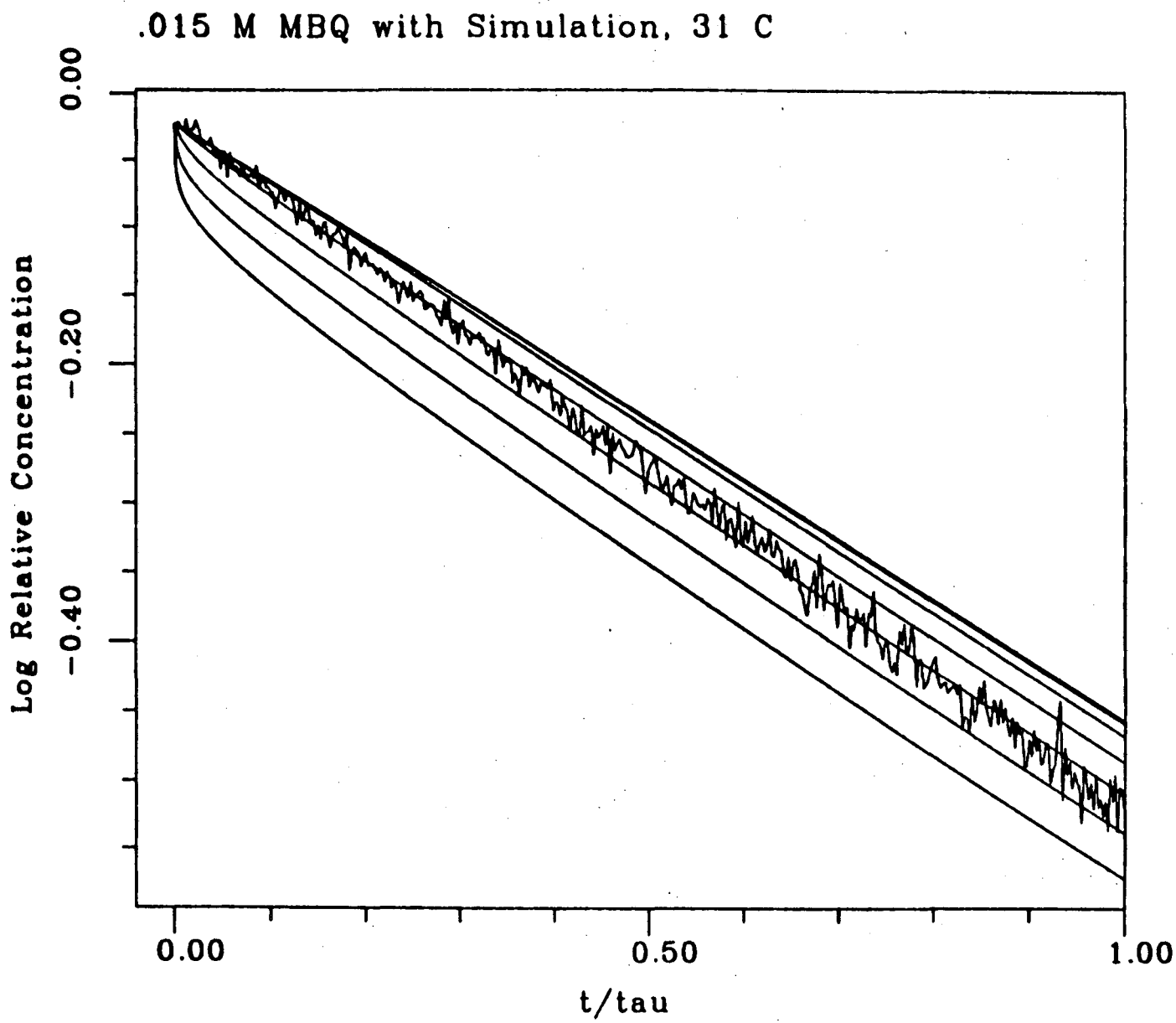
Simulations with overlayed experimental transients, 31° C

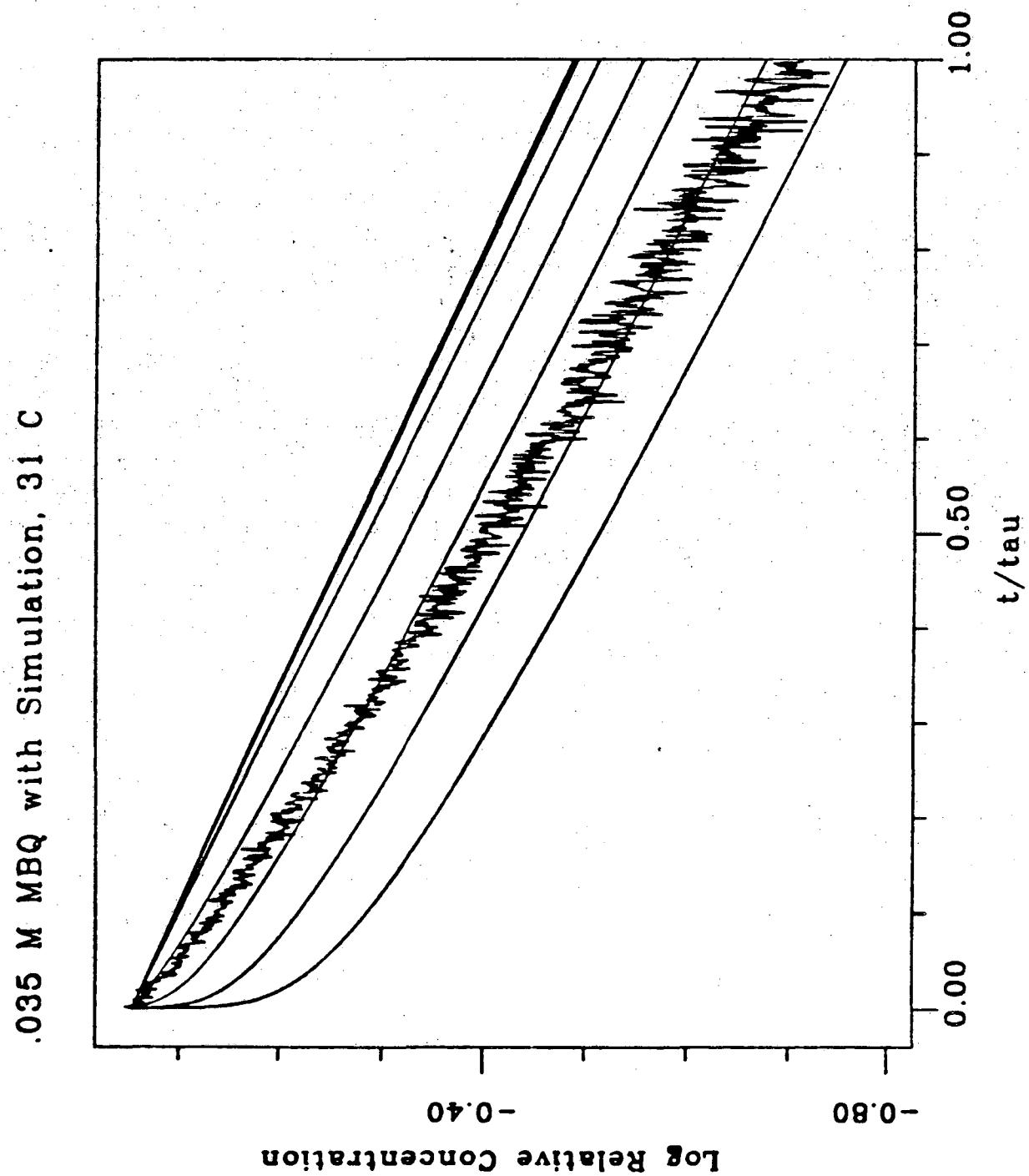
Simulated ν = 0, 10^{3} to 10^{8} s^{-1}.

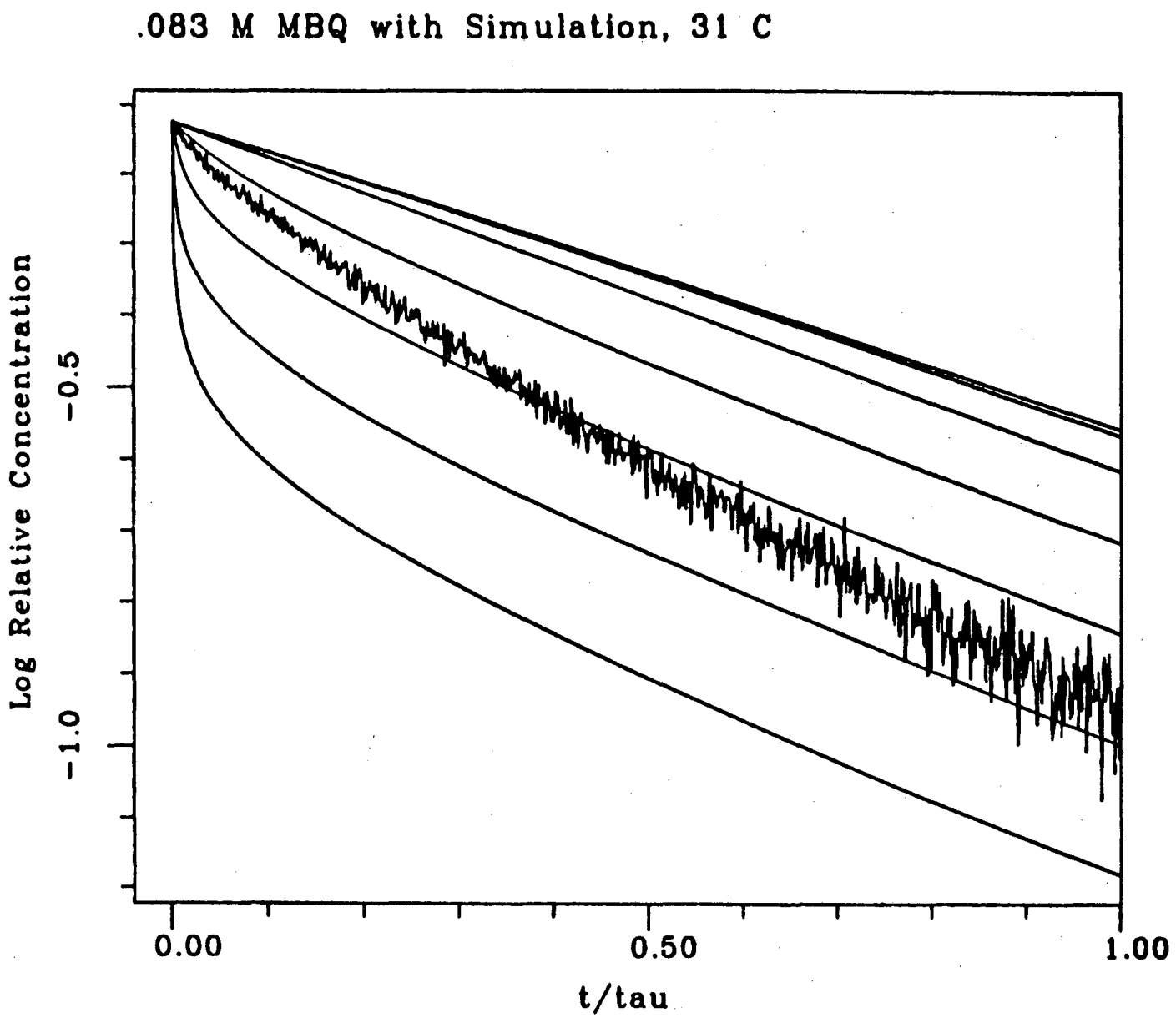
Donor lifetime = 39.9 ms.

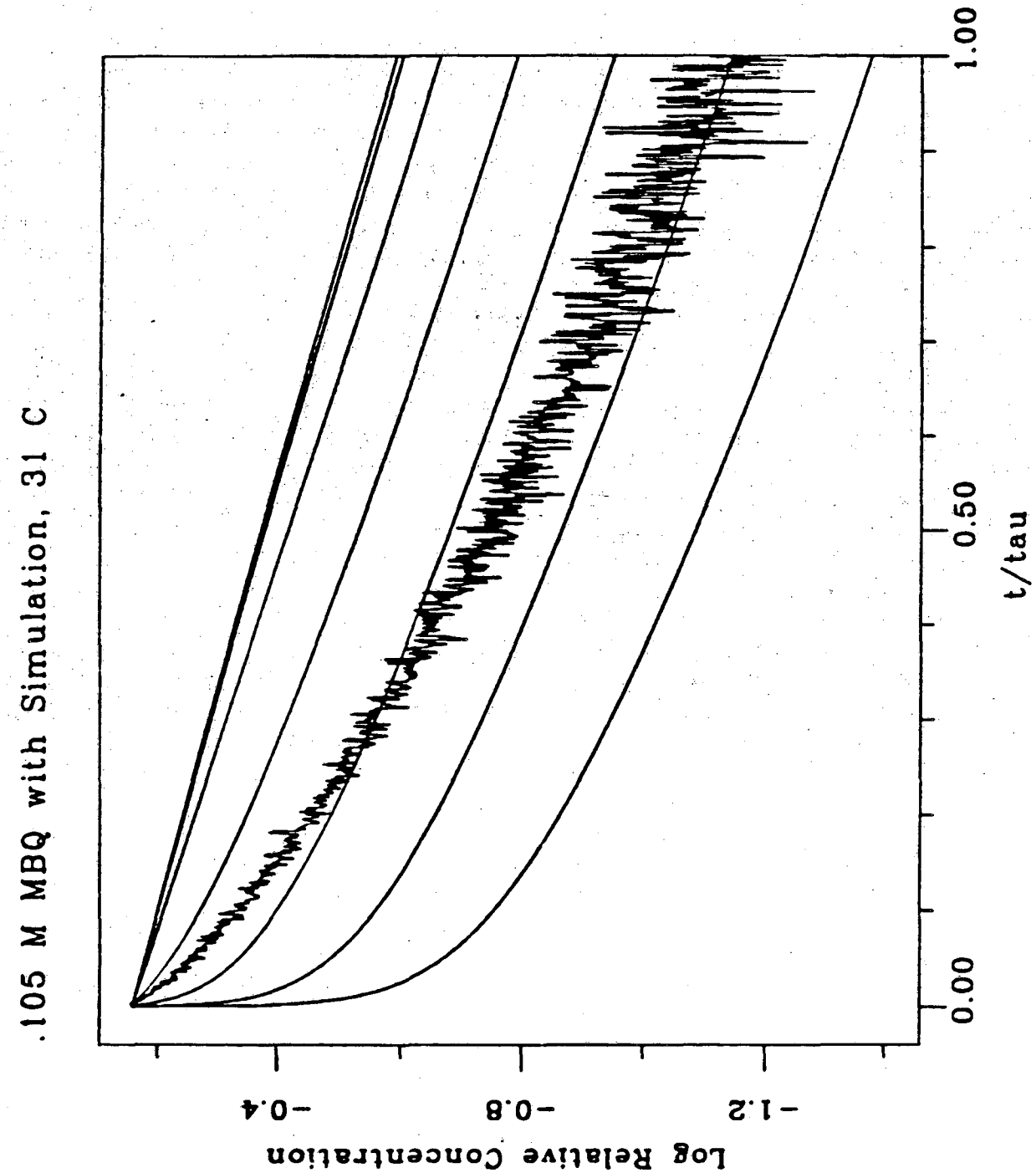
Singlet quenching radius = 11 Angstroms.

Acceptor concentration /M	
0.015	Figure (21)
0.035	Figure (22)
0.083	Figure (23)
0.105	Figure (24)


.015 M MBQ with Simulation, 31 C
Log Relative Concentration
0.00
-0.20
-0.40
0.00
0.50
1.00
t/tau


.035 M MBQ with Simulation, 31 C
Log Relative Concentration
-0.40
-0.80
0.00
0.50
1.00
t/tau


.083 M MBQ with Simulation, 31 C
Log Relative Concentration
-0.5
-1.0
0.00
0.50
1.00
t/tau


.105 M MBQ with Simulation, 31 C
Log Relative Concentration
-0.4
-0.8
-1.2
0.00
0.50
1.00
t/tau

Angstroms [34]. This program used routines of the Interactive Mathematical and Statistical Library (IMSL) in double precision to obtain the best fitted curve. Table 3 shows the results of these calculations. Figure 25 shows a sample fit.

The .105 M sample does not fit the simulations well. Nor is the accuracy of the fit to equation (19) very good. I tend to believe that there was something wrong with this sample, either with the concentration or the temperature during the measurement. This should be redone.

Taking the average of ν for the three lower concentrations at 21° gives a value of $\nu = 3.4 \pm .6 \times 10^4\ s^{-1}$.

Transients at temperatures higher than 21° C could not be fitted to equation (19).

Table (3). Results of fitting experimental transients from t/τ = 0 to .5 to equation (19). a was fixed to 0.75 Angstroms

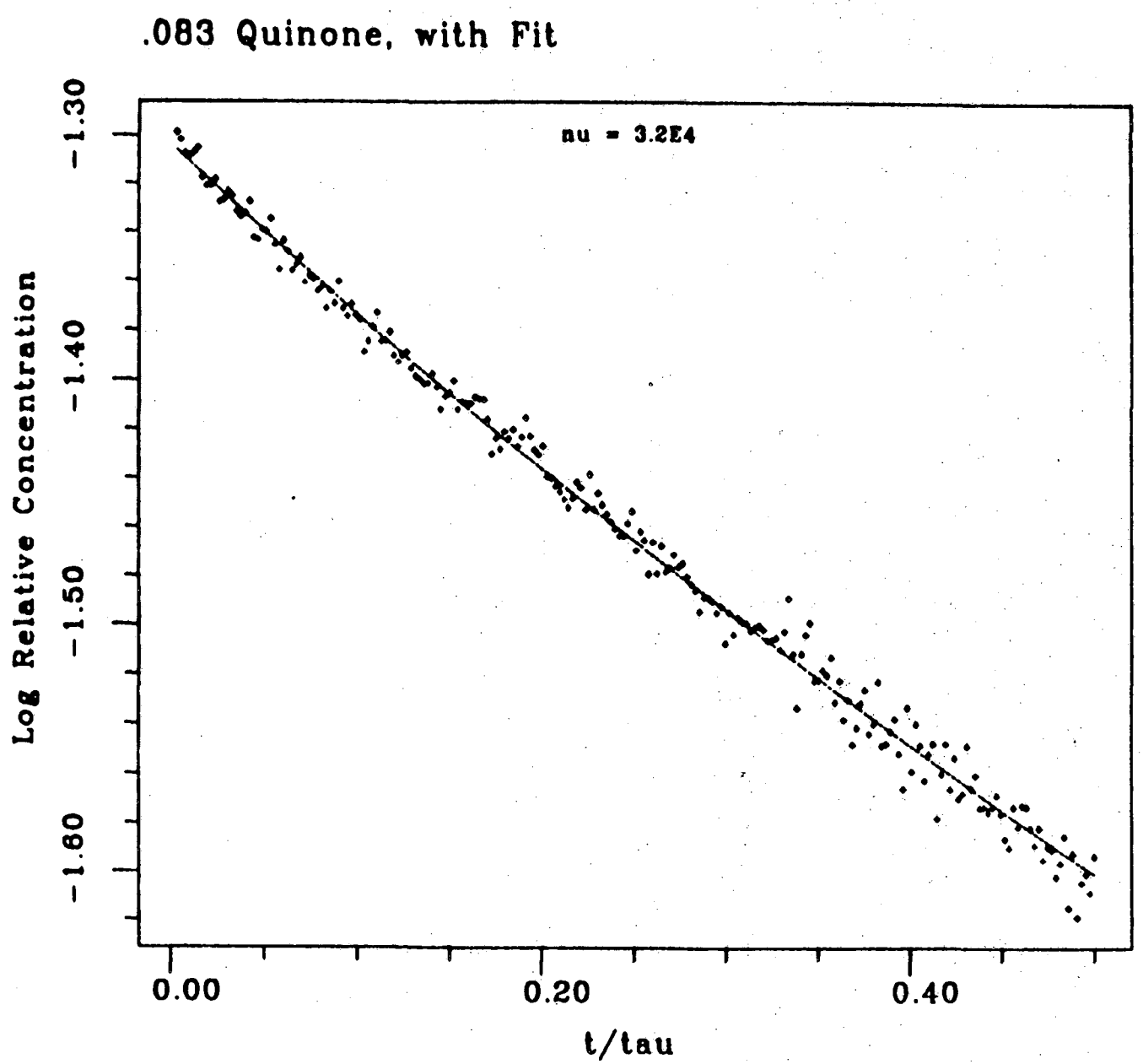
Quinone Concentration /(M)	ν/ s^{-1}
0.015	2.9×10^4
0.035	4.1×10^4
0.083	3.2×10^4
0.105	1.1×10^5

Figure (25)

Decay of ^{3}(ZnTPP) with .083 M added quinone, 21° C. Experimental points with fit to equation (19), with a set to 0.75 Angstroms.

ΔA_o = .066

ν = 3.2×10^4 s^{-1}


.083 Quinone, with Fit
nu = 3.2E4
Log Relative Concentration
-1.30
-1.40
-1.50
-1.60
0.00
0.20
0.40
t/tau

CONCLUSIONS

We will interpret the quenching of both excited singlet and triplet ZnTPP as due to electron transfer. Thus, we must rule out other possible mechanisms - namely, electronic energy transfer, formation of donor - acceptor complexes while the solution is still fluid, and triplet complex formation after excitation.

Energy transfer is easy to rule out. The excited singlet and triplet states of ZnTPP are fairly low in energy (1.9 and 1.5 eV, respectively, estimated from the emission wavelengths.) This compares with gas phase singlet and triplet energies of 2.75 and 2.30 eV for benzoquinone [35]. Energy levels for methylbenzoquinone should be similar; and are much higher than those for ZnTPP.

No changes in the absorption or emission spectra were seen upon combination of the quinone and porphyrin. Such changes would indicate ground state complexation. Also, Harriman et al [33] saw no evidence of ground state complexation between ZnTPP and benzoquinone in either ethanol or toluene.

In that study, benzoquinone was found to quench the triplet state of ZnTPP in fluid solution via two routes. The first was

electron transfer, verified by the long lived $ZnTPP^+$ absorption at 409 nm [36,37]. This is the dominant mode of deactivation in polar solvents.

In nonpolar solvents, flash photolysis was shown to give a transient attributed to a triplet porphyrin - quinone complex [38]. Sucrose octaacetate is nonpolar. However, for such a triplet complex to form, the porphyrin and quinone would have to be in very close proximity. Donor - acceptor pairs separated by such a short distance would be expected to react via singlet state electron transfer, prior intersystem crossing to the triplet. Thus, we do not feel that this mode of complex formation is important.

We should consider the energetics of electron transfer quenching. Equation 20 may be used to estimate the free energy change for the reaction [14] -

$$\Delta G^o_{ET} = E(T_1) - (E(D^+/D) + E(A/A^-) + \frac{e^2}{ER} \qquad (20)$$

The last term is a correction for the Coulombic energy associated with charge transfer.

In acetonitrile solution [37],

$$ZnTPP^{+} + e^{-} \quad ZnTPP \quad \Delta\varepsilon^{o} = 1.05\ V \tag{21}$$

and also in acetonitrile [39],

$$MBQ + e^{-} \quad MBA^{-} \quad \Delta\varepsilon^{o} = -0.34\ V \tag{22}$$

Making the somewhat hazardous estimate that these are the potentials in sucrose octaacetate, one finds that

$$\Delta G^{o}_{ET} = 0.16\ eV + \frac{e^{2}}{er} \tag{23}$$

Since the last term will always be positive, the free energy of electron transfer should always be negative.

From this we conclude electron transfer is the favorable route for quenching of both the porphyrin singlet and triplet states by methylbenzoquinone.

The model developed earlier works well at 21°. As the temperature increases, it breaks down. One must ask why. We think the answer is diffusion. At 30°, cracked sucrose octa-acetate solutions anneal. At 46°, they flow. This indicates that diffusion is taking place. Rhodamine 6G fluorescence is not depolarized, but it has a lifetime of ns, and we are looking at processes over tens of ms. Thus, the lack of depolarization is nearly irrelevant.

What would we expect to see in a solution where electron tunnelling and slow diffusion were present? We might expect to see a combination of the two processes. At short times, we can approximate that the molecules are very nearly fixed in their positions. One would expect the kinetics over this short time scale to be best described by electron tunnelling.

Over longer time scales, the molecules are no longer fixed, but moving relative to each other. The kinetics now approach the much faster rates of a second order, diffusion controlled process.

This is exactly the deviation from predicted behavior we observe at temperatures of 31° and above. At 31°, the kinetics may be well described in terms of fixed distances up to times of t/tau equal to 0.2, but the rate of disappearance of triplet

ZnTPP is faster at longer times. At higher temperatures (lower viscosity, faster diffusion), the assumption of fixed distances doesn't hold over any time scale - the rate of ZnTPP depletion is just too fast.

Thus, at 21° we see no evidence of diffusion in the observed kinetics (with the possible exception of the highest quinone concentration, 0.105 M). At 31° and above, we have both macroscopic and microscopic evidence of diffusion. This evidence is glass annealing and fluid flow, and the apparent breakdown of the assumption of fixed distances in the rate of depletion of the ZnTPP triplet.

At 21°, the rate of electron transfer as a function of distance is given by equation (5), with a = .75, and $\nu = 3.4 \times 10^{-4}\ s^{-1}$,

$$k(r) = (3.4 \times 10^{-4}\ s^{-1}) \exp -\left[\frac{(r - 9\ \mathring{A})}{.75\ \mathring{A}}\right] \qquad (24)$$

This is a relatively small number for ν, as the maximum could be up to $\nu = 10^{13\pm1}\ s^{-1}$ [13]. This low number is not completely unexpected, in light of the low exothermicity of the reaction. One theoretical formulation of electron transfer rates gives the

following dependence of the frequency factor on the exothermicity of the reaction [13,40,41]:

$$\nu = \nu_0 \exp \left[-(\Delta G^o_{ET} + \lambda)^2 \Big/ 4\lambda kT \right] \tag{25}$$

where λ is the reorganization energy of the molecules as they change geometry and solvation after electron transfer. Sutin [42] has catalogued values of λ for various inorganic electron transfer reactions. For the reactions he has considered, λ ranges from 0.5 to 2.5 eV.

Equation (25) states that the rate of electron transfer will decrease as ΔG^o_{ET} decreases below the reorganization energy. Miller and co-workers did find that the rate decreased with decreasing exothermicity of reaction. So our small value for ν is not unexpected, considering the small exothermicity of our reaction.

Armed with the frequency factor, we can now estimate ^3R_q, the quenching radius for electron transfer from the triplet state. Starting with the definition of the quenching radius, that distance where the rate of electron transfer is equal to the rate of normal excited state decay, we can say that

$$\frac{1}{\tau} = \exp - \left(\frac{(R_a - R_0)}{a} \right) \tag{26}$$

where is the inverse of the first order rate constant for triplet decay. Rearrangement gives -

$$R_a = R_0 + a \left| n\nu\tau \right. \tag{27}$$

Using values of ν = 43.4 ms, a = 0.75 Angstroms, R_0 = 9 Angstroms, and $\nu = 3.4 \times 10^4\ s^{-1}$ gives a value for the quenching radius ^3R_q = 15 Angstroms. This value is somewhat smaller than quenching radii measured in the steady state through phosphorescence quenching [14], but the donors used in that study had longer lifetimes (about 7 seconds) and the reactions were more exothermic (with ΔG^0_{ET} at least 1.0 eV).

PROSPECTUS

In the experiments done so far, diffusion of the reacting species was a problem. It would be worthwhile to get some idea of what the viscosity of sucrose octaacetate is as a function of temperature. Greenspan and Fischer [43] have developed a fairly straightforward method of determining high viscosities. They timed the penetration of a weighted glass rod into highly viscous solutions, and compared the penetration rates with those in solutions of known viscosity (glycerol). An Arrhenius plot of log viscosity vs. 1/temperature can then be extrapolated to lower temperatures (higher viscosities).

Knowledge of the viscosity allows one to estimate the diffusion coefficient, D, through the Stokes - Einstein relation [45]:

$$D = \frac{kT}{6\pi\eta g} \tag{28}$$

where η is the viscosity, and g the radius of the molecule. Knowledge of the diffusion coefficient would allow us to determine if diffusion is a realistic explanation for the observed high temperature deviation from predicted behavior.

Measurement of the kinetics at a lower temperature would also be useful. From this, we could see if temperature had any effect on the rate of electron transfer. Several theories predict rates that do not change with temperature at low temperatures, with a transition to an Arrhenius rate expression with increasing temperature [45].

One could check the affect of the solvent on these rates by switching to another room temperature glass such as decalindiol, or a polymer such as polymethylmethacrylate. This might also expand the available temperature range.

One of the large disappointments of this study was the inability to observe the intermediate photoproducts, the oxidized porphyrin and/or the reduced quinone. With these, we could determine the distance dependence rate of the back reaction. At the beginning, we hoped to observe these products through the strong absorption of the oxidized porphyrin at 409 nm. However, methylbenzoquinone proved to be a much less effective quencher than we had anticipated. Thus, we had to add a higher concentration to get observable quenching. Methylbenzoquinone has a weak, rather broad featureless absorption in the blue, λ_{max} = 430 nm, with an extinction coefficient of about 19 M^{-1}-cm^{-1}. This is enough to obscure any other absorbance of wavelength greater than 500 nm.

Attempts to observe the radical photoproducts at other wavelengths did not work. There are simply too many chemical species absorbing from the ultraviolet out to 500 nm to be able to pick any one wavelength to monitor.

It appears another method must be found to observe the photoproducts in this system. Time resolved epr may be the answer. The porphyrin ground state and quinone will be epr "transparent", as they are diamagnetic. One would only have to separate the porphyrin triplet signal from the porphyrin and quinone radicals. This is definitely worth further investigation.

Another alternative would be to go to another system altogether, with a different donor and acceptor. These two species should be nearly transparent in the visible, with strongly colored oxidized and reduced radicals. An example of such an electron donor is p-N,N,N',N'-tetramethylpheylenediamine (TMPD). The excited triplet of this molecule is a very strong reducing agent, the ground state is transparent in the visible, and both the triplet state and the cation radical are highly colored in the visible. It turns out that the TMPD cation radical and triplet spectra are nearly identical, so actually this may not be the best molecule to use. A donor with similar

properties, but with markedly different triplet and cation radical spectra, would be ideal.

I would like to take this discussion one last step, and assume it will be possible to monitor the radical photoproducts. The first point deals with orientation effects. The rate of electron transfer should be dependent on the orientation of the donor acceptor pair, as well as the distance of separation. Neither the treatment presented in this paper nor any others take the orientation into account. This may be because, so far, no one has observed any experimental property that would allow one to examine the orientation dependence. I would like to propose such an experiment.

The initial laser excitation is polarized. It will excite molecules in some orientations, but not in others. This results in a macroscopic orientation of the excited molecules, which can be observed (for instance, in fluorescence polarization). If the electron transfer is dependent on orientation, the collection of oxidized and reduced photoproducts might also be macroscopically oriented. This could be seen by the polarization of the absorption of visible light (optical detection) or microwaves (epr) by these transient species.

Lastly, if the rate of the back reaction were much slower than the rate of forward reaction, electron exchange between acceptors might compete with the back reaction. The approximation that each donor acceptor pair is isolated from the rest of the system would not be valid. This would not change the observed decay of the donor. But, one would expect to see a large increase in the overall yield of the radical photoproducts (since their rate of depletion is slowed), and these products would decay much more slowly. In addition, any optical or epr polarization would disappear. This might be another point to consider if and when we can observe the radical photoproducts.

REFERENCES

1. For a review, see M. Graetzel, Acc. Chem. Res., 14, 376 (1981).

2. a) S.A. Alkaitis, G. Beck, and M. Graetzel, J. Amer. Chem. Soc., 97, 5723 (1975).

b) P.A. Brugger and M. Graetzel, J. Amer. Chem. Soc., 102, 2461 (1980).

c) C.K. Graetzel and M. Graetzel, J. Phys. Chem., 86, 2710 (1982).

d) R.H. Schmehl and D.G. Whitten, J. Amer. Chem. Soc., 102, 1938 (1980).

e) R.H. Schmehl and D.G. Whitten, J. Phys. Chem., 85, 3473 (1981).

f) T. Matsuo, T. Sakamoto, K. Takuma, K. Sakura, and T. Ohsako, J. Phys. Chem., 85, 1277 (1981).

g) M.P. Pileni, Chem. Phys. Lett., 71, 317 (1980).

h) K. Kalyanasundrum, Chem. Soc. Rev., 7, 453 (1978).

3. a) I. Willner, W.E. Ford, J.W. Otvos, and M. Calvin, Nature (London), 280, 823 (1979).

b) D. Meisel and M.S. Matheson, J. Amer. Chem. Soc., 99, 6577 (1977).

c) C.D. Jonah, M.S. Matheson, and D. Meisel, J. Phys. Chem., 83, 257 (1979).

d) R.E. Sasson and J. Rabani, J. Phys. Chem., 84, 1319 (1980).

e) S. Kendler and J. Rabani, J. Phys. Chem., 85, 1637 (1981).

f) R.E. Sasson and J. Rabani, Isr. J. Chem., 22, 138 (1982)

4. a) W.E. Ford, J.W. Otvos, and M. Calvin, Nature (London), 274, 507 (1978).

b) W.E. Ford, J.W. Otvos, and M. Calvin, Proc. Natl. Acad. Sci. USA, 76, 3590 (1979).

c) P.P. Infelta, M. Graetzel, and J.H. Fendler, J. Amer. Chem. Soc., 102, 1479 (1980).

d) M.S. Tunuli and J.H. Fendler, J. Amer. Chem. Soc., 103, 2507 (1981).

e) P. Tundi, D.J. Kippenberger, M.J. Politi, P. Klahn, and J.H. Fendler, J. Amer. Chem. Soc., 104, 5352 (1982).

5. a) J.M. Clear, J.M. Kelly, D.C. Pepper, and J.G. Vos, Inorg. Chim. Acta, 33, L139 (1979).

b) J.M. Calvert, J.V. Casper, R.A. Binstead, D.T. Westmoreland, and T.J. Meyer, J. Amer. Chem. Soc., 104, 6620 (1982).

c) K. Ageishi, T. Endo, and M. Okawara, J. Polym. Sci. Polym. Chem. Ed., 19, 1085 (1981).

6. M. Calvin, I. Willner, C. Laane, and J.W. Otvos, J. Photochem., 17, 195 (1981).

7. a) K. Kalyanasundrum, E. Borgarello, and M. Graetzel, Helv. Chim. Acta, 64, 362 (1981).

b) D. Duonghong, J. Ramsden, and M. Graetzel, J. Amer. Chem. Soc., 104, 2977 (1982).

c) M. Graetzel and A.J. Frank, J. Phys. Chem., 86, 2964 (1982).

d) M.D. Ward, J.R. White, and A.J. Bard, J. Amer. Chem. Soc., 105, 27 (1983).

e) J.R. Harbour and M.L. Hair, J. Phys. Chem., 81, 1741 (1977).

f) J.R. Darwent and G. Porter, J. Chem. Soc. Chem. Comm., 145 (1981).

g) Z. Alfassi, D. Bahnemann, and A. Henglein, J. Phys. Chem., 86, 4656 (1982).

8. T.F. Ho, A.R. McIntosh, and J.R. Bolton, Nature (London), 286, 254 (1980).

9. M.A. Bergkamp, J. Dalton, and T.L. Netzel, J. Amer. Chem. Soc., 104, 253 (1982).

10. J. Miller, Science, 189, 221 (1974).

11. J. Beitz and J. Miller, J. Chem. Phys., 71, 4579 (1979).

12. J. Miller and J. Beitz, J. Chem. Phys., 74, 6746 (1981).

13. J. Miller, J. Peeples, M. Schmitt, and G.C. Closs, J. Amer. Chem. Soc., 104, 6488, (1982).

14. J. Miller, K. Hartman, and S. Abrash, J. Amer. Chem. Soc., 104, 4296 (1982).

15. M. Tachiya and A. Mozumunder, Chem. Phys. Lett., 28, 87 (1974).

16. A. Kira, J. Phys. Chem., 85, 3047 (1981).

17. T. Guarr, M. McGuire, S. Strauch, and G. McLendon, J. Amer. Chem. Soc., 105, 616 (1983).

18. S. Strauch, G. McLendon, M. McGuire, and T. Guarr, J. Phys. Chem., 87, 3579 (1983).

19. D. DeVault, Quart. Rev. Biophys., 13, 390 (1981), and references within.

20. J.A. Jortner, J. Amer. Chem. Soc., 102, 6676 (1980).

21. J.J. Hopfield, Proc. Natl. Acad. Sci. USA, 71, 3640 (1974).

22. M. Inokuti and F. Hiriyama, J. Chem. Phys., 43, 1978 (1965).

23. A. Namiki, N. Nakashima, and K. Yoshihara, J. Chem. Phys., 71, 925 (1979).

24. Also mentioned in ref. 19 are the unpublished results of Miller and co-workers.

25. R.K. Huddleston and J.R. Miller, J. Phys. Chem., 86, 200 (1983).

26. S. Chandrasekhar, Rev. Mod. Phys., 15, 1 (1943).

27. G. Gamow, Z. Phys., 51, 204 (1928).

28. DeVault, in ref. 20, uses 'a' to represent the inverse of the term used in this work.

29. N. Turro, "Modern Molecular Photochemistry", Academic Press, New York (1973).

30. L. Pekkarinen and H. Linschitz, J. Amer. Chem. Soc., 82, 2407 (1960).

31. J.M. Yang, Ph.D. Thesis, University of California, Berkeley (1981).

32. A. Harriman, G. Porter, and N. Searle, J. Chem. Soc. Faraday II, 75, 1515 (1979).

33. Program SAB1.EXE.

34. Program DDDD.EXE.

35. J.R. McDonald and L.E. Brus, J. Chem. Phys., 59, 4966 (1973).

36. J. Fajer, D.C. Borg, N. Forman, A. Dolphin, and R.H. Felton, J. Amer. Chem. Soc., 92, 3451 (1970).

37. A. Wolberg and J. Manassen, J. Amer. Chem. Soc., 92, 2982 (1970).

38. P.A. Shakhverdov, Optikai Spektroskopiya, 30, 42 (1971).

39. M.E. Peover, J. Chem. Soc., 4540 (1962).

40. a) R.A. Marcus, J. Chem. Phys., 24, 966 (1956).

b) V.G. Levich, Adv. Electrochem. Eng., 4, 249 (1966).

41. J. Ulstrup and J. Jortner, J. Chem. Phys., 63, 4388 (1975).

42. N. Sutin, Acc. Chem. Res., 15, 275 (1982).

43. H. Greenspan and E. Fischer, J. Phys. Chem., 69, 2466 (1965).

44. P.W. Atkins, "Physical Chemistry", W.H. Freeman and Company, San Francisco; page 835.

45. See p. 437 in ref. 20 for a discussion of the different theories.

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