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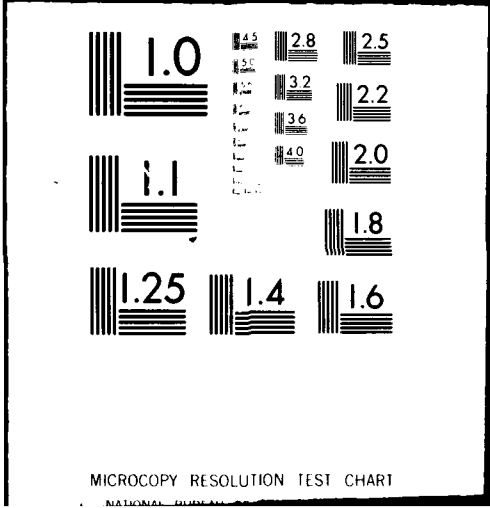
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THE CASE OF TWO REACTIVE AND INTERCOMMUNICATING EXCITED STATES. (U)  
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The Case of Two Reactive and Intercommunicating Excited States

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# The Case of Two Reactive and Intercommunicating Excited States

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## Abstract

*Cr(en)<sub>3</sub> 3+*

The exact kinetics of a pulsed laser experiment producing two potentially reactive and potentially intercommunicative states is examined in detail, with special reference to aqueous *Cr(en)<sub>3</sub> 3+*. The various possible regimes of rate constant values in all cases but one lead to physically questionable absolute values. The acceptable regime is that in which the first doublet thexi state is directly chemically reactive. A challenge to the reading of earlier results on the monitoring of the rate of appearance of the primary photoproduct is discussed, and dismissed.

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### Introduction

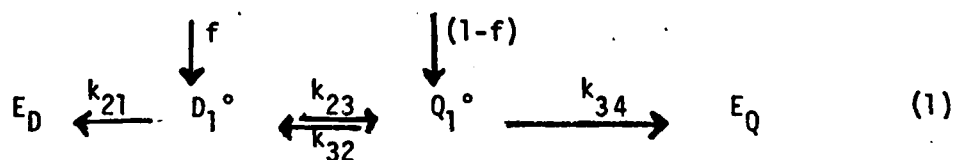
A situation that is important in the case of Cr(III) photochemistry and which is now emerging in that of Rh(III) complexes,<sup>1</sup> is one in which excitation may lead to two different excited states, each of which has the possibility of undergoing chemical reaction. The appearance of the two states may be prompt, that is, faster than the time resolution of the equipment (in our case, about 3 nsec).<sup>2</sup> The appearance mechanism may either be one of prompt intersystem crossing, pisc, during thermal equilibration of the initially produced Franck Condon state, or by intersystem crossing, isc, after thermal equilibration of the Franck Condon state. There may be back intersystem crossing, bisc. The scheme, labeled for the case of a  $d^3$  complex, is shown in Figure 1.

The purpose of the present writing is several fold. The general kinetic treatment, while now new,<sup>3,4</sup> seems not to have been applied fully, although various special cases have been presented.<sup>5,6</sup> Several kinetic regimes are possible, each carrying important implications and limitations. The analysis that follows is intended to explore these, and is presented in sufficiently general form to be useful for other excited state systems than those of Cr(III). In Figure 1, however, the two states are designated  $D_1^\circ$  and  $Q_1^\circ$ , the thermally equilibrated excited (thexi) doublet and quartet states in the  $d^3$  case. For Rh(III), the states might be singlet and triplet (or quintet). The states could alternatively be of the same spin, perhaps derived from a common state in  $O_h$  symmetry.

A second purpose is to analyze the physical implications of the various kinetic regimes, and their chemical reasonableness, in the case of certain Cr(III) complexes. There will be special emphasis on aqueous  $Cr(en)_3^{3+}$ , en denoting ethylenediamine. It will be necessary to respond to a direct attack by Kirk.<sup>7,8</sup>

### The Kinetic Scheme

To pursue the labeling in Figure 1,  $f$  is the fraction of initially formed Franck Condon state,  $Q_{FC}$ , that arrives promptly at  $D_1^\circ$ .  $D_1^\circ$  may exit the excited state system by emission, by non-radiative relaxation to the ground state,  $Q_0^\circ$ , or by chemical reaction to product, P. The respective rate constants are  $k_r$ ,  $k_{nr}$ , and  $k_{cr}$ ; the total exiting rate constant is  $k_{21} = k_r + k_{nr} + k_{cr}$ . Similarly, for  $Q_1^\circ$ , we define  $k_{34} = k'_r + k'_{nr} + k'_{cr}$ . The direct yield or efficiency of chemical reaction from  $D_1^\circ$  is  $\phi_D' = k_{cr}/k_{21}$ , and that from  $Q_1^\circ$  is  $\phi_Q' = k'_{cr}/k_{34}$ . Finally, the rate constants for bisc and isc are denoted  $k_{23}$  and  $k_{32}$ , respectively. The kinetic scheme is thus:



At time zero, initial concentrations  $(D_1^\circ)^\circ$  and  $(Q_1^\circ)^\circ$  have been established by fast thermal equilibration and by pisc of  $Q_{FC}$  formed by an excitation pulse (the steady state case will be noted later). The general solution to (1) has been published,<sup>3,4</sup> and we proceed to the aspect of interest here. The rate at which exiting occurs from  $D_1^\circ$  is given by  $k_{21}(D_1^\circ)$ , and the total exiting up to time  $t$ , by  $E_D = k_{21} \int_0^t (D_1^\circ) dt$ . Taking  $(Q_{FC})$  as unity, so that  $(D_1^\circ)^\circ = f$ , analysis gives

$$E_D = \frac{k_{21}}{\lambda_2 - \lambda_1} \left\{ \begin{array}{l} \frac{f(\lambda_2 - \alpha) + (1-f)k_{32}}{\lambda_1} (1 - e^{-\lambda_1 t}) \\ - \frac{f(\lambda_1 - \alpha) + (1-f)k_{32}}{\lambda_2} (1 - e^{-\lambda_2 t}) \end{array} \right\} \quad (2)$$

where  $\alpha = k_{21} + k_{23}$  and  $\beta = k_{32} + k_{34}$ . The decay constants are given by

$$2\lambda_{1,2} = (\alpha + \beta) \pm [(\alpha - \beta)^2 + 4k_{23} k_{32}]^{1/2} \quad (3)$$

Similarly, the rate of exiting from  $Q_1^{\circ}$  is  $k_{34}(Q_1^{\circ})$ , and the total exiting is given by  $E_Q = k_{34} \int_0^t (Q_1^{\circ}) dt$ .<sup>9</sup> Taking  $(Q_1^{\circ})^{\circ}$  as just  $(1-f)$ ,

$$E_Q = \frac{k_{34}}{\lambda_2 - \lambda_1} \left\{ \begin{array}{l} \frac{f k_{23} + (1-f)(\lambda_2 - \beta)}{\lambda_1} (1 - e^{-\lambda_1 t}) \\ - \frac{f k_{23} + (1-f)(\lambda_1 - \beta)}{\lambda_2} (1 - e^{-\lambda_2 t}) \end{array} \right\} \quad (4)$$

Equations (2) and (4) may be abbreviated:<sup>10</sup>

$$E_D = A(1 - e^{-\lambda_1 t}) + B(1 - e^{-\lambda_2 t}) \quad (5)$$

$$E_Q = C(1 - e^{-\lambda_1 t}) + D(1 - e^{-\lambda_2 t}) \quad (6)$$

The total yield of photoproduct as a function of time following a fast excitation pulse is then

$$\phi = (\phi'_D A + \phi'_Q C) (1 - e^{-\lambda_1 t}) + (\phi'_D B + \phi'_Q D) (1 - e^{-\lambda_2 t}) \quad (7)$$

In the case of Cr(III) amines in room temperature solution,  $\lambda_1$  will typically be a large number, and  $\lambda_2$ , around unity, if time is measured in microseconds. Events completed in nanoseconds or less will be termed "fast", and those requiring of the order of microseconds, "slow". The two categories are distinguished in nanosecond pulse laser photolyses, and it is to this type of experiment that much of the analysis is

directed. At time small compared to  $1/\lambda_2$  but large compared to  $1/\lambda_1$ , we speak of prompt photoproduct formation,  $\phi_{fast} = (\phi_D' A + \phi_Q' C)$ . With additional time lapse, further product formation occurs, the eventual additional yield being  $\phi_{slow} = (\phi_D' B + \phi_Q' D)$ . The grow-in of  $\phi_{slow}$  will have the lifetime  $1/\lambda_2$ ; this is the same lifetime as for the decay of emission from  $D_1^0$  since the emission rate is given by  $k_r(D_1^0)$ . While  $k_r$  determines the emission intensity, it is not otherwise important, that is, we take  $k_r \ll k_{21}$  (as well as  $k_r' \ll k_{34}$ ).

If a quencher is present, such that  $D_1^0$  emission is quenched,  $k_{21}$  is increased by the term  $k_q$  (quencher). With complete quenching,  $k_{21}$  is now large compared to  $k_{cr}$ ;  $\phi_D'$  approaches zero. Further,  $k_{21}$  is now large compared to  $k_{23}$  so that only  $\phi_{fast}$  remains. The "unquenchable" fraction of the normal quantum yield is thus  $\phi_{fast}/\phi$ . (We suppose that there is no chemical reaction induced by the quenching encounters--not always a safe assumption.)

#### The Case of Aqueous $Cr(en)_3^{3+}$

It is both helpful as a specific, and required by current dispute, to consider the case of  $Cr(en)_3^{3+}$  in room temperature aqueous solution. The total photoproduct yield is known to be  $\phi = 0.37$ ,<sup>11,12</sup> and, from our monitoring studies,<sup>2</sup> 70% of the photochemistry is slow or quenchable, so that  $\phi_{slow} = 0.26$  and  $\phi_{fast} = 0.11$ . Quenching studies from other laboratories give only 50% to 60% quenchable photochemistry,<sup>12,13</sup> but we will assume our finding to be the more correct one; not being based on quenching, it is not potentially reduced by reaction during quenching encounters.<sup>14</sup> The  $D_1^0$  emission lifetime  $\tau$ , is 1.8  $\mu\text{sec}$  at 25 °C, or 1.8 if time is expressed in microseconds.<sup>12,15</sup> In the calculations that follow, however, we have chosen round numbers for key rate constants so as to make it easier to compare various effects. Except where

quenching is introduced, our  $\lambda_2$  values will be around unity; and scaling of all rate constants in a set by the factor  $1.8 \lambda_2$  will give the actual values needed to agree with  $\tau$ , in microsecond time units. Such scaling will not be necessary for the comparisons involved, however.

Equations (2) and (4) contain four rate constants and, clearly, an extensive mapping would be needed to cover all combinations in gradation. We will concentrate on several clear-cut regimes, representing various proposed and possible physical situations. The calculations are summarized in Table 1.

Regime IA. - This is the regime which we have proposed.  $D_1^\circ$  is populated by pisc, there is no bisc, and photochemistry occurs by chemical reaction both from  $D_1^\circ$  and from  $Q_1^\circ$ . It is assumed that  $k_{23}$  is small compared to the exiting rate constant,  $k_{21}$ , so that  $\tau$  is primarily controlled by  $k_{21}$ , and that  $k_{34}$  is relatively large, so that reaction from promptly formed  $Q_1^\circ$  is "fast". A corollary assumption is that  $k_{32}$ , for isc, is small compared to  $k_{34}$ . The schematic picture is shown in Figure 2(a), the width of the arrows suggesting relative magnitudes of rate constants.

Five calculations are given in Table 1. Calculation (1) is for  $f = 0.3$ , the value given by our monitoring results; case (2) is for  $f = 0.7$ , chosen so that  $\phi_D' = \phi_Q'$ , and case (3) is for  $f = 0.89$ , the maximum allowable value if  $\phi_{fast}$  is to be the experimental value of 0.11. Thus the observables,  $\lambda_2$ ,  $\phi_{fast}$ , and  $\phi_{slow}$  can be obtained for any  $f$  in the range 0.3 (actually 0.26) to 0.89. The matter of the actual value of  $f$  will be discussed further below.

Calculation (4) illustrates that a 100 fold increase in  $k_{32}$  has negligible effect; it is only important that  $k_{32}$  be small compared to  $k_{34}$  in this regime. Case (5) represents quenching, with  $k_{21}$  now set at 1000, and  $\phi_D'$  taken to be zero; as expected,  $\phi = \phi_{fast} = 0.11$ .

Since  $\phi_D'$  cannot be less than 0.29, this regime requires that  $k_{nr}$  not be very large compared to  $k_{cr}$ . The emission lifetime,  $\tau$ , is given essentially by  $1/k_{21}$  or by  $1/(k_{cr} + k_{nr})$ . Experimentally, the variation of  $\tau$  with temperature gives a linear Arrhenius plot, which would not be expected if  $k_{nr}$  were appreciable relative to  $k_{cr}$ ; since the temperature dependencies of the two rate constants should be different, the relative importance of  $k_{nr}$  should vary with temperature, making the Arrhenius plot of  $\tau$  non linear. Further, from the slope, the apparent activation energy is 10 kcal, <sup>12,15</sup> a figure which is physically reasonable for  $k_{cr}$  but large for  $k_{nr}$ . Non-radiative relaxation rates are not usually so temperature dependent (see the discussion in Ref. 15). In this regime, then, the most plausible case on general grounds is that of calculation (1) for which  $k_{nr} \ll k_{cr}$ . The  $f$  value for this case is the one we found, and which is disputed.

A second comment is that pisc is almost certainly very fast if it is to occur at all. This is to be expected on physical grounds in that the relaxation of  $Q_{FC}$  should not take more than a few solvent diffusional jump times, or about  $200 - 1000 \times 10^{-13}$  sec. We assume that some solvent cage rearrangement must occur as  $Q_{FC}$  changes bond lengths and angles to become  $Q_1^\circ$ . Experimentally, we see no measurable rise time to  $D_1^\circ$  emission so that any pisc occurs in less than about 1 nsec. Further, in the cases of certain Cr(III) thiocyanato complexes,  $D_1^\circ$  absorption appeared within short psec of excitation, <sup>16</sup> setting a yet larger rate for pisc in regime IA.

Regime IB. - It is not necessary to the essential features of Regime I that pisc occur.  $D_1^\circ$  may alternatively be formed promptly through a fast isc. We continue to assume that  $k_{23}$  is small compared to  $k_{21}$ , so that  $\phi_{\text{slow}}$  is still due to reaction from  $D_1^\circ$ . The situation is illustrated in Figure 2(b).

The calculations show that it is now the ratio  $k_{32}/k_{34}$  that determines the ratio  $(D_1^\circ)^\circ/(Q_1^\circ)^\circ$ . Cases (6), (7), and (8) duplicate the observables of cases (1), (2), and (3), although  $\lambda_1$  is now larger because of the contribution of  $k_{32}$ ,  $k_{34}$  having been kept constant. Calculation (9), for quenching, gives the same observables as does (5).

It is to be expected that a line of situations intermediate between Regimes IA and IB would also reproduce the observables. That is, linear combinations of pisc and fast isc (with no bisc) will be acceptable insofar as the data are concerned. However, as discussed above, we expect  $k_{\text{nr}} \ll k_{\text{cr}}$ , or  $\phi_D'$  to be large rather than of intermediate value. Thus the acceptable combination would be with cases (1) and (6).

Referring to the discussion about pisc above, in Regime IB it is now isc that must be very fast. If  $D_1^\circ$  is to appear within a few hundred vibration times of excitation,  $k_{32}$  must be  $\sim 10^{10} - 10^{11} \text{ sec}^{-1}$  (or  $10^4 - 10^5$  in our time scale). This means that  $k_{34}$  is also in this range of values since it is necessary in this regime that  $0.4 < k_{32}/k_{34} < 8$ . Further, since chemical reaction competes with other processes,  $k_{\text{cr}}'$  must also be in this range. This last requirement poses a problem. It is the reaction from  $Q_1^\circ$  that tends to obey the photolysis rules<sup>11</sup> in the case of non- $O_h$  complexes, that is, in the case of at least two different kinds of ligand present. Theoretical rationalization of the rules has been made, for example, on the basis that the reacting state has an antibonding electron,

true for  $Q_1^\circ$ , but not for  $D_1^\circ$ .<sup>17</sup>  $Q_1^\circ$  reactions are highly stereospecific (and often antithermal in type)<sup>14</sup> and such specificity implies the presence of kinetic barriers sufficient to allow choice between reaction modes, that is, some activation energy is expected. Thus the required magnitude of  $k'_{cr}$  seems too large to be comfortable in the context of the reaction chemistry of  $Q_1^\circ$ .

Another aspect is that by microscopic reversibility,  $K_{32} = k_{23}/k_{32}$ . The energy difference between  $Q_1^\circ$  and  $D_1^\circ$  for  $Cr(en)_3^{3+}$  has been estimated to be 4-5 kK,<sup>18</sup> or about 13 kcal mole<sup>-1</sup>. Neglecting entropy contributions, one thus estimates  $k_{23}/k_{32} \approx 3 \times 10^{-10}$ , or  $k_{23} \approx 3 \text{ sec}^{-1}$ , or  $3 \times 10^{-6}$  on our microsecond time scale. So small a value is marginally acceptable in this regime since all that is required is that  $k_{23}$  be small compared to  $k_{32}$  and  $k_{21}$ , but will cause difficulty in the case of Regime IIB below.

In summary, Regime IB suffers in the context of all the available information in implying an unreasonably large value for  $k'_{cr}$ . Of the two, Regime IA is to be preferred.

Regime IIA. - We abandon  $D_1^\circ$  as a chemically reactive state and suppose that all chemical reaction occurs from  $Q_1^\circ$ , the slow portion via bisc from  $D_1^\circ$  formed by prompt intersystem crossing. This is essentially the regime proposed by Balzani and co-workers<sup>12</sup> (or Regime IIB). The emission lifetime is now likely to relate to  $k_{23}$ , to which we now give the reference value of unity. The rate of  $Q_1^\circ$  exiting must still be rapid, to allow for a  $\phi_{fast}$ , and, as for Regime IA, we assume  $k_{32}$  to be negligible. Since  $k_{21}$  is now a wasting process, leading to no chemical reaction, it is taken to be small compared to  $k_{23}$ . The scheme is illustrated in Figure 2(c).

Case (10) provides a sample calculation which produces the observed yields. Note the resemblance to case (2). This is a requirement, since  $\underline{f}$  must be 0.7 (more if  $k_{21}$  is not negligible) for 70% of  $\phi$  to be slow;  $\phi'_0$  must be the same as  $\phi$ , or 0.37. If  $k_{21}$  is comparable to  $k_{23}$ , then, as illustrated by case (11),  $\underline{f}$  and  $\phi'_0$  increase compensatorily. In calculation (12) the  $k_{21}/k_{23}$  ratio is at the maximum possible value to obtain the observed yields. Case (13) illustrates that it is not necessary that  $k_{32} \ll k_{23}$ ; the rate constants may be comparable, with appropriate adjustment in  $\underline{f}$ , although again, draining of the system through the non-productive  $k_{21}$  path must be limited.

A problem is that  $\lambda_2$  is now determined primarily by  $k_{23}$  (if  $k_{21}$  is small), so that in real time,  $k_{23} \approx 10^6 \text{ sec}^{-1}$ . From the discussion under Regime IB, it follows that  $k_{32} \approx 10^6/3 \times 10^{-10} = 3 \times 10^{15} \text{ sec}^{-1}$ , or unacceptably fast, as is also true for  $k_{34}$  and hence  $k'_{cr}$ . We discard Regime IIA.

Regime IIB. - An alternative, it can be assumed that  $D_1^\circ$  is populated promptly by  $isc$  rather than by  $pisc$ . As with Regime IB, the ratio  $k_{32}/k_{34}$  largely determines  $(D_1^\circ)^\circ/(Q_1^\circ)^\circ$  and hence  $\phi_{slow}/\phi_{fast}$ . The absolute values of the rate constants are not important provided that  $k_{32} \gg k_{23}$ . The scheme is illustrated in Figure 2(d).

Calculation (14) gives an acceptable result, and case (15) illustrates that the results are not sensitive to the magnitudes of  $k_{32}$  and  $k_{34}$  at constant ratio. Note that  $\lambda_2$  is no longer approximately equal to  $k_{23}$ ; it is less than it by approximately the factor  $k_{34}/(k_{32}+k_{34})$  if  $k_{21}$  is small, essentially because each occurrence of  $D_1^\circ \rightarrow Q_1^\circ$  is partly nullified by that fraction of  $Q_1^\circ$  which returns rapidly to  $D_1^\circ$ .

It is relevant to examine the sensitivity of  $\lambda_2$  to various parameters since it is not identifiable with any single one. This can be done analytically, but it is sufficient here to examine some cases empirically.

First,  $k_{21}$  need not be negligible compared to  $k_{23}$ . Cases (16) and (17) illuminate this dependence of  $\lambda_2$ . A 10% increase in  $k_{21}$  leads to a 4% increase in  $\lambda_2$ , but note that changes in the  $k_{32}/k_{34}$  ratio are required to obtain the observed yields. Also,  $k_{21}$  cannot be increased beyond about 0.5 without lowering  $\phi$  below 0.37. Comparison of cases (18) and (15) show that a 10% increase in  $k_{23}$  increases  $\lambda_2$  by 9% if  $k_{21}$  is small, and comparison of cases (19 and (16) shows about the same sensitivity at the larger  $k_{21}$  level, although now a change in the  $k_{32}/k_{34}$  ratio is needed to maintain the observed yields.

The physical acceptability of Regime IIB may be questioned. It requires that  $k_{21} < k_{23}$  although both are non-radiative transitions between states, with the activation energy for  $k_{21}$  expected to be small while that for  $k_{23}$  must approximate the 10 kcal mole<sup>-1</sup> obtained from the temperature dependence of  $\tau$ . The  $k_{23}$  process, moreover, involves a spin change, while the  $k_{21}$  process does not. It is thus highly unlikely that  $k_{21}$  is in fact less than  $k_{23}$ ; it should be much larger.

Another problem is that  $\lambda_2$ , which is the observed  $1/\tau$ , is not identifiable with  $k_{23}$  exactly, but depends in a complex manner on the  $k_{21}/k_{23}$  and  $k_{32}/k_{34}$  ratios. With such a mixed dependence, a linear Arrhenius plot is not expected for  $\tau$ , contrary to observation. Further, in real time,  $k_{23}$  is about  $10^{-6}$  sec<sup>-1</sup>, and as noted above,  $k_{32}$  becomes inacceptably large, as does  $k_{34}$  and  $k'_{cr}$ . Thus quantitative considerations make Regime IIB unacceptable.

Summary for the four Regimes.- Rate constant values can be chosen for each of the four regimes such that the observed  $\tau$ ,  $\phi_{slow}$ , and  $\phi_{fast}$  are obtained. In the cases of Regimes IB, IIA, and IIB, however, quantitative difficulties appear when physically reasonable constraints are placed on the absolute values of the rate constants and on the

$k_{23}/k_{32}$  ratio. Such quantitative considerations form an essential, too often neglected part of the picture. Here, they lead to a rather firm rejection of these regimes. Only Regime IA is free of such problems and is therefore the one to be postulated in the absence of truly compelling evidence otherwise. Note, however, that the choice of Regime IA does not absolutely settle the question of the value of  $f$ , although quantitative considerations give strong preference to a value around 0.3, so that  $\phi_D'$  approaches unity and  $\tau$  is controlled primarily by a single process,  $k_{cr}$ , thus giving good Arrhenius behavior. We have pointed out the likely importance of  $k_{cr}$  in determining  $\tau$  values for Cr(III) amines generally,<sup>15</sup> a conclusion that has found recent support both for  $\text{Cr(en)}_3^{3+}$  and for other Cr(III) complexes.<sup>19,20</sup>

#### The Prompt Intersystem Crossing Yield

The above analyses have invoked only the unquestioned constraints, namely those imposed by  $\tau$ ,  $\phi_{slow}$  and  $\phi_{fast}$ . The experiments in which we observed the rate of appearance of primary photoproduct, by monitoring the increased absorbance,<sup>2</sup> provided a fourth constraint. This was the value of  $\phi_{D_1^\circ}$ , that is, the yield of  $(D_1^\circ)^\circ$ . This yield is given by

$$\phi_{D_1^\circ} = B\lambda_2/k_{21} \quad (8)$$

and the various calculated values are given in the last column of Table 1. For Regimes IIA and IIB,  $\phi_{D_1^\circ}$  is  $> 0.7$ . This is a consequence of requiring all chemical reaction to occur from  $Q_1^\circ$ . Only for Regimes IA and IB are smaller values allowed.

The monitoring results in fact gave  $\phi_{D_1^\circ}$ , or  $f$  in the case of Regime IA, as  $0.33 \pm 0.09$ , and this figure alone rules out Regimes IIA and IIB. On various grounds, we proposed Regime IA as the probable one.

We come now to the claims by Kirk.<sup>7</sup> The monitoring traces provided a ratio of optical density differences,  $R$  (see Eq. (6) in Ref. 2), and it was the value of  $R$  for 620 nm monitoring that was especially important in allowing the above estimation of  $f$ . Kirk's extrapolation procedure, on which he bases his recalculated  $R$  values is, in fact, not a useful one since it emphasizes the long time region of a trace, a region which is made quite inaccurate by the noise width of the trace; an example is given in Figure 3. The ripple which sometimes showed in traces, probably due to dust, developed relatively slowly, and, in fact, in cases showing such ripples, the initial increase in absorbance as read directly is more likely to be correct than that from some attempt to fit an exponential curve through a ripple.<sup>21,22</sup> We have re-examined our copies of the oscilloscope traces, in view of Kirk's claims, and conclude that our original readings were correct. We again report an  $R$  value at 620 nm of about 4, and definitely reject both the value and the error limits that Kirk proposes.

Our conclusion that  $D_1^\circ$  is directly chemically reactive rests on several legs: the quantitative analyses detailed above, the monitoring results, and the recent studies comparing solid and solution emission lifetimes (Refs. 19 and 20). As Kirk notes, an additional experiment might be to measure the quantum yield for aquation of  $\text{Cr(en)}_3^{3+}$ , on irradiation at the wavelength of a doublet absorption feature. An increase in yield would be confirmatory of our conclusion. A lack of significant increase would, unfortunately, not be fully diagnostic since the experiment is a difficult one, and there are several factors that could make the apparent yield too small.<sup>24</sup> Also, a non-increase in yield would not, of course, distinguish between  $D_1^\circ$  and  $Q_1^\circ$  as the source of  $\phi_{\text{slow}}$ .

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- (8) Reference is made in Ref. 7 to some of our Polaroid photographs of oscilloscope traces.<sup>2</sup> A response to this re-reading of our own data is provided further below.
- (9) These equations were provided to Kirk in a memorandum from the senior author.
- (10) Kirk's equations 1A and 1B can be obtained for steady state irradiation. They are not in general valid for pulse photolysis, and are obtainable from Eqs. (2) and (3) only with several approximations.<sup>7</sup> These amount to  $D_1^\circ$  functioning as a steady state source for any reaction from  $Q_1^\circ$  via bisc.
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- (14) Conductimetric changes following laser pulse photolysis confirm that 70% of the photochemistry is indeed slow, that is, implicates  $D_1^\circ$ . W. L. Waltz, R. T. Walters, and R. J. Woods, private communication.
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- (21) Experiments at 620 nm were difficult because of the low  $\text{Cr(en)}_3^{3+}$  and product absorbances. Careful millipore filtering of the solutions was needed to eliminate dust-related artifacts, and, to reduce Raman scatter which might saturate the photomultiplier, the monochromator slits were set at the lowest practical value. It was essential that the laser and detector train be operating at specifications; this required expert, experienced operation. The trace shown in Figure 3 is one of several that were essentially artifact-free, and is reproduced from a Xerox copy of a photographic enlargement of the

original Polaroid prints, made at the time of writing Ref. 2.

(We cannot find the original prints for the 620 nm runs in our library of prints.) The R value for Figure 3 is about 3.5; the average value which we reported for 620 nm was  $4.0 \pm 0.5$ .<sup>2</sup>

- (22) Kirk's conclusions are based on monitoring data taken during a brief visit,<sup>23</sup> which on our casual inspection were not of sufficient quality to be useful (some must have been taken after cracking of the doubling crystal so that hot spots could have been present), and, apparently, on Xerox copies made by him of some of our Xerox copies of the original Polaroid photographs of oscilloscope traces. Not all of the original data were in the section of the laboratory notebook that Kirk examined and copied, nor did Kirk discuss his questions with the second author, who obtained most of the original data. This original data acquisition was based on over a year of careful optimizing of the performance of this equipment.
- (23) Kirk acknowledges our financial support for his visit. His instruction in and use of the laser equipment was, more specifically, assisted in a quite major way by Dr. A. Lees.
- (24) The report of unchanged yield by Chen and Porter<sup>25</sup> was in abstract form, and has not been published in detail. Potential sources of error in a direct irradiation experiment include the presence of traces of dust so that the measured (low) extinction coefficient is too high, correction for the bandwidth of the irradiating light exceeding the line width of the doublet absorption feature, and the question of whether excitation of other than the 0-0 quartet to doublet transition will give the correct reaction yield from  $D_1^\circ$ .
- (25) S. Chen and G. B. Porter, Abstracts of the 10th Informal Conference on Photochemistry, Stillwater, Oklahoma, 1972.

Legends for the Figures

Figure 1. Excited state scheme for a  $d^3$  system. Heavy lines denote thermally equilibrated states. Light lines denote successive stages of relaxation of the solvent cage; at each stage, as indicated by the small parabolas, there is a vibrational potential well.

Figure 2. The four regimes. (a) Regime IA, (b) regime IB, (c) regime IIA, (d) regime IIB.

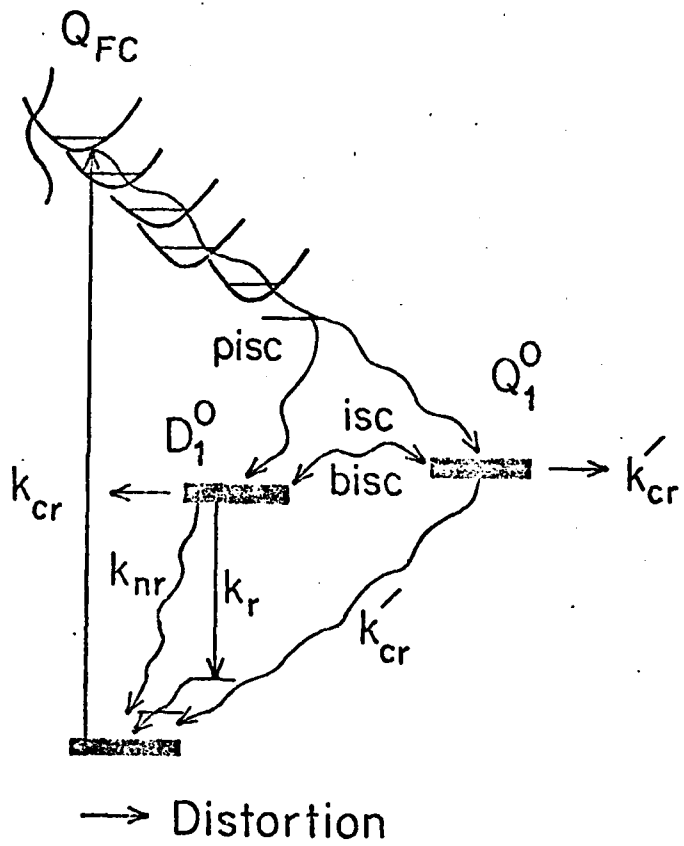
Figure 3. Transient absorbance changes under 620 nm monitoring. The ordinate voltage scale is offset by 6.5 scale divisions.

Table 1

Case	$k_{21}$	$k_{23}$	$k_{32}$	$k_{34}$	$f$	$\lambda_1$	$\lambda_2$	$A^a$	$B^a$	$C^a$	$D^a$	$\phi_D^1$	$\phi_Q^1$	$\phi_{slow}$	$\phi_{fast}$	$(D_1^\circ)^b$
<u>Regime IA (see Figure 2(a))</u>																
1	1	0.01	0.01	1000	0.3	1000	1.01	$7 \times 10^{-9}$	0.297	0.700	0.003	0.87	0.16	0.26	0.11	0.30
2	1	0.01	0.01	1000	0.7	1000	1.01	$3 \times 10^{-9}$	0.693	0.300	0.007	0.37	0.37	0.27	0.11	0.69
3	1	0.01	0.01	1000	0.89	1000	1.01	$1.1 \times 10^{-9}$	0.981	0.110	0.009	0.292	1.00	0.26	0.11	0.88
4	1	0.01	1	1000	0.3	1001	1.01	$7 \times 10^{-7}$	0.298	0.699	0.003	0.87	0.16	0.26	0.11	0.30
5	1000	0.01	1	1000	0.3	1001	1000	0.689	0.990	0.689	0.010	0	0.16	0.001	0.11	---
<u>Regime IB (see Figure 2(b))</u>																
6	1	0.01	428.6	1000	0	1429	1.01	$2 \times 10^{-4}$	0.298	0.700	0.002	0.87	0.16	0.26	0.11	0.30
7	1	0.01	2338	1000	0	3338	1.00	$2 \times 10^{-4}$	0.699	0.300	0.002	0.37	0.37	0.26	0.11	0.70
8	1	0.01	8091	1000	0	9091	1.00	$1 \times 10^{-4}$	0.889	0.11	0.001	0.29	1.00	0.26	0.11	0.89
9	1000	0.01	428.6	1000	0	1429	1000	0.70	1.00	0.700	0.000	0	0.16	0	0.11	---
<u>Regime IIA (see Figure 2(c))</u>																
10	0.01	1	0.01	1000	0.7	1000	1.01	$3 \times 10^{-11}$	0.007	0.300	0.694	0	0.37	0.26	0.11	0.70
11	1	1	0.01	1000	0.82	1000	2.00	$2 \times 10^{-9}$	0.410	0.179	0.411	0	0.63	0.26	0.11	0.82
12	0.01	1	1000	1000	0.4	2001	0.51	$2 \times 10^{-6}$	0.014	0.300	0.687	0	0.38	0.26	0.11	0.70
13	0.01	1	10	1000	0.7	1010	1.00	$3 \times 10^{-8}$	0.007	0.296	0.697	0	0.37	0.26	0.11	0.70
<u>Regime IIB (see Figure 2(d))</u>																
14	0.01	1	1000	400	0	1401	0.296	$5 \times 10^{-6}$	0.024	0.285	0.690	0	0.37	0.26	0.11	0.71
15	0.01	1	$1 \times 10^4$	4000	0	$1.4 \times 10^4$	0.296	$5 \times 10^{-7}$	0.024	0.286	0.690	0	0.37	0.26	0.11	0.71
16	0.2	1	1000	180	0	1181	0.352	$1 \times 10^{-4}$	0.481	0.152	0.367	0	0.72	0.26	0.11	0.85
17	0.22	1	1000	170	0	1171	0.365	$2 \times 10^{-4}$	0.515	0.145	0.340	0	0.76	0.26	0.11	0.85
18	0.01	1.1	$1 \times 10^4$	4000	0	$1.4 \times 10^4$	0.324	$5 \times 10^{-7}$	0.022	0.286	0.692	0	0.38	0.26	0.11	0.71
19	0.2	1.1	1000	200	0	1201	0.383	$1 \times 10^{-4}$	0.435	0.166	0.399	0	0.66	0.26	0.11	0.83

(a) Coefficients of Eqs. (5) and (6); while the A values are generally small and negative, this does not mean that Eq of Eq. (5) is ever negative. The  $\lambda_1$  and  $\lambda_2$  values are not sufficiently disparate for the A and B terms to be fully distinct.

(b) As given by Eq. (8);  $(D_1^\circ)$  is relative to  $(Q_{FC}) = 1$ .



*Fig 1*

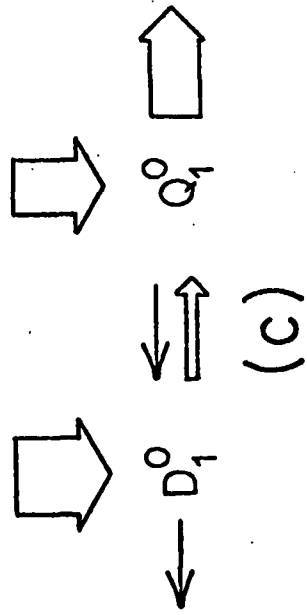
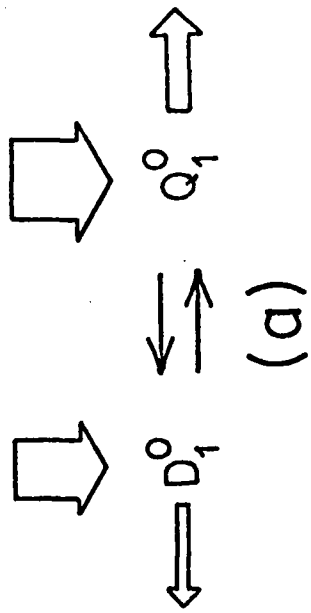
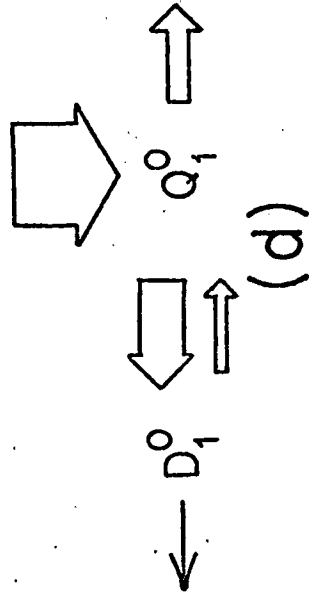
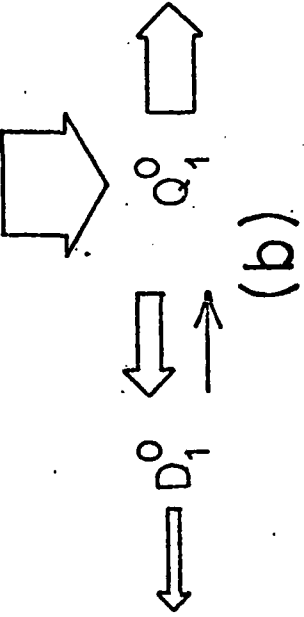
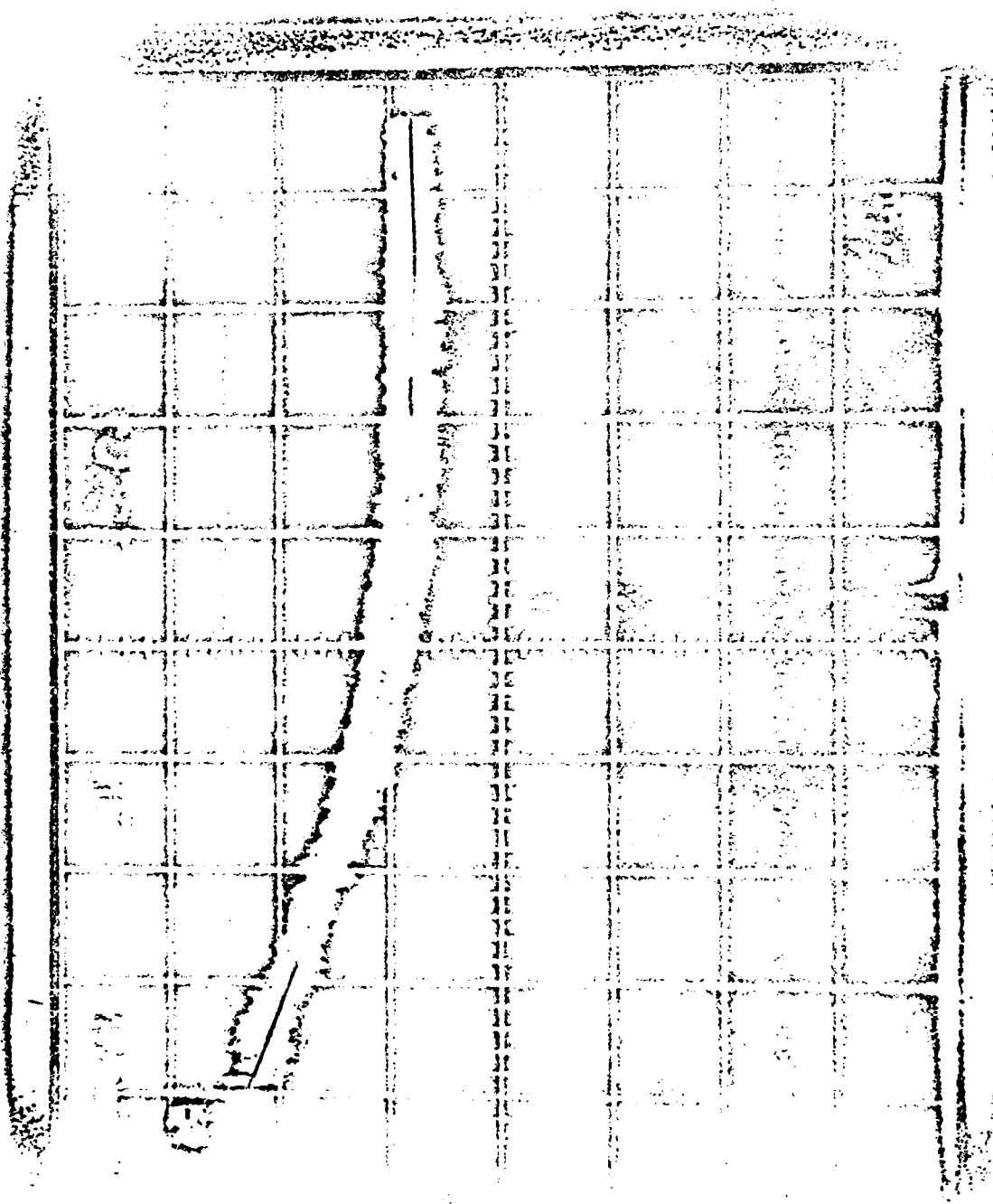


Fig. 2

6



$V_0 = 13.35$   
 $V_{inf} = 12.80$   
 $V_{inf} = 11.32$   
 $R = \frac{V_0 - V_{inf}}{\log \frac{V_0}{V_{inf}}} = \frac{13.35 - 11.32}{\log \frac{13.35}{11.32}} = \frac{2.03}{.0170} = 3.07$   
 $T_p = 5 \frac{1}{2} \text{ min}$   
 $\approx 200$

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